

Catalytic role of graphene in green hydrogen production

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Abstract. This comprehensive study aims at analyzing graphene-based technologies in enhancing hydrogen production via three methods including electrocatalysis, photocatalysis and plasma-assisted reforming. Graphene stands out as an excellent catalytic material due to its exceptional attributes which include large surface area, exceptional electrical and thermal conductivity, adjustable electronic properties and outstanding mechanical strength. The research explores graphene's contributions to hydrogen evolution through three main strategies including lowering energy barriers, escalation of active sites and enhanced electrical charge transport. The study also focuses on graphene's performance when functionalized with metal catalysts and heteroatoms, enhancing its capability in charge separation and absorption of light during photocatalysis. The application of plasma to graphene improves catalytic reaction in hydrogen production with improved resistance to energy consumption. Large-scale industrial adoption of this technology remains restricted in terms production cost, synthesis scalability and environmental safety issues. The research suggests an outlook for enhancing production technologies, improving process sustainability, and tackling scale-up technology to boost graphene's incorporation into green and effective hydrogen energy production.

1 Introduction

Hydrogen has arisen to be the most useful clean energy carrier because of its zero emission of greenhouse gas (GHG). It stands as the most abundant element across the cosmos (see Figure 1) [1] and provides a flexible option for storing high amounts of energy across numerous operational domains and systems such as transportation, electricity generation, and industrial processes [2]. The use of hydrogen in fuel cells results in zero greenhouse gas emissions which earns it an essential position in mitigating climate change and zero dependence on carbon-based energy sources [3]. One of the major benefits of hydrogen usage as an energy carrier emerges from its efficient mechanisms in energy storage and transportation. Hydrogen can be derived from four main production techniques, namely: electrolysis of water, refining of natural gas, processing from biomass and industrial waste product retrieval [4, 5]. Green hydrogen production stands as the optimal sustainable choice since it relies on renewable energy from solar energy, wind power or hydroelectric power to

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split water molecule (H_2O) into H_2 and O_2 through electrolysis. As a result, that this production method generates zero emissions, it is established that it is the sustainable replacement for traditional fossil fuels exploration and exploitation. Moreover, hydrogen demonstrates versatility for storage through different forms which include compression in liquid and solid states, therefore, making it an effective solution for handling intermittent power sources from renewable energy systems [6]. Hydrogen plays a vital role in fuel cell technology through its electrochemical reaction with oxygen to produce electric power. Fuel cells transform chemical energy to electrical energy through their efficient mechanism while producing water and heat as the by-products [7]. Fuel cells that run on hydrogen appear as a perfect option for zero-emission transportation system and provide power to hydrogen fuel cell electric vehicles (FCEVs), buses, trains and aircraft. Time for refuelling cars using hydrogen fuel cells is in minutes, quite unlike cars that use batteries which require hours for re-charging. Hence, hydrogen fuel cells are a more reliable and sustainable power source for heavy-duty and long-range transportation. Several industrial operations including steel productions, ammonia synthesis and chemical manufacturing, presently, rely on the use of fossil fuels for their high temperature production process. Unfortunately, fossil fuels, besides being non-renewable, is the primary cause of climate change from GHG emissions [8, 9].

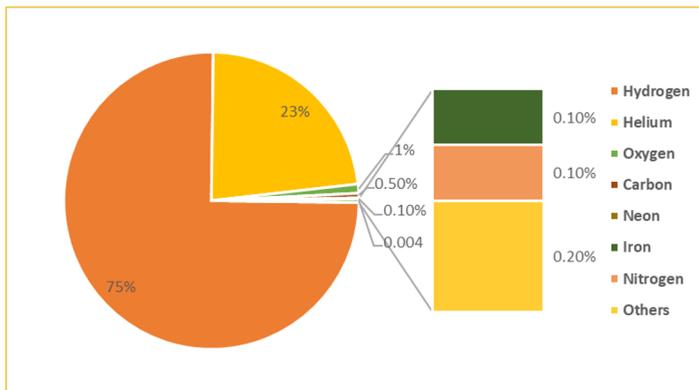


Fig.1. Elements in the universe displaying 75% abundance of hydrogen [1].

Hydrogen can be used to replace coal and natural gas in those industrial applications as a clean source of energy. This is because the energy is clean, renewable, innocuous with highest calorific among other common natural energy sources (Figure 2) [10].

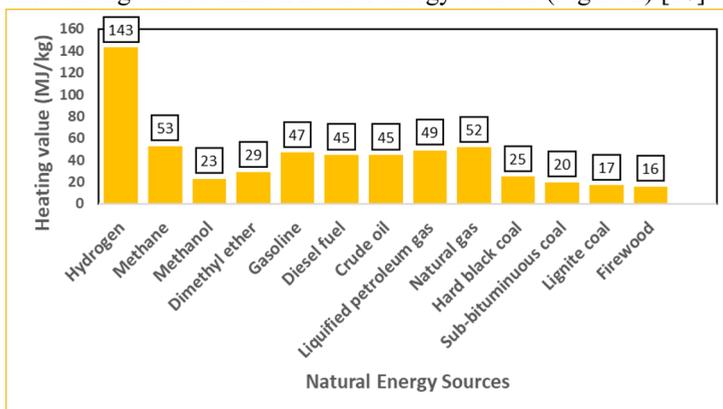


Fig. 2. Heat values of some natural energy sources [10].

The existing natural gas pipelines can utilize hydrogen blending to generate a mixture with reduced carbon content which supports the transition toward hydrogen-based energy economy. According to S&P Global Platts Analytics [11], hydrogen consumption was forecasted to drop to 73 million metric tons in 2020. The global pandemic triggered a drop in oil product demand which led to the decline in hydrogen usage. The projected growth of refinery production capacity amounts to 1 million metric tons in 2020 whereas previous predictions had reached 1.7 million metric tons. A substantial increase to 4.25 million metric tons of yearly hydrogen production will occur during the next ten years, as projected (see Figure 3). The continued increase in the demand of hydrogen energy implies that the production and technological innovations into cost efficient production of hydrogen is imperative. Although there are concerted efforts to increase the production of hydrogen to meet global demand, it was reported that 98% of hydrogen production is from grey hydrogen, a product of steam methane reforming (SMR), which involves splitting of methane (CH₄) into hydrogen and carbon dioxide [12]. This is a major source of GHG emissions. Only 2% of the hydrogen production is green hydrogen produced from renewable source (solar, wind, hydro), which involves electrolysis of water to generate hydrogen with zero GHG emission. Therefore, much is still needed in transiting from grey hydrogen production to green hydrogen.

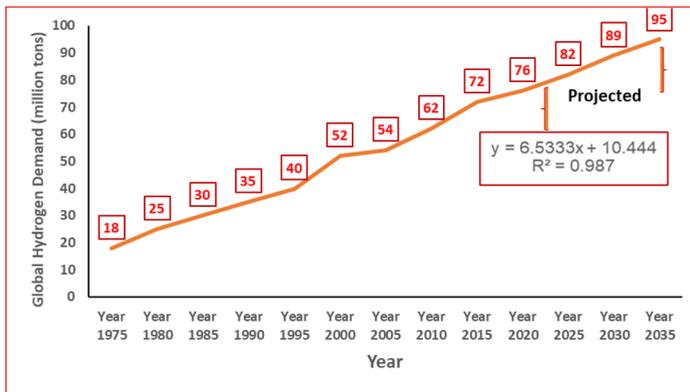


Fig. 3. Global hydrogen demand from 1975 to 2018 and projected to 2035 [11].

1.1 The role of graphene in hydrogen production

Graphene (Gr), a 2-D single-layered carbon nanomaterial has drawn extensive research interest for its function as a catalyst, an electrode material and in hydrogen storage because of its distinctive electrical, electronic, thermal and mechanical properties. A combination of its large surface area (see Figure 4), high electrical conductivity [13], chemical stability and adjustable electronic property [14] makes graphene ideal for improving hydrogen production technology. The integration of graphene-based materials into the production technologies of hydrogen like, electrocatalysis, photocatalysis, plasma-assisted reforming and hydrogen sorption improves the hydrogen yield and efficiency of the system [15]. Graphene demonstrates excellent potential in electrocatalytic splitting of water, which is one of the efficient methods of hydrogen production. In electrocatalysis of water, there occurs hydrogen evolution reaction (HER) at the cathode to produce hydrogen, and oxygen evolution reaction (OER) at the anode to release oxygen [16]. Traditionally, platinum-based catalysts have been the dominant catalyst for the reaction. Even though its efficiency is high, its cost undermines its commercial viability. There are three groups of graphene-based catalysts, namely, nitrogen-doped graphene, graphene-doped transition metals (Gr-MoS₂-, Gr-Ni-, Gr-Co-), and

metal-free graphene-based catalysts which are very cost effective and efficient in hydrogen production [17]. These graphene-based catalysts, according to research, elevate charge transfer rates, lower reaction energy thresholds and stimulate efficient hydrogen production [18].

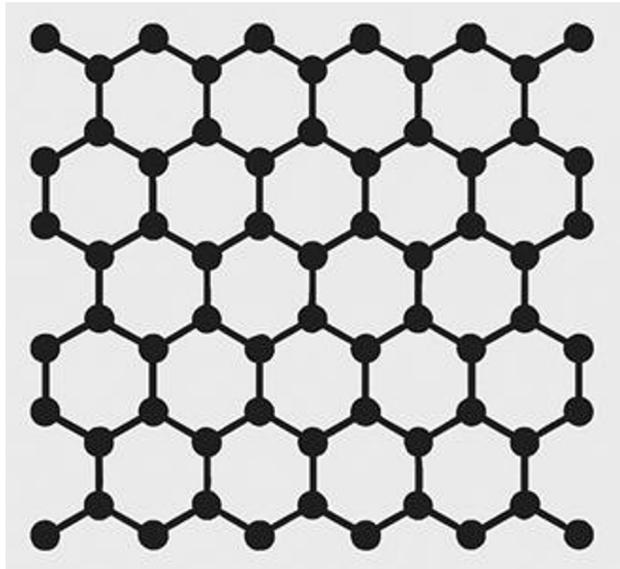


Fig. 4. A graphene sheet.

Another process of producing hydrogen is through photocatalysis. This involves splitting of water using solar power which may need catalytic action of graphene [19]. The capacity of graphene to stimulate charge separation and enhance electron transfer makes it as a unique co-catalyst in photocatalysis [20]. It was reported that the photo-reactivity of titanium dioxide (TiO_2) as a photocatalyst is limited because of sudden electron-hole recombination during photocatalysis [21]. But when doped with graphene, its reactivity increases effectively. When elements like nitrogen, sulfur and boron are doped in graphene, their activity as co-catalysts for photocatalysis of water are highly enhanced, as the graphene's active sites for hydrogen evolution is increased with appropriate modification of its electronic structure [22]. More so, some other innovative use of graphene is in the production of hydrogen through plasma-assisted methods. Hydrocarbon or water molecules can be broken down into hydrogen and oxygen by employing high-energy plasma as an operating medium. Graphene-based catalysts serve to lower the energy of reaction threshold, increase reaction kinetics and elevate hydrogen yield [23]. Research has it that production of hydrogen via graphene-plasma reforming of methane is more environmentally friendly than the traditional steam methane reforming (SMR) [23]. However, the incorporation of graphene into the catalysts enhances the efficiency of converting biomass to hydrogen resulting in an increase in hydrogen yield.

The need for sustainable clean energy has instigated increased research into hydrogen energy as a prospective replacement for fossil fuels. Due to rapid progress in this domain, there is the need to develop a systematic review in the area to evaluate graphene-based hydrogen production processes and benchmark them against traditional approaches. While other studies have concentrated on the roles of graphene in electrocatalysis [24], photocatalysis [25], and thermochemical [26] production of hydrogen, there is a gap of holistic analysis that systematically assesses and correlates these processing methods. This study will incorporate multifarious research results to proffer a unique outlook on how graphene improves hydrogen synthesis efficiency, lowers energy usage, and promotes sustainable technology in hydrogen production. This review, therefore, will examine graphene-based procedures for hydrogen production by categorizing them while assessing

their energy efficiency, environmental impacts, and analyzing barriers to their commercial scalability. It will identify recent advancements in hydrogen energy technology and provide useful insights beneficial to the research community, industries and policy-making agencies in developing improved clean graphene-based hydrogen production technology.

2 Methods of hydrogen production using graphene

2.1 Electrocatalytic splitting of water

The electrocatalytic splitting of water is important for creating sustainable H₂ energy as H₂O is broken down into H₂ and O₂ through this electrochemical reaction assisted with catalysts [27]. Two electrodes operate in the electrochemical system comprising a vessel containing electrolytes that is powered by an external voltage source (see Figure 5). At the cathode a hydrogen evolution reaction (HER) occurs where protons (2H⁺) from water acquire electrons to become H₂ gas (2e⁻ → H₂) [80]. The oxygen evolution reaction (OER) at the anode transforms water molecules into oxygen gas while producing protons and four electrons (2H₂O → O₂ + 4H⁺ + 4e⁻) [28].

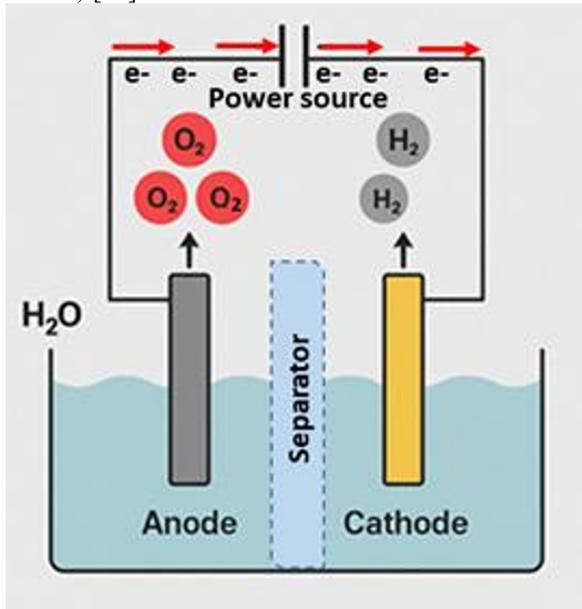


Fig. 5. Electrochemical splitting of water.

Platinum has acquired high popularity as the cathode for hydrogen evolution reaction while anode materials use transition metal oxides iridium oxide (IrO₂) and ruthenium oxide (RuO₂) for oxygen evolution reaction [29]. Meanwhile, with the support of graphene catalyst, the reaction is beefed up by lowering the overpotential and increasing the charge transfer rate, hence, making electrocatalytic water splitting a highly effective process for hydrogen production [30].

Moreover, when graphene is used as a supportive agent for metal-based catalysts, the efficiency of HER is boosted. Noble metals like platinum exhibit exceptional HER activity, but their high cost and scarcity limit scalability. Research reports higher performance in HER with reduced noble metal content when graphene with large active surface area and efficient electron transfer is anchored to Pt nanoparticles [31]. Metal catalysts like MoS₂, CoP and NiFe alloys, when incorporated into graphene, demonstrate superior HER performance

through the combination of their H₂ yielding characteristics [32]. The combination of graphene with metal catalysts creates an optimal environment for stable electron transfer and protected catalytic site function which lowers reaction overpotential, reduces current density and increases hydrogen yield. The research on hydrogen evolution employs graphene-based catalysts because they possess three essential properties: tuneable electronic property, flexible structure and strong interactions with metal and semiconductor catalysts. Research developments in doping, defect engineering and catalyst hybridization systems will lead to advancements in practical scalable and economical hydrogen production technologies.

2.2 Photocatalytic splitting of water for hydrogen generation

The sustainable method of photocatalytic hydrogen generation produces H₂ from water splitting by using solar power and photocatalytic materials to generate O₂ and H₂. The photocatalytic reaction mimics photosynthetic reaction by employing semiconductor catalysts that receive sunlight to energize electrons which initiate redox reaction in water electrolyte to produce hydrogen and oxygen [33]. Through photocatalysis, hydrogen generation system provides low-energy-consuming-clean fuel from renewable solar energy which is more sustainable and environmentally friendlier than conventional steam methane reforming (SMR) and electrolysis processes. The photocatalytic process operating on semiconducting photocatalysts undergo three fundamental steps: (i) photon absorption above the catalyst's bandgap threshold, producing electron-hole pairs, (ii) charge carrier separation, occurring within the chip material, and (iii) water molecule interaction with the electrons and holes [34] (see Figure 6). Therefore, photocatalytic production of hydrogen involves three main steps including light absorption, charge separation and surface reactions. The photocatalysts (e.g. titanium dioxide (TiO₂), cadmium sulfide (CdS) and graphene-based nanocomposites) excite electrons from the valence band to the conduction band when it absorbs photons from the sun which have complete or greater energy than its bandgap threshold [35]. This process leaves behind positively charged holes. The excited electrons react with H⁺ (proton), reducing it to H₂ while the hole oxidizes the water to release O₂ as a byproduct. The improvement in the system efficiency requires additional co-catalysts such as platinum, molybdenum sulfide, and nickel phosphide to hasten charge transfer rate and decrease the occurrence of charge recombination.

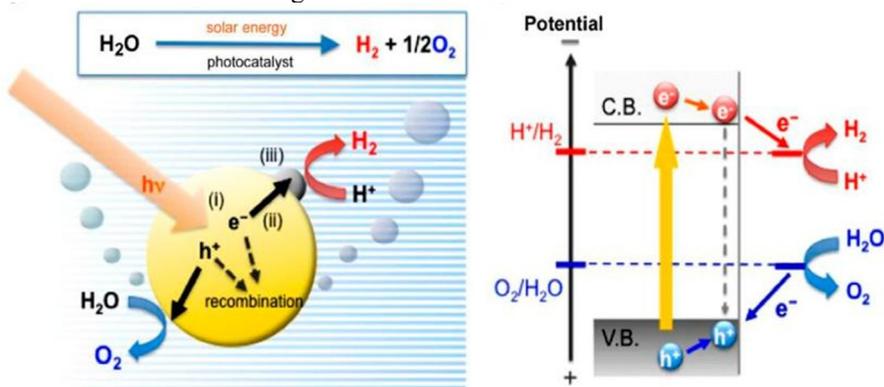


Fig. 6. Photocatalytic splitting of water to produce hydrogen. Reproduced with permission from [34].

A key obstacle in photocatalytic hydrogen production is when photogenerated electrons and holes fail to start the redox reactions, forcing them to recombine before the reactions can begin, thus reducing system efficiency [36]. The remedy proposed by researchers includes use of heterojunctions, plasmonic nanoparticles and 2D nanomaterials (e.g., graphene, MXenes, and black phosphorus) which can improve electron mobility while sustaining

charge separation [37]. Photocatalysts based on graphene demonstrate maximum effectiveness because of their high electrical properties, large surface area and efficient carrier transfer characteristics. Photocatalysis of water can also be categorized in two forms, namely, single-step, otherwise called overall water splitting (OWS) and multi-step, also known as Z-scheme or dual-photon system. In single-step technique, a single photocatalyst facilitates both hydrogen (H_2) and oxygen (O_2) evolution [38]. The material needs to possess bandgaps between 1.8 and 2.2 eV for achieving efficient solar light absorption and electron-hole creation during this procedure. Material with adequate stability under reaction conditions together with high activity are the major challenges of this OWS technique [39]. To maintain high efficiency the photocatalyst needs effective mechanisms for separating and transporting charge carriers without recombination reaction. Research is on in exploring the efficiency of metal oxides, nitrides and sulfides for this role. However, it has been reported that 2-D material like graphene-C₃N₄ which has an effective charge separation capacity and large surface area shows strong potential in this application [40]. The Z-scheme system operates as a natural photosynthetic system with two photocatalysts connection and an electron mediator which optimizes charge transfer efficiency [41].

2.3 Plasma-assisted hydrogen production

Utilizing plasma energy has been perceived as another strategy to enhance hydrogen production technologies. Plasma represents the fourth state of matter that contains highly energized combination of ions, electrons and neutral particles. This high-energy state promotes swifter molecular dissociation and chemical reaction while facilitating better catalytic performance, thus making it an effective method for improved hydrogen production. The presence of graphene doubles the rate of reaction in hydrogen production via plasma-assisted hydrogen production technique [42]. The large surface area of graphene provides sufficient hydrogen adsorption sites thereby promoting molecular interaction with radicals generated by the plasma and subsequently stimulating higher hydrogen yield. The high thermal stability of graphene makes it the choice material for plasma-based hydrogen production as the reaction is majorly at very high temperature.

Several research have found graphene-based catalysts to hold great potential in the plasma reforming process of converting hydrocarbon into hydrogen. Plasma reforming of hydrocarbons functions via ionized gases (plasma) which activate the hydrocarbon molecules at temperatures below those needed by conventional thermal techniques. The incorporation of graphene into this process improves the catalytic performance of the process as it provides exceptional physicochemical properties like high surface area, superior electrical conductivity and thermal stability [43]. In plasma environments, graphene promotes uniform dispersion of active metal nanoparticles like Ni, Co, Pt, preventing their sintering and enhancing their thermal stability [44]. The metal-graphene composites stimulate effective C–H and C–C bond breaking processes in hydrocarbon molecules like methane, ethane and heavier alkanes, thereby enhancing hydrogen generation efficiency [45].

Plasma treatment of graphene material creates an innovative method to boost hydrogen production techniques via water splitting and hydrocarbon reforming. In this method, non-thermal plasma (NTP) produces high-energy electrons capable of activating graphene surfaces through physical and chemical changes that generate essential active sites for catalytic reactions. Exposure of graphene to plasma results in its surface functionalization and ‘defect’ engineering processes. The addition of vacancies, edges sites and oxygen-containing functional groups on graphene creates increased chemical reactivity [46]. The catalytic role of such defects includes their ability to adsorb and activate water and hydrocarbon molecules after which they break H–O and C–H bonds for hydrogen evolution [23]. Plasma treatment allows for optimal dispersion and anchoring of nanoparticles (Ni, Pt,

Fe, P, N) [109] on graphene surfaces, enhancing synergistic catalysts performance for hydrogen production.

3 Prospects, challenges and outlook of graphene-assisted hydrogen production

The operational lifetime of hydrogen production technologies relies heavily on the stability and durability of catalysts. Researchers are extensively studying graphene-based catalysts in recent times because of their exceptional features that help in maintaining catalytic effectiveness and resilience in harsh operating environments [16]. These materials present a promising solution for designing stable and durable catalysts that can operate in different hydrogen production methods such as thermochemical reforming, photocatalytic water splitting and electrochemical hydrogen evolution reactions. Graphene possesses outstanding thermal conductivity, high mechanical stability and exceptional chemical stability. These naturally inherent properties qualify graphene as an excellent material to anchor active metal sites for Ni, Pt, Co; or to work independently as a catalyst through engineered defective surfaces [23]. Its resistance against sintering and agglomeration of active metal nanoparticles enhances the stability of graphene-based catalysts [47]. During the elevated-temperature-based hydrogen production like steam catalysis or plasma-assisted reforming, conventional catalysts usually experience nanoparticle coarsening, leading to inactivation. But graphene's unique and enlarged surface area, and strong interfacing with metal catalysts promote particle distribution on the substrate, and forestall their sintering and agglomeration, thus sustaining their catalytic reactivity for a long period of operation [14, 48].

The major challenges to extensive deployment and commercial use of hydrogen production through graphene technologies with its prospective advantages are numerous. Successful implementation of graphene-based hydrogen technologies requires overcoming key difficulties in the synthesis, functionalization, catalytic integration, and system design of the technology. One of the obstacles is the synthesis of cost-effective, high-quality and scalable graphene. The production of graphene with desirable properties through chemical vapor deposition (CVD), mechanical exfoliation and chemical reduction of graphene oxide (GO) requires expensive precursors, complex equipment and involves multiple purification steps [49]. More so, retaining uniform layer thickness, defect density, and surface integrity is critically needed for catalytic efficiency of graphene. Incidentally, these properties are not only difficult to control but costly to mass produce [50]. Even though graphene delivers unique activation aid to metal catalysts during synthesis of hydrogen, the attaching active sites of transition metals like Pt, Ni, Co may not be stable over time. Reaction performance decreases through aggregation and leaching of metal nanoparticles present during multiple reaction cycles. Non-doped graphene displays chemical inertness that hinders its interaction with catalytic species thus complicating synthesis due to additional functionalization needs [51]. When functionalization is conducted to alter the chemical inertness, graphene tends to lose its structural stability.

The future of graphene-based synthesis of hydrogen is bright, symbolizing increased interest in utilizing its unique properties to enhance effectiveness, scale-up, and sustainability in green energy development. Progresses in 'clean' and scalability of graphene production require stringent measures to subdue the present costly and environmentally unfriendly methods. Innovative techniques can create high quality, less energy-demanding and less chemical waste systems, making graphene-assisted techniques more efficient, resilient and sustainable for industrial production of hydrogen. State-of-the-art advancements, like heteroatom doping (N, S, B) or graphene-based nanocomposites are believed to be able to enhance graphene's electronic and catalytic characteristics, tuning its properties in electrocatalytic, photocatalytic and plasma-based hydrogen evolution systems [20, 52].

Furthermore, incorporating graphene into innovative reactor designs, like plasma-induced or light-based hydrogen synthesis can provide avenue for low temperature production with enhanced energy consumption effectiveness. Research outlook should also focus on in-situ testing and computational approach, providing in-depth knowledge of reaction kinetics with smart development of robust and sustainable graphene catalysts. In all, graphene's versatility in properties situates it as a principal innovation in the universal transition to hydrogen-based energy systems, but only if the present drawbacks of longevity, environmental issues and costliness are adequately handled via sustained research and development.

4 Conclusion and recommendations

A thorough analysis by this study demonstrates how graphene induces revolutionary changes in three hydrogen synthesis technologies which include electrocatalysis, photocatalysis and plasma-assisted reforming. Its exceptional material properties such as enlarged surface area, adjustable electronic configuration, high mechanical stability with remarkable electrical and thermal conductivity make graphene an ideal synthetic hydrogen efficiency booster. Graphene-assisted catalysts improve hydrogen evolution reaction by both decreasing reaction overpotentials and improving hydrogen yield reactivity sites. This superior strength equips catalysts with outstanding chemical stability and allows them to protect against 'coking' and offers perfect binding for metal and non-metal catalysts.

The extensive technological potential of graphene in hydrogen production faces various barriers that impede general commercial deployment. The primary downsides stem from expensive manufacturing techniques, short product lifecycle, environmental impact as well as limitations in large-scale production. Research needs to establish both economical and eco-friendly manufacturing systems for better quality graphene production. A complete analysis needs to focus on studying how graphene-based catalysts interact with hydrogen production in diverse operating environments during its reactions. The future research needs to focus on creating efficient graphene functionalization techniques which will use defect engineering tools with metals and semiconductors to optimize hydrogen production while ensuring sustainability goals. Life cycle assessments combined with techno-economic studies need to track technical innovations to validate graphene-based hydrogen methods which fulfil sustainability requirements while being suitable for worldwide commercial clean energy deployment.

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