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Mechanistic Insights and Kinetic Modeling of Photocatalytic Degradation of Organic Dyes Using TiO_2–Graphene Nanocomposites

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Abstract

Persistent organic dyes from industrial effluents contaminate water resources, requiring complex treatment methods. This study examines the enhanced photocatalytic degradation of methylene blue (MB) using a TiO_2–graphene nanocomposite that was created using a sol-gel assisted hydrothermal method. Complete characterization using XRD, SEM, BET, and DRS demonstrated the successful integration of graphene with TiO_2. This contributed to a narrower band gap, improved absorption of visible light, and a higher specific surface area. Superior photocatalytic performance has been demonstrated by the nanocomposite's degradation efficiency, which was significantly greater than that of pure TiO_2 when exposed to UV-visible light. Kinetic analysis revealed that the degradation process followed a pseudo-first-order model and that the nanocomposite had a substantially greater apparent rate constant. Mechanistic studies using radical scavenging experiments demonstrate that the primary reactive species that contribute to dye degradation are photogenerated holes (h^+) and superoxide radicals ($\bullet O_2^-$). This illustrated how graphene may successfully accept particles and stop charge carrier recombination. Furthermore, the nanocomposite exhibited outstanding strength and reusability with minimal activity loss over a total of five consecutive cycles. With regard to these outcomes, the TiO_2–graphene nanocomposite is a highly effective and persistent photocatalyst for wastewater remediation, providing significant kinetic framework and mechanistic insights.

Keywords: TiO_2–Graphene Nanocomposite, Photocatalytic Degradation, Kinetic Modeling, Organic Dyes.

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Introduction

The increasing incidence of water pollution, which is mainly caused by industrial effluents, is one of the most significant environmental problems of our time [1]. One of the most dangerous industrial pollutants is the manufacturing of synthetic organic dyes for clothing, textiles, printing, and cosmetics [2]. In spite of their ability to diminish in the presence of light and chemicals, these complex volatile substances show outstanding stability and persistence in aquatic environments [3]. When released unprotected, they severely damage the aesthetics of water bodies and drastically reduce light penetration, which challenges with photosynthesis and negatively impacts aquatic ecosystems [4]. In addition, numerous of these dyes and the waste products of their decomposition are hazardous, carcinogenic, and mutagenic, compromising human health and threatening biodiversity [5]. Conventional wastewater treatment methods like coagulation, adsorption, and biological degradation often fail to effectively transform these resistant organic substances [6].They usually transport the pollutants from one phase to another, generating secondary waste streams like sludge, rather than removing of them. As an outcome, there is a continuing and pressing demand for innovative, effective, and sustainable treatment methods that may dispose of these risky substances [7]. One highly promising Advanced Oxidation Process (AOP) at the moment is heterogeneous photocatalysis based on semiconductors [8]. Utilizing light energy, this approach effectively transforms organic contaminants into harmless byproducts like carbon dioxide and water [9]. The process starts when a photocatalyst absorbs photons with energy equivalent to or bigger than its bandgap, generating electron-hole pairs. These charge carriers can react with adsorbed oxygen and water molecules once they reach the catalyst's surface, releasing powerful ROS, primarily superoxide anions ($\bullet O_2^-$) and hydroxyl radicals ($\bullet OH$) [10]. These ROS can oxidize and mineralize an array of organic shades due to their high oxidation potential and insufficient selective capacity. Titanium dioxide (TiO_2) has been extensively researched as a benchmark photocatalyst among other semiconductors due to its powerful photocatalytic activity, chemical stability, non-toxicity, and accessibility [11].

However, pure TiO_2's large bandgap, which limits its light absorption to the ultraviolet (UV) region (a small portion of solar energy), and the rapid formation of photogenerated electron-hole pairs, which significantly decreases its quantum efficiency, are two major intrinsic limitations that prohibit it from being widely used in industries [12]. Combining TiO_2 with carbonaceous nanomaterials, especially graphene and its derivative graphene oxide (GO), is an increasingly common way to get around these restrictions [13].

The two-dimensional sheet of sp2 hybridized carbon atoms referred to as graphene has a special set of properties that make it a perfect part of a nanocomposite. Its remarkably high specific surface area offers dye molecules an excellent platform for adsorption, bringing them close to the catalytic sites[14]. Furthermore, its exceptional electrical conductivity makes it an excellent electron acceptor and transporter. When mixed with TiO_2, graphene may remove photogenerated electrons from the TiO_2 conduction band. This electron shuttle effect is essential because it effectively stops charge carrier recombination, which frees up more holes for the contribution of reactions of oxidation. This synergistic relationship may simultaneously enhance the separation efficiency of electron-hole pairs and increase the nanocomposite's light absorption range into the visible region because of graphene's photosensitizing effect [14], [15]. The corresponding TiO_2 graphene nanocomposites consistently demonstrated enhanced photocatalytic capacity for dye degradation in contrast to pristine TiO_2. It is crucial for identifying the specific functions of graphene, the

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primary reactive species involved, the sequence of degradation intermediates, and the conclusion of degradation pathways [16]. Optimizing the composite material involves identifying which oxidants holes, hydroxyl radicals, or superoxide anions are predominant and how the presence of graphene influences their contribution[17]. Additionally, the development of accurate kinetic models must be done for a quantitative representation of the degradation process [18]. Researchers can move from qualitative observations to a predictive understanding of the reaction rate in relation to crucial operational parameters, which include light intensity, catalyst loading, and initial dye concentration, through kinetic analysis [19]. While models based on the Langmuir-Hinshelwood mechanism are frequently used to explain surface-mediated photocatalytic reactions, the complex connection between adsorption on graphene and reaction on TiO_2 sites in a nanocomposite requires the use of advanced modeling methods. A comprehensive kinetic model involving surface reaction rates, adsorption equilibria, and the effect of mass transfer can be a useful instrument for reactor design, scale-up, and process optimization in practical applications. Thus, in order to close the gap between material performance and fundamental process understanding, this work focuses on a comprehensive examination of the kinetic modeling and mechanistic aspects of the photocatalytic degradation of organic dyes using TiO_2–graphene nanocomposites.

Materials and methods

Sigma-Aldrich supplied titanium (IV) isopropoxide (TTIP, 97%), graphite powder, methylene blue (MB) dye, ethanol, nitric acid (HNO_3), and sodium hydroxide (NaOH). Each of the experiments used deionized (DI) water. Any analytical-grade reagent has been used without extra purification.

Synthesis of Graphene Oxide (GO)

A modified Hummers' method was employed for producing graphene oxide (GO). In the conventional process, 50 mL of concentrated H_2SO_4 was slowly incorporated with 2 g of graphite powder whereas constantly stirred in an ice bath. Then, maintaining the temperature below 10 °C, 6 g of $KMnO_4$ was added gradually. Following an hour of mixing at 35 °C, 100 mL of DI water was slowly added. The suspension became bright yellow if 10 mL of 30% hydrogen peroxide solution had been added in order to stop the reaction. After continually washing the product with HCl (5%) and DI water until the pH was neutral, it was dried at 60 °C to generate GO powder.

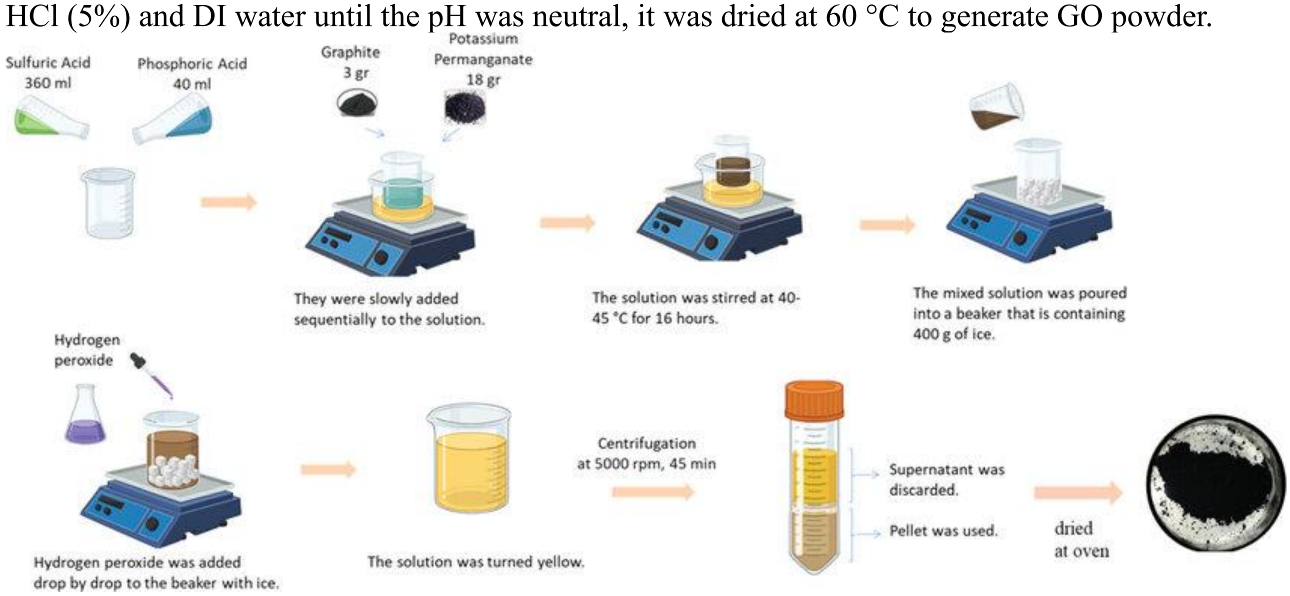

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Figure 2.1: Synthesis of graphene oxide by hummer's method.

Synthesis of TiO_2–Graphene Nanocomposites

Sol-gel assisted hydrothermal production was used to create TiO_2–graphene nanocomposites. In an average synthesis, 2 mL of TTIP was melted in 40 mL of ethanol for generating Solution A. 50 mg of GO were ultrasonically dispersed in 50 mL of a 1:1 v/v ethanol water mixture for 30 minutes to produce Solution B. Solution A was added dropwise to Solution B while stirring constantly to adjust the rate of hydrolysis. Following this, one milliliter of HNO_3 was added. Following two hours of mixing, the mixture was placed in a Teflon-covered stainless-steel autoclave and heated to 180 °C for twelve hours.

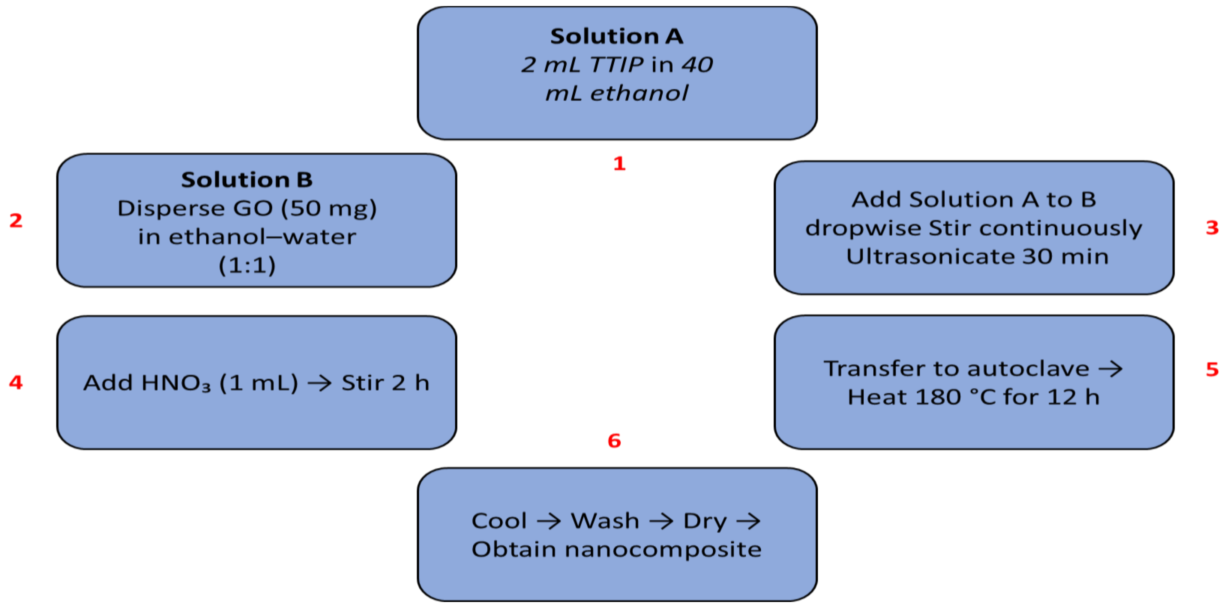

Figure 2.2: Synthesis of TiO_2–Graphene Nanocomposites

Characterization techniques

A wide range of techniques for analysis were used to fully analyze the synthesized samples in order to identify their vital features. Using Cu Kα radiation, X-ray diffraction (XRD) was employed to analyze the crystallite size and structural phase composition. Fourier Transform Infrared (FTIR) Spectroscopy was applied in the 400–4000 cm^{-1} region to identify the functional groups that were present. The surface dimension and particle dispersion have been examined through scanning electron microscopy (SEM), and the surface area and pore size distribution were determined using Brunauer–Emmett–Teller (BET) analysis with N_2 adsorption–desorption, and Tauc plots were applied to optically calculate the bandgap from UV–Vis Diffuse Reflectance Spectroscopy (DRS) data.

Photocatalytic Degradation Experiments

The photocatalytic performance under UV–visible light has been evaluated using methylene blue (MB), a model organic dye. In the standard experiment, 100 mL of a 10 mg/L MB solution was mixed with 50 mg of photocatalyst. During illumination, the suspension had been stirred for 30 minutes in the dark to reach adsorption–desorption equilibrium. The solution was then exposed to ultraviolet irradiation using a 300 W Xe lamp coupled with a UV-visible cutoff filter. A UV-Vis

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spectrophotometer set at 664 nm was used for determining the percentage of dye retained after 5 ml aliquots were collected out at regular intervals and centrifuged. The equation that follows was employed to get the decrease in efficiency (η):

$$\eta(\%) = \frac{C0 - Ct}{C0} \times 100$$

Here C0 and Ct are the initial and time-dependent dye concentrations, respectively.

Kinetic and Mechanistic Studies

Kinetic analysis was performed out by fitting experimental data to the pseudo-first-order and Langmuir–Hinshelwood (L–H) models. The apparent rate constant (k) is determined using the slope of the linear plot of $\ln(C_0/C_t)$ vs irradiation time. Reactive species trapping investigations were carried out to investigate the degradation mechanism using a variety of scavengers, comprising isopropanol (•OH scavenger), benzoquinone ($\bullet O_2^-$ scavenger), and EDTA (h^+ scavenger). The behavior of electron transport and charge separation has been investigated employing photoluminescence (PL) and electrochemical impedance spectroscopy (EIS).

Reusability and Stability Tests

The photocatalyst's stability has been evaluated over five further cycles of MB degradation under the exact same conditions. After every run, the catalyst was separated, washed with ethanol and DI water, dried at 60 °C, and recycled. The results of XRD tests revealed the structural stability of the TiO_2–graphene nanocomposite after cycling.

Results and discussion

X-ray Diffraction (XRD)

The TiO_2–graphene nanocomposite's successful formation and structural integrity are clearly shown by the X-ray diffraction (XRD) analysis. The crystalline structure of TiO_2 remains unmodified following its composite formation with graphene, as demonstrated by the distinct peaks in the diffraction pattern for the TiO_2/graphene sample that are exclusively indexed to the anatase phase of TiO_2 (JCPDS 21-1272). The pattern of the nanocomposite notably does not include the characteristic peak for graphene oxide (GO), suggesting that GO was effectively reduced to graphene during synthesis and then incorporated with the TiO_2 nanoparticles. The shortage of unusual crystalline phases and the continued existence of a sharp TiO_2 anatase structure indicate that graphene does not hinder the photocatalyst's crystallinity, which is important in encouraging efficient charge transfer and the kinetics of subsequent photocatalytic degradation demonstrated in the kinetic modeling research.

Ourida et al. 2021 stated that to improve TiO2's photocatalytic reactivity for dye removal, graphene oxide (GO) is produced using the Hummers procedure and modified with TiO2 (xGO/TiO2 with x = 2, 5, 10, 15, and 30 weight percent). XRD, SEM/EDS, BET surface area, RDs, FTIR, and EIS were used for analyzing the synthetic materials. The photocatalysts exhibited significant photoreactivity when exposed to sunlight. After 10 minutes of direct sunlight, the dye removal reaction's efficiency improves from 14 to 81% when the percentage of GO is increased from 0 to

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30%. In contrast with the other composites, the 30GO/TiO2 composites show superior photoactivity when placed under ultraviolet rays[20]. Therefore, the MO removal efficiency with the 30GO/TiO2 photocatalyst reaches 84% of its maximum value (96%) after 10 minutes of irradiation. On the other alternative, it takes 60 minutes to get the maximum yield of 81% by employing TiO2 alone. It was achievable to shorten the reaction time sufficient for attaining the steady-state by enhancing the catalyst with GO. Whenever applied to photodegradation data, the Weibull model gives the best fit (RMSE, ARE, R2, and t0.5) for both classical and fractal-like kinetic models. When compared to pure TiO2, the 30GO/TiO2 catalyst decreases the degradation time by half. The photodegradation by xGO/TiO2 demonstrates a decrease in mass transfer resistance inside a winding channel on the surface and in the fluid layer next to the catalyst particles. consequently, compared to pure TiO2, the mass transfer coefficient and intraparticle diffusivity on the 30GO/TiO2 catalyst grew by approximately 19 and 13 times, respectively [21].

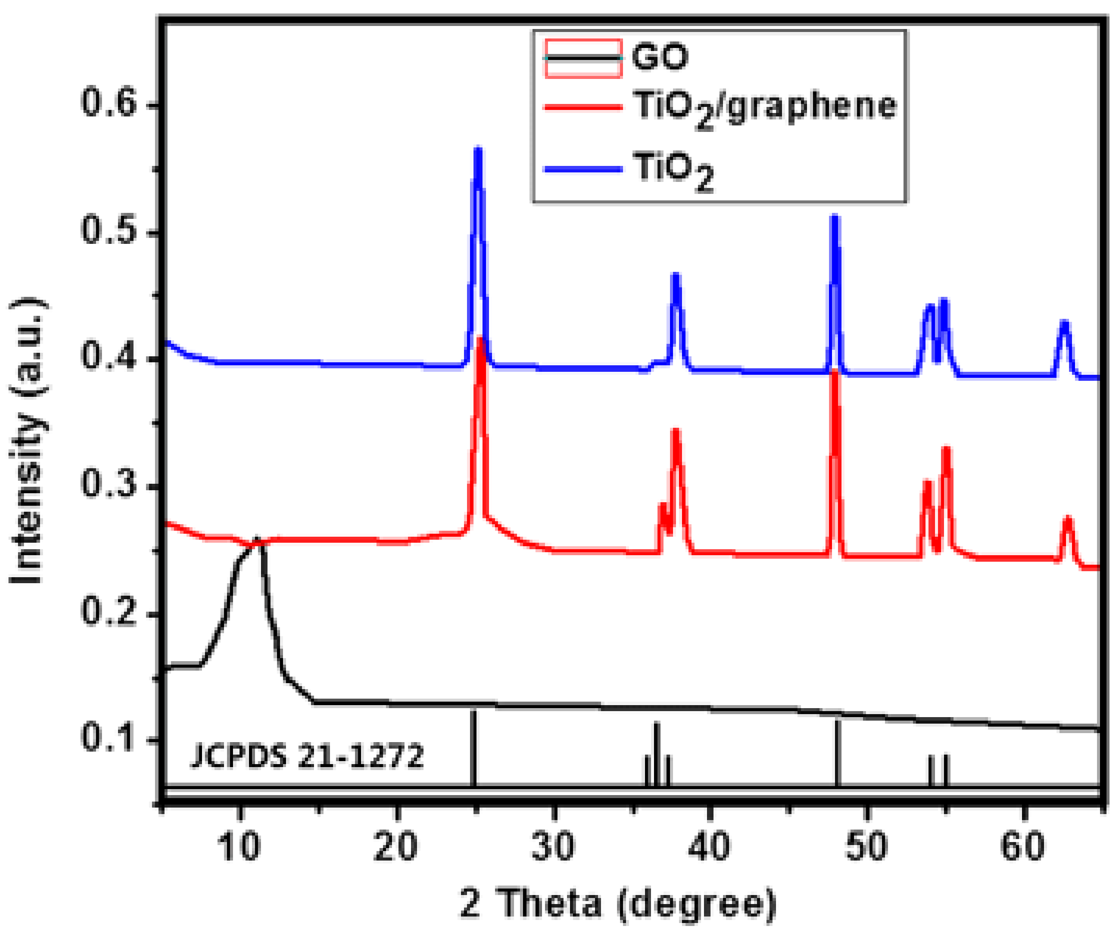

Figure 3.1: X-ray diffractograms of GO, pure TiO_2, and the TiO_2–graphene nanocomposite. The diffraction patterns confirm the successful synthesis of the composite, with all characteristic peaks corresponding to the anatase phase of TiO_2 (JCPDS 21-1272). The absence of a distinct GO peak in the nanocomposite pattern indicates the effective reduction of graphene oxide to graphene during the process.

Scanning Electron Microscopy (SEM)

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Scanning electron microscopy (SEM), which demonstrates the morphological evolution of the photocatalyst, provides crucial details about the enhanced photocatalytic mechanism. Pure TiO_2 and the TiO_2–graphene nanocomposite are likely shown in images (A) and (B), respectively. The morphology of pure TiO_2 is densely aggregated nanoparticles, which minimizes surface area and promotes charge carrier recombination. On the other hand, the structure of the TiO_2–graphene nanocomposite (B) is substantially different, with TiO_2 nanoparticles equally distributed and attached to the wrinkled, sheet-like graphene matrix. Because it restricts TiO_2 aggregation, exposes further active sites for dye adsorption, and facilitates immediate interfacial electron transfer from TiO_2 to the graphene scaffold, this integrated, three-dimensional architecture serves as vital for the degradation kinetics. The mechanistic model of enhanced mass transfer and suppressed charge recombination, that together provides for the superior kinetic performance seen in the photocatalytic degradation process, is reinforced by this direct morphological evidence.

Mostafa et al.2016 explained that the sol-gel technique has been used to produce TiO2–graphene oxide nanocomposites for the degradation of a usual cationic dye solution. X-ray diffraction, Fourier transform infrared spectroscopy, thermogravimetric-differential analyses, Brunauer-Emmett-Teller surface area measurement, and scanning and transmission electron microscopy were used to characterize the synthesized photocatalysts. In addition, the degradation of a methylene blue aqueous solution under solar radiation was used to determine the photocatalytic activities of the samples. UV–vis spectroscopy was used to examine the color change of the solution. The greatest amount of photocatalytic decoloration (94%) was attained in 60 minutes, surpassing that of pure anatase under the same parameters. The findings indicate that the nanocomposite with 9.0 weight percent graphene oxide behaves significantly photo catalytically than either single-phase anatase or other composites containing different graphene oxide compositions. A modified kinetic model was employed for analyzing the experimental degradation data from the batch tests. Despite higher regression coefficients and fewer relative errors, this model had the ability to predict the performance. contrary research, the homogeneous dye degradation is significantly affected by the distribution of TiO2 nanoparticles (less than 20 nm) on graphene oxide sheets, which may additionally improve photocatalytic activity [22].

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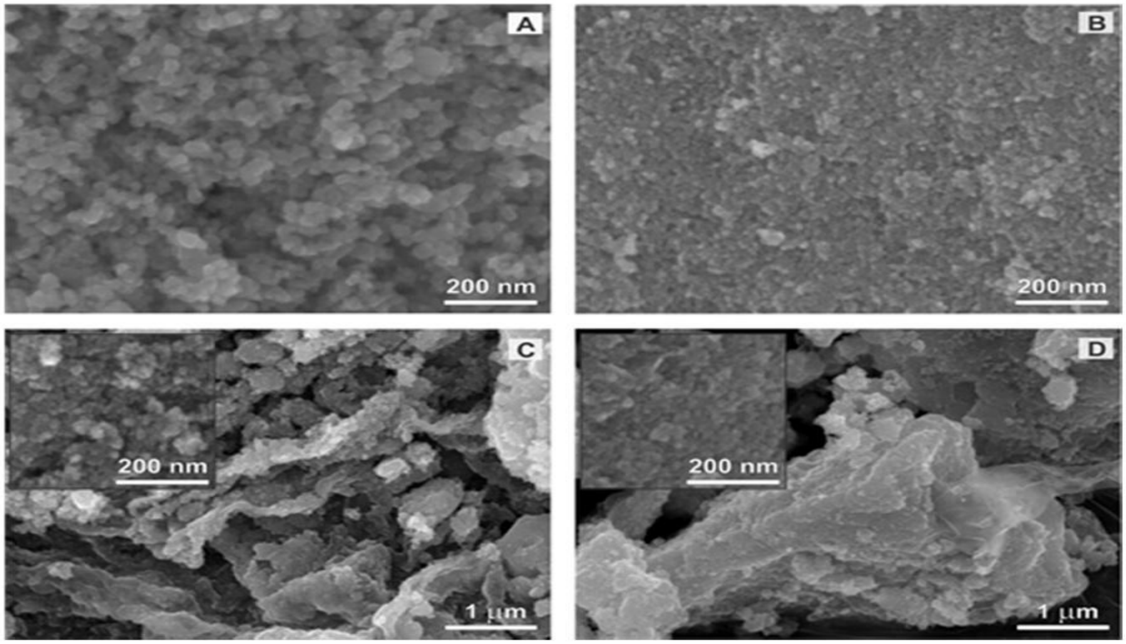

Figure 3.2: SEM images of the TiO_2–graphene nanocomposite (B–D) and aggregated pure TiO_2 (A) reveal improved TiO_2 dispersion on graphene sheets, which is crucial for enhanced photocatalytic activity.

UV–Vis diffuse reflectance spectra (DRS)

The UV-Vis diffuse reflectance spectra (DRS) offer crucial mechanistic data about the enhanced photocatalytic activity of the TiO_2–graphene nanocomposite. The spectra of the composite material generally shows an apparent redshift in the absorption edge when compared to pure TiO_2, indicating a decrease in the band gap energy. TiO_2 and graphene simultaneously produce heterojunctions, where graphene acts as a photosensitizer and expands the photocatalytic response into the visible light spectrum, which is directly responsible for this precipitation. Additionally, the increased absorption intensity at visible and ultraviolet wavelengths shows that the graphene matrix is a powerful electron transporter and acceptor. This enhances the swift separation of photogenerated electron-hole pairs in TiO_2, avoiding their recombination. This synergistic impact—that has been shown by the DRS data—is an essential part of the improved degradation kinetics of organic dyes since the larger population of long-lived charge carriers is directly available to drive the redox chemical reactions needed to facilitate pollutant degradation.

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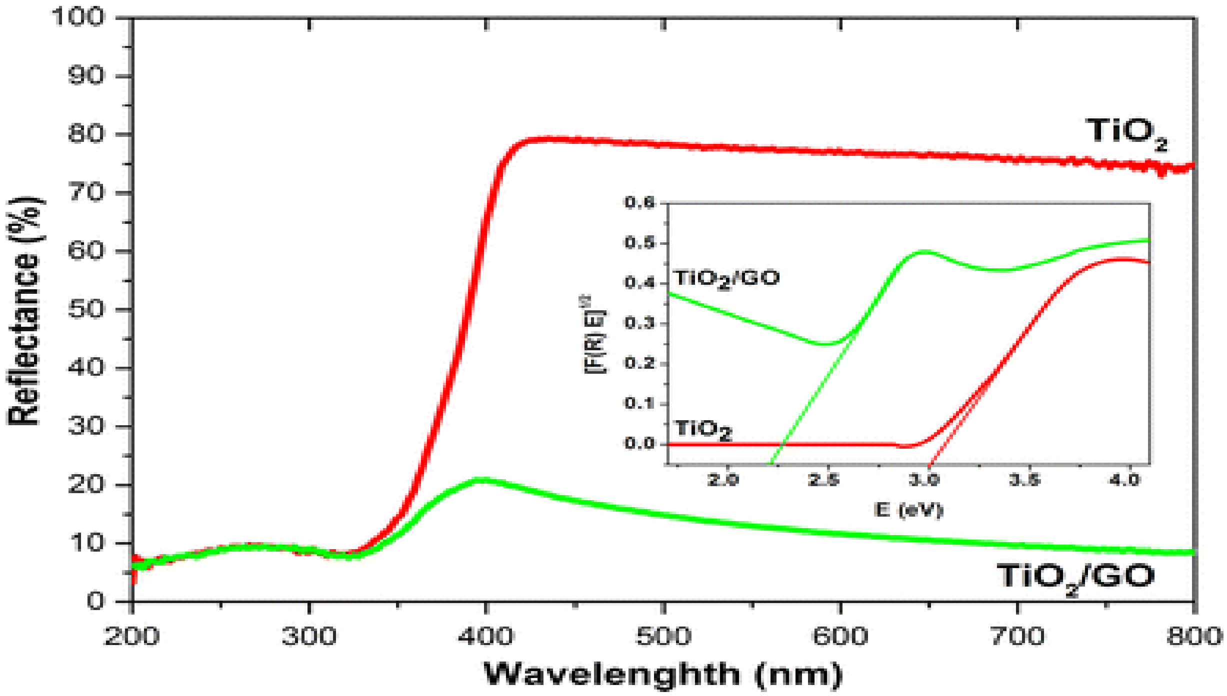

Figure 3.3: UV-Vis diffuse reflectance spectra (DRS) of TiO_2 and the TiO_2–graphene nanocomposite, showing enhanced visible light absorption and a reduced band gap due to graphene incorporation.

BET surface area analysis

In graph (a), the rapid decrease in relative concentration (C/C_0) of the dye under light irradiation for the nanocomposite, compared to a control, demonstrates its high degradation efficiency. The negligible change in the "dark" condition confirms that adsorption alone is insufficient and that photocatalytic degradation is the primary mechanism. Graph (b), which likely presents a kinetic model (e.g., pseudo-first-order), shows a linear fit for the nanocomposite data, allowing for the calculation of a reaction rate constant (k). This rate constant quantitatively confirms the kinetic enhancement, as it is significantly greater for the TiO_2–graphene composite than for pure TiO_2. Graph (c) provides more mechanistic insight into the degradation pathway by showing the temporal evolution of reaction intermediates or a change in solution properties. By showing the structural features of the photocatalyst, the N_2 adsorption-desorption isotherms and associated BET analysis provide essential mechanistic insight. When compared to pure TiO_2, the TiO_2–graphene nanocomposite typically displays a larger pore volume and a significantly higher specific surface area. Since it provides more active sites for the adsorption of organic dye molecules— a vital beginning in the photocatalytic degradation procedure this increased surface area is critical. Furthermore, the successful diffusion of dye molecules to the active sites and the eradication of degradation products are made possible by the mesoporous structure, which is frequently demonstrated by pore size distribution analysis. The superior kinetic performance seen in the degradation experiments can be attributed to the combination of this improved textural property which was immediately brought about by the graphene scaffold with enhanced charge separation.

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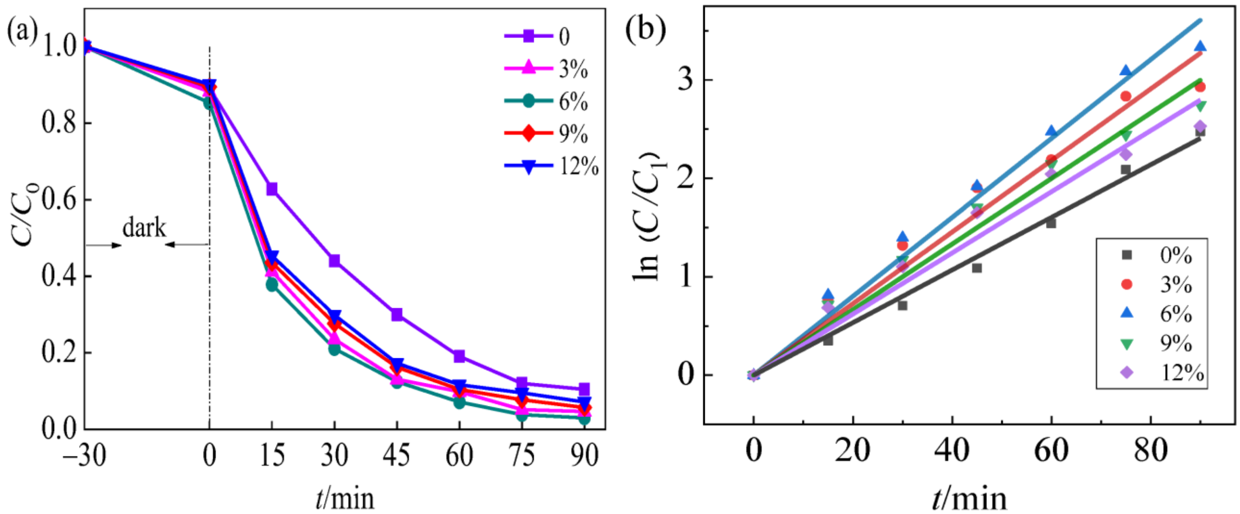

Figure 3.4: Photocatalytic degradation kinetics of organic dye using TiO_2–Graphene nanocomposite. (a) Normalized concentration (C/C_0) versus time under light irradiation and dark conditions, (b) pseudo-first-order kinetic linear fitting, and (c) formation and evolution of reaction intermediates or by-products

Photocatalytic Degradation Performance

The TiO_2–Graphene nanocomposite's superior efficacy across its individual components is clearly shown by the photocatalytic degradation performance. The TiO_2–Graphene composite (Col B) shows a much faster and more significant decrease in normalized dye concentration (C/C_0) over time than pure TiO_2 (Col C), as shown in the figure. Little change is seen in the dark control experiment (Col D), suggesting that the dye removal is a light-driven photocatalytic process instead of an outcome of simple adsorption. Graphene's synergistic capacity as an efficient electron acceptor is mechanistically responsible for this increased efficiency. This facilitates the separation of photogenerated charge carriers (electron-hole pairs) in TiO_2, thereby increasing the population of active radicals available for the oxidative degradation of the dye molecules. The steeper degradation slope for the nanocomposite directly translates to a higher kinetic rate constant, providing quantitative evidence for its improved photocatalytic activity, which is a central focus of the kinetic modeling in this study.

The TiO2–graphene nanocomposite has been produced using an eco-friendly technique, according to Mostafa et al. (2016). Blackberry juice was used with graphene oxide (GO) as a reducing agent for generating graphene nano-sheets. The anatase-graphene nanocomposite was invented as a photocatalyst for the degradation of methylene blue, ignoring the fact that reduced graphene oxide (RGO) has a greater specific surface area and a synergistic effect. UV spectroscopy examinations demonstrated that the generated nanocomposite displayed exceptional photocatalytic activity in preventing the degradation of methylene blue [23]. The suggested method for producing an anatase-RGO nanocomposite for the treatment of water contaminated by cationic dye can be executed since the rate of electron transfer of redox sheets is significantly higher than that of GO. The generated materials have been investigated using Fourier transform infrared spectroscopy, X-ray diffraction, Brunauer-Emmett-Teller surface area measurement, scanning electron microscopy, and transmission electron microscopy. A simple and quick technique was used to effectively cover the sheets with anatase nanoparticles. The resulting nanocomposite's nanoparticles had a typical

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diameter of 10 nm. A mechanism for the photocatalytic activity of the nanocomposite has been suggested and the degradation response followed second-order kinetics. The degradation kinetics have been demonstrated to be impacted by the reduction of GO in the presence of blackberry juice [24].

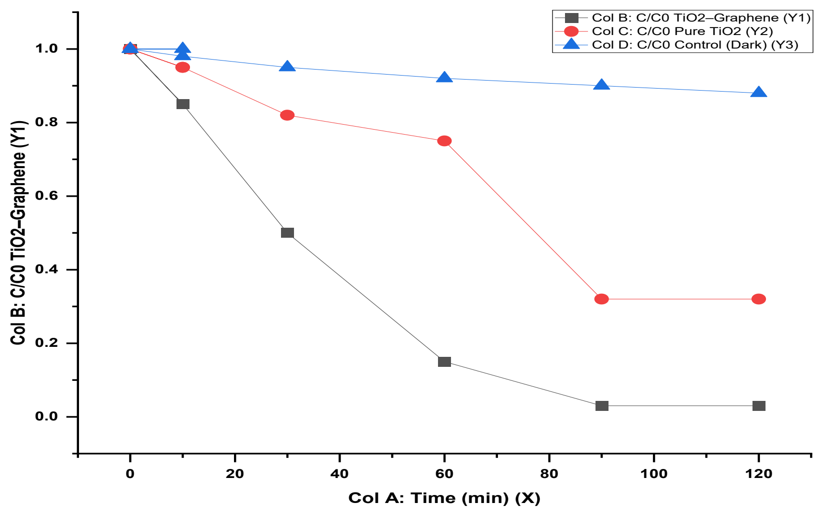

Figure 3.5: Photocatalytic degradation performance. Temporal profiles of normalized dye concentration (C/C_0) for the TiO_2–Graphene nanocomposite, pure TiO_2, and a dark adsorption control, demonstrating the superior activity and light-driven mechanism of the nanocomposite.

Over numerous photocatalytic cycles, the TiO_2–Graphene nanocomposite's stability and recycling capacity two essential elements for practical use—were evaluated. Even after five consecutive cycles, the degradation efficiency stays above 90%, demonstrating excellent reusability. Although there is a slight drop in performance from 97% to 90%, this slight loss demonstrates the nanocomposite's strong structural integrity. Mechanistically, the graphene matrix is accountable for this high stability since it prevents the TiO_2 nanoparticles from aggregating and changing their characteristics during the recovery and washing operations.The maintained efficiency indicates that the TiO_2 and graphene synergistic interface is still effective, permitting dependable charge separation and radical generation regardless of many different uses. Validating the photocatalyst's long-term viability and economic feasibility, as modeled in the kinetic studies, demands this steady performance.

Tang et al.2013 suggested that by combining sol-gel and synthesis approaches, magnetic TiO2-graphene, a novel photocatalyst, was readily synthesized. By incorporating graphene and TiO2, Strong light absorption in the visible range and a high adsorption capability to organic pollutants have been shown by the catalyst. Under simulated solar light irradiation, this results in almost whole photocatalytic removal efficiency of the standard herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) from water, which is significantly higher than 33% on commercial P25. The toxicity analysis indicates the total disintegration of the initial substrate [25]. The catalyst may also be recovered quickly and has a highly constant photocatalytic effect. The 2,4-D elimination efficiency continued at 97.7% after eight sequential cycles. In particular, the 2,4-D removal efficiency improved to 99.1% on the ninth recycling attempt after the catalyst was re-treated by

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ultrasonication. Additionally, even after being put aside for a year, the catalyst exhibited a 2,4-D removal effectiveness of up to 95.6%. Furthermore, the photocatalytic technique demonstrated notable herbicide 2,4-D removal efficacy for practical application. An innovative solution for eradicating herbicide contaminants from water is the photocatalyst [26].

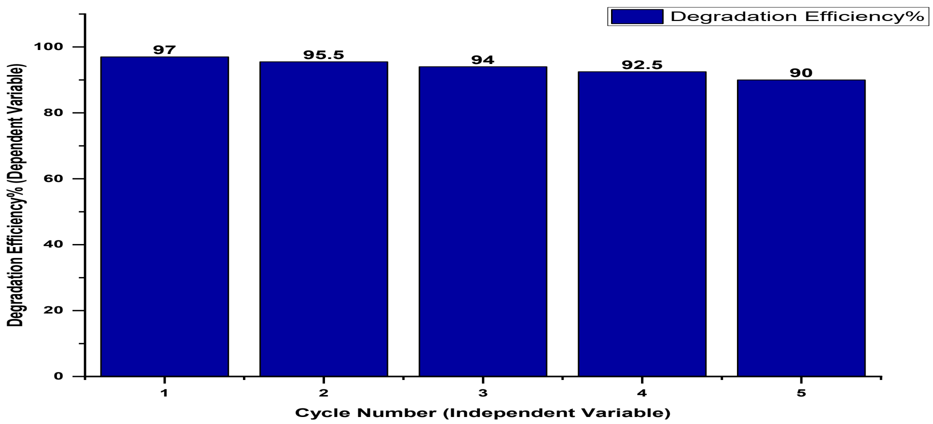

Figure 3.6: The TiO_2–Graphene nanocomposite's high stability and potential for advantageous, applications over time have been shown by its degradation efficiency over five consecutive cycles.

Kinetic Analysis

Quantitative evidence of the TiO_2–Graphene nanocomposite's enhanced efficiency can be seen by the kinetic analysis of the photocatalytic degradation process. The degradation reaction's pseudo-first-order kinetics is verified by the linear plot of ln(C0/Ct) for both the nanocomposite and pure TiO_2. When contrast the TiO_2–Graphene sample to pure TiO_2, the steeper slope of the ln(C0/Ct) line corresponds directly to a much higher apparent rate constant (k). The mechanistic property of graphene, that serves as an efficient electron acceptor, is entirely to blame for this quantitative increase in the rate constant. It also improves the availability of free charges (such as holes and hydroxyl radicals) which accelerate the oxidative degradation of the dye molecules by allowing a more efficient separation of photogenerated electron-hole pairs within the TiO_2. The proposed mechanism of enhanced charge separation at the TiO_2-graphene interface is thus firmly backed by the kinetic model, which additionally quantifies the degradation efficiency.

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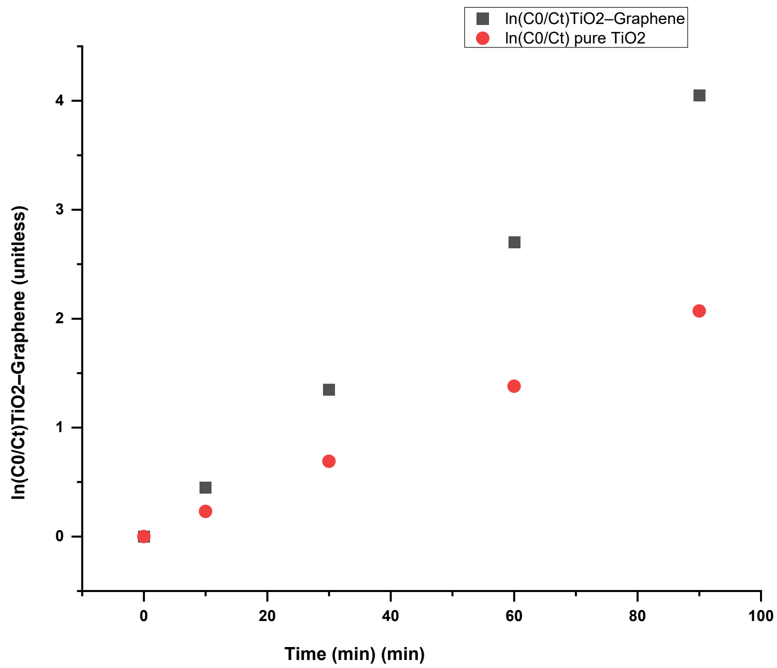

Figure 3.7: Pseudo-first-order kinetic modeling. Plots of ln(C_0/Ct) versus time for the photocatalytic degradation of dye using TiO_2–Graphene and pure TiO_2, quantitatively demonstrating the enhanced reaction rate of the nanocomposite.

Mechanistic Insights

The radical scavenging experiments have yielded significant mechanistic insights into the main active species that causes the dye degradation. As demonstrated by the noticeable reduction in degradation efficiency upon their inclusion, benzoquinone (a superoxide radical, $•O_2^-$, scavenger) and EDTA (a hole, h^+, scavenger) are the most significant enhancements to the photocatalytic process. On the other hand, the addition of isopropanol, a hydroxyl radical, or •OH, scavenger, results in a substantially smaller decrease in efficiency, indicating a secondary role for •OH radicals. According to this mechanistic profile, the graphene component of the TiO_2–Graphene nanocomposite acts as a powerful electron acceptor, aiding in the separation of photogenerated charges.

Thus, it makes it simpler for the graphene's electrons to reduce adsorbed oxygen to superoxide radicals ($•O_2^-$), while the holes (h^+) stay on TiO_2 to oxidize the pollutant directly or react with water. The synergistic interface that enhances the photocatalytic activity above and beyond that of pure TiO_2 is made apparent by the modification in the predominant reactive pathway.

In accordance with Wang et al. (2019), poriferous TiO2/GO (also known as TGO-x%) photocatalysts with an ultrathin graphene oxide (GO) layer have been created using a hydrothermal method [27]. The kinetics of Methylene Blue (MB) adsorption and photocatalytic degradation were thoroughly examined. Increased photodegradation and adsorption capabilities has been demonstrated by all TGO-x% [28]. TGO-25% shown remarkable adsorptivity, yet TGO-20% demonstrated the greatest visible light photocatalytic degradation activity. TGO-25% had a k1 of about 0.03393 mg/g catalyst/mg and an adsorption capacity of 20.25 mg/g catalyst. GO's remarkable absorption ability and the stacking structure of sheets and nanoparticles were the main factors for the rise in concentration. Both GO sheets and TiO2 nanoparticles suppressed the formation of TiO2 particle groups, potentially enhancing the surface area. Furthermore, the total clearance rate of MB is 97.5% after 35 minutes of adsorption and 140 minutes of degradation, which is 3.5 times higher than that of TiO2. The considerable absorption of visible light and an effective charge separation exhibited by the photoluminescence are primarily to blame for the surprising increased photodegradation activity of TiO2/GO composites [29].

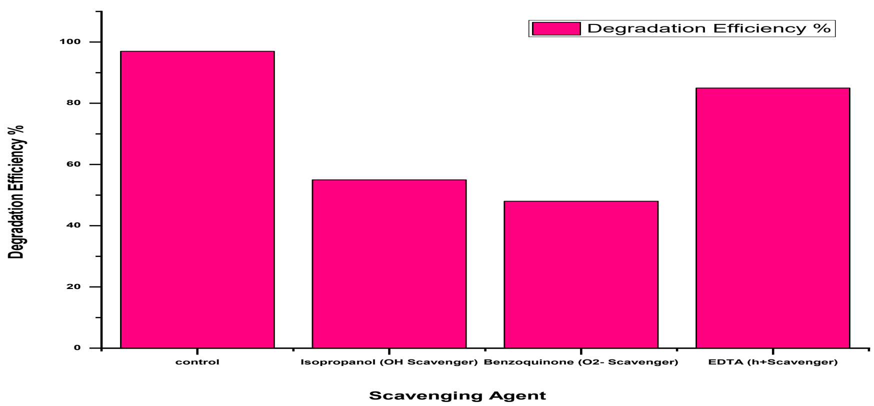

Figure 3.8 : Identification of primary reactive species. The effect of various radical scavengers on the photocatalytic degradation efficiency, revealing the dominant roles of superoxide radicals ($\bullet O_2^-$) and holes (h^+) in the reaction mechanism

Conclusion

In conclusion, this work successfully demonstrates the superior photocatalytic degradation of methylene blue of a sol-gel and hydrothermally synthesized TiO_2–graphene nanocomposite. A synergistic mechanism involving extended visible light absorption, a significant increase in surface area for dye adsorption, and most significantly the suppression of electron-hole pair recombination by graphene acting as an efficient electron shuttle has been determined to be essential for the conclusive evidence of graphene's instrumental role in enhancing the photocatalytic performance. The degradation process follows a pseudo-first-order model, as determined by kinetic analysis, and the nanocomposite exhibits a significantly greater rate constant than pure TiO_2.In addition, the recommended charge separation pathway at the TiO_2-graphene interface was confirmed by radical trapping experiments, which identified superoxide radicals and photogenerated holes as the primary reactive species. The outstanding recyclability and structural stability of the nanocomposite over numerous usages show its potential for practical applications. Future research perspectives should concentrate on bridging the gap between profitable laboratory-scale activities and practical uses. The objective must be to speed up the synthesis of the nanocomposite in a way that is economical and sustainable. Its performance should be evaluated against complex, real-world industrial effluents with competing ions and multiple chemicals in order to assess its robustness. In addition, advancing the creation of immobilized catalyst systems, such as coatings on stable substrates, would deal with the problems that accompany powder recovery in continuous-flow water treatment facilities.Further expanding the light absorption into the visible spectrum and enhancing quantum yield might be attainable by examining the possibilities of doping with more compounds or producing ternary composites. In order to properly evaluate the sustainability and commercial viability of this revolutionary technology for environmental remediation, a comprehensive life-cycle assessment and economic analysis constitute vital next steps.

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