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Fabricating advanced functional materials for Hydrogen evolution reaction applications

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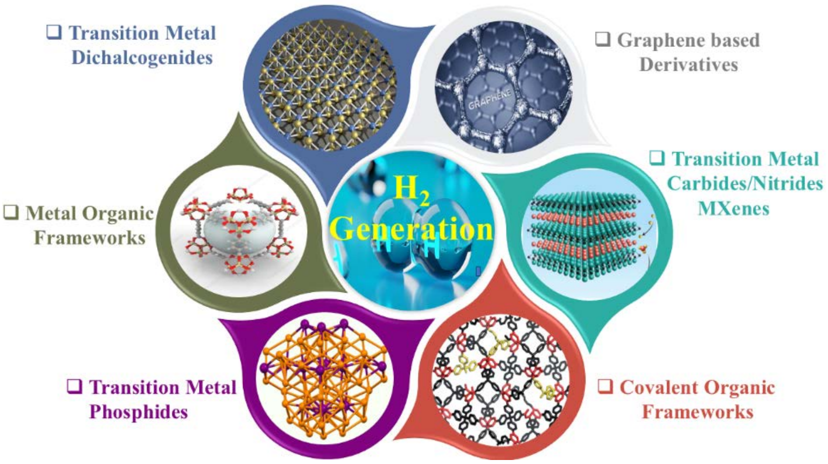
Review

ABSTRACT



Nano-engineering advanced functional materials for hydrogen evolution reaction via overall water splitting is an emerging area that is currently the epicentre for producing green hydrogen as a sustainable energy resource. Hydrogen evolution reaction (HER) is one-half of the water-splitting process (the other being the oxygen evolution reaction, and demands the surface of the catalytic system to lower the activation energy of the overall water splitting (OWS) process. Fabricating the highly active catalysts involves the development of nanostructured, multi-metallic, and heterostructured catalysts with a focus on improving catalytic efficiency, stability, and cost-effectiveness. Bottom-up approaches such as hydrothermal synthesis, sol-gel route, chemical vapor deposition, and reverse-micellar methods are key in producing materials with high surface areas, well-exposed active sites, and facilitated electron transfer capabilities. Herein, we have categorized the different next-generation catalytic systems employed for HER applications based on their classes, synthetic routes, and performance during OWS. We have also given a precise understanding of the role of advanced functional nanomaterials in hydrogen storage applications. We believe this article will provide conceptual guidance to the researchers aiming to contribute to energy conversion applications.

Keywords: *Nanostructures; Advanced materials; Hydrogen energy; Bottom-up routes; Sustainable adaptability.*

INTRODUCTION

The present economy of the energy sector is heavily dependent upon fossil-derived energy (coal, oil, and natural gas) and these non-renewable resources continue to be the dominant sources of global energy. However, there is a paradigm shift underway due to the alarming stage of climate change, international environmental protocols, technological advancements, and evolving economic landscapes. Fossil derivatives still account for the majority of the world's energy supply, for instance, despite its high carbon footprints, coal remains a primary energy source for electricity generation, especially in nations such as China and India. However, the global exhaustion of coal is peaking or slightly declining as nations phase out coal plants, specifically in the countries where coal deposits are not found. Similarly, oil remains the primary supply for automobiles and comprises nearly 31% of the global energy mix [1-4]. It is pivotal for almost every transportation mode, however, its dependency is gradually limiting across the world as sustainable energy adoption is increasing. Sustainable energy solutions encompass renewable energy technologies, efficiency measures, storage solutions, and innovative ideas for energy management and reduction in carbon footprints [5-7]. These approaches systematically aim to create an energy ecosystem that involves sustainable processes and is capable of meeting the needs of a growing population and simultaneously mitigating environmental impacts. Scaling up these solutions is crucial to addressing the twin challenges of climate change and energy security while fostering sustainable economic growth. Hydrogen (H_2) fuel has the potential to significantly contribute to a sustainable energy future. It can be generated via renewable energy (green H_2) and serves as an

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energy carrier for hard-to-decarbonize sectors, like heavy industry, long-haul transport, and shipping. H_2 can also be used in fuel cells to generate electricity with zero emissions. Therefore, many industrial sectors and policy-makers are routing toward H_2 energy carriers to fulfill energy demands as it is lucrative for sustainable adaptability.

For realizing efficient green H_2 production, heterogeneous catalysis via overall water splitting (OWS) is considered one of the most viable routes as it involves renewable input energies such as photon or electrical energy to initiate redox reactions over the surface of semiconducting/metallic catalytic systems [8-11]. H_2 and oxygen evolution reactions (HER and OER) are the key processes in water splitting. These processes primarily require active catalysts to reduce energy barriers and increase reaction efficiency. Several different classes of catalysts have been exploited and categorized based on their compositions, physicochemical properties, and activity during water splitting. Among the front runners as active HER-material, two-dimensional (2D) materials such as graphdiyne and graphene-based derivatives [12, 13], MXenes [14], MBenes [15], transition metal dichalcogenides [16], and phosphides [17] (TMDs and TMPs) have emerged as viable materials on account of their remarkable physicochemical properties and layered structure that facilitate the electron transfer during HER via OWS as well depicted in figure 1 [18]. Similarly, other catalysts such as metal/covalent organic frameworks (MOFs/COFs) [19, 20], metal oxides [21, 22], and perovskite derivatives [23, 24] are cost-effective semiconductors that have the potential to be exploited for scalable HER applications. Advanced functional materials for H_2 evolution are designed with special features to improve efficacy, sustainability and practicality that should lower the activation energy for H_2 generation or oxidation reactions with high specificity towards H_2 evolution, suppressing side reactions. They have resistance to degrade under mild conditions, comprising extreme pH, temperature, and potential and have high electrical conductivity for effective electron migration in electrochemical processes which are efficient for energy conversion. For photocatalysts, an optimal bandgap (~1.8–2.2 eV) to absorb visible light effectively and to ensure compatibility between catalyst and reaction intermediates for better charge migration is needed which are characteristic features of functional materials. Therefore, the researchers are trying to optimize these advanced functional materials by taking into consideration their chemical properties and stability to utilize them for efficient energy conversion, and environmental and sensing applications [25-27]. Several routes such as reverse micelles, solvothermal, hydrothermal, citrate precursor, etc. [28-33] have been used in literature to design various significant catalytic systems. The development of unique catalysts focuses on maximizing activity, lowering cost, and improving stability, especially for large-scale H_2 production [34-36]. Heterostructure catalytic systems are a kind of materials that are constructed via two or more different components with well-defined interfaces. These systems influence the synergistic effects arising from the amalgamation of different materials to improve catalytic activity. The concept builds upon the principles of nanomaterials, surface chemistry, and catalysis offering a versatile platform for addressing challenges in energy conversion, chemical synthesis and environmental remediation. Designing heterostructured catalytic systems by tailoring compositional and structural properties has motivated researchers to focus more on tandem catalysis by involving two or more active materials simultaneously in HER applications. Therefore, in this progressive review, we have focused more on the applicability of heterostructured catalytic systems. Herein, we have reviewed the recent achievements in the photochemical and photo-/electrochemical HER operations in the light of advanced functional materials. Before that, we discussed several important routes of fabricating these active HER materials that hold industrial significance for the large-scale applications of advanced materials. We have also discussed the role of advanced functional materials in H_2 storage based on their physicochemical properties.

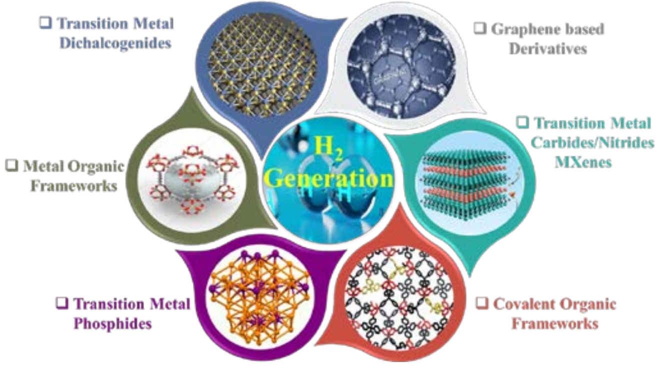

Figure 1. Schematic representation of different advanced functional materials for H_2 generation.

FABRICATION OF ADVANCED FUNCTIONAL MATERIALS:

The field of advanced functional materials is rapidly evolving, and perseverant innovations in fabrication techniques are pivotal to fully capitalize on these materials in next-generation technologies. The advanced functional materials possess unique electrical, optical, thermal, and mechanical features that make them suitable for cutting-edge technologies in research areas like energy storage, environmental sustainability, biomedical devices, and nanotechnology. The development of materials that are active for energy-conversion applications involves the preparation and engineering of materials with superior physicochemical properties tailored for high performance [37, 38]. The fabrication of advanced nanomaterials is broadly categorized into two main approaches, 1) top-down and 2) bottom-up methods as shown in figure 2. These approaches symbolize fundamentally different pathways for preparing nanoscale materials. Both these approaches have their inherent advantages, bottlenecks, and applications in the field of nanotechnology. The basic principle of top-down methods is reducing the size of larger materials to the nanoscale. The top-down methods are usually commenced with bulk precursor and involve its nano-scaling or cutting down into nanoscale structures via mechanical, chemical, or physical procedures, often by mechanical means, etching, or lithographic techniques [39-41].

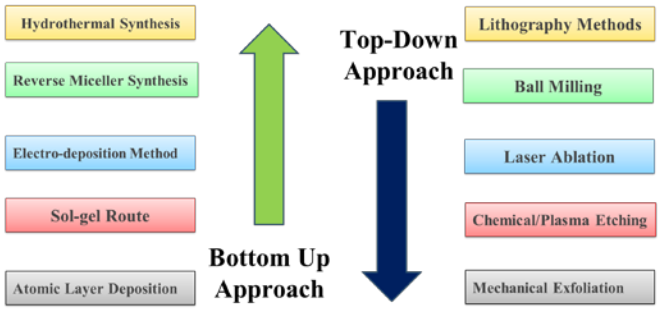

Figure 2. Different fabrication techniques to design advanced nanomaterials.

Top-down routes are significant for constructing well-defined nanostructures and patterned surfaces. These methods hold relevance in the areas where uniform nanostructures are requisite such asfor electronics, photonics, and photovoltaic applications [42]. Several top-down routes have the potential to realize the scalable applicability of advanced materials such as lithography methods [43], different etching ways [44], ball milling [45, 46], laser ablation [47], and many more. Among these routes, lithography is a widely employed method to fabricate nanoscale patterns over a substrate for mass-producing integrated circuits, microchips, and nanoelectronics. A mask is used to define the desired pattern, and the substrate is exposed to light (photolithography) [48], electrons (electron beam lithography) [49], or ions (ion-beam lithography) [50], which transfer the pattern to the surface. Another important top-down approach is ball milling [51], where bulk material is usually placed into a rotating cylinder containing hard balls. The impact and shear forces generated by the ball's movement break the material into uniform nanoscale particles. Ball-milling method is considered a pivotal technique for the scalable fabrication of metallic nanoparticles, ceramics, alloys, and heterostructures [52]. Chemical/Plasma etching involves selectively removing bulk precursors from a surface to prepare nanoscale patterns using etchant solutions [53, 54]. This is often done chemically or through plasma etching, where reactive ions etch away specific regions. The etching process has been utilized in microelectronics to develop precise patterns for transistors and other devices, as well as for nanostructured surfaces. Other than these routes, laser ablation is also a crucial top-down method in which a high-powered laser is focused on a bulk material to vaporize it, producing nanoparticles [55]. This method has found applications in designing a wide range of advanced functional nanomaterials. There are more top-down methods that are gaining the attention of researchers such as spark erosion, high-energy grinding, laser interference lithography, and mechanical exfoliation [56].

Despite their recent success [57], top-down methods have several obstacles in their large-scale applicability for desired applications such as the introduction of undesired defects at the nanoscale while breaking down bulk materials. The whopping cost of sophisticated equipment and a significant amount of waste material further limit the applications of top-down routes. Achieving atomic or near-atomic precision is more challenging in top-down methods compared to bottom-up techniques. On the other hand, bottom-up synthesis involves constructing nanoscale materials atom by atom via nucleation and growth processes. This approach mimics natural processes like crystal growth and generally allows for greater control over the physicochemical properties of the nanomaterials, such as size, shape, and specific surface area. Several important bottom-up approaches have been capitalized to tailor the physicochemical properties of advanced functional nanomaterials such as hydrothermal synthesis [58], reverse-micellar method [59], chemical vapor/electro-deposition [60, 61], sol-gel route [16, 62], atomic-layer deposition [63], and molecular beam epitaxy [64]. Unlike top-down approaches, bottom-up methods allow precise control over the atomic structure, resulting in high-purity and well-defined nanomaterials without a high quantity of defects and typically minimize material waste. In these methods, materials can be tailored at the nanoscale to achieve specific properties concerning the targeted applications. Some of the most important shortcomings of bottom-up methods are their scalability and complexity. These methods do not facilitate the mass production of advanced functional nanomaterials and demand precise control over the reaction conditions that can be technically challenging and expensive if sought for large-scale applications. Attaining uniformity and purity of the desired product can be tiresome, especially in large-scale manufacturing [64-67].

Among bottom-up methods, the hydrothermal method is the most common approach which involves chemical reactions in an aqueous (hydrothermal) or non-aqueous (solvothermal) solution at relatively higher pressure and temperature as compared to ambient conditions that facilitate the controlled growth of nanomaterials. The hydrothermal route is an important method to fabricate metal oxides, 2D materials like TMDs, MXenes, and nanostructured materials used in catalysis, sensors, and energy conversion applications. Another significant bottom-up method is a sol-gel process which is a wet chemical method where metal alkoxides or metal salts are hydrolyzed followed by condensation to form a gel. The gel is dried and calcined to produce fine particle-sized nanomaterials. Another interesting bottom-up route is atomic layer deposition (ALD) which implicates the sequential deposition of thin films, one atomic layer at a time, by introducing chemical precursors that react on the surface. This allows precise control over film thickness at the atomic level. In molecular beam epitaxial (MBE) growth of advanced functional materials, atomic/molecular beams are exposed over the heating substrate in vacuum conditions, where they condense to form high-quality crystalline nanostructures that are defect-free with atomic-level precision, such as thin films or quantum dots. In the electrodeposition technique, an ions-rich solution mixture is deposited onto a conductive substrate by exploiting electrical energy. This builds up thin films, nanowires, or nanoparticles on the substrate. Electro-deposition is a simple and cost-effective process that allows the precise control of the particle size and morphology of nanostructures. These are some of the important physical and chemical routes for fabricating advanced functional materials that have proved their mettle in the recent past [68-70]. Researchers are trying to optimize the scalability of these methods and simultaneously exploring new methods that can effectively synthesize multifaceted nanomaterials.

ADVANCES IN HER APPLICATIONS OF ADVANCED FUNCTIONAL MATERIALS:

As we know H_2 as energy carrier has been considered as a hybrid-modelled fuel alongside electric vehicles. However, for the direct application of H_2 fuel, researchers are trying to optimize the production and storage issues [71, 72]. In the scalable applicability of H_2 fuel, HER via OWS has emerged as a feasible and cost-efficient option to realize the direct applications of H_2 in automobile and household sectors. Figure 3 and 4 display the mechanism of photocatalytic H_2 generation and photo/-electrocatalytic H_2 generation in three electrode system respectively.

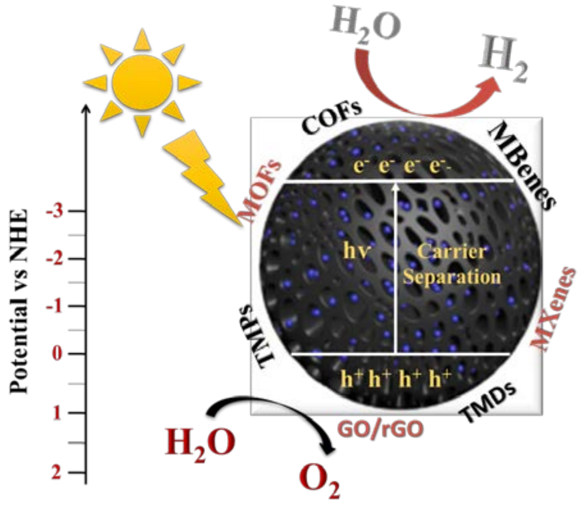

Figure 3. Mechanistic demonstration of photocatalytic water splitting for advanced functional materials such as metal organic frameworks (MOFs), covalent organic frameworks (COFs), transition metal phosphides, graphene oxide (GO), reduced graphene oxide (rGO), and transition metal dichalcogenides (TMDs).

For instance, Mehtab et al [73] developed cadmium selenide quantum dots (CdSe QDs) @g-C_3N_4 Z-scheme heterojunctions via successive ionic layer adsorption and reaction approach to ameliorate the HER performance of pristine g-C_3N_4. The optimized CdSe QDs@g-C_3N_4 heterojunctions yielded 4.3 mmol H_2/g_{cat} with ~24% AQY due to the facile Z-scheme heterojunction formation as illustrated in figure 5(a). Low overpotential values toward HER (147 mV) and OER (218 mV) processes also validated the electrochemical efficiency of CdSe QDs@g-C_3N_4 electrocatalyst owing to facilitated Mott-Schottky interface formation as shown in figure 5(b).To enhance the photochemical and photo-/electrochemical HER efficiency of ZnO, Ali et al [74] developed quaternary Te-$MoTe_2$-$MoSe_2$/ZnO heterostructures via a hydrothermal approach. The authors employed ultrafast transient absorption spectroscopy to evaluate the lifetime decays of pure ZnO and optimized Te-$MoTe_2$-$MoSe_2$/ZnO heterostructure in which the latter exhibited nearly 2.5-folds higher lifetime of electron carriers at the conduction band, inferring improved charge-transfer kinetics during HER process. Photocatalytic transformations revealed ~41% AQY for the quaternary heterostructure with as high as 5.25 mmol/g_{cat}/h H_2 production rate as indicated in figure 5(c). The authors ascertained the multi-functionality of the as-prepared catalyst by evaluating photo-/electrochemical OWS efficiency as shown in figure 5(d) and figure 5(e) respectively. Te-$MoTe_2$-$MoSe_2$/ZnO heterojunction depicted low overpotential and Tafel slope values for HER and OER, which confirmed its potential as an active HER/OER material for OWS. Kuznetsov et al [75] investigated the enhancement of HER efficiency by optimizing the active sites via the Co-substitution in the structure of Mo_2C MXene. This study ascertained that the substitution of Co creates a more favourable electronic structure, boosting charge transfer and reducing energy barriers for H_2 production. Experimental observations and computational studies showed a significant improvement in HER activity with lower overpotential and enhanced catalytic efficiency compared to pristine Mo_2C. The Co-modified MXene material demonstrated stable and efficient catalytic behaviour toward HER with a high turnover frequency. The findings signified the scope of single-atom doping strategies to tune the physicochemical properties of MXenes for HER applications.

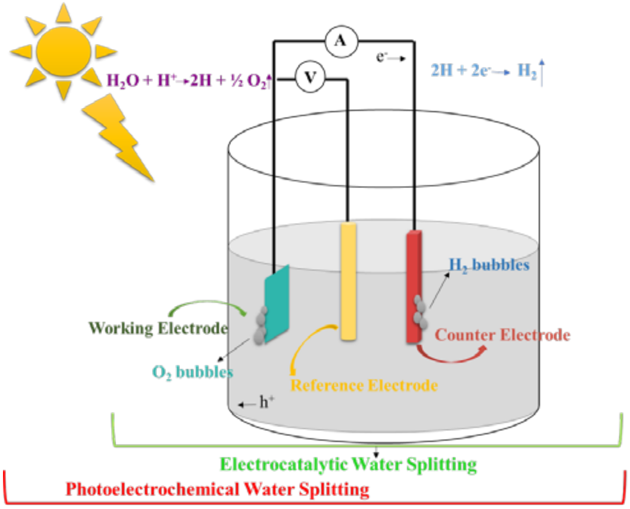

Figure 4. Mechanistic demonstration of photo-/electrochemical water splitting.

Mehtab et al [76] developed a bilayered MoS_2@g-C_3N_4 2D/2D Z-scheme heterojunctions for enhanced HER performance via photochemical and photo-/electrochemical routes. Due to their synergy, the amalgamation of MoS_2 and g-C_3N_4 created a highly efficient platform for photocatalytic and electrocatalytic H_2 generation. MoS_2 provided abundant active sites and excellent catalytic properties, while g-C_3N_4 improved light absorption and charge separation. The heterojunction structure facilitated electron transfer at the interface, minimizing recombination and enhancing HER performance compared to individual MoS_2 and g-C_3N_4. The heterostructure's electrocatalytic performance in alkaline media was also improved, showing lower overpotential (262 mV) at higher current density (20 mA/cm^2). This work highlights the potential of MoS_2/g-C_3N_4 heterojunctions for cost-

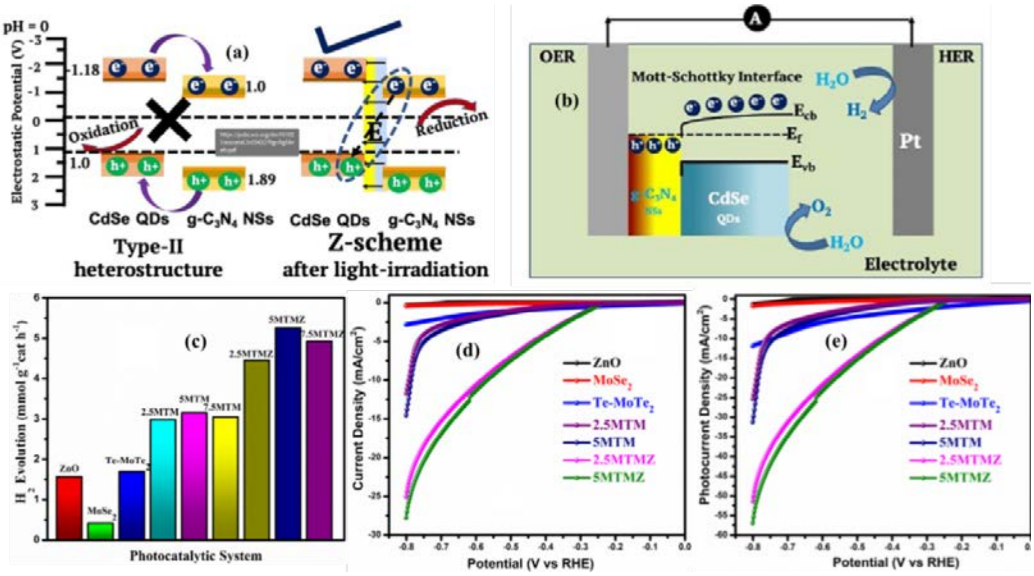

Figure 5. Mechanistic sketch of (a) Heterojunctions formation and (b) electrochemical water splitting in CdSe QDs@g-C_3N_4 electrocatalyst. H_2 production activity for (c) Photocatalysis, (d) Electrocatalysis, and (e) Photo-electrocatalysis. Reproduced with permission from reference 73 and 74, Copyright 2024, American Chemical Society and John Wiley and Sons, respectively.

effective, scalable hydrogen production through photocatalysis and photo-/electrocatalysis. Optimized MoS_2/g-C_3N_4 manifested two times higher HER activity with a whopping 34% AQY and 18.04 mmol/$g_{cat}^{-1}H_2$ rate as illustrated in figure 6(a). Verily, the electrochemical results also proved the low overpotential toward cathodic current density which represents high HER activity as shown in figure 6(b). Recently, Ali et al [77] investigated the novel S-scheme type Te-$MoTe_2$-MoS_2/ZnO quaternary heterojunctions to create multifaceted active material for enhanced HER efficiency. The S-scheme charge transfer pathway facilitated the separation of photogenerated electron-hole pairs, thus, minimizing recombination and enhancing the photocatalytic performance. Transient absorption spectroscopy revealed the ultrafast charge transfer and prolonged time scale of active electron carriers at the conduction band edge responsible for the HER process.The integration of Te-$MoTe_2$-MoS_2 with ZnO enhanced the catalytic activity toward photochemical and photo-electrochemical HER due to the improvement of light absorption and electronic conductivity. The combination of these materials resulted in a highly active and stable catalyst, with improved HER performance ascribed to favourable band alignment and efficient charge separation. This study excellently elucidates the potential of the S-scheme heterostructured materials for scalable and efficient green hydrogen energy production. The group reported photochemical HER activity as high as 20.8 mmol/g_{cat} with nearly 41% AQY as shown in figure 6(c). Alongside, electrocatalytic and photoelectrochemical investigations revealed excellent HER performance with a low overpotential value (-0.51 V and ~-0.3 V) to achieve a benchmark current density of 10 mA/cm^2 as revealed in figure 6(d, e) respectively.

Ali et al [78] developed a ternary MoS_2-BN/TiO_2 heterostructured photocatalyst for enhanced HER activity via water splitting. The rational design of the ternary heterostructure leveraged over the complementary properties of the components, MoS_2 provided the rich active sites for HER, BN improved the thermal stability against corrosiveness for photo-corrosion prone MoS_2, while TiO_2 aided in photocatalysis by lowering the recombination dynamics. The integration of these materials into a ternary heterostructure significantly ameliorated the charge separation and electron transfer during redox reactions over the surface of the catalyst as proven by the marvellous H_2 production activity of MoS_2-BN/TiO_2 photocatalysts.The ternary system showed lower overpotentials, increased current density, and stable performance in both electrochemical HER and OER processes in comparison to individual components or binary heterostructures. The synergistic relationship between MoS_2, BN, and TiO_2 resulted in improved overall catalytic activity for H_2 generation. This study stresses the potential of ternary heterostructures for efficient, scalable H_2 production through the OWS process. Ali et al [79] modulated the thermodynamically stable facet of anatase-TiO_2 with orthorhombic MoO_3 to augment the HER activity and ammonia-sensing performance of pristine TiO_2. The integration of MoO_3 with TiO_2 ameliorated the overall charge transfer and light absorption, boosting the photocatalytic efficiency for H_2 production. The optimized MoO_3-TiO_2 heterostructured photocatalyst exhibited a marvellous photocatalytic H_2 yield of 9.18 mmol/g/h at 36% AQY. Whereas, electrochemical and photoelectrochemical HER studies also inferred the low 0.7 V and 0.61 V overpotentials during water splitting. MoO_3-TiO_2 exhibited enhanced HER performance due to the symbiosis between the two materials, with MoO_3 facilitating improved separation of charge carriers and broadening the light absorption range. This study highlighted the dual applicability of MoO_3-TiO_2 in clean energy production and environmental monitoring and provided a cost-effective and sustainable approach to address key challenges in H_2 energy and ammonia sensing technologies. Ali et al [80] analyzed the in-situ development of MoO_3 into $SrTiO_3$ synthesis to develop MoO_3- $SrTiO_3$ heterostructured nanocatalysts for HER process and environmental remediation. The authors combined experimental synthesis with theoretical simulations to better elucidate the catalytic efficiency of this heterostructure. The optimized MoO_3-$SrTiO_3$ nanocomposite yielded 4-fold higher HER activity as compared to pure $SrTiO_3$

with nearly 16% AQY. Photo-/electrochemical studies ascertained the higher HER activity of 2% MoO_3–$SrTiO_3$ on account of the advanced current density at the lower potential. Theoretical simulations and photocatalytic reaction mechanisms explained the charge transfer mechanisms at the interface, highlighting the role of band alignment and subdued electron-hole recombination in boosting HER performance. To depict the augmented HER activity in bilayered TMDs/metal oxide heterojunctions, Ali et al [81] developed the unique S-scheme type $MoSe_2$-MoS_2/ZnO ternary heterostructures via an environmentally benign hydrothermal approach. The authors focused on enhancing charge separation and transfer via the S-scheme mechanism, based on efficient photo-induced hole trapping and electron transport. The $MoSe_2$–MoS_2 nanoflowers dispensed abundant active sites, while ZnO nanosheets acted as an electron acceptor, facilitating ultrafast charge transfer across the interface. The S-scheme architecture prevented the recombination of photogenerated electron-hole pairs resulting in excellent photocatalytic efficiency. Superior $MoSe_2$–MoS_2/ZnO catalyst depicted ~59% AQY with HER activity that was 5 times higher than pristine ZnO. Ultrafast assessments inferred prolonged time delay of active photo-electron carriers in ternary $MoSe_2$–MoS_2/ZnO heterostructure as compared to ZnO. The improved electronic conductivity, enhanced light absorption, and favourable band alignment led to the higher activity of the prepared photocatalyst. This work highlights the potential of $MoSe_2$–MoS_2/ZnO composites for sustainable hydrogen generation, demonstrating a promising strategy for maximizing charge transfer in photocatalytic systems.

Ali et al [82] incorporated $MoSe_2$ and BN over TiO_2 for enhanced photochemical and photo-electrochemical HER performance via improved separation of electron-hole pairs and extended light absorption due to visible light-active $MoSe_2$. In the developed catalyst, $MoSe_2$ played the role of an efficient electron donor having abundant HER active sites, while BN served as an insulating layer to minimize back recombination dynamics. TiO_2 contributed to the stability and light-harvesting capability of ternary photocatalyst. The ternary $MoSe_2$-BN/TiO_2 heterojunctions formed a favourable energy band alignment, facilitating efficient electron flow and suppressing charge recombination. Experimental results demonstrated significantly improved H_2 generation under light irradiation as shown in figure 6(f), attributed to the synergistic interaction between the $MoSe_2$, BN, and TiO_2. Superior $MoSe_2$-BN/TiO_2 and binary $MoSe_2$–TiO_2 heterostructures revealed 32 and 18 times superior photocatalytic HER activity as compared to pristine TiO_2, thus confirming the exponential rise in the HER performance. Similarly, photo/-electrocatalytic investigations also depicted lower overpotential values of $MoSe_2$-BN/TiO_2 and $MoSe_2$–TiO_2 heterostructures to obtain higher cathodic current densities symbolizing HER. This study presents promising nano-engineered ternary heterojunctions for sustainable hydrogen production, combining experimental validation with theoretical insights.

Wang et al [83] presented an excellent study on the development of Ni_3N/Mo_2N heterojunctions for enhanced HER activity via urea oxidation. The study focused on interfacial engineering to optimize the electron transfer and catalytic efficiency of the as-developed composite material. The

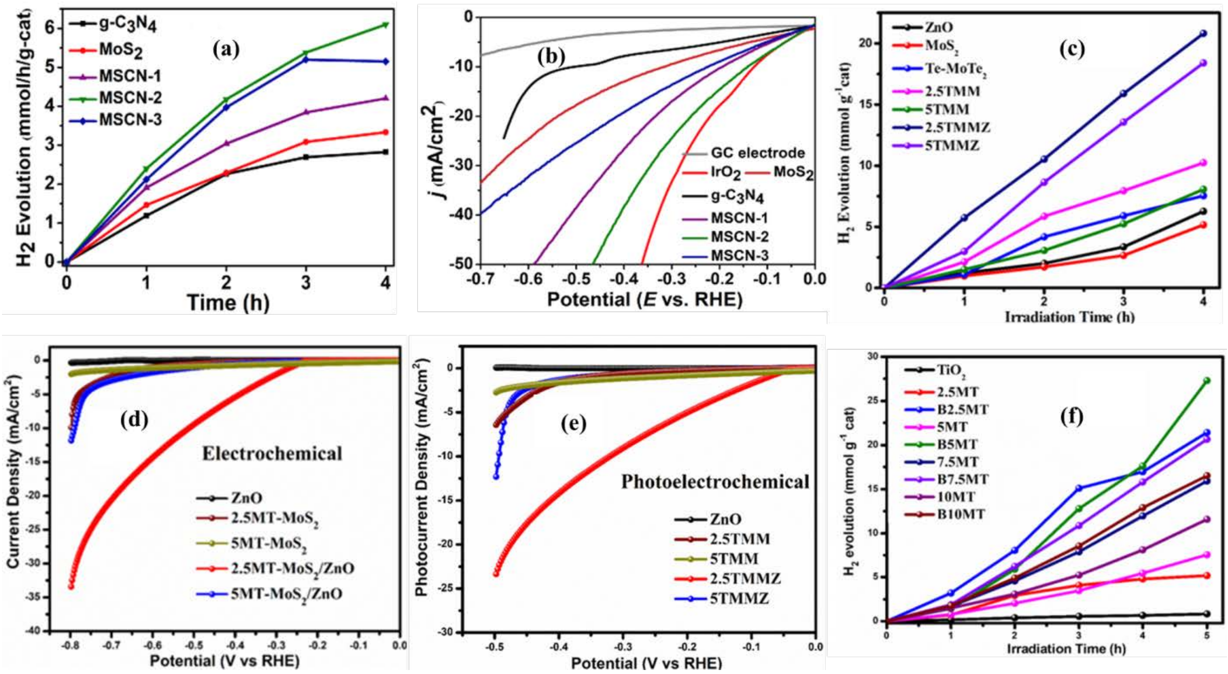

Figure 6. (a) Photochemical H_2 rate and (b) LSV curves of pristine MoS_2 and g-C_3N_4 and their composites. Reproduced with permission from reference 76, Copyright 2023, American Chemical Society. H_2 production activity for (c) Photocatalysis, (d) Electrocatalysis, and (e) Photo-electrocatalysis. Reproduced with permission from reference 77, Copyright 2024, American Chemical Society. (f) Photochemical H_2 rate of $MoSe_2$, BN, TiO_2 and their heterostructures. Reproduced with permission from reference 82, Copyright 2024, Elsevier.

combination of Ni_3N and Mo_2N resulted in a heterojunction formation, that facilitated efficient charge separation during the HER process. Authors coupled HER with the urea oxidation to further lower the required overpotential, making the process more energy-efficient. This tandem approach offers an environmentally benign way to generate H_2 while simultaneously addressing wastewater treatment through urea removal. This work demonstrates a promising strategy for improving H_2 generation efficiency and integrating sustainable processes with energy production. Khan et al [84] explored the application of $TbCrO_3$ nanoparticles as an active material for HER through electrocatalysis and photocatalysis. The study highlighted the unique multiferroic properties of $TbCrO_3$, which enabled efficient charge separation and transfer, critical for HER. The authors corroborated that coupling the hydrogen evolution with hydrazine oxidation led to a significant lowering of the overpotential (0.2 V) required for H_2 production. The authors also tested the photocatalytic activity of the $TbCrO_3$ and inferred the whopping 10 mmol/g/h H_2 production rate that further enhances the material's potential for sustainable hydrogen production. This work demonstrates $TbCrO_3$ as a promising single-perovskite material for dual-mode H_2 generation via OWS, offering energy-efficient solutions for clean energy applications. These marvellous recent developments in the advanced functional materials for efficient photochemical and electrochemical HER via OWS operations effectively demonstrate the progress in achieving scalability in sustainable energy conversion applications.

ROLE OF ADVANCED FUNCTIONAL MATERIALS IN HYDROGEN STORAGE:

H_2 storage is a significant area in the development of H_2 as a sustainable energy carrier, especially for fuel cells and environmental applications. Developing materials that can safely and efficiently store H_2 at ambient conditions is the need of an hour [85-88]. Transportation of H_2 is a major concern due to which many catalysts have been tried to combat this limitation such as metal/complex hydrides [89, 90], carbon derivatives [91, 92], liquid organic H_2 carriers [93, 94], MOFs [95], and other H_2 adsorption catalysts [96]. H_2 storage catalysts play an essential role in enhancing the kinetics of H_2 adsorption and release from storage materials. Development in H_2 storage catalysts is pivotal to making H_2 a viable energy carrier, particularly regarding safety, efficiency, and scalability. Advanced functional materials improve H_2 uptake, release kinetics, and lower operating temperatures for the applicability of H_2 fuel [97]. Hydrides are generally efficient for H_2 storage due to storing H_2 at a higher density than liquid H_2, such as MgH_2 can store a considerable amount of H_2 by weight. Several metal hydrides can reversibly absorb and desorb H_2 under appropriate pressure and temperature conditions. Hydrides serve a broad range of binding energies with H_2 permitting for applicability, based on the storage application. Some hydrides release H_2 at relatively low temperatures, turning them applicable for portable and industrial applications. They conventionally store hydrogen in a stable, solid form, reducing risks associated with high-pressure or cryogenic H_2 storage. Metal hydrides such as MgH_2 [98], $NaAlH_4$ [99], and $LiBH_4$ [100] are promising H_2 storage materials owing to their high H_2 density. Nevertheless, their pragmatic applicability is restricted by slow kinetics and high desorption temperatures. Decorating metal hydrides with metal ions (e.g., Ti^{4+}, Fe^{3+}, Ni^{2+}) or co-catalysts can escalate the adsorption and release of H_2 from metal hydrides [101]. For instance, transition metals are viable options for improving the adsorption of H^+ ions and desorption kinetics. Reducing the particle domain of metal hydrides and incorporating advanced nanomaterials can also significantly upgrade H_2 storage properties by increasing exposed active sites and reducing diffusion pathways for H-atoms. Complex borohydrides ($NaBH_4$ [102], $LiBH_4$ [103]) and alanates ($NaAlH_4$ [104]) have high H-capacities but suffer from high desorption temperatures and sluggish kinetics. Advanced materials are often used to lower the temperatures required for hydrogen release. For instance, introducing Ti-based catalysts/ionic liquids to metal hydrides like $NaAlH_4$ can effectively reduce the decomposition temperature and increase the H_2 desorption rate [105]. In the same way, Ru, Ni catalysts have been also used to enhance the kinetics of borohydrides. Ionic liquids can be amalgamated with complex hydrides to improve H_2 storage capacity and release [106].

Carbon derivatives such as graphene, carbon nanotubes (CNTs), and activated carbon are light weight and have high surface areas that can adsorb significant amounts of H_2, thus making them viable H_2 storage catalysts. Carbon-based materials are versatile and efficient for storage due to their structural and surface features such as activated carbon and graphene have a large surface area per unit mass, that improves their capability to adsorb gases like H_2, CH_4, or CO_2 . The porous structure of carbon-based materials facilitates gas adsorption, micropores and mesopores act as reservoirs improving storage capacity. Carbon-based materials are comparatively lighter than metal-based systems making them attractive for applications like H_2 storage in transportation. The surface chemistry of carbon can be modified to improve binding interactions with stored material, enhancing storage capacity and efficacy. Carbon materials remain stable under numerous conditions, that are important for maintaining durability. However, without catalysts, their H_2 storage capacity is often limited. Introducing heteroatoms/metal nanoparticles into carbon structures can enhance hydrogen adsorption [107, 108]. These doped or functionalized carbons can act as catalytic sites to facilitate H_2 storage and release. Liquid organic hydrogen carriers (LOHCs) such as N-ethylcarbazole [109], and methyl cyclohexane [110] have shown potential in recent years to reversibly store hydrogen through chemical bonding. Metallic nanoparticles or semiconductors are important for the hydrogenation and dehydrogenation processes. Metallic nanoparticles such as Pd, Pt, or Ni are used in these systems to catalyze the addition and removal of H_2. The small size of metallic nanoparticles offers a high surface area relative to their volume, revealing more active sites for catalytic reactions. This improves the efficiency of hydrogenation and dehydrogenation methods by easing the interaction between the catalyst and the reactants. Metals such as Pd, Pt and Ni have a high affinity for

H_2, they can dissociate molecular H_2 into atomic hydrogen, an important step in both hydrogenation and dehydrogenation. Nanostructured semiconductors also offer high surface area, that is fruitful for supporting catalytic species or directly participating in the reaction. They can ease charge migration method when merged with metallic nanoparticles or doped with elements to create active sites for catalytic reactions. These catalysts must be efficient at mild conditions to make LOHCs feasible for practical applications. Metallic nanoparticles possess a higher propensity toward H-atoms which make them suitable H_2 adsorption catalysts. Metallic nanoparticles are capable of enhancing H-adsorption onto surfaces with high surface areas at low temperatures such as porous materials, and zeolites [111, 112]. The anchoring of metallic nanoparticles can improve the interaction between H_2 and the porous materials, leading to enhanced H_2 uptake. Therefore, based on the physicochemical properties of advanced functional nanomaterials, H_2 generation as well as storage can be elevated for its scalable applications as an energy carrier.

CONCLUSIONS

H_2 generation via water splitting is a key technology for sustainable H_2 production, essential for transitioning to a clean energy economy. In this review, we have accounted the significance of advanced functional nanomaterials in escalating the scale of HER via OWS. Herein, we have precisely presented the advances and progress of state-of-the-art photochemical and electrochemical catalytic systems in light of recent achievements. We have detailed several important synthetic protocols based on the top-down and bottom-up classifications to nano-engineer the advanced nanocatalysts. In addition, we have thoroughly examined the recent reports of photochemical and photo-/electrochemical HER and presented critical commentary over these results. We have also highlighted the role of advanced functional nanomaterials in resolving the H_2 storage issues taking into account their excellent physicochemical properties. We believe that this review article will contribute to the thorough understanding of H_2 production via water splitting through advanced nanomaterials.

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CONFLICT OF INTEREST

The authors declare no financial competing interest.

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