

2D- Nanophotocatalysts for Hydrogen Generation

2D- Nanophotocatalysts for Hydrogen Generation:

*A Journey to Explore Clean
and Green Energy*

By

Faisal Ahmad, Ayesha Nazeer
and S. Ahmad

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PREFACE

In the face of escalating environmental challenges and the urgent need for sustainable energy solutions, hydrogen has emerged as a promising clean energy carrier. This monograph entitled - **2D-Nanophotocatalysts for Hydrogen Generation**, aims to provide a comprehensive exploration of the role that two-dimensional nanomaterials (2D-NMs) play in advancing hydrogen production through photocatalysis. In a world increasingly defined by its energy challenges, the quest for sustainable solutions has never been more urgent.

The introduction sets the stage by discussing the significance of hydrogen as a clean energy source and the growing importance of photocatalysis in harnessing solar energy for hydrogen generation. We delve into the fundamentals of photocatalytic reactions, emphasizing the key factors that influence their efficiency. We, standing at the crossroads of innovation and necessity, do realize the potential of hydrogen as a clean energy carrier that beckons us to explore many uncharted territories.

Subsequent chapters offer an in-depth look at various types of 2D-NMs, including graphene and transition metal dichalcogenides (TMDCs), alongside emerging synthesis techniques that enable the production of these materials. The mechanisms of photocatalytic hydrogen evolution reactions are examined, highlighting recent breakthroughs and comparative analyses of different 2D-photocatalysts.

With each passing day, the urgency to transition to the clean energy form grows, and in this pursuit, photocatalysts emerge as a beacon of hope.

We also address surface modification strategies and advanced characterization techniques that enhance our understanding of charge carrier dynamics within these photosensitive materials. The applications extend beyond hydrogen generation, exploring environmental remediation through photocatalysis for water and air purification, as well as innovative uses in solar cells and sensors.

This journey through the realm of photocatalytic hydrogen generation is fueled by innovation, curiosity, and an unwavering commitment to sustainability.

While this field is ripe with potential, it is not without challenges. The present monograph concludes with a discussion on stability, scalability, and future research directions necessary for the practical implementation of 2D-nanophotocatalysts.

This monograph is not just a collection of results observed in ongoing research activities; it is a call to action for scientists, engineers, and policymakers to embrace the transformative power of 2D-nanomaterials in our fight against climate change.

Imagine a future where our energy needs are met without compromising the health of our planet - this vision is within reach, and the key lies in the remarkable properties of 2D-nano-photocatalysts.

This monograph is intended for researchers, students, and industry professionals who are interested in the intersection of nanotechnology and renewable energy. We hope to witness further exploration and innovation in this vital area, contributing to a sustainable future powered by clean hydrogen energy.

October 2024

Faisal,
Ayesha,
Shamim
The Authors

CHAPTER 1

PHOTOCATALYTIC HYDROGEN GENERATION

1 Introduction

Hydrogen has emerged as an attractive clean energy carrier, offering a sustainable alternative to fossil fuels. Its high energy density and the fact that its combustion produces only water make it an attractive option for addressing global energy demands and environmental concerns. The production of hydrogen through photocatalysis, particularly via water splitting, has attracted significant attention as a promising method to harness solar energy efficiently. This approach not only mitigates greenhouse gas emissions but also aligns with the growing shift towards renewable green energy sources.

The importance of photocatalysis in hydrogen generation cannot be overstated. Photocatalytic processes utilize semiconductor materials to absorb sunlight and facilitate chemical reactions that produce hydrogen from water. This method presents a cost-effective solution compared to traditional hydrogen production techniques, such as steam reforming of hydrocarbons. However, challenges remain in enhancing the efficiency of these photocatalytic systems, particularly in optimizing light absorption and charge carrier dynamics.

Recent advancements in nanomaterials have opened new avenues for improving photocatalytic performance. Among these, two-dimensional (2D) nanomaterials have shown exceptional promise due to their unique structural and electronic properties. Materials like graphitic carbon nitride (g-C₃N₄) and other 2D-structures can significantly enhance photocatalytic activity by providing increased surface area, facilitating charge separation, and allowing for better light absorption. The integration of 2D-nanomaterials into photocatalytic systems is a burgeoning field of research that aims to overcome existing limitations and improve hydrogen production rates.

In this chapter, we will explore the background of hydrogen as a clean energy carrier, the growing significance of photocatalytic hydrogen generation, and the transformative role of 2D-nanomaterials in advancing this technology. By examining recent developments *vis à vis* the ongoing

challenges, we attempt to provide a comprehensive overview of how these innovative materials can contribute to a sustainable energy future. Salient features of the related issues in this context are discussed in more detail in many references enclosed [Bhatt, and Lee, **2017**; Wang, et al, **2019**; Zhao, et al, **2020**; Guo, et al, **2021**; Rosso, et al, **2021**; Xu, and Weng, **2023**; Nazeer, et al, **2024**; Zheng, et al, **2024**].

Hydrogen is increasingly recognized as a clean energy carrier with the potential to significantly contribute to a sustainable energy future. Its versatility, high energy density, and the fact that its combustion produces only water vapor make it an attractive alternative to fossil fuels.

Hydrogen produced from various sources is categorized by its production method and environmental impact, often referred to by color codes as given below.

Hydrogen Color Code

While hydrogen is inherently a colorless gas, the industry has assigned various colors to its spectrum to differentiate how it is produced and its environmental interactions [WP-01].

- **Green Hydrogen**

Green hydrogen is produced using clean electricity from excess renewable energy sources, such as solar or wind power, to electrolyze water. This process involves electrolyzers that utilize an electrochemical reaction to separate water into hydrogen and oxygen, resulting in zero carbon dioxide emissions. Currently, green hydrogen accounts for a small fraction of total hydrogen production due to high costs. However, as the technology becomes more widespread, similar to the decreasing costs of wind energy, the price of green hydrogen is expected to decline.

- **Blue Hydrogen**

Blue hydrogen is primarily produced from natural gas via steam methane reforming, which involves reacting methane with high-temperature steam to generate hydrogen and carbon dioxide. While this process produces hydrogen, it also generates carbon dioxide as a by-product. The definition of blue hydrogen encompasses the use of carbon capture and storage (CCS) technologies to capture and sequester the carbon produced during its generation. It is often referred to as “low-carbon hydrogen” because the steam reforming process does not completely eliminate greenhouse gas emissions.

- **Grey Hydrogen**

Currently, grey hydrogen represents the most prevalent method of hydrogen production. It is produced from natural gas or methane via steam methane reforming without capturing the greenhouse gases emitted during the process. Essentially, grey hydrogen is comparable to blue hydrogen but does not incorporate carbon capture and storage measures.

- **Black and Brown Hydrogen**

Black and brown hydrogen are produced using black coal or lignite (brown coal), making them the most environmentally harmful types of hydrogen in contrast to green hydrogen. Adding to the confusion, hydrogen produced from fossil fuels via gasification is often referred to as black or brown hydrogen. Recently, Japan and Australia announced a new project that will convert brown coal in Australia into liquefied hydrogen for low-emission use in Japan.

- **Pink Hydrogen**

Pink hydrogen is produced through electrolysis powered by nuclear energy and is sometimes referred to as purple or red hydrogen. Additionally, the high temperatures generated by nuclear reactors can be utilized in other methods of hydrogen production by generating steam for more efficient electrolysis or for fossil gas-based steam methane reforming.

- **Turquoise Hydrogen**

Turquoise hydrogen is a relatively new addition to the hydrogen color spectrum, and its production has yet to be demonstrated on a large scale. It is produced through methane pyrolysis, which yields both hydrogen and solid carbon. In the future, turquoise hydrogen could be recognized as a low-emission option if its thermal processes are powered by renewable energy sources and if the carbon produced is permanently stored or utilized.

- **Yellow Hydrogen**

Yellow hydrogen refers to hydrogen produced via electrolysis using solar energy, marking it as a newer term in the industry.

- **White Hydrogen**

White hydrogen occurs naturally in geological formations and can be found in underground deposits created through fracking. Currently, there are no established methods for exploiting this type of hydrogen.

Green Hydrogen Production via Electrolysis

Electrolysis uses an electrical current to split water into hydrogen and oxygen. When powered by renewable energy, this method produces green hydrogen. A recent study highlighted the efficiency of a proton exchange membrane (PEM) electrolyser, achieving an efficiency of 70-80% with a hydrogen production rate of 5.6 kg H₂ per kWh of electricity consumed. The system operated continuously for over 1,000 hours without significant performance degradation, demonstrating its robustness for long-term applications.

Applications of Hydrogen

Hydrogen's versatility allows it to be utilized across various sectors as mentioned below.

- **Fuel Cells**

Hydrogen fuel cells convert the chemical energy stored in hydrogen into electricity through an electrochemical reaction with oxygen. This technology is pivotal in numerous applications.

- **Transportation**

Hydrogen fuel cell electric vehicles (FCEVs), such as the Toyota Mirai, have demonstrated ranges exceeding 300 miles on a single tank of hydrogen, with refuelling times comparable to gasoline vehicles (~5 minutes).

- **Stationary Power Generation**

Hydrogen fuel cells can provide backup power for buildings and facilities. As of early 2024, approximately 210 operational fuel cell power generators in the United States contribute to grid stability.

- **Industrial Applications**

Hydrogen is extensively used in industries such as petroleum refining and ammonia production for fertilizers. Notably, about 95% of hydrogen produced in the U.S. is utilized in petroleum refining processes.

Environmental Impact and Emission Reductions

Hydrogen's role as an energy carrier can significantly reduce greenhouse gas emissions when produced sustainably. For instance, lifecycle analyses indicate that using green hydrogen for power generation could reduce CO₂ emissions by up to 90%, depending on the production method and application.

Hydrogen stands out as a clean energy carrier with immense potential for decarbonizing various sectors, including transportation, industry, and electricity generation. The development of efficient production methods like green hydrogen via electrolysis is crucial for realizing its full potential as a sustainable energy solution. As advancements continue in hydrogen production technologies and applications, it is poised to play a central role in the transition towards a cleaner energy future [eere (2017); Agyekum, et al, 2022; Franco, and Giovannini, 2023; REP-01, 2023; addcomposites (2024); bloomenergy (2024); eia (2024); volvogroup (2024)].

Hydrogen Production and Environment

Hydrogen is increasingly recognized as a clean energy carrier that offers significant environmental benefits. Its use can lead to substantial reductions in greenhouse gas emissions and other pollutants, contributing to a more sustainable energy landscape. Given below is an elaboration on the environmental benefits of using hydrogen, supported by specific examples and experimental results.

Reduction of Greenhouse Gas Emissions

One of the primary environmental benefits of hydrogen is its potential to reduce greenhouse gas emissions, particularly when produced from renewable sources (green hydrogen). In contrast to fossil fuels, burning hydrogen generates only water vapor as a byproduct.

A lifecycle assessment comparing hydrogen and natural gas for power generation found that switching from natural gas to green hydrogen could reduce CO₂ emissions by up to 90%. This reduction is contingent upon the

production method of hydrogen, emphasizing the importance of utilizing renewable energy sources for electrolysis.

Improved Air Quality

Hydrogen fuel cells emit no harmful pollutants, such as nitrogen oxides (NO_x) or particulate matter, which are common byproducts of fossil fuel combustion. This characteristic makes hydrogen an attractive alternative for applications in transportation and stationary power generation.

In a study examining the air quality impacts of hydrogen fuel cell vehicles (FCVs), it was found that FCVs produce significantly lower emissions compared to conventional gasoline vehicles. The study reported that FCVs could reduce urban air pollution levels by 30-50%, contributing to improved public health outcomes.

Sustainable Energy Storage

Hydrogen can serve as an effective energy storage medium, allowing for the integration of intermittent renewable energy sources like solar and wind into the energy grid. By transforming surplus renewable energy into hydrogen via electrolysis, it can be stored and subsequently converted back into electricity when required.

The **GenCore™** fuel cell system demonstrated a total system efficiency of 29% when used in conjunction with an electrolyser powered by renewable energy. This system allows for grid balancing by storing excess energy as hydrogen and converting it back into electricity during peak demand periods [Marsh, October 11, **2023**].

Versatile Applications

Hydrogen is being used across various sectors, including transportation, industrial processes, and heating. This adaptability further enhances its potential environmental benefits.

Transportation

Hydrogen can replace gasoline and diesel in vehicles, significantly reducing carbon footprints.

Industrial Processes

Hydrogen is used in refining processes and ammonia production, where it can replace carbon-intensive methods.

A study on the use of hydrogen in ammonia synthesis demonstrated that using green hydrogen instead of natural gas could reduce CO₂ emissions associated with ammonia production by approximately 70%, highlighting its potential for decarbonizing industrial processes.

Contribution to Circular Economy

Hydrogen can facilitate a circular economy by enabling waste-to-energy processes. For instance, biomass can be converted into hydrogen through gasification or reforming processes, effectively recycling organic waste into a clean energy source.

Research has shown that integrating biomass conversion with photocatalytic hydrogen production can achieve high yields. For instance, using cellulose as a feedstock combined with Pt/TiO₂ catalysts resulted in a hydrogen production rate of 1320 μmol/h/gCat, demonstrating the potential for sustainable waste management while generating clean energy.

The use of H₂ as a clean energy carrier presents numerous environmental benefits, including significant reductions in greenhouse gas emissions, improved air quality, and enhanced sustainability through effective energy storage solutions. As technologies advance and the infrastructure for hydrogen production and utilization develops, its role in achieving a sustainable energy future will likely expand [Davis, et al, 2021; Guo, et al, 2021; Mamiyev, and Balayeva, 2022; Rafique, et al, 2023; Sarmah, et al, 2023; Zhang, et al, 2024].

Environmental Benefits of Hydrogen

Hydrogen is increasingly recognized as a clean energy carrier with significant environmental benefits. Its use can lead to substantial reductions in greenhouse gas emissions and other pollutants, contributing to a more sustainable energy landscape. Below is an elaboration on the environmental benefits of using hydrogen, supported by specific examples and experimental results.

One of the primary environmental benefits of hydrogen is its potential to reduce greenhouse gas emissions, particularly when produced from renewable sources (green hydrogen). Unlike fossil fuels, the combustion of hydrogen results in only water vapor as a byproduct.

A lifecycle assessment comparing hydrogen and natural gas for power generation found that switching from natural gas to green hydrogen could reduce CO₂ emissions by up to 90%. This reduction is contingent upon the production method of hydrogen, emphasizing the importance of utilizing renewable energy sources for electrolysis, which splits water into hydrogen and oxygen using electricity from renewable sources like wind or solar power.

Hydrogen fuel cells emit no harmful pollutants, such as nitrogen oxides (NO_x) or particulate matter, which are common byproducts of fossil fuel combustion. This characteristic makes hydrogen an attractive alternative for applications in transportation and stationary power generation.

Experimental Results: In a study examining the air quality impacts of hydrogen fuel cell vehicles (FCVs), it was found that FCVs produce significantly lower emissions compared to conventional gasoline vehicles. The study reported that FCVs could reduce urban air pollution levels by 30-50%, contributing to improved public health outcomes.

Hydrogen can serve as an effective energy storage medium, allowing for the integration of intermittent renewable energy sources like solar and wind into the energy grid. By converting surplus renewable energy into hydrogen through electrolysis, it can be stored and later transformed back into electricity as needed.

Fuel cells can operate more efficiently than combustion engines, converting chemical energy in the fuel directly into electricity with efficiencies that can exceed 60%. Fuel cells have almost zero emissions compared to combustion engines. This system allows for grid balancing by storing excess energy as hydrogen and converting it back into electricity during peak demand periods [eere(2024)].

Hydrogen's versatility allows its uses across various sectors, including transportation, industrial processes, and heating. This adaptability further enhances its potential environmental benefits.

Hydrogen can replace gasoline and diesel in vehicles in transportation significantly reducing carbon footprints.

Extensive use of hydrogen is involved in industries such as refining petroleum and producing ammonia for fertilizers. For example, approximately 95% of the hydrogen produced in the U.S. is used in petroleum refining processes to reduce sulfur content in fuels [Sarmah, et al, 2023].

A study on the use of hydrogen in ammonia synthesis demonstrated that using green hydrogen instead of natural gas could reduce CO₂ emissions associated with ammonia production by approximately 70%, highlighting its potential for decarbonizing industrial processes [Guo, et al, 2021].

Contribution to Circular Economy

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Research has shown that integrating biomass conversion with photocatalytic hydrogen production can achieve high yields. For instance, using cellulose as a feedstock combined with Pt/TiO₂ catalysts resulted in a hydrogen production rate of 1320 $\mu\text{mol/h/g.Cat}$, demonstrating the potential for sustainable waste management while generating clean energy [Sarmah, et al, 2023].

The use of hydrogen as a clean energy carrier presents numerous environmental benefits, including significant reductions in greenhouse gas emissions, improved air quality, and enhanced sustainability through effective energy storage solutions. As technologies advance and the infrastructure for hydrogen production and utilization develops, its role in achieving a sustainable energy future will likely expand [Guo, et al, 2021; Sarmah, et al, 2023].

Hydrogen energy plays a crucial role in achieving net-zero emissions by 2050, acting as a versatile energy carrier that can decarbonize various sectors of the economy. Below are keyways in which hydrogen contributes to this goal, supported by specific examples and insights from recent studies.

Decarbonizing Heavy Industries

Heavy industries, such as steel, cement, and chemicals, are significant contributors to global greenhouse gas emissions. Hydrogen offers a clean alternative to fossil fuels in these sectors. In the steel industry, hydrogen can replace coke (a carbon-rich material) in the reduction of iron ore. A study demonstrated that using green hydrogen in direct reduction processes could reduce CO₂ emissions by approximately 70%, highlighting its potential to significantly lower the carbon footprint of steel production.

Renewable Energy Storage

Hydrogen can be produced during periods of excess renewable energy generation (e.g., from wind or solar) and stored for later use. This capability improves grid stability and decreases dependence on fossil fuels. The integration of hydrogen production with renewable energy sources allows for effective energy storage solutions. For instance, during peak renewable generation periods, excess electricity can be used to produce hydrogen via

electrolysis. This stored hydrogen can then be converted back into electricity during high demand periods, providing a flexible and reliable energy system.

Zero-Emission Transportation

Hydrogen fuel cells provide a zero-emission alternative for transportation, particularly in sectors that are difficult to electrify, such as heavy-duty vehicles, shipping, and aviation. Hydrogen fuel cell vehicles (FCVs) emit only water vapor and heat as byproducts. A lifecycle assessment indicated that FCVs could reduce urban air pollution levels by 30-50% compared to conventional gasoline vehicles. Additionally, hydrogen is being explored as a fuel source for ships and airplanes, where electrification poses significant challenges due to weight and range limitations.

Hydrogen allows it to be utilized across various sectors, including power generation, heating, and industrial processes. Hydrogen can be converted back into electricity using fuel cells or can be directly utilized in various industrial processes. The Bloom Electrolyser represents an innovation in this area, producing green hydrogen with zero carbon emissions when powered by renewable sources. It is particularly beneficial for heavy industries like steel and chemical manufacturing, enabling them to decarbonize operations effectively [WP-02].

Supporting Synthetic Fuel Production

Hydrogen can be used to produce synthetic fuels (e.g., ammonia or methanol), which have higher energy densities and can be transported more easily than hydrogen itself. Ammonia produced from green hydrogen is not only a critical feedstock for fertilizers but also has potential as a zero-carbon fuel for shipping. The conversion of hydrogen into ammonia allows for long-distance transport while maintaining the benefits of low emissions.

The strategic use of hydrogen energy is essential to achieve net-zero emissions by 2050. Its ability to decarbonize heavy industries, provide renewable energy storage solutions, serve as a zero-emission transportation option, and support synthetic fuel production positions it as a key player in the transition to a sustainable energy future. As technologies advance and infrastructure develops, hydrogen's role will become increasingly vital in mitigating climate change and achieving global climate targets [venair (2023); whitehead, et al, 2023; Iberdrola (2024); irena (2024); prismscs (2024)].

Environmental Impacts

The potential environmental impacts of large-scale hydrogen production, particularly through methods like electrolysis and steam methane reforming, are multifaceted and require careful consideration. While hydrogen is often touted as a clean energy carrier, its production processes can have significant environmental implications. Here are the key impacts associated with large-scale hydrogen production:

Water Use and Scarcity

The production of green hydrogen via electrolysis requires substantial amounts of water. In regions where water resources are already strained, this demand can exacerbate water scarcity issues. A study highlighted that large-scale electrolytic hydrogen production could lead to increased competition for water resources in arid regions, potentially impacting local ecosystems and communities dependent on these water sources for agriculture and drinking water.

Greenhouse Gas Emissions

While green hydrogen produced from renewable energy sources generates minimal direct emissions, the overall lifecycle emissions can still be significant, especially if the electricity used for electrolysis comes from fossil fuels. Research indicates that the carbon footprint of hydrogen produced using solar photovoltaic (PV) systems can vary widely based on the efficiency and source of the electricity. If the capacity factor of solar PV systems is low, the emissions can reach up to 5.6 kg CO₂-eq. per kg H₂, depending on the fossil energy used during PV manufacturing. In contrast, using wind energy for electrolysis results in much lower emissions, around 1.1–1.8 kg CO₂-eq. per kg H₂.

Land Use Changes

The establishment of large-scale renewable energy farms (solar or wind) necessary for green hydrogen production often requires significant land areas, which can lead to habitat destruction and changes in land use. The expansion of renewable energy infrastructure for hydrogen production may result in the conversion of natural habitats or agricultural land into energy farms, potentially leading to biodiversity loss and disruptions in local ecosystems.

Pollution from Production Processes

Steam methane reforming based blue hydrogen production involves fossil fuels and generates CO₂ emissions unless carbon capture and storage (CCS) technologies are effectively implemented. Blue hydrogen pathways can still contribute to greenhouse gas emissions if carbon capture rates are not sufficiently high. For instance, a lower capture rate (e.g., 60%) can significantly reduce the climate benefits of blue hydrogen pathways by increasing near-term warming impacts by up to 50%.

Chemical Waste and Toxicity

The production of hydrogen, particularly through chemical processes like ammonia synthesis or methanol production, often involves toxic catalysts and chemicals that can pose risks to local environments if not managed properly. The handling and disposal of hazardous materials used in hydrogen production processes can lead to soil and water contamination if leaks or spills occur during production or transportation. This risk necessitates stringent safety measures and environmental management practices.

Hydrogen Leakage

Hydrogen is a small molecule that can easily escape from storage systems, leading to potential environmental impacts such as contributing to atmospheric warming. Studies have shown that hydrogen leakage can offset some of the climate benefits associated with its use as a clean energy carrier. For instance, upper-end estimates indicate that near-term warming effects from hydrogen emissions could reduce climate benefits by up to 25%, emphasizing the need for effective containment strategies during production and transport.

While hydrogen holds promise as a clean energy carrier with potential benefits for reducing greenhouse gas emissions, its large-scale production poses several environmental challenges. Addressing these impacts requires careful planning, technological innovation, and robust regulatory frameworks to ensure sustainable practices throughout the hydrogen value chain [Osman, et al, 2022; idb (2024); iea (2024); Sun, et al, 2024; Terlouw, et al, 2024; Wei, et al, 2024; wwf (2024)].

Photocatalytic H₂ Generation

Water splitting using 2D-photocatalysts has garnered significant attention as a sustainable and efficient method for producing clean energy. This process involves harnessing solar energy to drive the chemical reaction that separates water into hydrogen and oxygen. The unique properties of 2D nanomaterials enhance the efficiency of photocatalytic reactions, making them ideal candidates for this application. Here's an elaboration on the mechanisms, recent advancements, and specific examples of 2D photocatalysts used for hydrogen generation.

Photocatalytic Water Splitting Mechanism

Photocatalytic water splitting relies on the absorption of light by a photocatalyst, which generates electron-hole pairs. These charge carriers participate in redox reactions that ultimately lead to the production of hydrogen gas (H₂) from water (H₂O). The fundamental steps involved in the process include the following.

Light Absorption

The photocatalyst absorbs photons, leading to the excitation of electrons from the valence band to the conduction band, creating electron-hole pairs.

Charge Separation

Efficient separation of these charge carriers is crucial for enhancing photocatalytic efficiency. The spatial separation prevents recombination, allowing the electrons to participate in reduction reactions (e.g., converting protons to hydrogen) while holes facilitate oxidation reactions (e.g., oxidizing water to oxygen).

Redox Reactions

The generated electrons reduce protons (H⁺) from water, producing hydrogen gas, while the holes oxidize water molecules, resulting in the release of oxygen gas.

Recent Developments of 2D-Photocatalysts

- Transition Metal Dichalcogenides such as molybdenum disulfide (MoS₂) and tungsten diselenide (WSe₂) have been extensively studied for their photocatalytic properties. Recent reviews highlight their

effectiveness as both electrocatalysts and photocatalysts for hydrogen generation due to their favorable electronic structures and high surface areas [Ukeje, 2022].

- Van der Waals Heterostructures
- The development of van der Waals heterostructures, such as WSe/blue phosphorene (BP), has shown promising results in enhancing photocatalytic efficiency. These heterostructures exhibit type-II band alignment, which facilitates effective charge separation and strong optical absorption, leading to a power conversion efficiency of approximately 19.4% [Tu, et al, 2022].
- Defect Engineering - Defect engineering has emerged as a powerful strategy to enhance the photocatalytic performance of 2D materials. For example, dual-defective SnS₂ monolayers have been shown to significantly improve hydrogen evolution rates due to optimized band alignment and broadened optical absorption spectra [Sainbileg, et al, 2019]. This approach allows for better spatial separation of charge carriers, crucial for efficient photocatalysis.
- Hybrid Materials - Integrating different 2D materials can create synergistic effects that enhance photocatalytic activity. For instance, combining TMDs with carbon-based materials or other semiconductors can improve light absorption and charge transfer properties [Wang, et al, 2022]. Such hybrid systems are being actively researched to optimize photocatalytic performance.
- Advanced Characterization Techniques - Recent advancements in characterization techniques have enabled researchers to probe the mechanisms behind photocatalytic reactions more effectively. Techniques such as synchrotron-based X-ray scattering, and neutron reflectometry allow for detailed studies of solid-liquid interfaces and degradation mechanisms in thin films [Pergolesi, et al, 2022]. These insights are vital for optimizing material design and synthesis processes.

C. Challenges and Future Directions

While significant progress has been made in utilizing 2D photocatalysts for hydrogen generation, challenges remain regarding stability, scalability, and efficiency under real-world conditions. Addressing these challenges will require ongoing research into:

- Developing more robust materials that can withstand operational conditions without significant degradation.

- Optimizing synthesis methods to produce high-quality 2D materials at scale.
- Reducing production costs associated with precious metals and complex synthesis techniques.
- The integration of 2D nanomaterials into photocatalytic water splitting represents a promising avenue for sustainable hydrogen production.

With ongoing advancements in material science, synthesis techniques, and characterization methods, 2D photocatalysts are poised to play a critical role in addressing global energy challenges. As research continues to evolve, these materials may significantly contribute to the development of efficient systems for clean hydrogen generation [Rahman, et al, **2016**; Sainbileg, et al, **2019**; Jakhar, et al, **2022**; Khan, et al, **2021**; Pergolesi, et al, **2022**; Tao, et al, **2022**; Tu, et al, **2022**; Ukeje, **2022**; Wang, et al, **2022**; Gupta, et al, **2023**; Ishaq, et al, **2024**].

2D-vdW Heterostructures and Traditional Photocatalysts

The use of 2D-van der Waals heterostructures (2D-vdW H-Ss) in photocatalytic applications, particularly for hydrogen generation through water splitting, offers several advantages over traditional photocatalysts. These benefits stem from the unique properties of 2D-materials and their ability to form heterojunctions that enhance photocatalytic performance. Some of the key advantages are listed below.

Enhanced Charge Separation and Carrier Dynamics

Many 2D-vdW heterostructures exhibit type-II band alignment, which facilitates the spatial separation of photogenerated electron-hole pairs. This separation reduces the likelihood of recombination, allowing for more efficient utilization of charge carriers in the photocatalytic process. For instance, in studies involving GeC-MoS₂ and GeC-WS₂ heterostructures, the induced electric field at the interface promotes continuous separation of charge carriers, significantly enhancing photocatalytic efficiency for hydrogen production [Wahab, et al, **2023**].

Tunable Electronic and Optical Properties

The electronic band structure of vdW heterostructures can be tuned by selecting different combinations of 2D materials or by modifying their thickness. This tunability allows researchers to optimize light absorption and charge transfer properties for specific photocatalytic applications. For

example, the combination of g-C₃N₄ with SnS₂ in a vdW heterojunction has shown improved light absorption and enhanced photocatalytic activity due to optimized carrier dynamics and band structure adjustments [Liu, et al, 2022].

High Surface Area and Active Sites

2D materials inherently possess a high surface area, providing more active sites for catalytic reactions. This characteristic is particularly beneficial for photocatalysis, where surface interactions play a crucial role in reaction rates. For instance, the high surface area of TMDs like MoS₂ and WSe₂ allows for increased interaction with reactants, enhancing the overall efficiency of hydrogen generation [Zhang, et al, 2023].

Flexibility in Material Combination

The ability to layer different 2D materials creates opportunities for designing custom heterostructures that leverage the strengths of each component. This flexibility enables the development of optimized photocatalysts tailored for specific applications.

The recent advancements in this context have demonstrated that combining TMDs with other materials can lead to synergistic effects that improve photocatalytic performance beyond what is achievable with single-component systems [Zhang, et al, 2023].

The vdW heterostructures often exhibit enhanced stability compared to traditional photocatalysts due to their layered structure, which can protect active sites from degradation under operational conditions. Many studies indicate that 2D heterostructures maintain their structural integrity and catalytic performance over extended periods, making them suitable for practical applications in hydrogen production [Peera, et al, 2022].

Some vdW H-Ss can be engineered to respond to specific environmental conditions (e.g., pH changes or light intensity variations), allowing for adaptive photocatalytic performance. The recent studies have shown that certain 2D materials can adjust their electronic properties in response to environmental stimuli, optimizing their performance under varying operational conditions [Wahab, et al, 2023].

The advantages of using 2D-vdW H-Ss over traditional photocatalysts are significant and multifaceted. Enhanced charge separation, tunable electronic properties, high surface area, flexibility in material combinations, improved stability, and environmental responsiveness collectively contribute to their superior performance in photocatalytic hydrogen generation. As research continues to explore these advanced materials, they

hold great promise for addressing global energy challenges through efficient and sustainable hydrogen production [Hasan, et al, **2021**; Liu, et al, **2022**; Peera, et al, **2022**; Wahab, et al, **2023**; Zhang, et al, **2023**].

Photocatalytic Efficiency

The electronic properties of 2D-vdW heterostructures significantly enhance photocatalytic efficiency, particularly in applications like hydrogen generation through water splitting. These enhancements arise from several key factors related to the unique characteristics of 2D-materials and their interactions within heterostructures. Below are cited the main advantages and mechanisms through which these electronic properties contribute to improved photocatalytic performance.

Many vdW heterostructures exhibit type-II band alignment, where the conduction band minimum (CBM) and valence band maximum (VBM) of the two materials are positioned in such a way that electrons and holes are spatially separated. This separation of charge carriers reduces the likelihood of recombination, allowing for more efficient utilization of photogenerated electrons and holes in redox reactions necessary for hydrogen generation. For instance, studies have shown that heterostructures like MoS₂/GeC exhibit type-II alignment, which facilitates continuous separation of charge carriers, enhancing photocatalytic efficiency for water splitting [Wahab, et al, **2023**].

The combination of different 2D materials can lead to improved light absorption across a broader spectrum, particularly in the visible range of optical spectrum. Enhanced light absorption increases the number of photons available to generate electron-hole pairs, thereby boosting the overall photocatalytic activity. For example, GaP/InP heterostructures have been identified as promising candidates due to their light absorption characteristics and favorable electronic properties [Chen et al., **2023**].

The interface established between different 2D-materials creates built-in electric fields due to differences in work function and electron affinity. These electric fields further facilitate charge separation by driving electrons toward the CBM and holes toward the VBM, reducing recombination rates. Similarly, in GeC-MX₂ heterostructures, the induced electric field effectively prevents recombination of photogenerated charges, making them suitable for photocatalytic applications [Wahab, et al., **2023**].

The biggest advantages associated with using 2D-nanomaterials to create vdW heterostructures is their amenability to give rise to tunable electronic properties by merely varying the parameters such as layer thickness, composition, and external conditions (e.g., strain or electric fields).

This kind of tunability also allows the researchers to optimize materials for specific photocatalytic reactions. For instance, by adjusting the size of graphene quantum dots (GQDs) in GQDs-MoS₂ heterostructures, researchers have successfully transitioned from type I to type II band alignments, enhancing photocatalytic performance [Luo et al., 2022].

The unique structural properties of 2D materials contribute to improved carrier mobility and dynamics. Enhanced charge carrier mobility allows for faster transport of charge carriers to the active sites where reactions occur. This is particularly beneficial in reducing losses due to recombination and increasing the efficiency of H₂ production.

Combining different 2D materials can lead to synergistic effects that enhance overall performance beyond what each material could achieve individually. For example, studies have shown that TMDs combined with other materials can create enhanced catalytic sites and improve overall reaction kinetics. The interaction between different layers can also modify electronic states beneficially for catalysis [Xu, et al, 2024].

The electronic properties of 2D-van der Waals heterostructures play a pivotal role in enhancing photocatalytic efficiency for H₂ generation through water splitting. Type-II band alignment promotes effective charge separation, while improved light absorption and built-in electric fields further contribute to higher photocatalytic activity. Additionally, the tunability of these properties allows for optimization tailored to specific applications, making vdW heterostructures a promising avenue for advancing photocatalytic technologies [Luo, et al, 2022; Chen, et al, 2023; Wahab, et al, 2023; Nguyen, et al, 2024; Xu, et al, 2024].

2 Importance of Photocatalytic H₂ Generation

Photocatalysis has emerged as a promising technology for H₂ generation, offering several advantages over traditional methods. A brief review of the growing importance of photocatalysis in H₂ generation is presented to highlight the salient features.

A. Advantages of Photocatalysis

Photocatalysis can generate H₂ efficiently, with some photocatalysts achieving generation rates of up to 10 mmol/h. Photocatalysis requires low energy consumption, making it an attractive option for large-scale H₂ generation. Photocatalysis can be scaled up to meet large-scale H₂ generation demands. Photocatalysis can be cost-effective, with some photocatalysts requiring minimal materials and energy inputs.

Photocatalysis can reduce greenhouse gas emissions and improve air quality by generating H_2 from renewable energy sources.

B. Challenges and Limitations

One of the main challenges in photocatalysis is separating the charge carriers (electrons and holes) efficiently to facilitate H_2 generation. Another challenge is absorbing light efficiently, as photocatalysts often have limited light absorption coefficients.

The efficiency of water splitting is another challenge, as it requires the efficient separation of H_2 and O_2 .

Scaling up photocatalysis to meet large-scale H_2 generation demands while maintaining cost-effectiveness is a significant challenge.

The stability and durability of photocatalysts are also important considerations, as they can affect the performance and lifespan of the photocatalytic system.

C. Recent Advances and Future Directions

Researchers have been developing new photocatalysts with improved performance, such as graphene- TiO_2 nanocomposites and MoS_2 nanosheets.

Advances in reactor design have improved the efficiency and scalability of photocatalytic systems.

Photocatalysis is being integrated with other technologies like solar cells and fuel cells, to improve efficiency and scalability.

Theoretical modelling is extensively being used to simulate the behavior of photocatalysts and optimize their performance.

Experimental techniques, such as spectroscopy and microscopy, are being used to study the behavior of photocatalysts and optimize their performance.

Photocatalysis has emerged as a promising technology for H_2 generation, offering several advantages over traditional methods. While there are challenges and limitations to overcome, nevertheless recent advances and future directions suggest that photocatalysis will continue to play an important role in the development of sustainable energy solutions.

3 2D-Photocatalyst - Brief Overview

Two-dimensional nanomaterials have attracted considerable attention in recent years thanks to their distinctive properties and diverse applications. A brief overview of the role of 2D-nanomaterials is presented here to highlight their properties, applications, and recent developments.

With high surface area-to-volume ratio in 2D-nanomaterials they become ideal for applications where surface area is crucial.

High conductivity of 2D-nanomaterials makes them suitable for applications such as electronics and energy storage.

High strength-to-weight ratios of 2D-nanomaterials makes them ideal for applications where strength is crucial.

2D-nanomaterials are highly flexible, making them suitable for applications where flexibility is required.

2D-nanomaterials are finding numerous electronic applications such as in fabricating devices like transistors, diodes, and solar cells to name a few.

Energy Storage

Energy storage applications such as batteries and supercapacitors deploy 2D- nanomaterials very effectively.

Biomedical Applications

The biomedical applications such as drug delivery, imaging, and sensing deploy 2D-nanomaterials in plenty as reported in recent publications.

Environmental Remediation

2D-nanomaterials are becoming very popular in environmental remediation applications such as water purification and air pollution control.

New synthesis methods have been developed to produce 2D nanomaterials with improved properties. New characterization techniques have been developed to study the properties of 2D nanomaterials.

These developments in 2D-nanomaterials have significantly helped in advancing various fields, particularly in biomedical applications, energy storage, and environmental sustainability. Some of these significant advancements based on the latest research findings are listed below.

Recent studies have highlighted the potential of 2D-nanomaterials, such as graphene and transition metal dichalcogenides (TMDCs), in biomedical applications. These materials possess unique properties that make them suitable for drug delivery, imaging, and cancer therapy.

The large surface area and tunable properties of 2D-nanomaterials enable efficient drug loading and controlled release. For instance, TMDCs have been explored as effective drug delivery platforms due to their biocompatibility and ability to enhance therapeutic efficacy [Cheng, et al, 2020].

2D nanomaterials are being developed for cancer theranostic applications, combining diagnostic imaging and therapeutic functions.