

*Research Article*

Promotion of Nickel-Modified Titanium Dioxide Photocatalysts with Graphene and Graphitic Carbon Nitride for Hydrogen Production from Water–Glycerol Mixtures

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Abstract: In photocatalytic hydrogen production, the influence of different promoters on the charge transfer behavior in nickel-modified titanium dioxide remains insufficiently understood, particularly in direct comparisons under the same catalyst platform. This study aimed to compare graphene and graphitic carbon nitride as promoters in Ni-G/TiO₂ and Ni-g-C₃N₄/TiO₂ composites and to elucidate their effects on the photocatalytic hydrogen evolution from water–glycerol mixtures. The composites were synthesized by wet impregnation followed by calcination and characterized using X-ray diffraction, ultraviolet–visible spectroscopy, and Fourier transform infrared spectroscopy to evaluate their structural and optical properties. Photocatalytic hydrogen production was tested under ultraviolet irradiation for 4 h in a batch photoreactor. Among the investigated materials, Ni-G/TiO₂ exhibited the highest hydrogen production of 12.8 mL, outperforming TiO₂ (8.3 mL), graphitic carbon nitride (7.4 mL), and Ni-g-C₃N₄/TiO₂ (9.0 mL). The superior performance of Ni-G/TiO₂ is attributed to the higher conductivity of graphene, which promotes more efficient electron migration and suppresses charge recombination more effectively than the band-alignment-dominated charge transfer in Ni-g-C₃N₄/TiO₂. These findings demonstrate that promoter selection governs electron transfer pathways and strongly influences photocatalytic performance. This study provides comparative insight into promoter-dependent electron transfer and establishes a design basis for improving the hydrogen production of titanium dioxide-based photocatalysts.

Keywords: g-C₃N₄; Graphene; Hydrogen production; Nickel; Photocatalysis; TiO₂

1. Introduction

As a renewable energy source, hydrogen holds great potential as an environmentally friendly alternative fuel because it does not emit CO₂ into the atmosphere (Carmen & V, 2008). However, the current utilization of hydrogen heavily relies on conventional technologies, such as steam reforming, coal gasification, conventional electrolysis, and partial oxidation, which are not environmentally friendly (Sutarno & Malik, 2016). In this context, photocatalytic water splitting has emerged as a promising technology for hydrogen production, offering improved energy efficiency and environmental sustainability (Slamet et al., 2015).

Photocatalytic hydrogen production from renewable sources, such as water and glycerol, involves concurrent oxidation-reduction reactions propelled by solar energy (Bednarczyk & Gmurek, 2024). Glycerol is commonly employed as a sacrificial agent because it readily scavenges photogenerated holes, suppresses electron–hole recombination, and enhances the efficiency of hydrogen evolution. Glycerol is an abundant and low-cost by-product of the biodiesel industry, making it an attractive renewable feedstock for sustainable photocatalytic hydrogen production.

This concerted process results in the creation of a pristine energy reservoir, devoid of contributions to both greenhouse gas emissions and concerns about global warming (Ramamurthi et al., 2000). Titanium dioxide (TiO_2) stands as a prevalent choice for an efficacious photocatalyst (Kustiningsih & Slamet, 2014) because of its outstanding photocatalytic performance, chemical robustness, non-toxic nature, corrosion resistance, cost-effectiveness, and adaptability across diverse applications (Kurniawan, 2018). However, TiO_2 does exhibit inherent limitations, notably inefficient absorption of visible light due to a large band gap of 3.2 eV, along with a relatively elevated rate of recombination for electron-hole pairs (Yu et al., 2019).

One of the most potent strategies for enhancing the effectiveness of TiO_2 photocatalysts involves the introduction of transition metal dopants (Choi & Hoffmann, 2010). Ni, a representative transition metal, possesses the ability to engender supplementary acceptor and donor states situated above the valence band and below the conduction band within TiO_2 photocatalysts (Shen et al., 2015). The integration of nickel metal demonstrates notable potential in amplifying the activity of TiO_2 photocatalysts, functioning as an electron capturer to impede the undesired electron-hole recombination process. In addition, this integration facilitates the heightened absorption of visible light, thereby augmenting the photocatalytic performance (Bhanvase et al., 2017). Nonetheless, the incorporation of an additional promoter becomes imperative to fully exploit these advantageous attributes. This promoter would further curtail the rate of electron-hole recombination, thereby expediting an efficient electron relay toward the targeted redox pairs.

Graphene, a two-dimensional material consisting of a single layer of graphite with a thickness of approximately one carbon atom, is characterized by remarkable electrical conductivity, charge carrier mobility, and high thermal conductivity (Norman et al., 2015). These exceptional properties render graphene highly suitable for photocatalytic applications. By acting as a promoter for TiO_2 , graphene expands the specific surface area, effectively providing the fast pathway for electrons to separate from holes in interacting with their respective redox targets (Yu et al., 2019). Furthermore, graphene possesses exceptional electrical conductivity, high electron mobility, and a large specific surface area, enabling efficient electron transport and suppressing charge recombination. These properties make graphene an attractive promoter for enhancing photocatalytic hydrogen production.

Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$), characterized by a band gap of 2.7 eV, shares a two-dimensional architecture akin to that of graphene, rendering it a compelling photocatalyst with wide-ranging applications (Ong et al., 2016; Saputera & Devianto, 2025). Positioned at approximately -1.3 V and 1.4 V vs. NHE at pH 7, the conduction and valence bands of $\text{g-C}_3\text{N}_4$ hold promising potential for catalyzing oxidation-reduction reactions in the context of photocatalytic water splitting (Baudys et al., 2020). Nevertheless, $\text{g-C}_3\text{N}_4$ is not exempt from certain limitations, encompassing the swift recombination of excited electron-hole pairs and a constricted specific surface area (Mun & Park, 2019). However, synergizing $\text{g-C}_3\text{N}_4$ with TiO_2 , which features conduction and valence bands positioned at approximately -0.5 V and 2.7 V vs. NHE, respectively (Mamba & Mishra, 2016), drives concerted electron-hole translocation at the semiconductor interface. In this composite design, electrons originating from the conduction band of $\text{g-C}_3\text{N}_4$ seamlessly navigate to the conduction band of TiO_2 , while holes emanating from the valence band of TiO_2 migrate to the valence band of $\text{g-C}_3\text{N}_4$. This alignment results in the effective separation and directed transport of charge carriers, which channel them adeptly toward their designated redox targets. In addition, $\text{g-C}_3\text{N}_4$ exhibits a moderate band gap (~ 2.7 eV), good visible-light responsiveness, good chemical stability, and suitable band-edge positions for photocatalytic hydrogen evolution. These characteristics make $\text{g-C}_3\text{N}_4$ a promising semiconductor for heterojunction photocatalysts.

Although graphene and $\text{g-C}_3\text{N}_4$ have been extensively studied as promoters in TiO_2 -based photocatalysts, direct comparisons between these materials under identical experimental conditions remain limited. Both materials are expected to enhance photocatalytic hydrogen production through different mechanisms. Graphene facilitates electron transport owing to its high

electrical conductivity and mobility, whereas g-C₃N₄ promotes charge separation through heterojunction formation and broadened light absorption. However, the relative effectiveness of these promotion strategies in Ni/TiO₂ photocatalysts remains unclear. Therefore, this study investigates the influence of graphene and g-C₃N₄ as promoters in Ni-X/TiO₂ composites (X = graphene or g-C₃N₄) for photocatalytic hydrogen production from water–glycerol mixtures. The effects of promoter selection on optical properties and hydrogen evolution performance were compared to elucidate the role of different charge-transfer enhancement mechanisms in TiO₂-based photocatalysts.

2. Methods

2.1 Material

Titanium dioxide (TiO₂ P25, Evonik Industries AG, Hanau, Germany), single-layer graphene (ACS Material LLC, Pasadena, CA, USA), nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, Merck KGaA, Darmstadt, Germany), urea (Merck KGaA, Darmstadt, Germany), methanol (Merck KGaA, Darmstadt, Germany), argon gas (Pro Gas, Bogor, Indonesia), and deionized water were used as received without further purification.

2.2 Synthesis of the photocatalyst

The composite of graphene-modified TiO₂ (G/TiO₂) was synthesized via a wet-impregnation technique. Initially, a solution containing 1 mg of single-layer graphene (ACS Material) dissolved in 100 mL of ethanol/water (volume ratio of 4:1) was subjected to 1 hour of sonication. Subsequently, 1 g of TiO₂ P25 (Evonik) was introduced into the solution, which was vigorously stirred for 1 hour, and followed by an additional hour of sonication. The resultant suspension underwent successive rounds of centrifugation, each lasting 1 hour, and was subsequently dried at 80°C in an oven for a duration of 2 hours. For the fabrication of Ni-G/TiO₂ composites, varying quantities of Ni(NO₃)₂·6H₂O (Merck) ranging from 0.5 wt% to 4 wt% were introduced into the suspension. The resulting precipitates were homogenized through grinding and subsequently subjected to calcination at 500°C for a period of 2 hours, conducted under a N₂ atmosphere.

The synthesis of g-C₃N₄ involved a multi-step procedure. Initially, 10 grams of urea was placed in a crucible container, which was then sealed with an aluminum foil-covered lid. The crucible was heated in a furnace and maintained at 550°C for 3 h, with the temperature being ramped up at a rate of 2°C min⁻¹. After cooling to room temperature (approximately 29°C), the resulting sample was meticulously ground into a powdered form. The resultant powder exhibited a distinct yellow color. The formulation of Ni-g-C₃N₄/TiO₂ was achieved using the wet-impregnation approach. Commencing with the mixing of 0.05 grams of g-C₃N₄ and 1 gram of TiO₂ within 40 mL of methanol contained in a beaker, the mixture was stirred using a magnetic stirrer for 1 h until homogeneity was attained. Subsequently, the beaker containing the g-C₃N₄, TiO₂, and methanol underwent ultrasonication within a bath-type ultrasonicator for a duration of 1 hour. Following this step, Ni(NO₃)₂·6H₂O was added to the solution, which was then stirred and heated to 80°C on a hot plate for 2 hours. The resulting Ni-g-C₃N₄/TiO₂ powder was subjected to careful grinding before calcination in the presence of flowing N₂ gas. The synthesis routes of G/TiO₂, Ni-G/TiO₂, g-C₃N₄, and Ni-g-C₃N₄/TiO₂ photocatalysts are schematically illustrated in Figure S1.

2.3 Material Characterization

The crystalline phase of the photocatalysts was confirmed through X-ray diffraction (XRD) analysis using a PANalytical Aeris instrument. The scanning range for the XRD measurements was set from $2\theta = 5^\circ$ to 80° , affording comprehensive insights into the samples' crystal structure. UV-Vis diffuse reflectance spectra (DRS) were recorded to appraise the optical ab-

sorption of the photocatalyst specimens. This endeavor was executed using an Agilent Cary 60 UV-Vis spectrophotometer, which spanned the wavelength spectrum from 200 to 800 nm. The DRS analysis facilitated an intricate examination of the absorptive characteristics of the samples. Fourier-transform infrared (FTIR) spectroscopy was employed to identify the inherent functional groups within the prepared photocatalysts. This analysis was conducted using a Thermo Scientific Nicolet iS5 instrument, operating across the infrared spectrum encompassing the range of 4000 cm^{-1} to 400 cm^{-1} . By leveraging FTIR, the presence of distinct functional groups within the photocatalysts was unequivocally verified. The conjoint use of XRD, UV-Vis DRS, and FTIR techniques engendered a holistic characterization of the photocatalysts, thus facilitating a nuanced understanding of their structural, optical, and chemical attributes.

2.4 Photocatalytic Hydrogen Production

Experiments on photocatalytic hydrogen production were conducted within an internally illuminated reactor. In each experimental run, 0.2 g of the photocatalyst was introduced into a 250 mL Pyrex reactor containing a 250 mL mixture of glycerol and water, with the glycerol content maintained at 10% v/v. Continuous stirring was applied throughout the reaction, and the headspace of the reactor was linked to a buret containing water at atmospheric pressure, enabling the measurement of the evolved hydrogen volume through the displacement of water. A cooling water system was integrated into the reactor, set at 20°C , to ensure isothermal conditions to counterbalance heat generation during photon exposure. Additionally, a thermometer was employed for real-time temperature monitoring within the reactor. Prior to light irradiation, an argon purge was instituted within the reactor for a span of 15 min, followed by a meticulous leak test to confirm the elimination of air and validate the absence of any leaks during the experimental process. The photocatalytic reaction was conducted for 4 h using a 20 W UV lamp as the irradiation source. The lamp provides broad UV emission and was positioned inside the reactor using a quartz sleeve, enabling an internal illumination configuration. This setup allows the reaction solution to be directly and uniformly irradiated without a defined lamp-to-reactor distance. The intensity of light at the reactor surface was not directly measured. The presence of hydrogen in the collected gas samples was subsequently confirmed through gas chromatography (GC) analysis conducted using a Shimadzu GC-8A instrument. After the photocatalytic reaction, gas samples were withdrawn directly from the buret and injected into the GC for hydrogen identification. The measured hydrogen volume was not corrected to standard temperature and pressure (STP). Figure S2 schematically illustrates the configuration of the photocatalytic hydrogen production reactor used in this study.

3. Results and Discussion

3.1 Synthesis of the photocatalyst

3.1.1 XRD Analysis

The characteristic diffraction peaks corresponding to the anatase and rutile phases of TiO_2 are displayed in Figure 1. The anatase phase of TiO_2 exhibited distinct peaks at 2θ values of 25.3° , 37.8° , 48° , 53.9° , 55.1° , 62.6° , 68.8° , 70.3° , and 75.1° , corresponding to crystal facets (101), (004), (200), (105), (211), (204), (116), (220), and (215), respectively (Ghadiry et al., 2016). In addition, a minor presence of the rutile phase in TiO_2 was observed, with peaks at 2θ values of 27.5° , 36° , and 41.4° , associated with crystal facets (110), (101), and (111), respectively (Haider et al., 2015; Zos'ko et al., 2023). The observed diffraction peaks correspond to the tetragonal crystal system of the anatase and rutile TiO_2 phases. The preservation of these characteristic peaks indicates that the incorporation of graphene and Ni did not alter the crystal structure of TiO_2 . According to the JCPDS data for nickel nanoparticles (no. 04-850), the diffraction peaks of nickel should be observed at 2θ values of 44.5° , 52° , and 78° , corresponding to the crystal facets (111), (200), and (220), respectively (Wang et al., 2008). However, no discernible nickel

diffraction peak was detected at those angles for the 4% Ni-G/TiO₂ sample. This absence can be attributed to the extremely low nickel concentration in the sample (Krýsa et al., 2004).

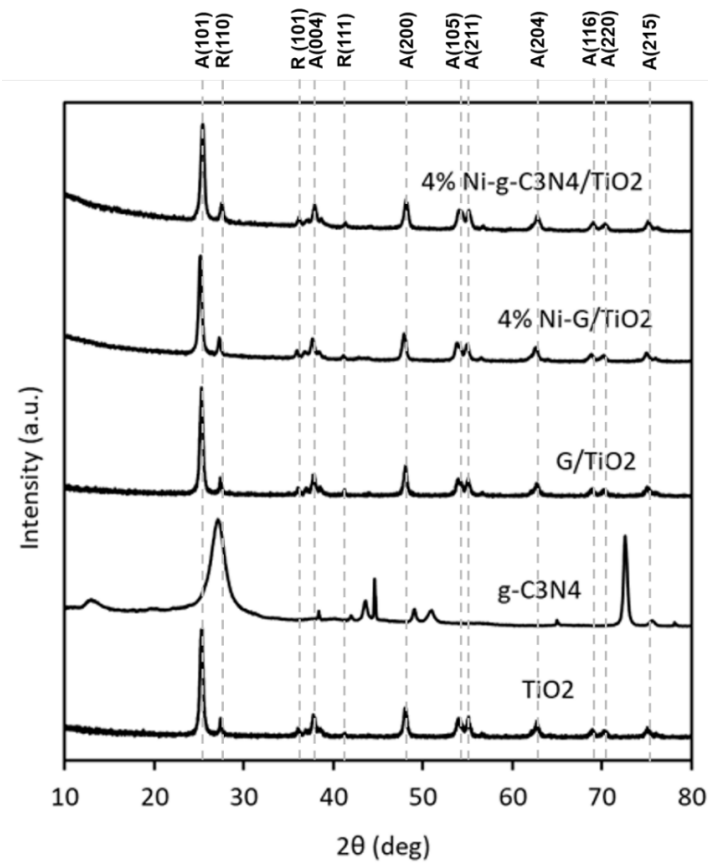


Figure 1 X-ray diffraction patterns of photocatalysts showing the characteristic diffraction peaks of anatase and rutile phases

The incorporation of graphene did not yield observable diffraction peaks, likely due to the amorphous arrangement inherent to graphene (Makki & Hussein, 2019). As a result, the XRD diffraction patterns of TiO₂ P25, G/TiO₂, and 4% Ni-G/TiO₂ samples displayed no marked disparities. This observation implies that the introduction of nickel and graphene did not deleteriously affect the crystalline structure of TiO₂, the principal light-harvesting constituent (Rahmatallah et al., 2021). The crystallite size (*D*) was estimated using the Scherrer equation (eq. (1)):

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where *D* is the crystallite size, *K* is the shape factor (0.9), λ is the X-ray wavelength (0.15406 nm for Cu K α radiation), β is the diffraction peak's full width at half maximum (FWHM) in radians, and θ is the Bragg diffraction angle. The crystallite size was calculated using the diffraction peak of anatase (101).

The crystallite size of the anatase (101) facet was derived using this method, as documented in Table 1. The crystallite sizes determined for the photocatalysts TiO₂ P25, G/TiO₂, and 4% Ni-G/TiO₂ were determined to be 17.88, 17.70, and 17.63 nm, respectively. These outcomes indicate that the inclusion of nickel in the capacity of transition metal dopants did not induce noteworthy modifications in the crystal properties of TiO₂. This negligible effect can be attributed to the relatively modest concentration of nickel, which constrains its capacity to appreciably influence the crystal dimensions of TiO₂ P25 (Vega et al., 2018).

Table 1 Crystallite size of anatase (101)

Photocatalyst	2θ	FWHM	Crystallite size (nm)
TiO ₂ (P25)	25.26	0.45	17.88
G/TiO ₂	25.26	0.46	17.70
4% Ni-G/TiO ₂	25.12	0.46	17.63

3.1.2 UV-Vis DRS analysis

To examine the optical characteristics of the photocatalyst sample and evaluate its absorption across both UV and visible light spectra, a series of UV-Vis diffuse reflectance spectroscopy (DRS) analyses were performed. The photocatalyst's absorption spectrum was recorded within a wavelength span encompassing 200–800 nm. Figure 2(a,b) shows the wavelength-absorbance profiles of the photocatalyst, capturing alterations in absorption intensity. All samples manifested a discernible red shift in their absorption spectra, indicating an augmented capacity of the photocatalysts to capture photons from the visible light domain.

The absorbance values in the UV wavelength region (200–400 nm) indicate distinct differences among the tested photocatalysts. Notably, g-C₃N₄ exhibits the lowest absorbance value, while 4% Ni-G/TiO₂ demonstrates the highest absorbance value. This observation suggests that 4% Ni-G/TiO₂ exhibits the most favorable response to UV light. Conversely, the absorption intensity differences among the photocatalysts are relatively subtle in the visible light wavelength region (400–800 nm). TiO₂ P25 shows the lowest absorbance value, whereas G/TiO₂ displays the highest. The incorporation of graphene into TiO₂, leading to the formation of Ti-O-C bonds, may account for the observed red shift in the UV-Vis spectrum (Park et al., 2006). Among the different variations of Ni loading on Ni-G/TiO₂ composites, similar absorption patterns and values are observed, with the most significant red shift occurring in the 4% Ni-G/TiO₂ composite. This red shift can be attributed to the introduction of Ni transition metal dopants, which enhance photon absorption in the visible light region by creating intermediate energy levels (Feng & Wu, 2020). Additionally, the red shift in Ni-G/TiO₂ can be attributed to the substitution of nickel metal and the presence of the graphene promoter, resulting in an intra-band state below the conduction band derived from the partially filled 3d orbital of nickel metal (Zhao et al., 2016).

Table 2 Band gap energies of TiO₂-based photocatalysts estimated from UV-Vis diffuse reflectance spectra using the Kubelka–Munk method and Tauc plot analysis

Photocatalyst System	Ni (wt%)	Band gap (eV)
TiO ₂ (P25)	–	3.28
g-C ₃ N ₄	–	2.68
G/TiO ₂	–	3.06
	0.5	3.05
	1.0	3.05
Ni-G/TiO ₂	2.0	3.00
	4.0	2.98
Ni-g-C ₃ N ₄ /TiO ₂	4.0	3.00

Table 2 presents the bandgap values of the synthesized composites assessed using the Kubelka-Munk function. The bandgap energies were estimated from the Tauc plots by assuming an indirect allowed transition ($(\alpha h\nu)^{1/2}$ vs. $h\nu$) (Figure S3), which is commonly applied for TiO₂-based materials. The 4% Ni-G/TiO₂ composite attains the smallest band gap among the examined photocatalysts, encompassing TiO₂ P25 and the five distinct Ni loading variations. The observed reduction in bandgap energy is expected and is consistent with previous studies

on Ni-modified TiO₂ photocatalysts. The introduction of Ni-related electronic states and the interaction between Ni and graphene can generate intermediate energy levels within the TiO₂ electronic structure, thereby reducing the energy required for electronic excitation. This observation highlights the notable bandgap attenuation through the Ni loading integration within the Ni-G/TiO₂ composite. The inclusion of the graphene promoter in tandem with the transition metal Ni facilitates this diminution through the formation of an intermediate energy band proximate to the conduction band of TiO₂. This dual modulatory effect culminates in a diminished band gap value, amplifying the TiO₂ modification process by the transition metal Ni and graphene promoter, particularly during visible light exposure (Low & Boonamnuayvitaya, 2013). The incorporation of Ni dopants into the TiO₂ lattice allows the excitation of Ni 3d electrons to the TiO₂ conduction band (Subagja & Widiarti, 2017). This dynamic engenders a heightened efficiency and activity within the composite. A narrower bandgap value imparts greater receptivity of TiO₂ to visible light wavelengths. A reduced bandgap energy is generally desirable for photocatalytic applications because it broadens the light absorption range and allows the photocatalyst to utilize a larger fraction of the available light spectrum. Consequently, more photogenerated charge carriers can be produced, potentially enhancing the photocatalytic activity. Note that the photocatalytic hydrogen production experiments in this study were conducted under UV irradiation. Therefore, although the observed red shift and bandgap reduction indicate improved light-harvesting capability, their direct contribution to visible-light-driven hydrogen production was not evaluated in this study. Thus, the optical characterization results should be interpreted as evidence of modified light absorption properties rather than visible-light photocatalytic activity. Furthermore, this abridged bandgap energy intensifies the photocatalytic potential by diminishing the requisite energy for electron excitation from the valence band to the conduction band (Putra, 2017). However, the photocatalytic performance is not determined solely by the bandgap energy. Other factors, such as charge separation efficiency, charge carrier mobility, recombination rate, surface active sites, and interfacial electron transfer processes, also play an important role in governing photocatalytic activity. Therefore, the superior hydrogen production observed for Ni-G/TiO₂ cannot be attributed exclusively to its lower bandgap energy but is also associated with the enhanced electron transport capability provided by graphene and the electron-trapping role of Ni.

3.1.3 FTIR Analysis

Figure 3 depicts the FTIR spectra of the synthesized photocatalysts, showcasing vibrational peaks within the wavenumber range of 3300–2800 cm⁻¹ for TiO₂, G/TiO₂, 0.5% Ni-G/TiO₂, 1% Ni-G/TiO₂, 2% Ni-G/TiO₂, and 4% Ni-G/TiO₂. These peaks signify the presence of the C-H functional group, characteristic of graphene (Hayyan et al., 2015). Additionally, within the wavenumber range of 1150–1000 cm⁻¹, the presence of the C-O functional group becomes obvious (Naebe et al., 2014). Transmission peaks arising in the wavenumber range of 650–500 cm⁻¹ indicate the existence of Ti-O and Ni-O bonds, denoting the incorporation of Ni metal (Zhang et al., 2016). In the g-C₃N₄ and 4% Ni-g-C₃N₄/TiO₂ specimens, broad transmission peaks spanning the range of 3300–3100 cm⁻¹ denote the stretching vibration of -NH bonds, which are intrinsic to the amine (-NH₂ and =NH) functional groups. The wavenumber at 3500 cm⁻¹ corresponds to the stretching vibration of the -OH group (Ma et al., 2020). Furthermore, the absorption peaks within the range of 2900–2850 cm⁻¹ signify the presence of C-H stretching vibrations (Putra, 2017). Absorption peaks spanning the range of 1650–1500 cm⁻¹ suggest the coexistence of N-H, N-O, C-O, and N-O constituents. Within the 4% Ni-g-C₃N₄/TiO₂ composite, an absorption peak in the range of 1600–1000 cm⁻¹ indicates the stretching vibration of C-N, concomitant with an absorption peak characteristic of TiO₂, thus confirming the presence of g-C₃N₄ within the composite (Senthil et al., 2017). The absorption peak within the wavenumber range of 850–500 cm⁻¹ for TiO₂ P25 and 4% Ni-g-C₃N₄/TiO₂ can be attributed to the influence of oxygen from the ambient atmosphere, which was adsorbed onto the surface of TiO₂ during the synthesis process (Marami et al., 2018).

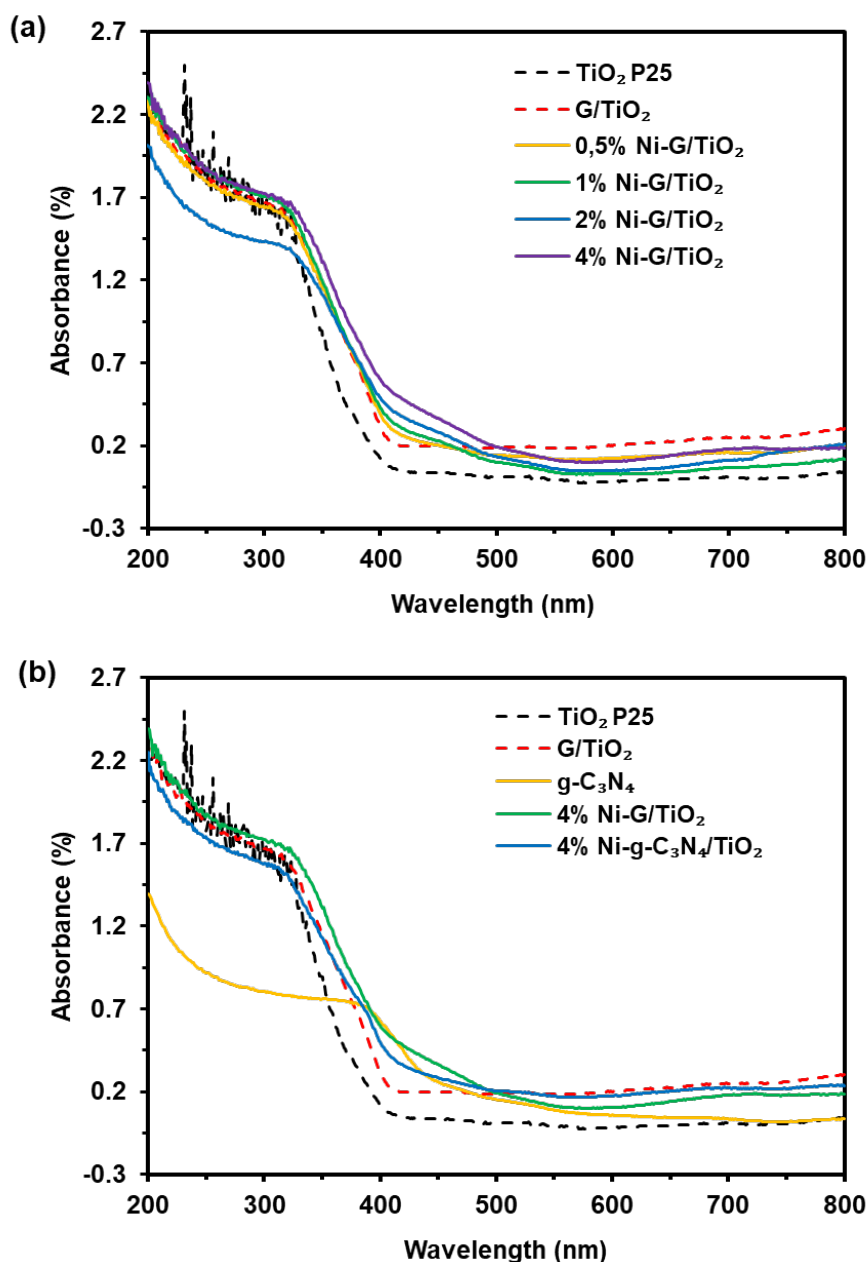


Figure 2 UV-Vis spectrum comparison of photocatalysts: (a) Ni loading content and (b) promoter type effect

3.2 Photocatalytic Activity for H₂ Production

3.2.1 Effect of Ni Loading on the Ni-G/TiO₂ Composite

As depicted in Figure 4, the 4% Ni-G/TiO₂ composite exhibited the highest hydrogen production among the tested samples, yielding 12.9 mL of hydrogen, which is 55% higher than TiO₂ P25, which can only produce 8.3 mL of hydrogen. This indicates that 4 wt% Ni provides the most favorable performance within the tested range for the Ni-G/TiO₂ system. Thus, the 4 wt% Ni loading was selected for the promoter comparison study because it provided the highest hydrogen production among the investigated Ni-G/TiO₂ samples. The incorporation of Ni loading in the Ni-G/TiO₂ composite is associated with an enhancement in hydrogen generation. These findings are consistent with those of Xu and Xu (2015), who emphasized the beneficial effect of nickel as a dopant for augmenting the activity of TiO₂ P25 photocatalyst. Ni incorporation can facilitate charge separation and improve catalytic performance (Xu & Xu,

2015).

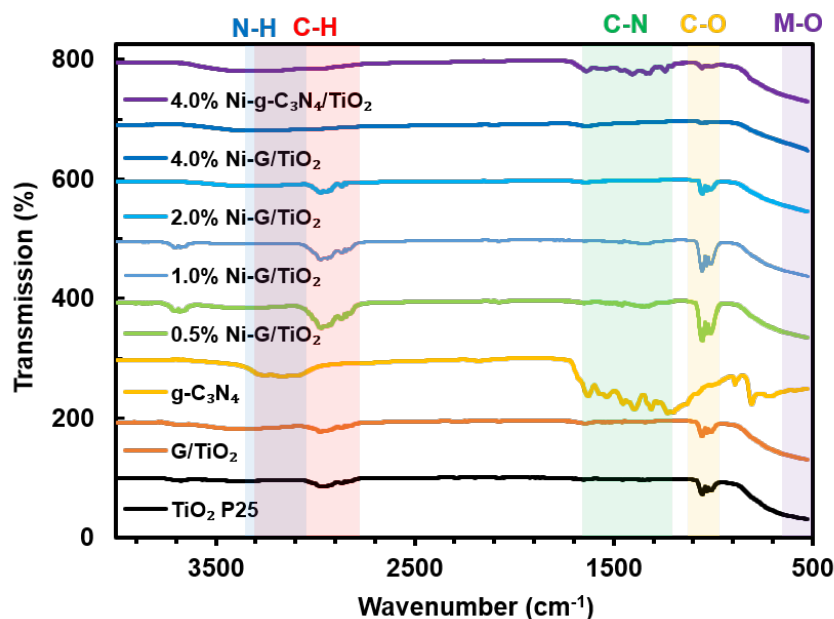


Figure 3 IR spectra of the photocatalysts showing the characteristic N–H, C–H, C–N, C–O, and M–O functional groups

The presence of graphene is likely to facilitate rapid charge transfer for better photocatalytic results. Ni and graphene play distinct roles in this composite and complement each other. Ni may act as an electron trapper, efficiently capturing excited electrons, while graphene serves as a relay, facilitating their transfer to the reduction target, as illustrated in Figure 6(a,b). Consequently, the combined effect of the transition metal Ni, graphene promoter, and TiO₂ mitigates electron-hole recombination, thus enhancing the photocatalytic hydrogen production performance (Ibadurrohman et al., 2022).

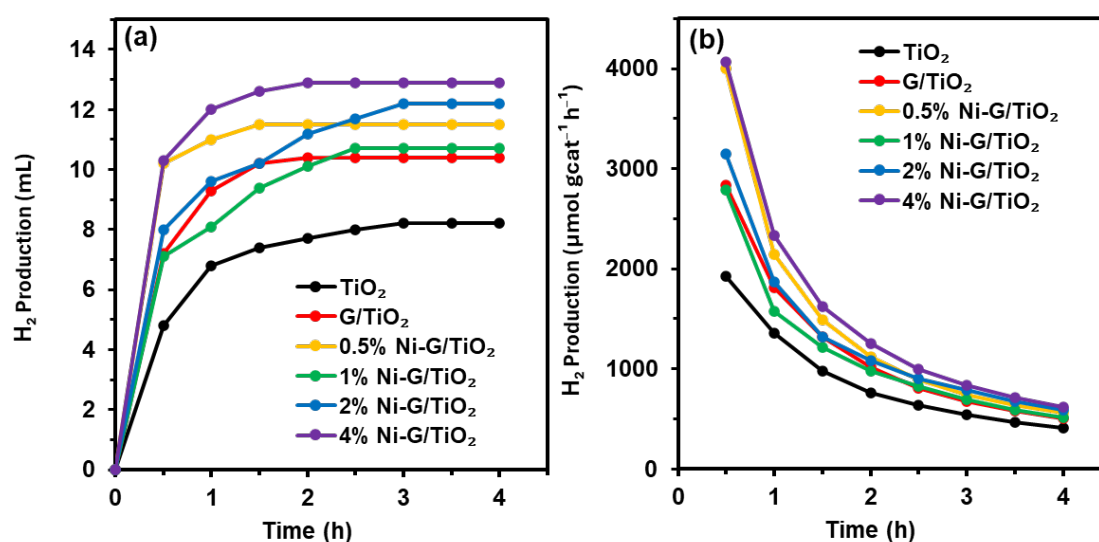


Figure 4 Hydrogen production with Ni-G/TiO₂ composite and 10% v/v glycerol at various Ni loadings in (a) mL and (b) $\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$

3.2.2 Effect of the X Promoter on the Ni-X/TiO₂ Composite

Subsequently, the same Ni loading was applied to the Ni-g-C₃N₄/TiO₂ system as a representative condition to enable comparison between different promoter systems. The optimal Ni loading may vary depending on the promoter type, and further investigation is required to determine the true optimum for each system. The results presented in Figure 5(a,b) demonstrate that g-C₃N₄ exhibited photocatalytic activity with comparatively lower performance, yielding only 7.4 mL of hydrogen, which is even less than TiO₂ with 8.3 mL of hydrogen produced. These findings are consistent with those of (Wang et al., 2008), who indicated that g-C₃N₄ is less active under UV irradiation, resulting in limited hydrogen generation (Irdhawati & Taufantri, 2016). The inferior activity of g-C₃N₄ can be attributed to the rapid recombination rate of electron-hole pairs, leading to relatively lower hydrogen production (Alcudia-Ramos et al., 2019).

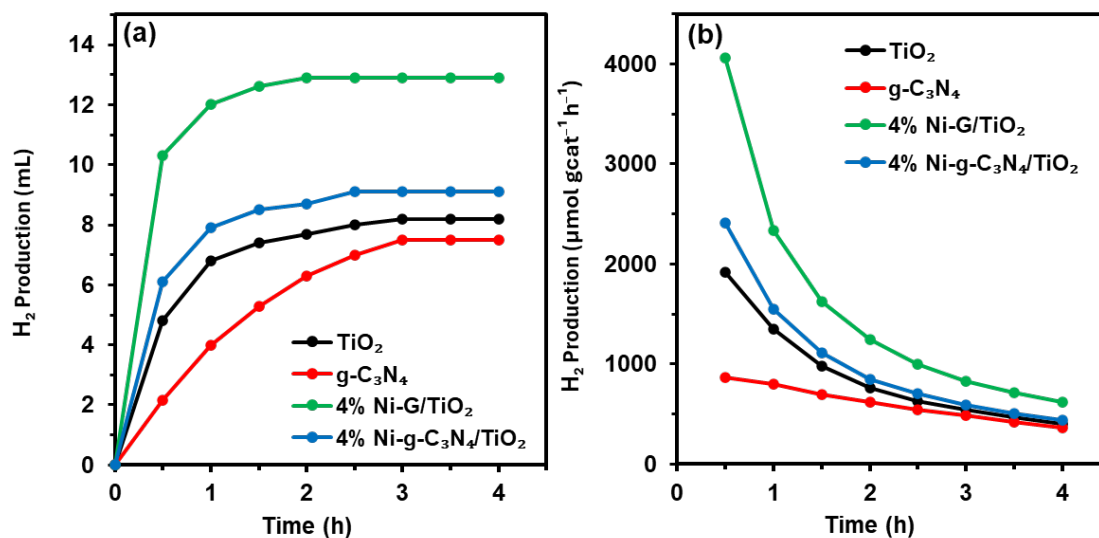


Figure 5 Hydrogen production on Ni-X/TiO₂ composite with 4% Ni loading in (a) mL and (b) $\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$

However, the use of g-C₃N₄ as a promoter for Ni-decorated TiO₂ photocatalysts (Ni-g-C₃N₄/TiO₂) resulted in the generation of 9 mL of hydrogen. This enhancement is likely attributed to the band alignment existing between TiO₂ and g-C₃N₄, as shown in Figure 6(a,b). Specifically, photogenerated holes originating from the valence band of TiO₂ migrate to the valence band of g-C₃N₄, facilitated by their electronic affinity, while electrons may be situated in the valence band of g-C₃N₄ transition to the conduction band of TiO₂ (Zhang et al., 2017). Subsequently, the Ni co-catalyst traps these electrons, where reduction reactions occur to yield hydrogen (Mun & Park, 2019). Therefore, Ni NPs are considered to act as electron accumulators, actively engaging in the hydrogen production process (Zhang et al., 2017). Note that the hydrogen evolution results presented in this study were obtained from single experimental runs. Therefore, statistical parameters, such as standard deviations and error bars, are not available. Although repeated measurements would provide a more rigorous assessment of reproducibility, the present results demonstrate the photocatalytic performance of the investigated photocatalysts under identical experimental conditions.

Based on the photocatalytic performance and optical characterization obtained in this study, the electron relay mechanism associated with graphene may be more effective than the heterojunction-assisted charge separation provided by g-C₃N₄ under the investigated conditions. This hypothesis is inferred from the experimental results and relevant literature rather than being directly demonstrated by charge-transfer characterization techniques. The enhanced performance of Ni-G/TiO₂ may be associated with the complementary roles of Ni and graphene in the Ni-G/TiO₂ composite. Ni is proposed to function as an electron-trapping site capable

of capturing photogenerated electrons, while graphene may serve as an electron relay that facilitates their transfer to the reduction sites for hydrogen evolution. In addition, graphene's high electrical conductivity and electron mobility may promote faster interfacial charge-transfer kinetics and suppress charge carrier recombination. In contrast, the enhancement provided by g-C₃N₄ is proposed to be mainly associated with heterojunction formation with TiO₂, which may facilitate charge separation through band alignment. Accordingly, these proposed mechanisms may explain the higher hydrogen production observed for Ni-G/TiO₂ under the investigated conditions. Nevertheless, further study is still needed to confirm these hypothesized mechanisms by performing direct charge-transfer characterization, investigating the effects of graphene and g-C₃N₄ contents, and conducting photocatalytic experiments under visible light illumination. The effect of glycerol oxidation byproducts on the overall photocatalytic performance was not specifically analyzed in this study and may warrant further investigation.

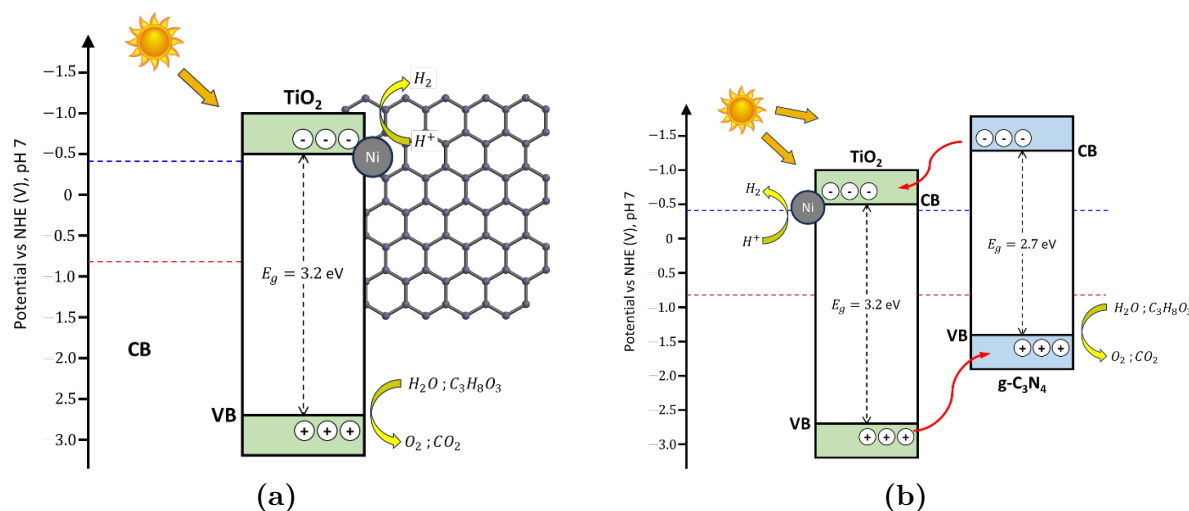


Figure 6 Schematic of the photocatalytic process in (a) Ni-G/TiO₂ and (b) Ni-g-C₃N₄/TiO₂

The present study focused on evaluating the structural, optical, and photocatalytic properties of the synthesized photocatalysts using X-ray diffraction (XRD), UV–Vis DRS, and Fourier transform infrared (FTIR) analyses. Therefore, the relative contributions of morphology, surface area, and electronic effects on the observed photocatalytic performance could not be distinguished. Moreover, because only the Ni-G/TiO₂ system was optimized with respect to Ni loading, whereas Ni-g-C₃N₄/TiO₂ was evaluated at a single Ni loading, the present study cannot conclusively determine whether the superior performance of Ni-G/TiO₂ arises predominantly from electronic effects, morphology, surface-area differences, catalyst dispersion, or a combination of these factors. In addition, although the photocatalytic performance and optical characterization results support the proposed charge-transfer pathway, no direct evidence of charge separation behavior was obtained. Accordingly, the proposed mechanism should be regarded as a hypothesis based on the experimental observations and relevant literature. Furthermore, although the optical characterization indicated enhanced visible-light absorption, the photocatalytic activity under visible-light irradiation was not evaluated in this study. Therefore, the effect of graphene and g-C₃N₄ on visible-light-driven hydrogen production remains to be experimentally verified. Further investigation using morphological and surface-area characterization, together with appropriate charge-carrier characterization techniques such as photoluminescence (PL) spectroscopy, would provide a more comprehensive understanding of the photocatalytic mechanism.

4. Conclusion

In summary, the incorporation of Ni and graphene into TiO₂ significantly enhanced photocatalytic hydrogen production from a water–glycerol mixture. Although g-C₃N₄ exhibited

lower photocatalytic activity than TiO_2 under UV irradiation, the incorporation of $\text{g-C}_3\text{N}_4$ as a promoter in $\text{Ni-g-C}_3\text{N}_4/\text{TiO}_2$ resulted in improved hydrogen evolution compared with $\text{g-C}_3\text{N}_4$ alone. Based on the photocatalytic performance and optical characterization results, the enhanced hydrogen production observed for $\text{Ni-G}/\text{TiO}_2$ is proposed to be associated with improved charge-transfer processes facilitated by the combined roles of Ni and graphene. Likewise, the performance improvement observed for $\text{Ni-g-C}_3\text{N}_4/\text{TiO}_2$ is inferred to be related to favorable band alignment and heterojunction formation between TiO_2 and $\text{g-C}_3\text{N}_4$. Under the investigated conditions, the graphene-promoted photocatalyst exhibited higher hydrogen production than the $\text{g-C}_3\text{N}_4$ -promoted photocatalyst. However, the proposed charge-transfer mechanisms remain inferential, and direct evidence of charge separation behavior was not obtained in this study. Therefore, further investigations involving advanced charge-transfer characterization techniques, such as PL, EIS, transient photocurrent, and Mott–Schottky analyses, are required to validate the proposed mechanisms and provide a more comprehensive understanding of the photocatalytic process.

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Author Contributions

Conceptualization, J.A. and M.I.; methodology, J.A. and M.I.; investigation, M.I.; data curation, M.I.; formal analysis, J.A., N.M. and M.I.; writing—original draft preparation, J.A., M.I., and N.M.; writing—review and editing, N.M. and M.I.; supervision, M.I.; project administration, M.I. All authors have read and agreed to the published version of the manuscript.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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