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Solar Fuels and Catalytic Water Splitting

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ABSTRACT

The widespread integration of particulate semiconductor photocatalysis into regional energy frameworks represents an indispensable paradigm shift for realizing global net-zero sustainability objectives. Among competing technical pathways, suspended particulate systems have garnered profound academic and industrial interest due to their potential for ultra-low-cost, scalable green fuel production. However, the foundational bottleneck remains the development of robust photocatalysts capable of achieving economically viable solar-to-hydrogen (STH) conversion efficiencies. Concurrently, contemporary engineering research focuses on large-scale panel deployment strategies while resolving critical safety challenges regarding the fluid-dynamic separation and collection of pure hydrogen from volatile stoichiometric oxyhydrogen mixtures. Recent literature heavily evaluates both single-stage and biomimetic two-step Z-scheme pathways for unassisted overall water splitting, alongside parallel poly generation systems that utilize water as an electron donor to drive photocatalytic carbon dioxide (CO_2) reduction into value-added solar fuels. Future commercial viability remains fundamentally contingent upon iterative advancements in chemical reactor design, long-term catalyst stability, macro-scale material manufacturing, and system-level explosion mitigation technologies.

Keyword: Photocatalytic water splitting, Solar fuels, green hydrogen, Renewable energy, Artificial photosynthesis Hydrogen economy, Charge recombination

1. INTRODUCTION

Fuels created by transforming solar energy into chemical energy are known as solar fuels. These fuels store solar energy for use in transportation, industry, and the production of electricity. Because solar fuels can be created utilizing plentiful natural resources like sunlight, water, and carbon dioxide, they are seen as renewable and environmentally favorable in contrast to traditional fossil fuels.

One of the most plentiful energy sources on Earth is solar energy. However, the fact that solar energy is intermittent—that is only available during the day and contingent on weather—is one of its main drawbacks. By storing solar energy in chemical bonds that can be transported and used whenever needed, solar fuels assist gets over this restriction.[1]

Natural photosynthesis, the process by which green plants transform sunlight, water, and carbon dioxide into chemical energy stored in carbohydrates, is the source of inspiration for the idea of solar fuels. To create fuels like hydrogen, methanol, methane, and ammonia, scientists use technologies like artificial photosynthesis, solar-driven electrolysis, and photo electrochemical systems, because it only creates water as a byproduct when utilized as fuel, hydrogen made from water using solar energy is regarded as one of the most promising solar fuels. As a result, solar fuels could be crucial in the shift to low-carbon, sustainable energy systems. As shown in figure 1a; 1b;1c

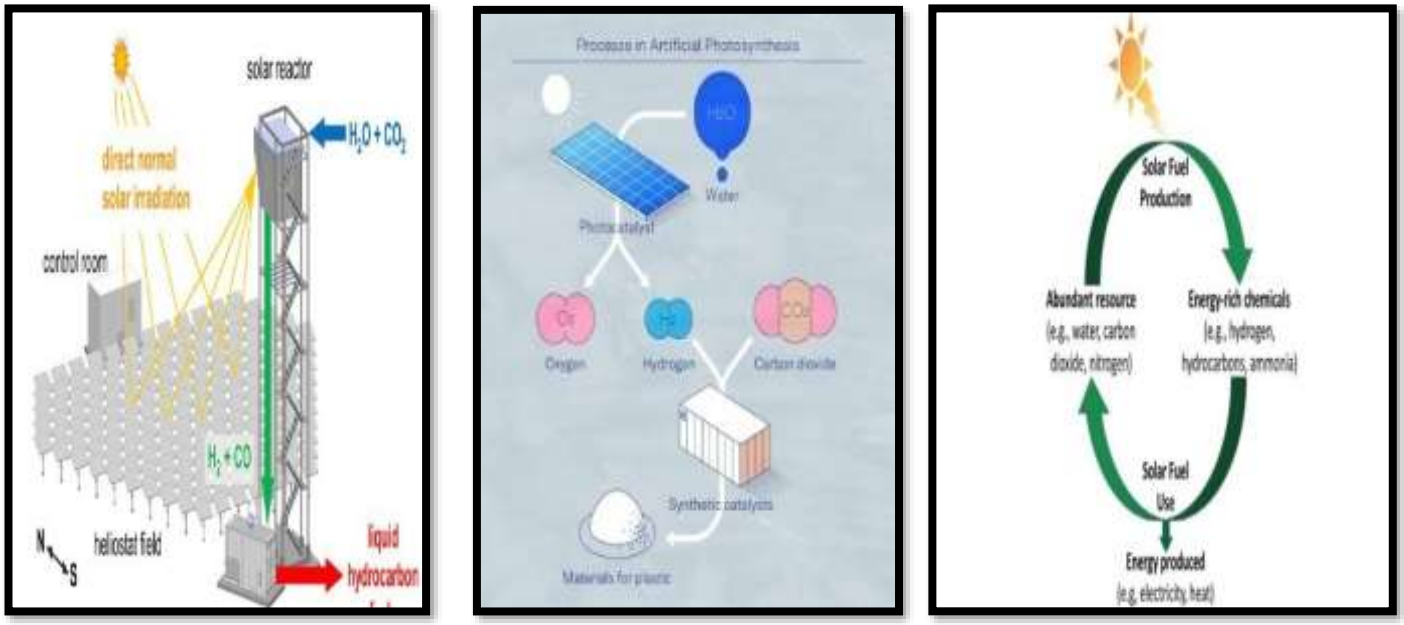


Figure 1a Solar Thermochemical Reactor System: 1b. Artificial Photosynthesis: 1c Solar Energy Capture
Source: https://www.chemistryworld.com, https://www.mcgc.com, https://www.nature.com/

1.1 RENEWABLE ENERGY NEED

1.1.1. Fossil Fuel Depletion

Conventional energy sources, such as coal and oil, are limited and running out. Companies must employ expensive, risky "extreme" techniques like hydraulic fracturing to sustain supply as conventional sources reach their peak. Fossil fuels alone cannot sustainably fulfil the estimated 3.6% yearly increase in global electricity demand through 2030. Making the switch to renewable energy is crucial to avoiding sharp price increases and guaranteeing a sustainable, ecologically sound substitute for our diminishing conventional resources.[2]

As global policy change toward renewable energy, investing in new fossil fuel infrastructure becomes riskier. These multibillion-dollar initiatives run the risk of becoming "stranded assets," which lose value before they break even. Depleting domestic reserves also pushes countries into "net-importer" status, making their economies susceptible to unstable energy markets and external geopolitical shocks.[2]

There are dangerous dependencies because 80% of the world's population depends on imports of fossil fuels from a small number of countries. Price spikes, such as the increase to $128/b in early 2026, result in extreme volatility. This volatility leads to "energy poverty," which makes basic transportation and heating costly.[2]

1.1.2. Preservation of the Environment

Over 75% of the world's greenhouse gas emissions come from the usage of fossil fuels, which release dangerous gases like CO_2 and SO_2. Coral reefs and other ecosystems are under risk due to these pollutants, which also contribute to ocean acidification and climate change. On the other hand, zero-emission electricity is produced by solar, wind, and hydropower. Making the switch to these renewable energy sources is essential to reducing global warming and safeguarding the delicate biodiversity of our world.[3]

While solar and wind power facilities need nearly little water for cooling, conventional power plants use billions of gallons. Fossil fuel combustion emits harmful chemicals that destroy biodiversity through acid rain and urban smog. Risks like catastrophic oil spills and acid mine drainage.

1.1.3. Diminished Global Warming

Global temperatures rise because of rising greenhouse gas concentrations, which trap heat like a blanket. Switching to renewable energy is crucial since burning fossil fuels for heat and power is the main source of carbon dioxide. Power is produced without combustion by solar, wind, and hydroelectric sources, greatly reducing this "heat-trapping blanket. “Energy is needed for manufacturing, however the "Carbon Payback" happens quickly. In comparison to coal's 820g CO_2/kWh, life-cycle emissions from wind (11g CO_2 /kWh) and solar (48g CO_2/kWh) are insignificant. While fossil fuel facilities constantly raise the atmosphere's potential for long-term warming every minute they run, these systems, once constructed, offer years of nearly carbon-free electricity.[4]

1.1.4. Sustainable Energy Provision

In 2026, we face the "Energy Trilemma": balancing security, fairness, and the planet's health. Moving from "finding and burning" fossil fuels to "harvesting and managing" nature’s flows is our only path forward. Unlike finite stocks of coal or oil that vanish once used, solar and wind are constant cycles that will persist for billions of years. This shift offers a predictable, free fuel source, ensuring a stable future for generations.[5]

1.1.5. Development of the Economy

The shift to renewable energy is a powerful economic engine for the twenty-first century, transforming how we build wealth. By moving from "extracting" to "harvesting," nations gain long-term financial stability. Unlike geographically restricted oil rigs, solar and wind projects can be built anywhere, bringing high-quality engineering and construction jobs to rural and underserved communities.[6]

Financially, renewables change the game. Since sunlight and wind are free, the cost of generating power is negligible once infrastructure is set. This allows businesses to lock in fixed energy rates for decades, shielding them from the volatile "price shocks" of global oil markets.

1.1.6. Access to Energy in Remote Locations

Traditional diesel generators are in remote areas, building massive power grids is often a financial impossibility, with costs sometimes outweighing a town's entire economic value. This is where distributed renewable energy changes the game. Unlike coal plants, these systems are modular; a village can start with a single solar panel for a clinic and scale up as they grow. Logistics trap, requiring expensive, hazardous fuel deliveries that fail whenever a storm hits, In contrast, wind and solar are fuel-free, harvesting energy directly from the environment. To bridge the gap during long winters or monsoons, surplus energy can be stored as **hydrogen**, ensuring total energy independence.[7]

1.2 CATALYTIC WATER SPILITING

Catalytic water splitting uses solar or electrical energy alongside a chemical catalyst to break water (H_2O) molecules into clean hydrogen (H_2) fuel and oxygen (O_2) gas, bypassing high energy barriers to produce sustainable, carbon-free green hydrogen.

1.2.1 Water splitting:

Water splitting is the endergonic chemical reaction in which water is broken down into oxygen and hydrogen as shown in figure 2. A hydrogen economy could be supported by a technological breakthrough in water splitting that is both economical and efficient. In photosynthesis, a form of water splitting takes place, but hydrogen is used ionically to power the Calvin cycle instead of being released. The hydrogen fuel cell based on the opposite of water splitting. Solar radiation-based water splitting has not yet been commercialised**.[**8**]**

$2\ H_2O \rightarrow 2\ H_2 + O_2$

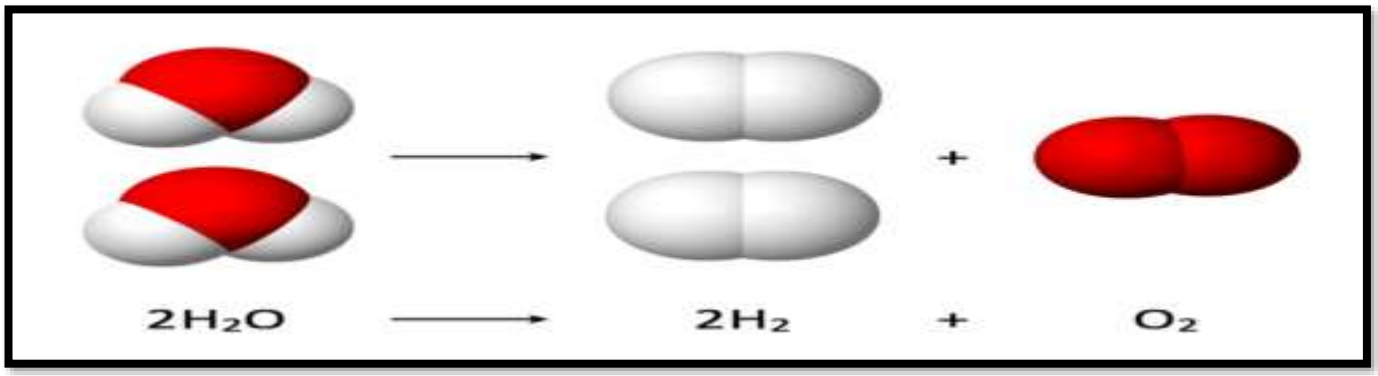


Figure 2. Water Splitting
Source: enwikipedia.or

1.2.2. Catalytic Water Splitting

In catalytic water splitting, water molecules (H_2O) break down into hydrogen (H_2) and oxygen (O_2) with the aid of catalysts that speed up the process and reduce the energy needed. It is among the most promising methods for producing hydrogen in a sustainable manner as shown in **figure 3.** This diagram illustrates an electrochemical water splitting cell divided by a membrane. Driven by an external power source, water is split at the cathode via a Hydrogen Evolution Reaction (HER) catalyst to produce hydrogen gas (a), while the anode uses an Oxygen Evolution Reaction (OER) catalyst to generate oxygen gas (b).[9]

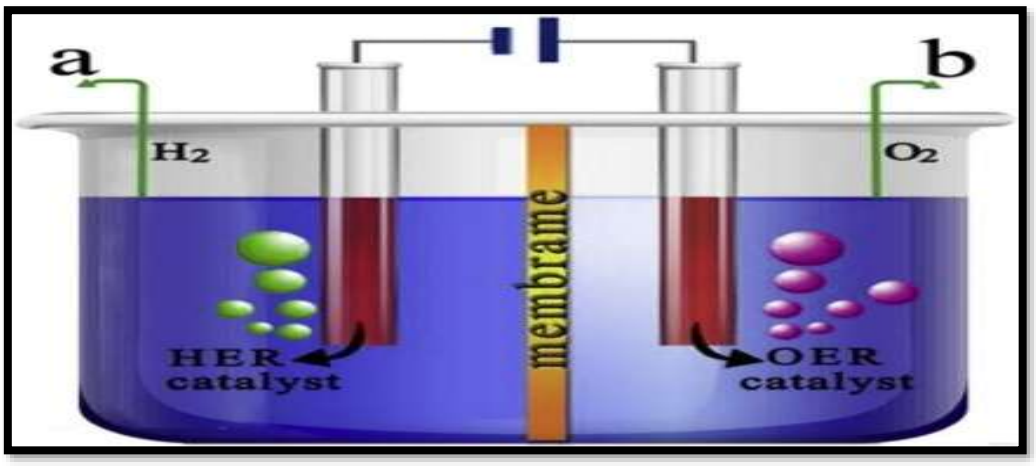


Figure 3. Electrochemical Water Splitting**, Source: https://www.researchgate.**

Key thermodynamic parameters:

- ✓ **Standard Gibbs free energy (ΔG°) ≈ 237.2 kJ/mol and Standard potential = 1.23 V**
- ✓ Reaction is **non-spontaneous**, therefore external energy is required.

Electrochemical Mechanism

(A) Hydrogen Evolution Reaction (HER)

In acidic medium: $2H^+ + 2e^- \rightarrow H_2$

In alkaline medium: $2H_2O+2e^- \rightarrow H_2+2OH^-$

(B) Oxygen Evolution Reaction (OER)

In acidic medium: $2H_2O \rightarrow O_2+4H^+ + 4e^-$

In alkaline medium: $4OH^- \rightarrow O_2+2H_2O+4e^-$

In photosynthesis, a form of water splitting takes place, but the electrons are sent to the electron transport chain in photosystem II rather than to protons. Carbon dioxide is reduced by the electrons and finally integrated into sugars.

Electrons are moved to several electron acceptors when photosystem I is photoexcited, eventually changing $NADP^+$ into NADPH. The oxidised photosystem I takes up electrons from photosystem II through a series of reactions involving plastoquinone, cytochromes, and plastocyanin. Oxidised photosystem II oxidises the oxygen-evolving complex (OEC), which converts water into O_2 and protons. Many studies have concentrated on employing synthetic Mn compounds as water oxidation catalysts since manganese is found in the OEC's active region.
In biological hydrogen production, the electrons generated by the photosystem are transferred to hydrogenases rather than a chemical synthesis apparatus, which produces H_2. A bioreactor is used to create this biohydrogen.[10]

2. WATER SPLITTING TECHNIQUE

Water splitting techniques utilize energy inputs such as solar, thermal, electric, or light energy—to dissociate water (H_2O) into hydrogen (H_2) and oxygen (O_2) gases, offering a clean, sustainable route for zero-emission energy production. Major approaches include photocatalytic water splitting, where semiconductors absorb light to generate electron-hole pairs for redox reactions; photoelectrochemical (PEC) cells, which separate oxidation and reduction half-reactions across photo-driven electrodes; thermochemical cycles, which use concentrated thermal energy to drive multi-step redox reactions; and traditional water electrolysis powered by renewable electricity. By integrating Earth-abundant catalysts and optimized material band structures, these techniques efficiently produce high-purity green hydrogen to serve as a versatile, eco-friendly energy carrier.[11]

2.1. Electrolysis of Water

The most used method for dividing water is electrolysis.the process of electrolysis involves passing an electric current through water to separate it into hydrogen (H_2) and oxygen (O_2). It is frequently employed in scientific experiments and the generation of hydrogen fuel.

$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

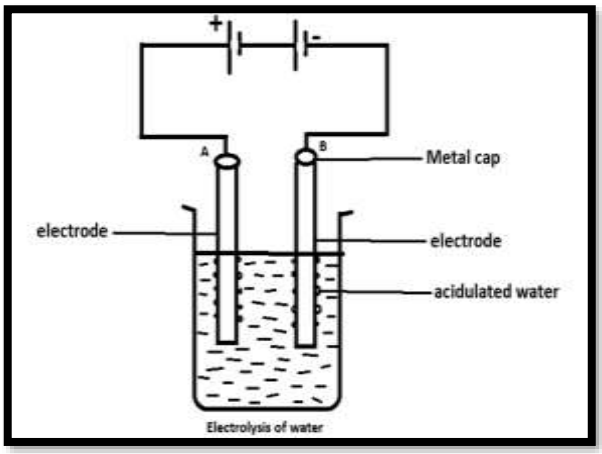
At Cathode (Negative Electrode): Reduction reaction occurs and it appears as a hydrogen gas bubbles.

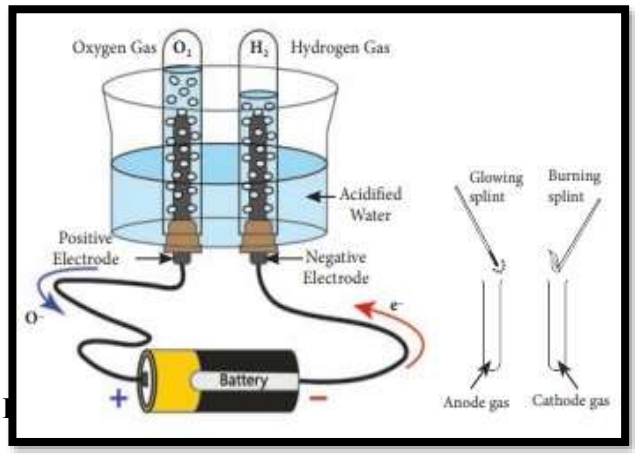
$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

At Anode (Positive Electrode): Oxidation reaction occurs and it appears as a oxygen gas bubbles.

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$$

The figure 4. illustrates the electrolysis of acidified water. An electric current splits water into oxygen gas at the positive anode and hydrogen gas at the negative cathode. The anode gas relights a glowing splint, while cathode gas burns actively.[12]





Source: https://www.vedantu.com/

Applications:

Production of Hydrogen Fuel:

The efficiency and "green" credentials of electrolysis depend heavily on the technology used and the source of electricity. The most developed commercial method is alkaline water electrolysis (AWE), which uses nickel-based catalysts and a liquid alkaline electrolyte (such as KOH). A solid polymer electrolyte is used in the proton exchange membrane (PEM). It is perfect for combining with renewable energy sources like solar and wind because of its high efficiency and quick response to varying power inputs. Solid Oxide Electrolyser Cell (SOEC): Using thermal energy to propel the process, this new high-temperature (500–850°C) technology provides exceptional electrical efficiency. [13],[14]

Laboratory Tests:

In the lab, electrolysis is about precision over scale. Using tools like the Hofmann Voltameter, researchers confirm water's 2:1 hydrogen-to-oxygen ratio by measuring gas displacement. Beyond theory, it's a practical way to produce "Heavy Water." Since light hydrogen reacts faster, long-term electrolysis leaves behind concentrated deuterium, a vital resource for nuclear research and high-end spectroscopy.[14]

Energy Storage and Fuel Cells:

Water electrolysis is the "missing link" that makes renewable energy truly reliable. Since wind and solar are unpredictable, electrolysis prevents wasted energy by converting excess electricity into hydrogen. Think of this hydrogen as a chemical battery that never loses its charge, unlike standard lithium-ion batteries.[15]

It can be stored in massive quantities for months, providing a vital energy reserve for winter. When needed, this hydrogen feeds into fuel cells to generate electricity, releasing only water as a byproduct. This "carbon-neutral loop" allows us to scale up storage cheaply and efficiently, ensuring power stays on even when the sun sets.[15]

Production of Industrial Hydrogen:

Industrial hydrogen is shifting from a fossil-fuel-based byproduct to a central strategy for global decarbonization. By using large-scale electrolysis, heavy industries are replacing "Grey Hydrogen" with clean alternatives. This transition is vital for the Haber-Bosch process, creating green ammonia for sustainable fertilizers. Similarly, refineries are integrating electrolyzers to purify crude oil and "crack" hydrocarbons, significantly reducing the carbon footprint of essential products like petrol and jet fuel.[16]

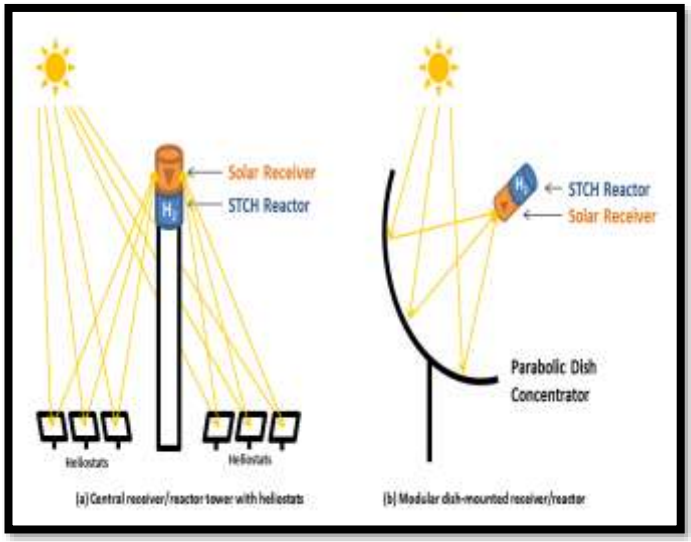
2.2. Thermochemical Water Splitting

Thermochemical water splitting utilizes high-temperature heat sources, such as concentrated solar collectors or advanced high-temperature nuclear reactors, to drive a multi-step redox reaction cycle. Intermediary materials—frequently metal oxides, sulphur-iodine compounds, or copper-chlorine complexes—react sequentially with water molecules, throughout these high-temperature steps, water is cleanly separated to yield pure hydrogen **(H_2)** and oxygen **(O_2)** gases at distinct stages. Crucially, all chemical intermediates, catalysts, and reactants are fully recovered, recycled, and reused within a closed-loop system, ensuring zero net chemical consumption while producing clean, emission-free energy.

Overall reaction: $2H_2O \rightarrow 2H_2+O_2$

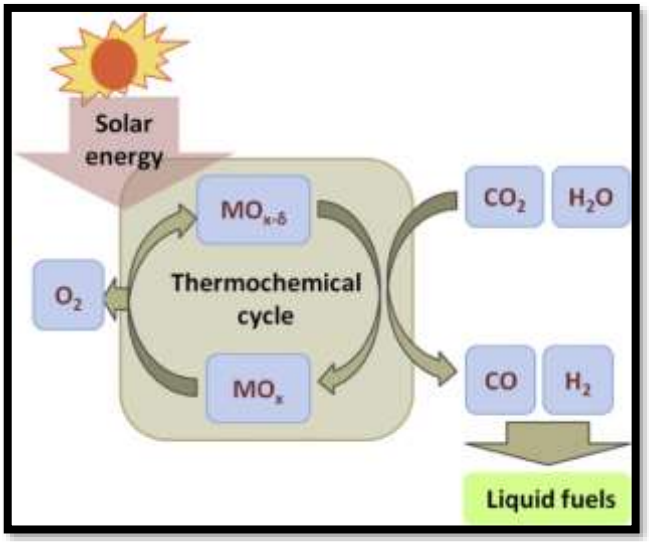
The figure **5(I)** This diagram illustrates two concentrated solar thermal systems used to drive hydrogen production. System (a) uses ground-based heliostats to focus sunlight onto a central tower receiver, while system (b) utilizes a parabolic dish to directly concentrate solar energy onto a modular receiver-reactor, and figure **5(II)** illustrates a two-step solar thermochemical cycle for fuel production. Concentrated solar energy thermally reduces a metal oxide (MO_x) to an oxygen-deficient state ($MO_{x-\delta}$), releasing oxygen (O_2). Next, the reduced oxide splits carbon dioxide (CO_2) and water(H_2O), regenerating MO_x and yielding carbon monoxide (CO) with hydrogen (H_2), which convert into liquid synthetic fuels.[17]

Figure 5: (I) Solar Thermal Chemical Hydrogen Cycle



Source: https://www.sciencedirect.com/

Figure 5: (II) Solar Two-Step Thermochemical



Source: https://www.researchgate.net/

Uses:

Production of Hydrogen for Fuel Cells: Thermochemical water splitting (TCWS) produces ultra-pure hydrogen, making it the perfect partner for sensitive fuel cells used in cars and trucks. Unlike traditional methods, TCWS is naturally free of carbon and sulfur—contaminants that typically "poison" and degrade engine components.[18]

By using solar-thermal heat to split water, we can harvest massive amounts of energy during the day. This "green hydrogen" can then power heavy-duty shipping and rail or stabilize the power grid at night, offering a clean, industrial-scale alternative to fossil fuels.

Storage of Renewable Energy in the Future:

Thermochemical water splitting (TCWS) is a breakthrough for energy storage, with the global market projected to hit **5.7 billion by 2026**. Unlike batteries that lose charge over time, TCWS stores energy in chemical bonds, enabling "seasonal storage"—holding summer sunlight as hydrogen to power homes all winter. As a high-density grid stabilizer, TCWS is moving toward the mainstream. Companies like New Hydrogen are pioneering technologies like Thermo Loop, which uses heat instead of expensive electricity to split water, creating a dependable, long-term fuel reserve.[19]

Production of Hydrogen in Industry:

Beyond power, hydrogen from thermochemical water splitting (TCWS) is a vital chemical feedstock. In 2026, the steel industry is pivoting toward a "Green Steel" revolution. By using TCWS-produced hydrogen instead of coal to reduce iron ore, manufacturers can produce high-quality metal with zero carbon emissions. Similarly, industrial hubs are swapping traditional, high-emission methods for TCWS to fuel the Haber-Bosch process. This transition enables "Carbon-Free" fertilizers, a massive step toward meeting global sustainability mandates for the food we eat.[20]

2.3. Photocatalytic Water Splitting:

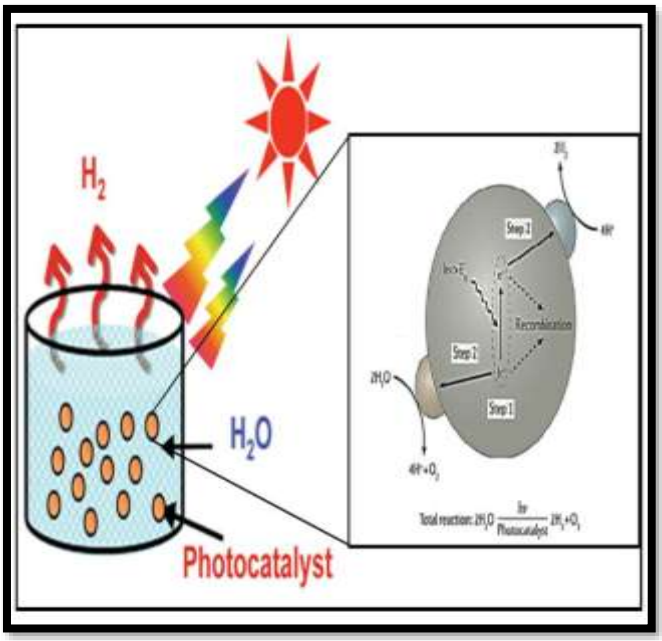
The process of splitting water (H_2O) into hydrogen (H_2) and oxygen (O_2) using sunlight and a semiconductor photocatalyst is known as photocatalytic water splitting, It is a significant technique for utilizing solar energy to produce clean hydrogen fuel.

Photocatalytic Water Splitting Mechanism
Step 1: Absorption of light, Sunlight is absorbed by photocatalysts.
Electrons transition from the valence band to the conduction band.
Step 2: Distinguishing charges: Pairs of electrons and holes are produced.
Step 3: Reduction reaction (formation of hydrogen)$2H^+ + 2e^- \rightarrow H_2$ Step 4: Oxidation reaction (formation of oxygen)

$$2H_2O + 4H^+ \rightarrow O_2 + 4H + 2H_2$$

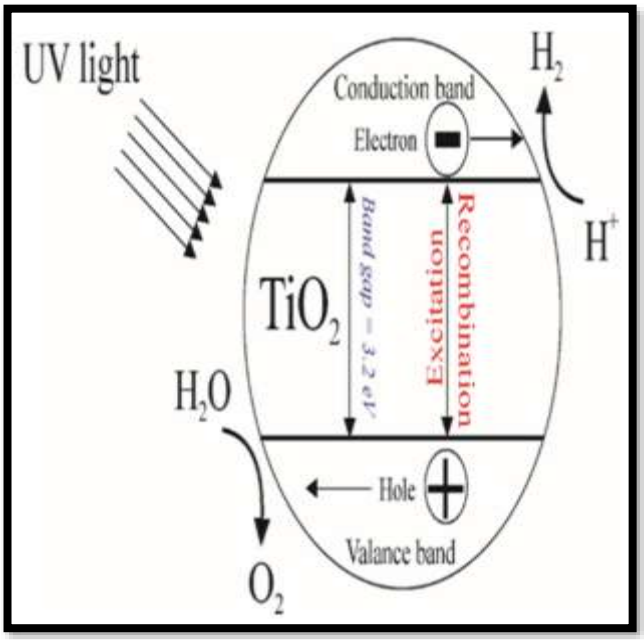
The figure 6(a) Sunlight photo-excites suspended photocatalyst particles, generating electron-hole pairs (e^-/h^+), holes migrate to the surface to oxidize H_2O into oxygen (O_2), while electrons reduce protons to hydrogen gas (H_2), overall splitting water into clean fuels. and figure 6(b) illustrate UV light exceeding the **3.2 eV** band gap excites electrons from the valence band to conduction band of TiO_2. Conduction band electrons reduce H^+ to H_2, while valence band holes oxidize H_2O to O_2.[21]

Figure 6: a) Photocatalytic Water Splitting



Source: https://solar.iphy.ac.cn/

Figure6: b) TiO_2 Band Structure Mechanism



Source: https://solar.dicp.ac.cn/

Uses:
Production of Green Hydrogen:

Because it replicates natural photosynthesis and produces hydrogen directly from sunlight and water without the necessity of complicated thermal reactors or an external power grid, photocatalytic water splitting (PWS) is frequently referred to as the "Holy Grail" of hydrogen generation. By 2026, the field has advanced from basic titanium dioxide (TiO_2) studies to high-efficiency, AI-designed materials that can reach the barrier for commercial feasibility. PWS functions at room temperature and pressure, in contrast to electrolysis, which needs electricity, and thermochemical splitting, which needs high-grade heat.[22]

Production of Solar Fuel:

Because photocatalytic water splitting (PWS) mimics natural photosynthesis to directly convert sunlight and water into hydrogen fuel without the need for intermediary energy, it is frequently referred to as the "Holy Grail" of solar fuel production. By 2026, the field will have advanced from simple laboratory tests to system-level engineering, concentrating on reaching the 10% Solar-to-Hydrogen (STH) efficiency threshold necessary for commercial viability.[23]

Systems for Artificial Photosynthesis:

In 2026, artificial photosynthesis evolved through three innovative systems. The "Solar-Thermal Leaf" uses the full solar spectrum—including infrared heat—to store energy in metal oxides, which then split water or CO_2 to create fuel.

Hybrid systems (PTC) split sunlight like a real leaf: visible light generates electricity while "waste" heat powers chemical reactions. This allows us to produce "solar kerosene," a carbon-neutral aviation fuel that mimics how plants store carbon, turning sunlight directly into liquid energy for planes.[24]

2.4. Photoelecto Chemical Splitting:

Water can be divided into hydrogen (H_2) and oxygen (O_2) via a process called photoelectrochemical (PEC) water splitting, which involves sunlight and semiconductor electrodes, it creates clean hydrogen fuel by combining photochemistry and electrochemistry.

Mechanism of Operation

First step: Absorption of light: The semiconductor photoelectrode is exposed to sunlight.
From the valence band to the conduction band, electrons migrate.
Step 2: Separation of charges, they produce holes (H^+) and electrons (e^-).
Step 3: Photoanode oxidation, Water oxidized by holes to produce oxygen $2H_2O + 4H^+ \rightarrow O_2 + 4H$
Step 4: Cathode reduction, as electrons move via the external circuit, hydrogen ions are reduced:
$2H^+ + 2e^- \rightarrow H_2$ as a result, hydrogen forms at the cathode and oxygen forms at the photoanode.

The figure 7(a) explain theSolar light excites electrons on the semiconductor photoanode ($h\nu > E_g$), generating holes that oxidize H_2O to O_2. Photogenerated electrons flow through the external circuit to the platinum counter electrode to reduce protons (H^+) into H_2,and figure 7(b) illustrate the Solar illumination excites electrons across the s semiconductor band gap (E_V to E_C) at the photoanode

releasing O_2. Transferred electrons move via an external circuit to the cathode compartment to reduce protons, generating separated H_2 gas.[25]

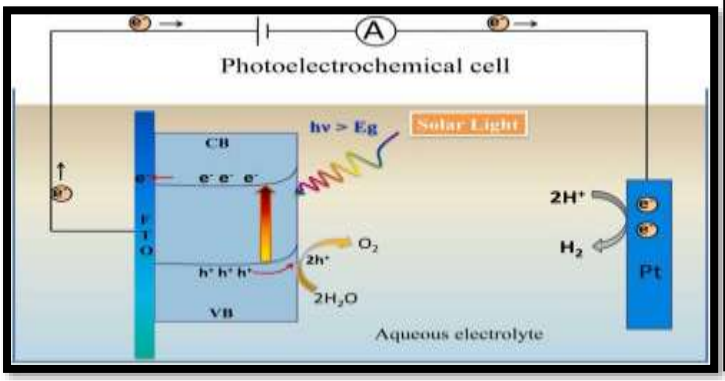


Figure:7(a) Photoelectrochemical (PEC) Cell Mechanism

Source: https://www.sciencedirect.com

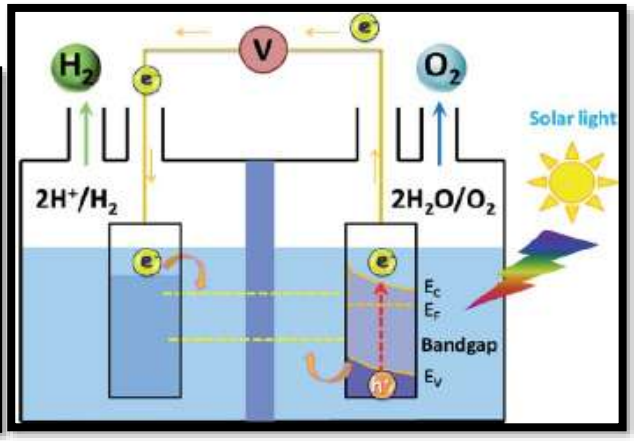


Figure 7(b)Two-Compartment PEC Cell Operation

Source: **https://www.sciencedirect.com**

3. TYPES OF CATALYST USED IN PHOTOCATALYTIC WATER SPLITING

a. Noble metal Catalysts

b. Transition Metal Catalysts

c. Metal oxide Catalysts

d. Metal Sulfide Catalysts

e. Metal Phosphide Catalysts

f. Perovskite Catalysts

3.1. Noble Metal Catalysts:

Noble metal catalysts are used in water splitting mainly because they make the reaction faster, more efficient, and stable. Splitting water into hydrogen and oxygen is naturally slow and requires high energy, so catalysts help lower the energy barrier. Materials like platinum, ruthenium, and iridium exhibit exceptional electrical conductivity and optimal intermediate binding energies. This drastically reduces overpotentials, ensuring superior catalytic activity, minimal energy losses, and long-term chemical durability during both hydrogen and oxygen evolution reactions.[26]

CATALYSTS	PROPERTIES
1.Paltinum	**Extremely high catalytic activity** **Very low overpotential** **Fast electron transfer** **Reaction: $2H^+ + 2e^- \rightarrow H_2$** **Best catalyst for hydrogen Evolution Reaction (HER)**
2. Iridium (Ir / IrO_2)	**High stability in acidic medium** **Strong OER activity** **Resistant to corrosion**
3. Ruthenium (Ru/RuO_2)	**Higher activity than IrO_2** **Good catalytic efficiency** **Can dissolve during long operation**

3.2. Transition Metal Catalysts: Since transition metals are far less expensive than noble metals yet nevertheless exhibit strong catalytic activity for the two essential processes, they are frequently employed as Earth-abundant catalysts for catalytic water splitting. Their variable oxidation states and tuneable electronic structures enable efficient charge transfer, significantly accelerating both the hydrogen and oxygen evolution reactions.

- Hydrogen Evolution Reaction (HER)
- Oxygen Evolution Reaction (OER)

Metal or metal oxide	Advantage
Nickel (Ni)	**Used for HER in Alkaline water electrolysis.** **Cheaper alternative to platinum**
Cobalt (Co)	**Used in OER catalysts** **Often used as cobalt Oxide or Cobalt phosphate.**
Iron (Fe)	**Used in combination with nickel (Ni – Fe) oxides.** **Good catalyst for OER**
Manganese (Mn)	**Inspired by natural water splitting system in photosynthesis.** **Used in Mn oxide catalysts**
Ruthenium (Ru)	**Highly active for OER** **Example: Ruthenium oxide (RuO_2)**
Molybdenum (Mo)	**Used in MoS_2 catalysts for hydrogen evolution.**
Iridium (Ir)	**Very stable catalysts for OER in acidic media.** **Example: Iridium oxide (IrO_2)**

3.3. Metal Oxide Catalysts:

Photocatalytic water splitting utilizing heterogeneous metal oxide semiconductors represents one of the most promising methodologies for scalable green hydrogen production. Metal oxides are widely favored due to their exceptional chemical stability, earth abundance, and highly tunable electronic structures. The fundamental mechanism involves the absorption of incident photon energy exceeding the semiconductor's band gap (E_g), prompting the excitation of photo-induced electron-hole pairs (e^-/h^+). These charge carriers subsequently migrate to the catalyst surface to drive

corresponding reduction and oxidation (redox) reactions. To achieve overall water splitting, the semiconductor's band gap must fulfil two thermodynamic criteria: it must be sufficiently wide to span the water oxidation/reduction potentials inclusive of required overpotentials (greater than 1.23 eV), yet narrow enough to efficiently harvest the visible light spectrum. Pristine metal oxides frequently exhibit intrinsic limitations, such as excessively wide band gaps or ultra-fast bulk charge recombination. To circumvent these bottlenecks, several engineering strategies are deployed. Anion/Cation Doping: Introducing foreign atoms (e.g., non-metals like N and S, or various transition metals) creates intermediate impurity states within the band gap, effectively shifting the absorption edge into the visible spectrum. Heterojunction Fabrication Coupling distinct semiconductors (e.g., TiO_2/CdS) establishes an internal macroscopic electric field at the interface, driving spatial separation of photogenerated electrons and holes in opposing directions'-catalyst Decorating the semiconductor surface with noble metals (Pt, Au) or transition metal oxides (RuO_2, IrO_2) lowers the activation energy barrier for gas evolution kinetics.

A persistent challenge in photocatalyst development is the "Stability-Efficiency Trade-off." Highly stable oxides, such as Titanium Dioxide (TiO_2), typically possess wide band gaps that limit their activity to the ultraviolet (UV) spectrum, which accounts for only ~5% of terrestrial solar irradiance. Conversely, narrow-band-gap oxides like Cuprous Oxide (Cu_2O) harvest visible light more efficiently but are highly susceptible to in situ photo-corrosion and self-reduction under aqueous conditions. To transcend these limits, current research heavily focuses on biomimetic Z-scheme architectures, which decouple the hydrogen and oxygen evolution reactions across two distinct light-harvesting units.[27]

3.4. Metal Sulphide:

Catalysts Because of their special optoelectronic characteristics, metal sulphide (MS) catalysts have become leaders in photocatalytic water splitting. Sulphides frequently have shorter bandgaps and more advantageous conduction band locations for hydrogen evolution, in contrast to many metal oxides, The Electronic Structure and Light Absorption of Tungsten Disulphide (WS_2) Because the valence band (VB), which is mainly made up of sulphur 3p orbitals, sits at a greater negative potential than the oxygen 2p orbitals found in oxides, the majority of metal sulphides are visible-light active, By narrowing the bandgap (Eg), the Bandgap Advantage for this placement enables the material to harvest a greater percentage of the solar spectrum. Sulphides with extremely negative Conduction Band (CB) potentials, such as CdS and ZnS, offer a powerful thermodynamic driving force for the reduction of protons into hydrogen (H_2). The "gold standard" for producing visible light H2 is cadmium sulphide (CdS), which has a band gap of about 2.4 eV. It is very efficient but prone to photo corrosion. Molybdenum Disulphide (MoS_2) catalyst is mostly utilised as a co-catalyst; its "edge sites" are very active for hydrogen evolution, Zinc Sulphide (ZnS) has a wide bandgap (UV active) of about 3.6 eV, making it good for H_2 evolution without co-catalysts due to very negative CB, Copper Indium Sulphide (Cu in S_2) has a band gap of about 1.5 eV and is a good light harvester that is frequently utilised in heterojunctions or ternary systems.[28]

3.5. Metal Phosphide Catalysts:

For photocatalytic hydrogen evolution, metal phosphides (Mx Py) have become a very effective and affordable substitute for noble metals such as platinum (Pt). Their main function is to act as a cocatalyst loaded onto a semiconductor (such as g-C3N4 or TiO_2) to promote the Hydrogen Evolution Reaction (HER), This explains their effectiveness and how they work in water-splitting systems, The semiconductor in a photocatalytic device creates electron-hole pairs by absorbing light, On the semiconductor's surface, metal phosphides serve as electron traps, They seize electrons produced by photolysis from the conduction band.

The "metal-like" conductivity of phosphides (such as Ni_2P, CoP, and FeP) enables speedy charge transfer by rapidly removing electrons, which lowers the rate of charge recombination and ensures that more electrons are available for the reduction of H^+ to H_2,The "Ensemble Effect" states that while the metal sites (M) bind the hydride, the phosphorus atoms (P) in the lattice function as proton-acceptor sites (H^+), Phosphorus's electronegativity drives electron density away from the metal during bonding, resulting in a negatively charged phosphorus and a positively charged metal centre, By

reducing the Gibbs free energy (Delta GH*) of hydrogen adsorption, this dual-site process makes it almost as effective as Pt.[29]

Common Metal Phosphide Catalysts: Ni_2P, CoP, Fe_2P, MoP, Cu_3P

3.6. Perovskite Catalysts:

Because perovskite oxides (ABO_3) are chemically resilient, highly adjustable, and less expensive than noble metals (such Pt or IrO_2), they have emerged as a key component of catalytic water splitting research. These materials are usually assessed for their performance in two half-reactions in the context of water splitting: the Hydrogen Evolution Reaction (HER) at the cathode and the Oxygen Evolution Reaction (OER) at the anode, The structure of perovskite (ABO_3): Perovskites' crystal structure gives them their versatility: A-site: Typically, a bigger alkaline-earth or rare-earth metal (e.g., La, Sr, Ba, Ca). These ions can adjust the B-site's oxidation state and mainly stabilize the crystal structure. A smaller transition metal, such as Co, Fe, Ni, or Mn, is typically found in the B-site, The real water-splitting chemistry takes place at this active catalytic site the oxygen anions in the O-site "Lattice Oxygen Participation," in which the oxygen in the crystal itself aids in the formation of O_2 bonds, is highlighted by recent study, To produce more active sites, "doping" or "exsolution" is the main focus of current research. [30]

e.g. $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3\text{-delta}}$ (BSCF), $CaSrFe_{0.75}Co_{0.75}Mn_{0.5}O_{6\text{-delta}}$, $LaNiO_3$, $SrIrO_3$

4. APPLICATION IN (HYDROGEN ECONOMY)

The sustainable creation of "green hydrogen" is the main use of photocatalytic water splitting, In order to reduce climate change and improve energy independence, this clean hydrogen is meant to take the place of fossil fuel-derived (grey) hydrogen in several industries.

4.1. Energy Storage:

Hydrogen energy storage is one of the most popular chemical energy storage, Hydrogen is storable, transportable, highly versatile, efficient, and clean energy carrier, it also has a high energy density, for energy storage application, off peak electricity is used to electrolyse water to produce hydrogen. The hydrogen can be stored either as compressed gas, liquefied gas, metal hydrides or nanostructures, the choice of the storage technology depends on the characteristics of available technologies in terms of technical, economical or environmental performance ,During the discharge phase, the stored hydrogen is either used in fuel cell or burnt directly to produce electricity. One major drawback in using hydrogen for electricity storage is the substantial energy losses during a single cycle.[31]

4.2. Renewable Energy:

Solar fuels revolutionize "hard-to-abate" industries like steel, cement, and shipping where batteries fail, Projects like Namibia's Oshivela use solar hydrogen for green steel, replacing coal, In a renewable energy hydrogen economy, excess solar or wind power powers water electrolysis to produce zero-emission green hydrogen. This hydrogen acts as a versatile, clean-burning energy carrier, addressing the intermittency of renewables by enabling long-term energy storage and sector coupling across heavy industries, transportation, and power grids.[32]

4.3. Industrial Processes:

In green steelmaking, solar fuels are replacing carbon-intensive coke as they move from research to industrial infrastructure, to decarbonise mining by 2027, big companies like Fortescue are speeding up green networks,

furthermore high-temperature thermochemical reactors that provide the intense heat required for chemical synthesis, glass and cement are now directly powered by concentrated solar energy.[33]

4.4. Transportation:

For "hard-to-abate" modes of transportation like shipping and aviation, solar fuels have a high energy density Companies like Synhelion produce solar kerosene and carbon-neutral green methanol, with the SAF market hitting 8.25 billion in 2026 In the meantime, solar hydrogen is used by fuel cell trucks made by companies like Tata Motors to refill more quickly than batteries.[34]

4.5. Power Generation.

Industrial efforts toward deep decarbonization in the power generation sector are increasingly leveraging the co-firing of green hydrogen (H_2) within existing natural gas turbine architectures. Initial integration frameworks target blending ratios of 20% to 30% by volume. Concurrently, major original equipment manufacturers (OEMs), including Mitsubishi Power and Siemens Energy, have pioneered "hydrogen-ready" turbine technologies capable of transitioning to 100% solar-derived hydrogen fuel supplies. Beyond simple combustion adjustments, contemporary research is shifting toward polygeneration frameworks that integrate freshwater production, waste heat recovery, and thermochemical hydrogen synthesis into unified, high-efficiency energy systems.[35]

4.6. Energy Independence:

Because solar fuels enable countries and people to "bottle" sunshine into chemical forms that can be stored and transported, they represent a crucial frontier for energy independence, Solar fuels (such as green hydrogen or solar methanol) can replace fossil fuels in industries that are challenging to electrify, in contrast to traditional solar power, which produces sporadic electricity, For nations that are net importers of petrol and oil, solar fuels offer a means of separating their economies from unstable international markets and geopolitical tensions, Utilise the Using "drop-in" solar fuels (synthetic petrol or methane) that operate in current pipelines, tankers and engines is one of the quickest routes to independence because it avoids the enormous expense of replacing a country's entire energy grid.[36]

4.7. Technological Advancements:

Renewable hydrogen production represents the primary pathway for solar energy vectoring. Specifically, recent advancements in Proton Exchange Membrane (PEM) electrolysis have enhanced operational durability via iridium-thrifty catalysts, optimizing compatibility with the intermittent profiles of photovoltaic generation. Concurrently, integrating High-Temperature Steam Electrolysis (HTSE) with concentrated solar power (CSP) leverages thermal energy assets to drastically reduce the specific electrical energy consumption required for water splitting.[37]

4.8. Scalability:

Seamless dimensional scalability—bridging milligram-scale laboratory discoveries to square-kilometre industrial utility plants—is the foundational link underpinning a commercial green hydrogen economy (Turner et al., 2024). While decoupled photovoltaic-electrolysis (PV-E) configurations currently predominate at advanced Technology Readiness Levels (TRLs), the development of monolithic, direct solar-to-fuel panels remains crucial. Although these direct photoelectrochemical (PEC) architectures circumvent the thermodynamic efficiency penalties associated with intermediate power conversion steps, their commercial viability remains fundamentally contingent upon solving macro-scale manufacturing challenges, namely large-area catalyst deposition techniques and enhanced long-term corrosion mitigation strategies.[38]

5. Challenges of Solar Fuels

Despite India’s rapid progress in solar energy adoption, several challenges continue to hinder its full potential. These challenges span across policy implementation, financial viability, infrastructure, and environmental concerns. Addressing them is crucial to ensuring a sustainable and reliable solar future.[39]

5.1. Efficiency:

Solar-to-Fuel efficiency remains low due to thermodynamic gaps and overpotentials; real-world water splitting requires 1.6–1.8 rather than the theoretical 1.23V, Bandgap mismatches necessitate complex tandem cells, while rapid charge recombination and material defects convert absorbed photons into wasted heat, significantly reducing overall quantum efficiency and fuel output.[40]

5.2. Catalyst Stability and Cost.

In 2026, solar fuel production faces a "Valley of Death" regarding stability and cost, High-efficiency catalysts often suffer from photo-corrosion and surface fouling, leading to rapid performance declines, to compete with cheaper "blue" hydrogen, solar fuel must overcome high production costs by developing catalysts durable enough to last ten years.[41]

5.3. Scalability and Reactor Design:

There are three major obstacles to solar reactor scaling, Surface-to-volume ratios and shadowing restrict light control, while big apertures result in substantial heat loss, Bubble shielding in which gas accumulation absorbs sunlight and increases resistance, is a problem for fluid dynamics, lastly thermal cycling poses a danger to material durability, sudden temperature changes during cloud cover or sunset result in thermomechanical fatigue and structural failure.[42]

5.4 Safety:

Extreme thermal conditions result when using thermochemical water splitting, leading to material fatigue and the potential formation of "hot spots," where structural failure could easily occur. In addition, there are significant safety issues associated with handling molten salts, as they create serious burn hazards, The chemical risk of using hydrogen as a solar fuel is also significant because it is highly combustible and can cause embrittlement, therefore specialised and secure storage and transportation systems need to be developed.[43]

5.5. Storage and Transportation: Storage and Transportation:

The transition to solar fuels will encounter tremendous mid-stream challenges by 2026, Considerably greater than fossil fuels, low specific volumetric energy density means that volume for storage will be much greater than that of conventional fuel, Global logistics mean reworking or replacing infrastructure, because existing pipelines could suffer embrittlement unless they are retrofitted at a high cost, Therefore it is common for hydrogen to be converted to ammonia or liquid carriers to be shipped and distributed internationally.[44]

5.6. Environmental and Waste Concerns:

the energy-intensive process of manufacturing solar fuel and mining for rare materials (usually destroyed while obtaining these materials) has an "upstream" environmental impact. Operationally, catalysts are likely to eventually corrode or become inactive, causing them to release hazardous materials or to require frequent replacement and create a lot of electronic waste (e-waste), Although some materials can be recycled, obtaining large quantities of high-purity silicon and rare metals poses significant technical and economic challenges.[45

5.7. Policy and Regulatory Inconsistencies:

Solar fuels lack universal regulation. Rigid "additionality" mandates, requiring dedicated solar arrays, significantly inflate project costs, additionally inconsistent international carbon accounting policies complicate cross-border credit claims, Fossil fuel inertia sustained by direct and indirect subsidies, creates an uneven playing field, consequently investors view the high capital expenditures required for solar fuel infrastructure as riskier than traditional, subsidised energy sources.[46]

5.8. Financial and Investment Barriers:

Because solar fuel facilities require specialised chemical apparatus, reactors, and storage infrastructure, their capital expenditures are substantial, These unproven large-scale technologies require high borrowing rates from risk-averse lenders, in contrast to well-established solar PV, Additionally the "Green Premium" continues to be economically

unattractive to profit-driven investors in the absence of global carbon pricing to penalise fossil fuel externalities, impeding the shift away from conventional energy sources.[47]

5.9. Land Acquisition Issues:

Solar fuel projects have a problem when it comes to getting the land they need, The thing is that solar fuel projects need a lot of land, We are talking about 3 to 10 acres for every megawatt, This is a lot of space especially when you compare it to gas plants, which do not need that room, the other issue with fuel projects is that a lot of the records for the land are not up to date or are not even available on computers, This causes a lot of problems because people start arguing over who owns the land, Sometimes people even say that the land has been in their family for a long time, but they do not have any papers to prove it, All these issues make it really hard for solar fuel projects to get the land they need to capture sunlight on a large scale, Solar fuel projects really need a lot of space to work properly, This is a big deal for solar fuel projects.[48]

6. Future Research and Directions for Solar Fuels

6.1. Advanced Photocatalyst Development:

By 2026, photocatalyst research will have shifted from discovering bulk materials to achieving atomic-level precision, Instead of focusing solely on light absorption, scientists now use data-driven design to improve the chemical bond environment, To ensure maximum efficiency, research emphasises single-atom and dual-atom catalysts (SACs/DACs). By anchoring isolated metal atoms onto supports like TiO_2, these systems reach nearly 100% atom utilisation, significantly lowering the cost of using noble metals like platinum.[49]

6.2. Photoelectrochemical (PEC) Cell Optimisation:

The goal of research is to optimise photoelectrochemical cells using anticorrosive coatings and interface engineering, Charge separation is improved by using 2D/3D heterojunctions, and tandem perovskite-on-silicon devices have reached 35% efficiency, by addressing recombination and corrosion, these developments open the door to integrated, highly effective solar-to-hydrogen generation systems.[50]

6.3. Artificial Photosynthesis Systems:

By 2026, research on artificial photosynthesis has shifted to focus on industrial chemical production, Scientists are addressing efficiency challenges with nanotechnology and "cyborg" bacteria, Breakthroughs in plant-inspired molecules now allow for the storage of four charges through stepwise excitation, additionally semiconductor-coated bacteria, such as cyborg. thermotactic, capture low-intensity sunlight, These bio-hybrid systems eliminate the need for lasers, using solar energy to fuel internal metabolic processes that change CO_2 into valuable compounds like acetic acid.[51]

6.4. CO_2 Reduction to Solar Fuels:

Artificial photosynthesis, the process of converting CO_2 into solar fuels, is approaching a critical stage as research on renewable energy moves away from hydrogen and toward carbon-neutral fuels, In order to protect active sites and guarantee >90% selectivity even in purely aqueous environments, scientists are employing "Steric Shields" and molecular anchoring (such as Ni-terpyridine complexes on CdS quantum dots), MOFs are being used as "molecular scaffolds" to trap CO_2 molecules in high concentrations near the catalytic sites, greatly increasing reaction rates, This is the main challenge in the CO_2 reduction reaction (CO_2).[52]

6.5 Computational and AI-driven Materials Discovery:

Closed-loop autonomous discovery has transformed solar fuel research by substituting AI-driven robots and high-throughput computing for conventional trial-and-error, AI models create certain atomic configurations that satisfy required physical requirements in place of human testing, These technologies significantly speed up the search for stable, earth-abundant catalysts by quickly screening materials like perovskites and metal-organic frameworks by discovering novel "descriptors" for catalytic activity.[53]

6.6 Water Splitting Efficiency Improvements:

By using Value-Added Organic Reactions (VAORs), future solar fuel research seeks to avoid the slow oxygen evolution reaction (OER), Researchers reduce thermodynamic potential, enhance charge transfer, and produce high-value compounds in addition to green fuel by combining hydrogen evolution with the oxidation of biomass or plastic waste rather than creating oxygen.[54]

7. CONCLUSION

Despite its enormous potential as a clean and sustainable method for hydrogen production, photocatalytic water splitting still faces several significant challenges that limit its large-scale commercial application. These include photo-corrosion of semiconductor materials, rapid recombination of photogenerated electron–hole pairs, wide bandgaps that restrict visible-light utilization, and poor solar energy absorption efficiency. To overcome these limitations, researchers are adopting a variety of advanced strategies aimed at improving both the activity and stability of photocatalysts. Catalyst engineering plays a key role by incorporating co-catalysts, introducing surface modifications, and designing nanostructured materials to enhance charge separation, accelerate interfacial charge transfer, and improve long-term stability. In addition, bandgap engineering through doping, alloying, and tandem photocatalytic systems extends light absorption into the visible region while enhancing redox reaction kinetics. Technological innovations that combine photocatalysis with electrochemical methods, as well as photonic and plasmonic effects, further increase light-harvesting efficiency and accelerate reaction rates. Furthermore, computational tools such as density functional theory (DFT) provide valuable mechanistic insights, while machine learning (ML) enables predictive modelling and rapid discovery of high-performance photocatalytic materials. These integrated approaches have significantly enhanced the performance of widely studied catalysts such as TiO_2 and CdS. Ultimately, the transition toward scalable, efficient, and cost-effective hydrogen production will depend on continued advances in materials design, computational optimization, and innovative synthesis techniques.

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