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Review article

Graphene in water splitting for hydrogen generation

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ABSTRACT

It has been shown that graphene is a viable option for improving water-splitting operations to produce hydrogen. The function of graphene and graphene-based materials in water splitting is critically examined in this review, with an emphasis on current developments, underlying mechanisms, and potential future applications. The most important graphene derivatives used for this purpose are graphene oxide (GO), reduced graphene oxide (rGO), graphene-based metal oxides, graphene-based metal chalcogenides, graphene-based perovskites, graphene-based ternary and quaternary compounds, and graphene quantum dots (GQDs). This article may be useful for academicians, researchers, and industry persons in the area of water splitting for green hydrogen generation.

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KEYWORDS

Graphene and its derivatives
Water splitting
Hydrogen production
Mechanism of water splitting
Future perspectives



1. Introduction

There is a great demand for green energy due to climate issues, the economy, and health-related matters. Besides, economic and social factors also demand green energy. The switch to green energy is essential as the globe confronts more and more issues with resource depletion, climate change, and energy security [1–6]. Everyone is talking about green environment and sustainability. We can achieve these tasks by developing and utilizing green energy for our future requirements. The primary drivers of the need for green energy in the future include the fight against climate change, the management of finite fossil fuel supplies, the preservation of ecosystems, energy independence and security, a decrease in dependency on imported fuels, decentralized energy production, the reduction of air and water pollution, health and well-being, the enhancement of quality of life, the scarcity of current resources, the expensive nature of energy, social and economic equity, economic growth, the creation of new industries and markets, and the creation of jobs. In essence, the need to battle climate change, manage resources responsibly, guarantee energy security, foster economic growth, and enhance public health will be the primary drivers of green energy's future demand. Switching to green energy will

lead to a more affluent, resilient, and fair future in addition to being necessary for the environment.

Among various green energies, hydrogen is considered the best one because of its ease of preparation and high energy value [7–12]. Zero emissions, efficiency, adaptability, ease of storage, long-term storage, ease of transportation, new markets, economic growth, and job creation are some of the other benefits of hydrogen as a green energy source. Hydrogen has enormous potential as a green energy source and can help achieve profound decarbonization, energy security, and a sustainable future. As long as the developments of clean energy technology and climate action remain global priorities, their influence is only going to increase. There are many methods of hydrogen production but water splitting is considered as the best one due to freely available water and sun energy. Furthermore, the water-splitting process is crucial for producing hydrogen for several reasons, especially when considering sustainable energy and environmental preservation. Additionally, water splitting provides zero carbon footprints i.e. zero involvement of carbon. Also, this method offers no byproducts with the potential for innovation and economic growth; leading to various jobs. Finally, the development of a clean and

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sustainable energy future depends on the water-splitting technology for hydrogen synthesis. It provides a technique to create hydrogen without emitting carbon dioxide, encourages the use of renewable energy sources, and is essential to the global initiative to decarbonize different economic sectors.

Normally, water splitting needs photo-catalysts to generate hydrogen [13–17]. Various photo-catalysts including metal oxides, nanoparticles, and nano-composites have been used for this purpose. Nowadays, graphene is considered the material of this century and has been used in a wide range of applications including water splitting for hydrogen generation. Many compounds of graphene have been prepared and used in a variety of applications including water splitting for hydrogen production. Keeping all the above facts into consideration, it was considered worthwhile to write an article on the application of graphene and its derivatives in water splitting for hydrogen production.

2. Graphene

One layer of carbon atoms organized in a two-dimensional honeycomb lattice is known as graphene. It serves as the fundamental structural component of other carbon allotropes, such as fullerenes, graphite, and carbon nanotubes. Because of its special set of qualities, graphene is frequently hailed as a miracle material. Research is still being done to fully realize this material's potential. This is often referred to as the century's substance. In 2004, Andre Geim and Konstantin Novoselov created the amazing material known as graphene, for which they were awarded a Nobel Prize in 2010. Since its discovery, graphene has garnered significant attention and importance, positioning it as the material of the twenty-first century. Nevertheless, the different graphene compounds and composites are not investigated. It has, nevertheless, been applied to a variety of fields, including robotics, energy, sorbent, sensors, electrics, and electronics. Graphene's unique properties allow for a wide range of applications; some are enumerated below[18].

- Carbon: regular hexagons with three atoms surrounding each carbon atom.
- Graphene: a hexagonal, honeycomb-shaped lattice formed by the sp^2 hybridization of carbon atoms.
- There are 3.35 \AA between two adjacent graphene layers.

- The hexagonal array's carbon-to-carbon distance is 1.42 \AA .
- Inter-planar bindings: larger than the inter-planar van der Waals forces, resulting from covalent and metallic bondings.
- The original definition of graphene was one layer of carbon.
- As of late, graphene also known as graphite nanoplatelets or graphite nanosheets ten or more layers.
- It is lightweight, extremely durable, flexible, and 200 times stronger than steel. It can also be bent or folded.
- Because of its small structure, it is the ideal barrier. Even helium is unable to get through it.
- Because of its very thin nature, transparent.
- Only 2.3% of light is absorbed; the remaining light is passed through and is essentially undetectable.
- The thinnest material that has been discovered has a surface area of about $2,700 \text{ m}^2$ per g.
- 1000 times more conductive than copper in both electrical and thermal domains.
- Graphene is incredibly cheap since carbon is the fourth most common and abundant element on Earth.
- Stretchable, allowing sheets to be changed and extended by up to 20% without causing flaws.
- Magnetic characteristics can be changed by stretching a sheet.
- A vast array of physical and chemical properties characterize graphene derivatives, which are chemically inert.

Based on an analysis of the aforementioned graphene properties, it can be inferred that graphene has potential applications in nearly every field of study and industrial production, including hydrogen production by water splitting. The purpose of this article is to investigate the potential applications of graphene and its constituents in hydrogen production by water splitting. The crystal structure of graphene is shown in Fig. 1. On the other hand, Fig. 2 shows the general structures of graphene, graphene oxide, and reduced graphene oxide.

3. Water splitting for hydrogen generation

Photocatalytic water splitting using solar light or other radiation is a suitable way for hydrogen production as our goal is to convert solar energy into hydrogen energy from water. In the process of photocatalytic water splitting, photocatalysts undergo simultaneous

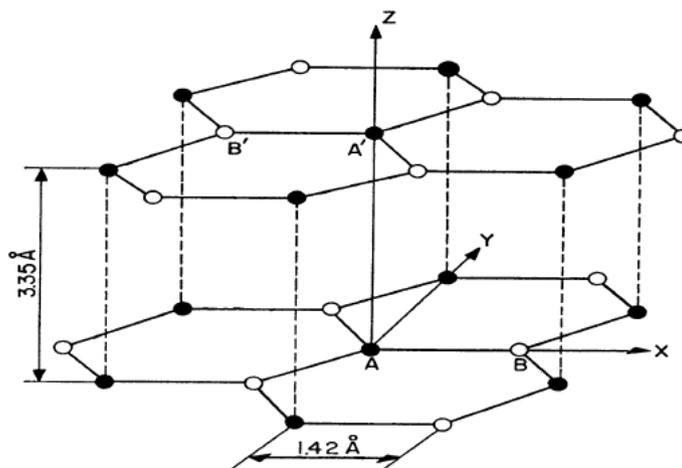


Fig. 1. Crystal structure of graphene.

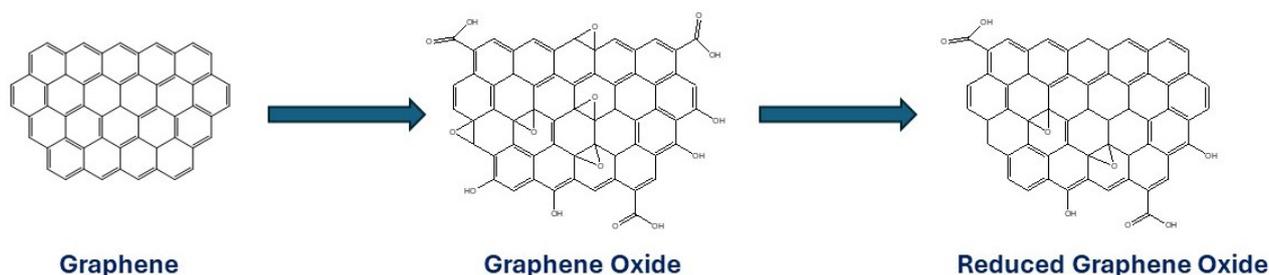


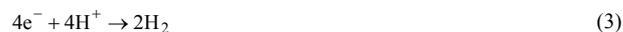
Fig. 2. Structures of graphene, graphene oxide, and reduced graphene oxide.

oxidation and reduction processes under sunlight or other radiation. Most of the photocatalysts are made from inorganic semiconductor materials. In 1972, Fujishima and Honda first reported water splitting into H_2 and O_2 using TiO_2 photo-electrodes [19].

Understanding water splitting's photochemistry is essential for comprehending the process and optimizing the conditions for hydrogen production. For water splitting the materials used are classified as semiconductors because they have an energy difference between the conduction band (CB) and valence band (VB). This is also known as band gap energy (E_g). These materials include atoms with energy levels having distinct populations of electrons and holes. Typically, in their ground state, electrons occupy low-energy states and can absorb photon energy ($h\nu$) in the presence of light, especially when $h\nu > E_g$. When a material absorbs energy, it can excite an electron from the valence band to the conduction band, leaving a hole in the valence band. This excited electron in the conduction band contributes to the material's conductivity. The H_2O molecules are already on the surface of the semiconductor or photo material which converts H_2O molecules into H_2 and O_2 molecules [20]. The four main stages in the mechanism of photocatalytic water splitting are illustrated in Fig. 3 (elementary stages i to iv).

In the first stage i) light is absorbed by the semiconductor and creates electron and hole (e^-h^+) pair. In the second stage ii) migration of e^- and h^+ via the photocatalyst towards the external surface. In the third stage iii) Reduction and oxidation reactions by h^+ and e^- that come into

contact with water. In the final stage iv) unfavorable charge recombination can occur either at the photocatalyst surface or during e^- and h^+ migration, leading to charge annihilation. The spontaneous combination of e^- and h^+ due to thermodynamically favorable and occurs instantly which can reduce the efficiency of water splitting. For water splitting the minimum band gap is required 1.23 eV. With proper radiation, this is simply achievable. The following equations help to understand the photochemistry of water splitting [21]. [19]



The above equations show that the photocatalyst absorbs radiation to create e^-/h^+ . Due to the pair of electrons in the O atom, when H_2O is oxidized with h^+ , it forms O_2 and H^+ . The H^+ ions are separated from water and undergo a 4-electron process CB to produce H_2 . Finally, the fourth equation shows the overall photocatalytic water-splitting process.

4. Graphene in water splitting for hydrogen generation

Because of its special qualities, graphene has demonstrated great promise for improving the efficiency of water splitting for the

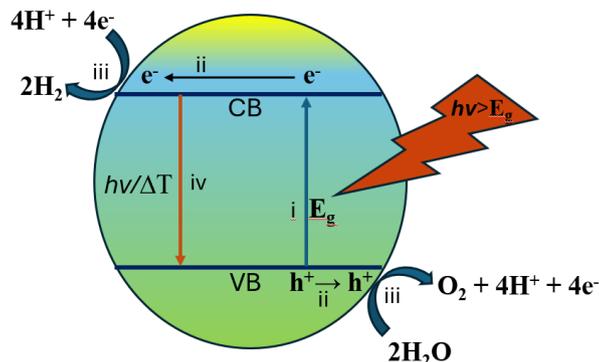


Fig. 3. Fundamental stages in photocatalytic water splitting: i) photoinduced charge formation, ii) charge transfer, iii) oxidation and reduction reaction, and iv) charge recombination.

production of hydrogen. The process of separating water molecules (H_2O) into hydrogen (H_2) and oxygen (O_2) using electrical energy is known as water splitting. Hydrogen production, a clean and renewable energy source, depends on this process. The main reasons for graphene being a good photo-catalyst are electrocatalyst support (high surface area, conductivity, stability), graphene-based composites (metal/metal oxide decorated graphene and graphene quantum dots), photo-catalysis (enhanced light absorption and reduction of recombination) and reduction of over-potential. In essence, research on graphene's potential in water splitting for hydrogen generation is still in its early stages, intending to maximize its benefits and figure out how to economically integrate it into commercial hydrogen production systems.

Despite having several exceptional qualities, such as a higher surface activity, strong mechanical capabilities, and superior electrical conduction, graphene is not an effective photocatalyst for splitting water to produce hydrogen. This is due to band gap limitations, poor charge separation, inert chemical surface, aggregation in water, and absence of catalytic active sites. Therefore, the researchers develop various derivatives of the graphene to explore new photo-catalysts in water splitting for hydrogen generation. Graphene frequently needs to be functionalized with other substances, such as metal oxides or sulfides, to create a band gap or catalytic sites, to enhance its photocatalytic capabilities. This complicates the substance, though, and it might not be as effective as conventional photo-catalysts.

5. Graphene compounds used in water splitting for hydrogen generation

Since graphene and its constituents have special physical, chemical, and electrical properties, there has been a lot of research done on them and their potential to improve water splitting for hydrogen generation. The following discusses the most significant graphene compounds that were investigated for this purpose.

5.1. Graphene oxide (GO)

Metal catalysts can be effectively anchored to graphene oxide's surface thanks to the abundance of oxygen-containing functional groups (such as carboxyl, epoxy, and hydroxyl groups). To increase the catalytic activity in water splitting, these functional groups must interact with

metal nanoparticles to improve their dispersion and stability. To increase the photocatalytic effectiveness of water splitting, GO can also function as a photocatalyst or be mixed with other semiconductors (like TiO_2). Better charge separation is made possible by the presence of oxygen groups, which slow down the recombination of e^-h^+ pairs.

Adding small quantities of oxygenated functional groups can convert certain graphene sp^2 C into sp^3 C. Increasing the oxygen concentration enhances the coexistence of conductivity sp^2 C and nonconductive sp^3 C domains, resulting in the development of a band gap. Because of its reduced electron motion, graphene oxide acts as a p-type semiconductor. The GO band gap ranges from 2.4 to 4.3 eV, based on oxidation state [22]. Increased oxygen concentration causes the band gap to widen as the VBM (valence band maximum) shifts from the graphene orbital to the O orbital, while the CBM (conductive band minimum) stays the same in the (graphene)* orbital. Yeh et al. [20] observed that GO had photocatalytic activity for water splitting, producing $2833 \mu\text{mol/h}$ with methanol as a sacrificial agent and $47 \mu\text{mol/h}$ without it. Later, the same scientists created various GO with varying oxygen concentrations for photocatalysts and examined the effect on photocatalytic water splitting activity [23]. It was shown that a decrease in VBM of GO increases the oxygen concentration. Thus, the graphene oxide with high OP (oxidation potential) produced O_2 , but the less oxygen-containing GO materials did not. The author finds that GO with the highest oxygen concentration had a VBM possible for OPS, but hydrogen evolution was seen in every case. However, highly oxidized graphene oxide had a wide band gap, which slowed light absorption to high Ultraviolet radiation, and due to this hydrogen production was reduced [24]. Fig. 4 illustrates the varying CBM and VBM for the various GO as a different oxygen concentration to the water reduction and oxidation.

Doping inorganic semiconductors and non-metallic atoms with oxides have been frequently stated in photocatalysts to increase the use of sunlight as energy, particularly in the visible portion of solar energy, where conventional semiconductors with wide band gaps are unable to absorb photons. In the instance of TiO_2 , it has been conventional that for increased photocatalytic activity doping with S and N-like elements the energy level is higher than the VBM of the semiconductor, resulting in a band gap reduction [25–27]. In the graphene example, replacing C atoms with B, N, P and other heteroatoms has been shown

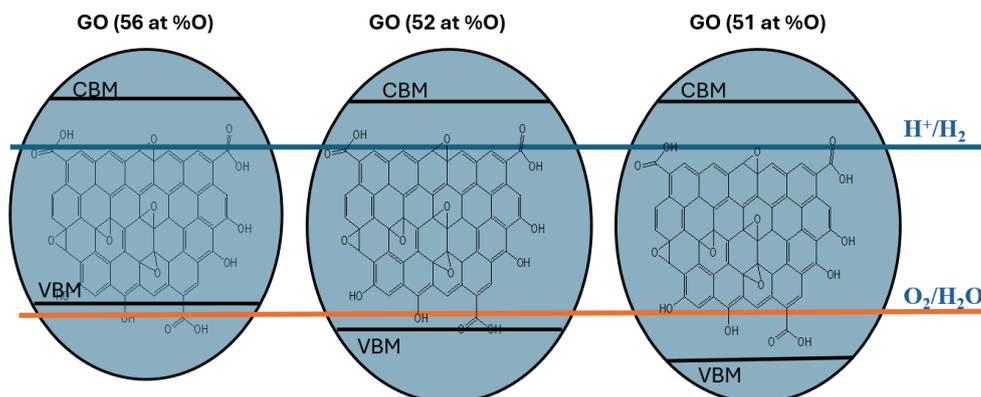


Fig. 4. VBM and CBM positions of graphene oxide materials as different oxygen content. Light Blue and orange lines correspond to the hydrogen reduction and water oxidation potential, respectively.

to affect the charge distribution on graphene, affecting band alliance as well as chemical and optical characteristics.

5.2. Reduced graphene oxide (rGO)

Because rGO has fewer oxygen-containing groups than GO, some of the electrical conductivity that was lost during graphene's oxidation is restored. Because of this, rGO is a superior conductor and can transmit electrons more effectively during the electrocatalytic water-splitting process. When rGO is combined with metal or metal oxide nanoparticles (such as Pt, CoO_4 , or MoS_2), composites that exhibit increased catalytic activity for the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) are frequently produced. N- and B-rGOs were produced by Putri et al. [28] by pyrolyzing graphene oxide with urea and boron anhydride. The authors also discussed reduced graphene oxide (rGO), a photocatalyst for the environmentally friendly synthesis of H_2 , which is doped with boron (B) and nitrogen (N). The significance of dopant atoms in graphene, according to the authors, makes doping a useful tactic to increase photocatalytic activity for stand-alone photocatalysts that are graphene derivatives. To split water, Samal et al. [29] synthesized rGO and $\text{Co}_3(\text{PO}_4)_2$ photo-catalyst. These $\text{rGO-Co}_3(\text{PO}_4)_2$ conjugates can be exploited to create more affordable and environmentally friendly photocatalysts. They demonstrated activity for water splitting and textile dye degradation in the visible range of solar radiation.

5.3. Graphene quantum dots (GQDs)

The electronic characteristics of graphene quantum dots (GQDs), which are minuscule bits of graphene usually smaller than 10 nm in size, can be altered by quantum confinement phenomena. For photocatalytic water splitting, this renders GQDs extremely efficacious in augmenting light absorption and charge transfer. When paired with semiconductors, GQDs can act as photosensitizers, increasing the effectiveness and improving the efficiency of visible-light-driven water splitting. They help extend the absorption range of the light spectrum and improve the separation of charge carriers.

N-doped graphene oxide QDs (GOQDs) with surface dimensions of below 0.1 μm have also been identified as promising photocatalysts. Thus, both the p- and n- domains function as interfacial junctions in

that place charge separation may occur. The band gap is 2.2 eV of N-doped GOQDs and under $\lambda > 420$ nm (visible light irradiation) in the single presence of water, hydrogen and oxygen quantities stoichiometrically measured [30]. Fig. 5 illustrates the reaction pathway in N-doped GOQDs with varying n- and p-type semiconductor domains.

In the same way, S-doped graphene oxide quantum dots (GOQDs) were produced hydrothermally utilizing $\text{HOC}(\text{CH}_2\text{CO}_2\text{H})_2$ (citric acid) as the GOQD precursor and sodium hydrosulfide as the intoxicating source. The goal of S doping was to improve GOQDs' light absorption in the visible range. The scientists found the S-doped GOQDs and graphene oxide band gaps, which were 2.3 and 2.8 eV, respectively. The Ultra Visible-Visible absorption spectra of S-doped GOQDs showed 3 absorption bands, with maximums at 524 nm, 395, and 333 nm respectively. At pH 8 and 95 °C, S-doped GO QDs produce 303 $\mu\text{mol g}^{-1}\text{h}^{-1}$ of H_2 . Adding 20% (v/v) $\text{C}_2\text{H}_5\text{OH}$ to the reaction mixture yielded 508 $\mu\text{mol g}^{-1}\text{h}^{-1}$ under the same conditions. Increasing the percentage of alcohol improved photocatalytic activity, reaching 1471 $\mu\text{mol g}^{-1}\text{h}^{-1}$ of H_2 with 80% (v/v) $\text{C}_2\text{H}_5\text{OH}$ [31]. Carbon QDs have also been utilized to support metal nanoparticles. Chen et al. [32] used a hydrothermal technique to produce NH_3 -modified N-doped GOQDs. Ammonia treatment converts pyrrolic/pyridinic groups to amide/amino groups in N-doped GOQDs. Modified N-doped GOQDs loaded with Pt nanoparticles (NPs) demonstrated 21% QY (quantum yield) in aqueous triethanolamine after irradiation.

5.4. Metal-decorated graphene

Noble metal nanoparticles such as platinum (Pt), palladium (Pd), or gold (Au) can be used to embellish graphene. The metal nanoparticles and the conductive graphene support work in concert to create these metal-decorated graphene composites, which make them excellent electrocatalysts for HER. On graphene or its derivatives, transition metals such as cobalt (Co), nickel (Ni), and molybdenum (Mo) can also be deposited to create highly efficient and economical catalysts. Ni/graphene and Co_3O_4 /graphene composites, for instance, are widely used for OER in alkaline media.

Reduced graphene oxide decorated containing Ni Nanoparticles (NPs) was created using a one-pot reaction with graphene oxide and nickel

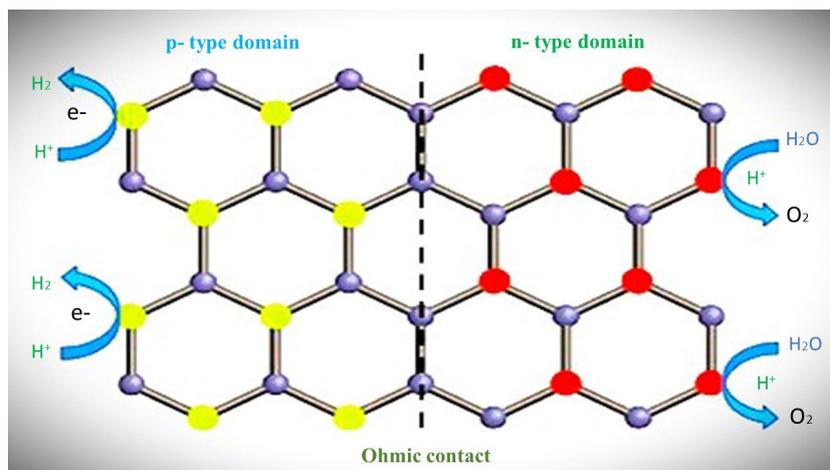


Fig. 5. Complete water splitting in N-doped GOQDs with variable n- and p-type semiconductor domains.

salt as precursors. Photocatalytic H₂ generation was shown to be enhanced by graphene oxide and Nickel Nanoparticles working in tandem. The author discovered that the synergy results from the interaction of Nickel Nanoparticles with reduced graphene oxide faults. At a nickel loading of 6 wt%, nickel-reduced graphene oxide (Ni-rGO) demonstrated at 470 nm photocatalytic activity ($\lambda > 420$ nm) in aqueous dispersions containing trimethylamine, with a QY (quantum yield) of 30.3% [33]. Oliva et al. [34] Ni(OH)₂ NP development on graphene films fabricated by casting method. These nanoparticles have spherical forms and are evenly dispersed on the surface of G. UV light excitation was used to investigate the H₂ production activity of graphene in H₂O with and without Ni(OH)₂ NPs. Graphene decorated with Ni(OH)₂ NPs produced 2.66 times more hydrogen than graphene without NPs. Li et al. [35] showed that utilizing graphene nanosheets decorated with CdS clusters as visible-light-driven photocatalysts resulted in high efficiency in photocatalytic H₂ generation. The materials were produced using a solvothermal technique, with GO as the support and Cd(Ac)₂ as the CdS precursor. At a graphene content of 1.0 wt% and Pt content of 0.5 wt%, these nanosized composites produce 1.12 mmol h⁻¹ (about 4.87 times greater than pure CdS nanoparticles) under visible light irradiation, with an apparent quantum efficiency (QE) of 22.5% at 420 nm. Graphene acts as an electron collector and transporter, increasing the lifespan of photogenerated charge carriers from CdS nanoparticles, resulting in strong photocatalytic H₂-production activity. This study demonstrates the possible use of graphene-based materials for energy conversion.

5.5. Graphene-based metal oxides

Combining graphene with mixed metal oxides (such as ZnFeO₂O₄ and NiCo₂O₄) can result in composite materials with strong water-splitting catalytic activity. These composites improve the performance of metal oxides by making use of graphene's higher surface activity and electrical conduction. The interaction between graphene and metal oxides often leads to improved catalytic properties, such as higher activity, better durability, and lower overpotential in both HER and OER.

Yadav et al. [36] created rGO/CuO heterostructures for hydrogen generation via photocatalytic water splitting. The comparison of CuO and rGO/CuO showed that the latter had enhanced photocatalytic effectiveness. The hydrogen production rate of rGO/CuO was approximately 20 mmol h⁻¹g⁻¹, 3 times greater than CuO. Du et al. [37] developed a Ru/G catalyst with highly catalytic activity for H₂ production. This notable increase in photocatalytic activity is thought to be due to Ru nanoparticles' synergistic impact with graphene. Diab et al. [38] developed a G/NiTiO₃ photocatalyst that had a faster hydrogen production rate than pure NiTiO₃ NPs. This is due to the effective charge carrier separation, significant visible light absorption, and reduced charge carrier recombination. Furthermore, these examples could open the way for developing more nanoparticles based on graphene to improve H₂ production. Iwase et al. [39] created a system in which graphene oxide was sediment on BiVO₄ combined with SrTiO₃- Ru:Rh. Synthesized material shows hydrogen as well as oxygen production.

5.6. Graphene-based metal chalcogenides

Graphene can be enhanced in its catalytic performance by combining it with molybdenum disulfide (MoS₂), a well-known HER catalyst.

Enhanced electrical conductivity and a large surface area for MoS₂ dispersion are provided by graphene, which results in increased catalytic activity. When coupled with graphene or its derivatives, other metal chalcogenides such as Cobalt disulfide (CoS₂) or tungsten disulfide (WS₂) have also been shown to exhibit similar advantages. In a separate methodology, MoS₂ NPs developed on rGO sheets in a one-pot synthesis by pyrolyzing powders or alginate films containing modest quantities of (NH₄)₂MoS₄ at 900 °C under Argon atmosphere. Synthesized material show more the one mmol g⁻¹h⁻¹ hydrogen production rate [39, 40].

5.7. Graphene-based perovskites

Perovskite materials such as BaTiO₃ or LaNiO₃ can be combined with graphene to create hybrid catalysts that are efficient for both photocatalytic and electrocatalytic water splitting. The graphene component improves charge transport and stability, which benefits these perovskites. Lv et al. [41] synthesized Reduced graphene oxide condensed LaNiO₃ materials in which LaNiO₃ NPs were encased in reduced graphene oxide sheets with a macroporous framework, which further promoted the capture of h⁺ and helped with the adsorption and diffusion of CH₃OH. The strong interaction between LaNiO₃ and reduced graphene oxide caused by the developing nickel-carbon bond served as a link to facilitate the efficient separation of e⁻ and h⁺. The as-prepared LaNiO₃-reduced graphene oxide nanoreactors showed significant stability and photocatalytic activity for hydrogen production from H₂O in the presence of CH₃OH as a scavenger. The LaNiO₃-5% rGO photocatalyst achieved a maximum H₂ generation rate of 3.22 mmol g⁻¹h⁻¹, which was 12 times greater than pure LaNiO₃ and had outstanding long-durable stability for 36 hours.

5.8. Graphene-based ternary and quaternary compounds

To maximize the efficiency of water-splitting catalysts, advanced composites containing metals, metal oxides, and other elements (e.g., N-doped graphene with Co₂O₄ and MoS₂) are being created. These substances seek to strike a balance between price, effectiveness, and longevity. Wang et al. [42] developed MoS₂/GO/g-C₃N₄ as an efficient for hydrogen production using solar power. Synthesized material is more active for hydrogen production compared to material without graphene. Khan et al. [43] synthesized CdS/GO/ZnO and CdS/GO/Al₂O₃ to investigate their photochemical activity. Both compounds had an improved photocatalytic activity, which was attributed to GO nanosheets, which provided a larger surface area for facile transfer of charge, reducing the frequency recombination of photo-induced e⁻-h⁺ pairs. These findings emphasize the unique properties of GO, which is an excellent material for carrying e⁻ and collectors that separate charge carriers. Furthermore, this development material is a very efficient graphene oxide-based heterostructured photo-catalyst activated by visible light, which may be used to generate H₂ via overall water splitting. Yu et al. [44] used MoS₂/ CdS/graphene heterostructures to investigate the H₂ generation rate via photocatalytic water splitting. The MoS₂/CdS/graphene composites had a high H₂ evolution rate of up to 1.9 mmol g⁻¹h⁻¹. This was due to the connected graphene acting as a charge transporter and e⁻ acceptor, resulting in outstanding performance. Charge recombination was inhibited in CdS due to the presence of graphene, and e⁻ transport in a synergistic system plays a vital role in increasing photocatalytic activity for hydrogen production. Yue et al. [45] synthesized another photocatalytic system

for H₂ generation: Nb₂O₅/CdS/N-doped G. After 8 hours of visible light irradiation, the greatest quantity of H₂ produced was 800 μmol g⁻¹h⁻¹, which was 7.7-fold more than pure CdS. The improved findings have been attributed to N-doped graphene's increased surface area, improved charge carriers, and superior electrical conduction. Khalid et al. [46] developed Eu-TiO₂/graphene material to study their photocatalytic water splitting performance. The outstanding Features of the synthesized materials, such as enhanced light absorption and slow recombination of e⁻-h⁺ pairs at the same time, were caused by the synergetic outcome of graphene and Eu, which show outstanding hydrogen evolution. Chang et al. [47] produced Ni-doped ZnS-graphene photocatalysts to examine their hydrogen production. The synthesized material demonstrated excellent results, with the greatest

photocatalytic activity for H₂ evolution produced at 8680 μmol g⁻¹h⁻¹. The improved findings were attributed to the synergistic impact of ZnS and graphene, which sped the transfer of e⁻, enhanced surface area, and boosted dispersion features. Xiang et al. [48] investigated WS₂/graphene/CdS heterostructure photocatalysts for the production of H₂ via photocatalytic water splitting. Because of the combined influence of WS₂ and graphene, the physicochemical features of the material reduced charge recombination and increased charge transfer, resulting in effective photocatalytic activity. WS₂/graphene-CdS with a four molar ratio of graphene and WS₂ to CdS had the greatest H₂ evolution rate (1842 μmol g⁻¹h⁻¹). The different graphene derivatives used in water splitting are summarized in Table 1.

Table 1. Hydrogen generation from water splitting using graphene and its derivatives.

Photo-materials	Types of radiation	H ₂ generated	Ref.
Graphene oxide (GO)			
GO	300 W Xe lamp ($\lambda > 420$ nm)	1.61 μmol g ⁻¹ h ⁻¹ (3.5 h)	[49]
GO (O: 28 wt%)	Water/methanol, 400 W Hg lamp	5.67 mmol g ⁻¹ h ⁻¹	[22]
rGO	Methanol, UV-visible (Hg)	2833 μmol g ⁻¹ h ⁻¹	[22]
N doped graphene	Methanol, ND-YAG laser	6 mmol g ⁻¹ h ⁻¹	[50]
N-doped defective graphene	300 W Xe lamp	6400 μmol g ⁻¹ h ⁻¹	[51]
Reduced graphene oxide (rGO)			
N/rGO (8.25 at%)	500 W Xe lamp with visible light	67 μmol g ⁻¹ h ⁻¹	[28]
B/rGO (3.59 at%)	500 W Xe lamp with visible light	65 μmol g ⁻¹ h ⁻¹	[28]
rGO-Co ₃ (PO ₄) ₂	300 W Xe lamp ($\lambda \geq 400$ nm)	6000 μmol g ⁻¹ h ⁻¹	[2]
Graphene-based metal oxides			
Ni/GO	Water/methanol, 400 W Hg lamp	70 μmol g ⁻¹ h ⁻¹	[52]
SrTiO ₃ -rGO	Methanol, 300 W Xe lamp	363.79 μmol g ⁻¹ h ⁻¹	[53]
Cu ₂ O-rGO	Methanol/water, 150 W Xe lamp 18%	264.5 μmol g ⁻¹ h ⁻¹	[54]
Graphene-based metal chalcogenides			
CdS/graphene nanoribbons	Lactic acid, 300 W xenon lamp	1.891 mmol g ⁻¹ h ⁻¹	[55]
MoS ₂ /rGO (MoS ₂ :52.7 wt%)	Water/triethanolamine, Xe lamp UV light	1.2 mmol g ⁻¹ h ⁻¹	[38]
Graphene-based perovskites			
LaNiO ₃ /rGO	-	3.22 mmol g ⁻¹ h ⁻¹	[39]
Graphene-based ternary and quaternary compounds			
Ag-TiO ₂ /G	Methanol/water, 300 W Xe lamp	225 μmol g ⁻¹ h ⁻¹	[56]
CdS/G/MoS ₂	Lactic acid/water, 300 W Xe lamp	1913 μmol g ⁻¹ h ⁻¹	[42]
Nb ₂ O ₅ /N-doped G/CdS	Na ₂ S/Na ₂ SO ₃ , 150 W Xe lamp	800 μmol g ⁻¹ h ⁻¹	[43]
Eu-TiO ₂ /G	Na ₂ S/Na ₂ SO ₃ , MX (metal halogen) lamp	100 mmol g ⁻¹ h ⁻¹	[44]
Ni-doped ZnS-G	Na ₂ S/Na ₂ SO ₃ , 300 W mercury lamp	8683 μmol g ⁻¹ h ⁻¹	[45]
Pt/TiO ₂ /rGO	Triethanolamine solar simulator	1075.68 μmol g ⁻¹ h ⁻¹	[57]
Cd _{0.5} Zn _{0.5} S/gC ₃ N ₄ /rGO	Na ₂ SO ₄ , Xe lamp	39.24 mmol g ⁻¹ h ⁻¹	[58]
Graphene quantum dots (GQDs)			
N/GQDs (N: 6 at%)	Pure water, 300 W Xe lamp with UV light	0.51 μmol g ⁻¹ h ⁻¹	[28]
S/GQDs (S: 1.9 at%)	water/propane-2-ol, 500 W Xe lamp	568 μmol g ⁻¹ h ⁻¹	[29]
S-GO QDs	Ethanol, 500 W Xe lamp	30,519 μmol g ⁻¹ h ⁻¹	[29]
GQDs/TiO ₂	Glycerol, solar light	29548 μmol g ⁻¹ h ⁻¹	[59]

6. Future perspectives

A single sheet of carbon atoms structured in a two-dimensional lattice, graphene has attracted a lot of interest due to its potential applications, including hydrogen generation through water splitting. Because of graphene's special qualities - such as its large surface area, remarkable electrical conductivity, and robustness hold great promise for improving the stability and efficiency of water-splitting operations. The future of graphene and its derivatives includes graphene-based photocatalysts (solar-to-hydrogen conversion and bandgap engineering), reduced overpotentials and cost-effective alternatives for electrocatalysts, scalability and commercialization (large-scale production and integration with renewable energy sources), and catalyst support materials (hybrid materials and enhanced stability and efficiency). With possible improvements in catalyst design, photocatalysis, and electrocatalysis, graphene's future in water splitting for hydrogen generation appears bright. However, stability, scalability, and cost issues must be resolved for graphene-based technology to be successfully commercialized. Graphene is a critical component in the shift to a sustainable hydrogen economy, and its full potential may be realized with further study and innovation in its synthesis, functionalization, and applications.

7. Conclusions

Because of its special qualities such as its large surface area, remarkable conductivity, and mechanical strength-graphene has great potential to transform water splitting for the production of hydrogen. Graphene can be used as a photocatalyst, a component of hybrid catalysts, or a catalyst support material to increase the stability and efficiency of processes involving the evolution of oxygen and hydrogen. But to reach its full potential, issues like cost-effectiveness, long-term stability, and scalability must be resolved. Graphene has the potential to significantly advance efficient and sustainable hydrogen generation, which would promote the wider use of clean energy technologies, with more study and development.

CRediT authorship contribution statement

Imran Ali: Conceptualization, Writing – original draft, Writing – review & editing.

Mohammad Hozaifa: Writing – original draft, Software.

Gunel Imanova: Conceptualization, Writing – review & editing.

Data availability

The data underlying this article will be shared on reasonable request to the corresponding author.

Declaration of competing interest

The authors declare no competing interests.

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