

Application of Graphene and Its Derivative Materials in the Field of Photocatalytic Hydrogen Production

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ABSTRACT

Graphene is a single-atom-thick two-dimensional (2D) carbon material, which exhibits excellent electrical conductivity, high electron mobility, large specific surface area, superior optical transmittance, and outstanding chemical stability. These inherent properties endow it with great suitability for photocatalytic applications. In practical photocatalytic research, graphene is commonly modified according to the catalytic conditions, catalyst composition, and target properties to be exploited; alternatively, graphene derivatives such as graphene oxide (GO) are adopted. Benefiting from the remarkable optoelectronic properties of graphene and its derivatives, they hold broad application prospects in the field of photocatalytic hydrogen evolution (PHE). Furthermore, with the in-depth understanding of their structure and properties, their role in the field of photocatalytic hydrogen evolution will be further consolidated and enhanced. Herein, we review the advances in the application of graphene and its derivatives in photocatalytic hydrogen evolution in recent years, and provide an outlook on their future development trends.

Keywords: Graphene; Photocatalysis; Hydrogen Production; Application

1. INTRODUCTION

Hydrogen is a clean secondary energy source with an ultra-high energy density. Against the backdrop of the increasingly severe impact of human activities on the global climate and the continuously rising global energy demand, there is an urgent need to develop efficient and green fuels to replace traditional fossil fuels ^[1]. The only combustion product of hydrogen is water, with no carbon dioxide or other pollutants generated. Meanwhile, hydrogen has a calorific value ranging from 120 to 143 MJ/kg, with an energy density 3 times that of gasoline, and is regarded as one of the most promising alternative clean energy sources ^[2]. Therefore, the development of sustainable and efficient hydrogen production methods is of paramount importance. Given the abundant solar energy supply and nearly inexhaustible water resources on Earth, photocatalytic water splitting for hydrogen production has emerged as a highly promising green hydrogen production approach.

Despite its broad prospects, the industrial application of photocatalytic water splitting for hydrogen production still faces numerous challenges. Low photocatalytic efficiency, short catalyst service life, and low solar energy utilization efficiency are the main factors restricting the development of photocatalytic hydrogen evolution (PHE) ^[3]. These challenges have driven extensive research on innovative photocatalysts, among which graphene has attracted widespread attention due to its unique physicochemical properties.

Graphene is a two-dimensional honeycomb lattice material composed of sp^2 -hybridized carbon atoms, featuring an ultra-large theoretical specific surface area, high electrical conductivity, and excellent chemical stability. These properties are conducive to improving photocatalytic efficiency ^[4]. Graphene oxide (GO), one of the graphene derivatives, is rich in oxygen-containing functional groups such as epoxy groups, carbonyl groups, carboxyl groups, and hydroxyl groups on its surface, and has better water solubility and modifiability compared with pristine graphene ^[5]. In addition, reduced graphene oxide (rGO) retains part of the functional groups in GO while restoring electrical conductivity to a certain extent ^[6]. Nitrogen-doped graphene can be obtained by doping nitrogen atoms into the graphene lattice, and nitrogen doping can significantly affect the properties and performance of graphene-based materials, thus enabling the tailored regulation of its performance according to application requirements ^[7]. Both graphene and its derivatives possess unique advantages, which have led to their wide application in the field of photocatalytic hydrogen evolution. Herein, this review summarizes the application progress of graphene and its derivatives in photocatalytic hydrogen evolution mainly from three aspects: heterojunction construction, coating structure design, and metal-free catalyst development. Meanwhile, the future development trends of these materials are prospected.

2. GRAPHENE AND ITS DERIVATIVES IN THE CONSTRUCTION OF HETEROJUNCTIONS

In photocatalysts, graphene and its derivatives are mainly used to enhance light harvesting capacity and improve the separation efficiency of photogenerated carriers. One of the most common applications is their participation in the construction of heterojunctions to boost the separation and transport efficiency of photogenerated carriers, thereby improving the overall photocatalytic efficiency.

2.1 Nitrogen-Doped Graphene in Heterojunction Construction

Dao et al. [8] innovatively applied hematite ($\alpha\text{-Fe}_2\text{O}_3$), a low-cost and environmentally friendly catalyst, to light-driven photocatalysis. They adjusted the electronic properties of graphene by doping N atoms into the lattice, enabling nitrogen-doped graphene (NGr) to function as an n-type semiconductor. Using 2D sliced layered hexagonal $\alpha\text{-Fe}_2\text{O}_3$ nanosheets as the core and 2D nitrogen-doped graphene as the shell, they constructed a heterojunction through the combination of the two via a core-shell structure, and incorporated Pt single atoms as the cocatalyst, finally fabricating a 2D/2D Z-scheme $\alpha\text{-Fe}_2\text{O}_3\text{@NGr}$ -Pt single-atom ternary core-shell heterojunction photocatalyst. During the experiments, specimens featuring NGr shell thicknesses of 1 nanometer, 3 nanometers, and 7 nanometers were fabricated. This was achieved by altering the quantities of supplementary glucose and DCDA precursors within the intervals of 10 to 20 milligrams, 20 to 30 milligrams, and 40 to 60 milligrams respectively. Subsequently, the corresponding core-shell structures were designated as $\alpha\text{-Fe}_2\text{O}_3\text{@NGr}_1$, $\alpha\text{-Fe}_2\text{O}_3\text{@NGr}_3$, and $\alpha\text{-Fe}_2\text{O}_3\text{@NGr}_7$. For Pt loading, three types of catalysts with 0.5 wt% and 2.0 wt% Pt loading were prepared for experiments: the Pt loading of NGr-Pt SAs and $\alpha\text{-Fe}_2\text{O}_3\text{@NGr}_3$ -Pt SAs was 0.5 wt%, and that of $\alpha\text{-Fe}_2\text{O}_3\text{@NGr}_3$ -Pt NPs was 2.0 wt%.

Photocatalytic Hydrogen Evolution (PHE) Performance Test:

50 mg of the photocatalyst to be tested was accurately weighed and uniformly dispersed in 50 mL of an aqueous solution containing 0.25 M Na_2SO_3 and 0.25 M Na_2S , which jointly acted as the hole sacrificial agent for the photocatalytic reaction. After dark pretreatment, the photocatalytic performance test under visible light was carried out using a 300 W xenon lamp (Asahi, Max 303) as the light source. Meanwhile, the PHE performance test under actual sunlight irradiation was conducted with the same reaction system, catalyst dosage, and pretreatment conditions.

Table 1. PHE Performance of Different Catalysts.

Catalyst	Pt Loading	PHE Rate ($\mu\text{mol mg}^{-1} \text{h}^{-1}$)	Multiple Relative to Pure NGr
NGr	-	0.39	1
$\alpha\text{-Fe}_2\text{O}_3\text{@NGr}_1$	-	1.24	3.18
$\alpha\text{-Fe}_2\text{O}_3\text{@NGr}_3$	-	1.95	5.00
$\alpha\text{-Fe}_2\text{O}_3\text{@NGr}_7$	-	1.52	3.89
NGr-PtSAs	0.5 wt%	1.80	4.62
$\alpha\text{-Fe}_2\text{O}_3\text{@NGr}_3\text{-PtSAs}$	0.5 wt%	6.40	16.41
$\alpha\text{-Fe}_2\text{O}_3\text{@NGr}_3\text{-PtNPs}$	2.0 wt%	5.25	13.46

As shown in Table 1, after 5 cycles (20 h), the ternary catalyst only lost 7.0% of its activity, while the binary $\alpha\text{-Fe}_2\text{O}_3\text{@NGr}_3$ and pure NGr lost 21.0% and 46.0% of their activity, respectively. The PHE rate of $\alpha\text{-Fe}_2\text{O}_3\text{@NGr}_3\text{-Pt SAs}$ under actual sunlight reached $6.7 \mu\text{mol mg}^{-1} \text{h}^{-1}$, which was slightly higher than that under visible light.

It is evident that the $\alpha\text{-Fe}_2\text{O}_3\text{@NGr}_3\text{-Pt SAs}$ catalyst exhibits superior PHE performance under visible light. The face-to-face contact interface formed by the 2D/2D core-shell structure and the formation of Fe-N bonds further enhance the interfacial bonding, shorten the charge transfer distance, provide an efficient channel for Z-scheme electron recombination, and avoid the light shielding and charge loss caused by the medium. The research idea of preparing photocatalysts by constructing a 2D/2D core-shell composite structure and utilizing the excellent electrical properties and high specific surface area of graphene has important reference value.

2.2 Graphene Quantum Dots in Heterojunction Construction

NaNbO_3 exhibits a typical perovskite structure, accompanied by a high absorption coefficient and excellent chemical stability. However, its wide band gap gives rise to sluggish reaction kinetics and a high recombination rate of photogenerated carriers, thus resulting in suboptimal photocatalytic activity [9]. Graphene quantum dots (GQDs) can significantly enhance the activity and durability of photocatalysts by accelerating the separation and transport of photo-generated carriers due to their excellent electron transport ability, remarkable quantum confinement effect, and abundant surface functional groups. Shao et al. [10] have innovatively combined the simple hydrothermal synthesis method with the self-assembly technology, and successfully prepared GQDs/ NaNbO_3 nanocomposites with dynamic oxygen vacancies. This innovative strategy effectively enhances the activity and stability of the composite material in the photocatalytic hydrogen production (PHE) reaction. In the process of synthesizing GQDs/ NaNbO_3 composite photocatalytic materials, the NaNbO_3 nanocrystal preparation needs to be compounded with graphene quantum dot (GQDs) dispersions with different mass ratios. Specifically, the doping mass fraction of GQDs in the composite material is combined with the NaNbO_3 matrix in the ratio of $x:100$ (where x takes values of 0.5, 1.0, 2.0, and 3.0). The prepared product is labeled as $x\%\text{GQDs}/\text{NaNbO}_3$. Figure 1 shows the construction mechanism of the GQDs/ NaNbO_3 nanocomposite. In this process, graphene quantum dots (GQDs) are anchored on the surface of the NaNbO_3 matrix in a uniformly dispersed manner, thereby constructing a heterojunction-type composite system.

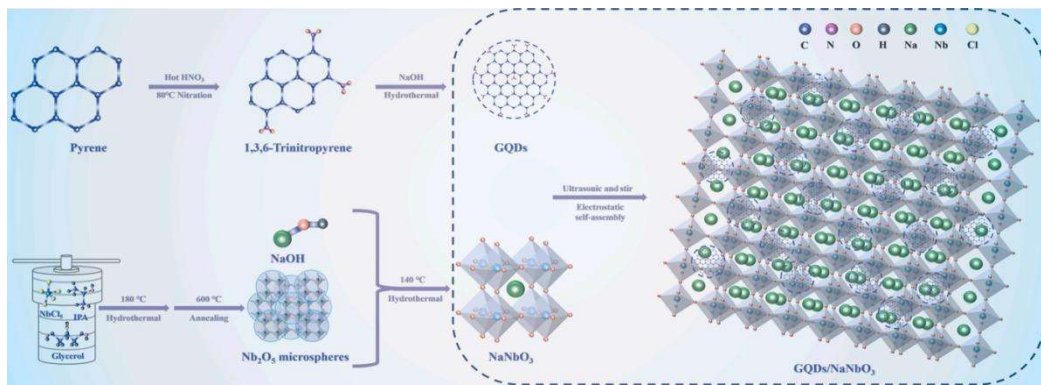


Figure 1. Schematic illustration of the preparation of GQDs/ NaNbO_3 composite. Adapted with permission from (Shao et al, 2025).

Photocatalytic Hydrogen Evolution (PHE) Performance Test:

A 300 W xenon lamp (HSX-F300) was used as the simulated sunlight source. 100 mg of the catalyst was uniformly dispersed in 100 mL of methanol aqueous solution ($V(\text{methanol}): V(\text{water}) = 10:90$), with methanol as the sacrificial agent. The PHE performance of pure NaNbO_3 , composites with different GQDs loadings (0.5%, 1.0%, 2.0%, 3.0%), and pure GQDs was tested.

Table 2. PHE Performance of Different Catalysts.

Catalyst	Total Hydrogen Production in 5 PHE Rate ($\mu\text{mol} \cdot \text{h}^{-1} \cdot \text{g}^{-1}$)		Performance Comparison (vs Pure NaNbO_3)
	$\mu\text{mol} \cdot \text{g}^{-1}$	$\text{g}^{-1} \cdot \text{h}^{-1}$	
NaNbO_3	2593.5	518.7	Baseline
0.5%GQDs/ NaNbO_3	3879.5	775.9	Increased to 1.5 times
1.0%GQDs/ NaNbO_3	2943.0	588.6	Slight increase
2.0%GQDs/ NaNbO_3	2681.0	536.2	Basically the same
3.0%GQDs/ NaNbO_3	2402.5	480.5	Lower than pure phase
GQDs	0	0	No PHE activity

As shown in Table 2, the optimal sample is 0.5%GQDs/NaNbO₃. In 5 consecutive cycle tests, the hydrogen production rate of the optimal sample was greatly improved in the second cycle, which was 1.5 times that of the first cycle, and the catalyst still maintained high activity after 5 cycles.

In their catalyst, GQDs act as efficient electron acceptors, form strong interfacial interaction with NaNbO₃, construct a rapid electron transport channel, and electrons are transferred from the surface of NaNbO₃ to GQDs at the interface. This realizes efficient spatial separation of photogenerated electron-hole pairs and greatly inhibits carrier recombination. This research proposed a dynamic oxygen vacancy strategy. Under light irradiation, the photogenerated electrons generated by NaNbO₃ are rapidly transferred to GQDs, and the photogenerated electrons interact with lattice oxygen to continuously generate new oxygen vacancies. During the cyclic reaction, the oxygen vacancies achieve a dynamic balance of “consumption-regeneration”, and their concentration continues to increase, thus realizing the increase rather than decrease of catalytic activity during the cycle. This has great reference significance for the industry pain point that traditional oxygen vacancies are prone to deactivation and the catalytic efficiency is difficult to maintain at a high level for a long time.

2.3 Heterojunction Construction Based on Graphene-Supported TiO₂ Nanosheet Arrays

TiO₂ is a photocatalytic hydrogen evolution material with non-toxicity, high chemical stability, and excellent photoelectric properties, which has great development prospects. However, pure TiO₂ has three main problems: first, its light harvesting capacity is seriously insufficient, and it can only absorb ultraviolet light with a wavelength less than 388 nm, accounting for no more than 5% of sunlight; second, the recombination rate of photogenerated electron-hole pairs is extremely high, making it difficult for photogenerated carriers to effectively participate in the surface catalytic reaction; third, its nanostructure is prone to agglomeration in aqueous solution, resulting in insufficient exposure of active sites. These problems greatly limit the industrial application of TiO₂. Hu et al. ^[11] combined graphene with high specific surface area, electronic conductivity, and high stability with TiO₂, successfully prepared graphene-supported TiO₂ nanosheet arrays (GT) via a hydrothermal method, and coupled CdS with the non-noble metal cocatalyst Ni₂P to construct a GT/CdS/Ni₂P (GTCN) composite photocatalyst with dual heterojunctions.

Photocatalytic Hydrogen Evolution (PHE) Performance Test:

A 300 W xenon lamp was used as the simulated sunlight source. 30 mg of the catalyst was uniformly dispersed in a mixed solution of 40 mL of water and 10 mL of methanol, with methanol as the sacrificial agent. The PHE performance of GT, pure CdS, GTC, GTCN, and GTN was tested.

Table 3. PHE Performance of Different Catalysts.

Catalyst	PHE Rate (mmol · h ⁻¹ · g ⁻¹)	Performance Comparison
GT	0.15	Reference sample
CdS	0.29	Pure phase sample
GTC	0.35	1.33 times higher than GT
GTN	0.84	4.6 times higher than GT
GTCN	1.91	11.7 times higher than GT

As shown in Table 3, the optimal sample is GTCN. After 5 cycle tests, GTCN still maintained excellent photocatalytic hydrogen evolution activity, with outstanding reusability and structural stability.

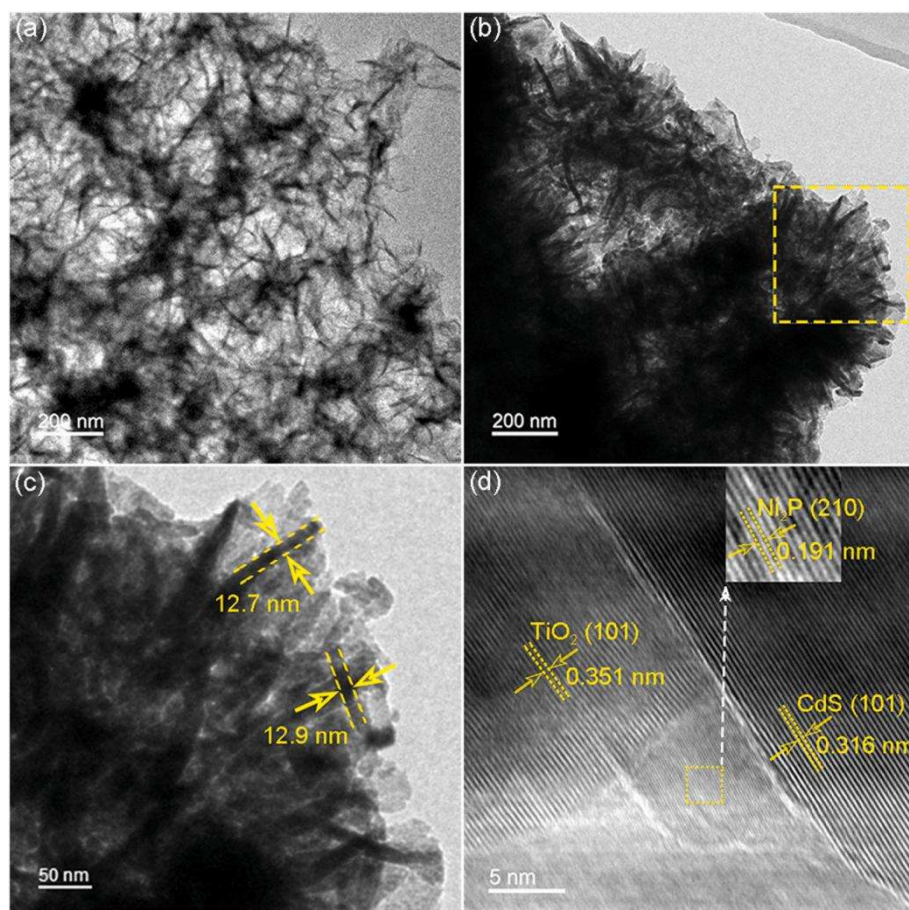


Figure 2. TEM images of (a) GT and (b, c) GTCN; (d) HRTEM image of GTCN. Adapted with permission from (Hu et al, 2025).

In their study, an in-situ growth technique was innovatively employed to realize the vertical growth of titanium dioxide (TiO_2) nanosheets on the surface of graphene substrates. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images (as shown in Figure 2) clearly demonstrate that the thickness of the as-prepared TiO_2 nanosheets is precisely controlled at approximately 12.7 nm. The vertically aligned TiO_2 nanosheets interweave with each other to construct a well-ordered array architecture. The synergistic effect of vertical growth and interlacing of graphene-based nanosheets significantly inhibits their own agglomeration, and at the same time constructs a large number of open channels and anchoring sites. This unique structural design not only endows the loaded TiO_2 nanosheet array with stable structural integrity through the interlaminar mutual support mechanism but also successfully constructs TiO_2/CdS type heterojunctions and $\text{CdS}/\text{Ni}_3\text{P}$ Schottky heterojunctions in the GTCN composite material system, realizing the effective regulation of the energy band structure and the improvement of the charge separation efficiency. The synergistic effect generated by these two heterojunctions constructs a double charge transport channel for photogenerated electrons, greatly improving the separation efficiency of carriers, not only maintaining the strong reduction characteristics of photogenerated electrons but also playing an important role in optimizing the kinetic process of the hydrogen evolution reaction. This unique nanosheet array structure provides a novel strategy for the rational design and fabrication of multicomponent graphene-based photocatalysts for photocatalytic hydrogen evolution.

2.4 Pyrene-Modified Chevron Graphene Nanoribbons in Heterojunction Construction

Owing to the quantum confinement effect, graphene nanoribbons (GNRs) exhibit tunable photoelectric bandgaps, high carrier mobility and prominent exciton effects. At the same time, molybdenum disulfide (MoS_2) is characterized by an octahedral layered S-Mo-S structure, which endows it with excellent electrical conductivity and a large number of active sites for hydrogen evolution reaction. Fang et al. [12] show that the large π -conjugated system of graphene nanoribbons can produce a stronger interaction with the layered crystal structure of molybdenum disulfide (MoS_2), thereby promoting the

charge transport efficiency between the two components and significantly inhibiting the recombination process of electrons and holes. Based on this property, a bottom-up liquid-phase preparation method (as shown in Figure 3) was adopted to synthesize pyrene-modified chevron graphene nanoribbons (cGNRs-Dipyrene), which were then composited with layered MoS₂ to construct a cGNRs-Dipyrene@MoS₂ heterojunction photocatalyst. The synthetic route of cGNRs-Dipyrene is shown in Figure 3, and the pyrene-modified chevron graphene nanoribbons (cGNRs-Dipyrene) were finally successfully prepared through a bottom-up synthesis strategy.

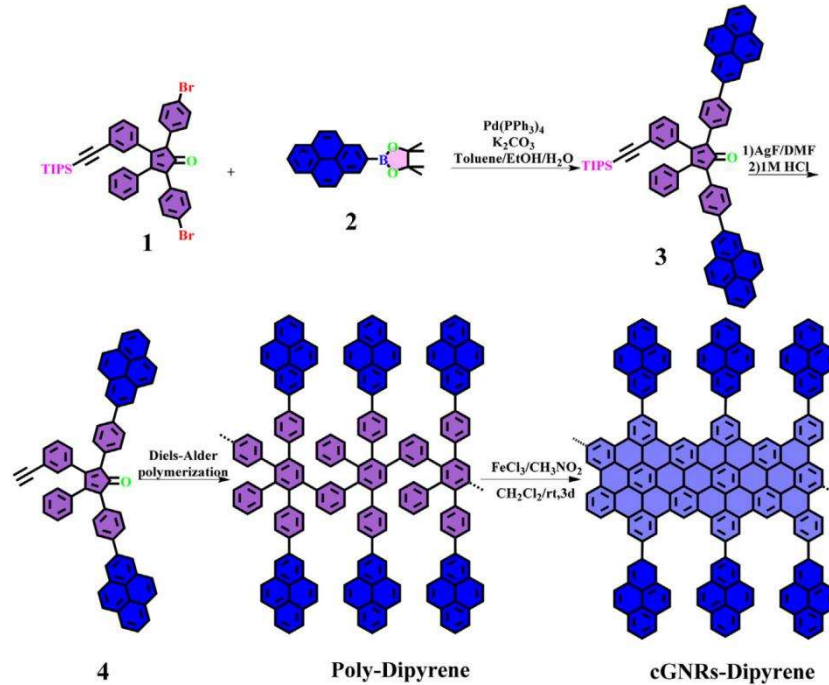


Figure 3. Synthetic route of compound cGNRs-Dipyrene. Adapted with permission from (Fang et al, 2025).

Photocatalytic Hydrogen Evolution (PHE) Performance Test:

A 300 W xenon lamp was used as the simulated sunlight source. 3 mg of cGNRs-Dipyrene@MoS₂ powder was uniformly mixed with 100 mL of 0.3 M ascorbic acid, and 5 wt% Pt was added. 0.3 M ascorbic acid was used as the hole sacrificial agent, and 5 wt% Pt was used as the cocatalyst.

Table 4. PHE Performance of Different Catalysts.

Catalyst	MoS ₂ Doping Ratio	Photocurrent Density	PHE Rate ($\mu\text{mol h}^{-1} \text{g}^{-1}$)
cGNRs-Dipyrene	0 wt%	0.24 $\mu\text{A}/\text{cm}^2$	Extremely low
MoS ₂	100 wt%	0.29 $\mu\text{A}/\text{cm}^2$	No obvious hydrogen production
cGNRs-Dipyrene@MoS ₂	13 wt%	2.64 $\mu\text{A}/\text{cm}^2$	1786

As shown in Table 4, the PHE performance test results show that neither pure cGNRs-Dipyrene nor pure MoS₂ can be used alone as a photocatalyst, which indicates that the cGNRs-Dipyrene@MoS₂ heterojunction enhances the PHE performance. Furthermore, following 5 rounds of extended light exposure (3 hours for each round, amounting to a total of 15 hours), the rate of hydrogen generation by the catalyst remained largely steady. This outcome validates the catalyst's excellent stability during photocatalytic cycling.

In their study, pyrene-modified chevron graphene nanoribbons were synthesized through a bottom-up liquid-phase synthesis strategy, and a cGNRs-Dipyrene@MoS₂ heterojunction was constructed with MoS₂. At the optimal MoS₂ doping ratio, a PHE rate of 1786 $\mu\text{mol h}^{-1} \text{g}^{-1}$ was achieved. This strategy of modifying graphene nanoribbons with conjugated groups and constructing heterojunctions with transition metal sulfides provides a good direction for the development of graphene nanoribbon-based photocatalysts and has great development potential.

3. GRAPHENE-COATED METAL CATALYSTS

Photocatalytic hydrogen production technologies are generally classified into two core pathways based on their reaction mechanisms and system architectures, namely Photocatalytic Hydrogen Evolution (PHE) and Photocatalytic Overall Water Splitting (POWS). The PHE system only proceeds with the water reduction half-reaction and necessitates the addition of sacrificial agents. In contrast, the POWS system drives both water oxidation and reduction half-reactions simultaneously and operates without the introduction of any sacrificial agents.

3.1 Selective Graphene Coating on Metal Cocatalysts

Typically, noble metals with high work functions, including Pt, Rh, and Pd, function as highly efficient cocatalysts for the hydrogen evolution reaction (HER). However, these noble metals also act as active sites for the reverse reaction, where they re-catalyze the recombination of H_2 and O_2 generated from water splitting into H_2O . This process results in a significant decline in hydrogen production efficiency, which represents the core bottleneck hampering the practical implementation of photocatalytic overall water splitting (POWS). Graphene features a unique two-dimensional honeycomb structure, in which the interstices between its aromatic rings are blocked by a dense π -delocalized electron cloud, theoretically allowing it to intercept the majority of gas molecules. Meanwhile, while inhibiting the permeation of gas molecules, graphene maintains high electrical conductivity for electron transport, thereby retaining its electron transfer capability. Based on this, Yang et al. ^[13] selectively coated single-layer graphene on the surface of metal cocatalysts via a chemical vapor deposition (CVD) method to fabricate core-shell structured metal@C cocatalysts. During the selective graphene coating via CVD, 1/2/4 layers of graphene coating were achieved by adjusting the volume of C_2H_2 (3 mL/6 mL/12 mL), and the corresponding samples were named Pt@3C/6C/12C/STO.

Photocatalytic Overall Water Splitting (POWS) Performance Test:

A 300 W xenon lamp was used as the simulated sunlight source. 20 mg of the photocatalyst was uniformly dispersed in 120 mL of deionized water.

Table 5. POWS Performance of Different Catalysts.

Catalyst	H_2 Evolution Rate ($\mu\text{mol} \cdot \text{h}^{-1}$)	Activity Retention Rate after 5 h	Performance Characteristics
Pt/STO	92	35%	Rapid 65% activity decline within 5 h, significant H_2 - O_2 reverse reaction
Pt@3C/STO	149	100%	Single-layer graphene coating, linear gas production rate maintained for 20 h continuous reaction, no activity attenuation
Pt@6C/STO	~100	100%	2-layer graphene coating, complete inhibition of reverse reaction, slight obstruction of electron transport, decreased activity
Pt@12C/STO	~61	100%	4-layer graphene coating, complete inhibition of reverse reaction, significant obstruction of electron transport, greatly decreased activity
Pt/STO/CoOOH	~146	-	Improved activity with CoOOH oxygen evolution cocatalyst, but still limited by reverse reaction
Pt@3C/STO/CoOOH	396	100%	Optimal system, performance 2.7 times that of Pt-based control, superior to the classic $Rh@Cr_2O_3$ system

As shown in Table 5, the optimal sample is Pt@3C/STO/CoOOH. Compared with the Pt/STO catalyst, its hydrogen evolution rate is greatly improved, and no activity attenuation is observed after the 5 h activity test, with greatly improved stability.

The H₂-O₂ reverse reaction is effectively inhibited for all catalysts coated with graphene layers. The gaps between the aromatic rings of graphene are completely blocked by the dense π -delocalized electron cloud, which intercepts O₂ molecules and prevents direct contact between O₂ and the internal Pt core. This greatly hinders the reverse reaction of photocatalytic overall water splitting. At the same time, the graphene coating also protects the Pt core, keeping it in a metallic state all the time and avoiding the deactivation of Pt due to oxidation. This strategy of selectively coating a graphene layer on the catalyst has great development potential, proposes a solution to the problem that photocatalysts are difficult to maintain high activity for a long time, and solves the problem of oxidative deactivation of noble metal cocatalysts. In addition, this scheme has universality and is applicable to a variety of noble metals.

3.2 Nitrogen-Doped Graphene Coated Ni Nanoparticles

At present, the main cocatalysts in the hydrogen evolution reaction are noble metals such as Rh and Pt. Although they have excellent catalytic performance, they have the disadvantages of high scarcity, high price, and prone to H₂-O₂ reverse reaction. As one of the candidate alternative metals, Ni also has two limiting factors: extremely easy oxidation and low catalytic activity. Aiming at the pain points of Ni cocatalysts, Liu et al. [14] adopted the strategy of carbon-coated Ni nanoparticles. This approach has the potential to boost the chemical stability of the catalyst and heighten the photocatalytic activity. In this investigation, SrTiO₃ (STO) was utilized as the model semiconductor support. First, Ni nanoparticles were deposited onto the support using an impregnation technique. Subsequently, N - doped graphene with adjustable structure was selectively coated on the Ni nanoparticles through chemical vapor deposition (CVD). By modifying the volume of the carbon source, graphene coatings with varying layer counts (1, 2, and 4 layers) were obtained. The corresponding samples were labeled as Ni@NC/STO, Ni@2NC/STO, and Ni@4NC/STO. At the same time, Ni@C/STO without N doping was prepared as a control sample.

Photocatalytic Overall Water Splitting (POWS) Performance Test:

A 300 W xenon lamp was used as the simulated sunlight source. 50 mg of the catalyst was uniformly dispersed in 100 mL of deionized water.

Table 6. POWS Performance of Different Catalysts.

Catalyst	H ₂ Evolution Rate ($\mu\text{mol} \cdot \text{h}^{-1}$)	Activity Multiple Relative to Ni/STO	Reaction Stability after 5h
Ni/STO	47	1.0	60% activity decline
Ni@C/STO	65	1.4	Basically stable
Ni@NC/STO	148	3.2	No obvious attenuation
Pt/STO	96	2.0	Continuous attenuation

As shown in Table 6, the optimal sample is Ni@NC/STO. Its photocatalytic hydrogen evolution rate is significantly higher than that of Pt/STO and Ni/STO, and no obvious activity attenuation occurs after the 5 h stability test.

The activity of Ni@NC/STO is greatly improved compared with Ni/STO, and the reaction activity is well maintained during the 5 h reaction, which is mainly attributed to the coating of the nitrogen-doped graphene layer. The graphene layer effectively isolates oxides and prevents them from contacting the Ni nanoparticles, fundamentally solving the problem that Ni is prone to oxidative deactivation in the POWS reaction. Owing to the work function mismatch between Ni and graphene, electrons migrate from Ni to the graphene coating. The nitrogen - doped graphene coating has the ability to promote the transfer of electrons from nickel atoms to the graphene layer. Additionally, it can modify the structure of the graphene layer through nitrogen doping, thereby speeding up the separation of carriers. This research offers an efficient approach to tackle the crucial problems associated with metallic nickel cocatalysts. Moreover, it further validates the significant application prospects of nickel - based cocatalysts in the realm of photocatalytic overall water splitting.

4. GRAPHENE-BASED CATALYSTS WITHOUT CONVENTIONAL METAL SEMICONDUCTORS

At present, the main catalysts for photocatalytic water splitting for hydrogen production are metal materials and semiconductor materials, most of which face problems such as insufficient light harvesting capacity and low light energy conversion efficiency. Wang et al. [15] focused on graphene, an emerging two-dimensional material, which can generate

high-energy hot/free electrons under conventional light irradiation due to its unique Dirac band structure and an Auger-like light-induced electron emission (LIEE) mechanism. Based on this property, the team constructed a 3D/2D graphene/MXene composite photocatalyst without the participation of traditional metal semiconductors.

In the experiment, graphene oxide (GO) was first prepared by the modified Hummers method, and GO was mixed with MXene dispersions of different ratios via a hydrothermal method and freeze-drying process (the graphene in the final prepared catalyst was rGO), to obtain a series of 3DGraphene/MXene composites with different MXene ratios, which were labeled as 3DGraphene/MXene-5, 3DGraphene/MXene-10, 3DGraphene/MXene-15, and 3DGraphene/MXene-20, corresponding to MXene mass ratios of 5%, 10%, 15%, and 20%, respectively. The synthesis process of 3DGraphene/MXene is shown in Figure 4. The reduced graphene nanosheets are cross-linked to form a porous network structure, and the two-dimensional MXene nanosheets are uniformly loaded on the 3D graphene to form the 3DGraphene/MXene composite structure. The rightmost figure shows the macroscopic morphology of the composite, which presents a black monolithic composite material.

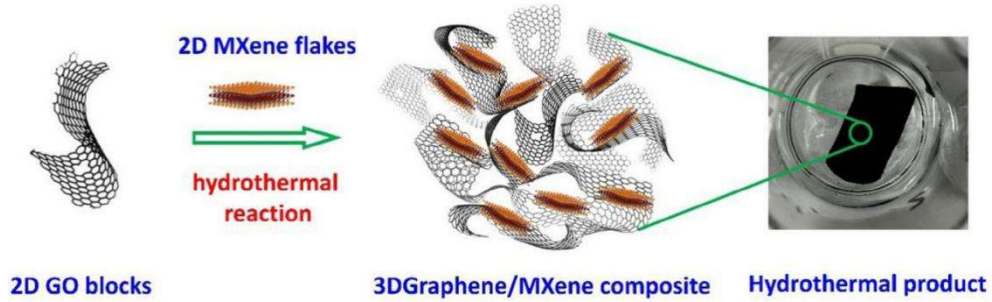


Figure 4. Synthesis procedure of 3DGraphene/MXene and representative photograph of the as-fabricated product (Wang et al, 2025).

Photocatalytic Hydrogen Evolution (PHE) Performance Test:

A 300 W xenon lamp was used as the simulated sunlight source, with methanol as the sacrificial agent.

Table 7. PHE Performance of Different Catalysts.

Catalyst	Average Hydrogen Evolution Rate in the First 0.5 h ($\mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$)	Average Hydrogen Evolution Rate in 4 h ($\mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$)
3DGraphene	392	576
3DGraphene/MXene-5	957	-
3DGraphene/MXene-10	1427	914
3DGraphene/MXene-15	1418	-
3DGraphene/MXene-20	1397	-

As shown in Table 7, the optimal sample is 3DGraphene/MXene-10, with the best hydrogen evolution activity at a MXene ratio of 10%. Excessive MXene will agglomerate on the graphene surface, hinder the absorption of incident light by graphene, and lead to the reduction of catalytic performance. Based on the unique properties of graphene itself, this study prepared a new type of photocatalyst, which has a wider light response range compared with traditional photocatalytic hydrogen evolution catalysts. It further explores the development potential of graphene and other two-dimensional materials in the field of photocatalytic hydrogen evolution, and has important reference value for the design and improvement of photocatalytic hydrogen production catalysts.

5. CONCLUSIONS

Graphene and its derivatives have attracted extensive attention since their discovery due to their unique two-dimensional structure and excellent properties. With their ultra-high electron mobility, tunable energy band, extremely large specific surface area, and unique structural characteristics, they have great development potential in the field of photocatalysis.

Overall, despite the considerable theoretical potential and application value of photocatalytic hydrogen production, the vast majority of reported catalysts remain at the laboratory research stage. Furthermore, photocatalytic performance evaluations are predominantly conducted using the PHE system, whereas the POWS system is far less widely adopted. Although the PHE system delivers high photocatalytic efficiency in tests, its reliance on the consumption of sacrificial agents not only incurs continuous costs for reagent replenishment but also prevents the realization of the ultimate goal of green and sustainable hydrogen production. By contrast, while the POWS system holds promise for achieving this goal, it faces critical challenges, including elevated costs arising from hydrogen-oxygen gas separation and intrinsically lower reaction efficiency. These issues severely constrain the industrialization process of photocatalytic hydrogen production and represent the primary challenges currently confronting this field. With the continuous advancement of graphene research, photocatalytic hydrogen production technologies are expected to break through existing technical bottlenecks.

In summary, this review summarizes several applications of graphene and its derivatives in the field of photocatalytic hydrogen production, and elaborates on the key properties applied therein. Graphene and its derivatives play three main roles in photocatalysis: 1. Accelerating electron transport, boosting the migration rate of photogenerated carriers and inhibiting carrier recombination; 2. Realizing interface regulation by adjusting the properties of graphene materials; 3. Isolating oxidizing substances from metal catalysts to protect the catalysts. Although many studies have prepared catalysts with excellent performance, accelerated the efficiency of photocatalytic hydrogen production to a certain extent, prolonged the catalyst service life, and made many advances in the field of photocatalytic hydrogen production, the following core problems still need to be solved:

- (1) Harsh catalytic conditions and high cost for industrial application
- (2) Complicated catalyst preparation process, which is difficult for industrial production
- (3) Still low catalytic efficiency
- (4) The stability and service life of the catalysts still need to be improved
- (5) Although the light absorption range has been improved to a certain extent, it is still at a low level, with low light energy utilization efficiency

Facing these challenges, more in-depth research is still needed in terms of reducing the cost of photocatalysts, simplifying the preparation process, and further improving the photocatalytic efficiency. Moreover, after laboratory tests, the photocatalytic performance of the catalysts should be tested in an environment closer to the actual application scenarios.

REFERENCES

- [1] Zhao, J., Zhang, J.-J., Li, Z.-Y., & Bu, X.-H. (2020). Recent Progress on NiFe-Based Electrocatalysts for the Oxygen Evolution Reaction. *Small (Weinheim an Der Bergstrasse, Germany)*, 16(51), e2003916. <https://doi.org/10.1002/smll.202003916>
- [2] Li, Z., & Xu, Q. (2017). Metal-Nanoparticle-Catalyzed Hydrogen Generation from Formic Acid. *Accounts of Chemical Research*, 50(6), 1449~1458. <https://doi.org/10.1021/acs.accounts.7b00132>
- [3] Tao, X., Zhao, Y., Wang, S., Li, C., & Li, R. (2022). Recent advances and perspectives for solar-driven water splitting using particulate photocatalysts. *Chem. Soc. Rev.*, 51(9), 3561~3608. <https://doi.org/10.1039/D1CS01182K>
- [4] Zhang, F., Liu, J., Hu, L., & Guo, C. (2024). Recent Progress of Three-Dimensional Graphene-Based Composites for Photocatalysis. *Gels*, 10(10), 626. <https://doi.org/10.3390/gels10100626>
- [5] Dayana Priyadharshini, S., Manikandan, S., Kiruthiga, R., Rednam, U., Babu, P. S., Subbaiya, R., Karmegam, N., Kim, W., & Govarthan, M. (2022). Graphene oxide-based nanomaterials for the treatment of pollutants in the aquatic environment: Recent trends and perspectives – A review. *Environmental Pollution*, 306, 119377. <https://doi.org/10.1016/j.envpol.2022.119377>
- [6] Razaq, A., Bibi, F., Zheng, X., Papadakis, R., Jafri, S. H. M., & Li, H. (2022). Review on Graphene-, Graphene Oxide-, Reduced Graphene Oxide-Based Flexible Composites: From Fabrication to Applications. *Materials*, 15(3), 1012. <https://doi.org/10.3390/ma15031012>
- [7] Xu, H., Ma, L., & Jin, Z. (2018). Nitrogen-doped graphene: Synthesis, characterizations and energy applications. *Journal of Energy Chemistry*, 27(1), 146~160. <https://doi.org/10.1016/j.jechem.2017.12.006>

- [8] Dao, V., Cipriano, L. A., Ki, S.-W., Yadav, S., Wang, W., Di Liberto, G., Chen, K., Son, H., Yang, J.-K., Pacchioni, G., & Lee, I.-H. (2023). 2D/2D Z-scheme-based α -Fe₂O₃ @NGr heterojunction implanted with Pt single-atoms for remarkable photocatalytic hydrogen evolution. *Applied Catalysis B: Environmental*, 330, 122586. <https://doi.org/10.1016/j.apcatb.2023.122586>
- [9] Zhang, D., Qi, J., Ji, H., Li, S., Chen, L., Huang, T., Xu, C., Chen, X., & Liu, W. (2020). Photocatalytic degradation of ofloxacin by perovskite-type NaNbO₃ nanorods modified g-C₃N₄ heterojunction under simulated solar light: Theoretical calculation, ofloxacin degradation pathways and toxicity evolution. *Chemical Engineering Journal*, 400, 125918. <https://doi.org/10.1016/j.cej.2020.125918>
- [10] Shao, W., Han, F., Hu, Y., Chen, W., Xie, Y., Wang, L., Chen, X., Zhang, F., & Ding, L. (2025). Generation of dynamic oxygen vacancies in graphene quantum dots/NaNbO₃ heterojunction for boosting photocatalytic hydrogen evolution. *Journal of Colloid and Interface Science*, 689, 137145. <https://doi.org/10.1016/j.jcis.2025.02.153>
- [11] Hu, H., Chen, F., Li, Y., Li, J., Cui, L., Jiang, D., Lin, X., & Gao, J. (2025). Construction of graphene supported TiO₂ nanosheet array/CdS/Ni₂P composite with dual heterojunctions for boosting photocatalytic hydrogen evolution. *Journal of Alloys and Compounds*, 1024, 180216. <https://doi.org/10.1016/j.jallcom.2025.180216>
- [12] Fang, J., Zhang, J., Han, Y., Xia, W., Li, M., An, J., He, X., & Liu, Y. (2025). In-situ synthesis of graphene nanoribbons with red-fluorescence-emission for constructing heterojunction with ultrafast electron transfer enhances photocatalytic hydrogen production. *Nano Materials Science*. <https://doi.org/10.1016/j.nanoms.2025.02.010>
- [13] Yang, X., Cui, J., Liu, X., Zhang, Q., Wang, D., Ye, J., & Liu, L. (2023). Boosting photocatalytic overall water splitting over single-layer graphene coated metal cocatalyst. *Applied Catalysis B: Environment and Energy*. <https://doi.org/10.1016/j.apcatb.2023.122369>
- [14] Liu, X., Yang, X., Cui, J., Wu, C., Sun, Y., Du, X., Chen, J., Ye, J., & Liu, L. (2023). Ni Coated with N-doped Graphene Layer as Active and Stable H₂ Evolution Cocatalysts for Photocatalytic Overall Water Splitting. *ACS Catalysis*, 13(21), 14314–14323. <https://doi.org/10.1021/acscatal.3c03405>
- [15] Wang, Q., Ye, Z., Zhao, X., Wang, H., Zhang, S., Zhang, S., Liu, H., Lu, Y., Jiao, M., Ma, Y., & Chen, Y. (2025). Enhanced Hot/Free Electron Effect for Photocatalytic Hydrogen Evolution Based on 3D/2D Graphene/MXene Composite. *Small*. <https://doi.org/10.1002/sml.202407863>