RESEARCH PAPER

Synergistic Effect of TiO$_2$ Nanorods Incorporated with Graphene Oxide for Photocatalytic Degradation of Multiple Dyes

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Abstract

The treatment of dye-contaminated wastewater is essential for mitigating environmental and health risks. In this study, we developed a novel nanocomposite, TiO$_2$-incorporated graphene oxide (TiO$_2$@GOn), aimed at enhancing the photocatalytic degradation of neutral red dye, which served as the target analyte. The photocatalysis technique was employed, leveraging the excitation of TiO$_2$ under UV light to generate reactive oxygen species for efficient dye degradation. TiO$_2$ nanorods were combined with graphene oxide to form the TiO$_2$@GOn nanocomposite, designed to improve charge separation and enhance catalytic activity. Nanocomposite characterization was carried out using X-ray diffraction (XRD) to determine crystallographic structure, scanning electron microscopy (SEM) to visualize surface morphology, and UV–Vis spectroscopy to evaluate the optical properties and photocatalytic behavior. The TiO$_2$@GOn nanocomposite demonstrated a synergistic catalytic effect, outperforming pristine TiO$_2$ and graphene oxide individually in dye degradation. This study introduces a highly efficient nanomaterial for environmental applications, offering a sustainable approach to the treatment of dye pollutants in wastewater.

Highlights

- **Development of TiO$_2$-incorporated graphene oxide nanocomposite (TiO$_2$@GOn).**
- **Catalytic degradation ability towards neutral red dye has been explored.**
- **Highly exposed surface area for the photocatalytic degradation process.**
- **Highly effective in the photocatalytic degradation of neutral red dye.**
- **Explored the possibility of employing TiO$_2$@GOn in dye degradation applications.**

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Introduction

The progression of human civilization has brought about significant adverse consequences for the environment. These negative effects have been exacerbated by air, water, and soil contamination, largely attributable to the rapid pace of industrialization, urbanization, and modern agricultural practices. In response to the growing concerns regarding environmental sustainability, ecological equilibrium, and human health, there is an increasing demand for measures aimed at environmental protection and energy conservation (Ahammed et al. 2020; Al-Amin et al. 2016). One prominent source of environmental pollution stems from organic

pollutants, focusing on organic dyes commonly generated by industries such as textiles and paper manufacturing. These dyes often exhibit high stability in aqueous environments, posing a substantial challenge to their removal and degradation. Some of these dyes are water-soluble, and their breakdown into secondary species can occur through processes like oxidation or exposure to sunlight (Nezafat et al. 2021; Chen et al. 2013).

Notably, the textile and paper industries alone produce approximately 106 tons of synthetic dyes annually globally. Shockingly, a significant portion of these dyes, around $1–1.5 \times 105$ tons, find its way into the environment through wastewater discharge. To combat this issue and reduce water pollution, wastewater treatment becomes imperative. Water pollution has dire consequences for aquatic life and disrupts the entire ecosystem as these pollutants enter the food chain. Moreover, many of these dyes have been identified as carcinogenic agents, increasing the risk of congenital disabilities and other health concerns(Sadia et al. 2021).To mitigate these detrimental effects, various wastewater treatment methods have been employed in recent years, including coagulation or flocculation, photodegradation of dyes into smaller molecules, adsorption, and chemical oxidation. Among these, the adsorption and photocatalytic degradation of dye molecules into smaller, less harmful components have emerged as highly efficient techniques for wastewater management. Nonetheless, it is worth noting that the challenge lies in obtaining catalysts with exceptionally high photocatalytic efficiency. This quest for superior catalysts underscores the ongoing efforts to address the complex issue of dye pollution and promote sustainable wastewater treatment practices (Liu et al. 2019).

When considering catalysts for photocatalytic degradation reactions, several key properties come to the forefront as essential criteria. These include a high surface area, physical and thermal stability, and biocompatibility. Nanomaterials are particularly well-suited for fulfilling these requirements and are, therefore, a primary choice for catalyzing the degradation of dyes. Among the myriad of nanomaterials, various types of metal nanoparticles, such as Ag and Au, as well as metal oxides like ZnO, NiO, and TiO_2, have been extensively explored for their efficacy in photocatalytic dye degradation processes. Among these photocatalysts, titanium dioxide (TiO_2) is one of the most promising candidates (Saraee et al. 2023; Padhi 2012). This is owing to its advantageous characteristics, including high chemical stability, affordability due to its low-cost availability, and strong oxidation capabilities. However, bulk TiO_2 particles possess inherent limitations, such as a relatively large band gap of approximately 3.2 eV, which can restrict their catalytic efficiency for dye degradation (Shujah et al. 2022).

To address this challenge, researchers have redesigned bulk TiO_2 material into nanoscale forms, which can significantly enhance its photocatalytic capabilities. Numerous strategies have emerged to overcome this limitation, including doping TiO_2 with other metals or metal oxides, coupling it with co-catalysts, and incorporating it with carbon-based nanomaterials like graphene, graphene oxides, or carbon nanotubes. Graphene oxide (GO) is a two-dimensional carbon material with exceptional mechanical strength, a vast surface area, and high chemical stability. These unique properties make GO an excellent candidate for serving as a supporting material for metal oxides, thus enabling it to act as a cooperative catalyst in photocatalytic dye degradation processes. By combining the attributes of TiO_2 and GO, researchers can capitalize on the synergistic effects between these materials to achieve superior catalytic performance in the degradation of dyes, furthering the development of effective and sustainable wastewater treatment solutions (Qamar et al. 2022).

Considering the paramount significance of dye degradation in the realm of wastewater management and the pivotal role played by metal oxide and graphene oxide (GO)-based materials in catalyzing dye degradation, our research endeavours led us to synthesize a novel nanocomposite known as TiO_2-incorporated graphene oxide (TiO_2@GOn). This nanocomposite was meticulously engineered to harness its catalytic potential for the degradation of neutral red dye, a common and persistent pollutant in various industrial effluents. Our investigation focused on evaluating the catalytic efficiency of the TiO_2@GOn nanocomposite and comparing it to the individual catalytic properties of pristine TiO_2 and GO. The central aim was to assess whether combining these two materials would yield synergistic benefits in the context of dye degradation. The catalytic capabilities of the nanocomposite were examined in detail, shedding light on its performance in the photocatalytic degradation of the neutral red dye.

Our results yielded promising outcomes, demonstrating that the TiO_2@GOn nanocomposite exhibited remarkably high effectiveness in the photocatalytic degradation of the neutral red dye.

Materials and Methods

Commercially sourced materials, including graphite, TiO_2 anatase, neutral red dye, and Azocarmine G2, were used in this study without prior purification. Purified water obtained from the Millipore Milli-Q water system was utilized for the analyses. UV–visible spectroscopic experiments were conducted using a Biochrome UV–visible spectrophotometer, which scanned 190–1100 nm. The

samples were subjected to medium-speed scanning within the 300–700 nm wavelength range. Fourier-transformed infrared spectra, spanning from 400 to 4000 cm^{-1}, were recorded using the Perkin Elmer Frontier MIR-FIR FT-IR spectrophotometer. Thermogravimetric analysis was carried out with a Thermal analyzer (Model TGA-50 & DSC-60, Shimadzu). For scanning electron microscopy (SEM) analyses, a JEOL JSM-6390LV SEM equipped with an Energy-Dispersive X-ray analyzer was employed. Powder X-ray diffraction patterns were obtained using a Rigaku Multiflex instrument that utilized a nickel-filtered CuKα (0.15418 nm) radiation source and a scintillation counter detector at scanning rate of 2 degrees per minute. Transmission electron microscopy analyses were conducted using the JEM-2100, a 200 kV instrument from Jeol.

Synthesis of GO Nanosheets [GOn]

Graphene oxide (GO) nanosheets were prepared using the Hummer's method (Maleki et al. 2024). Initially, a beaker containing 1 g of graphite powder was used to mix 25 mL of concentrated H_2SO_4 solution. This mixture was stirred until a uniform suspension was formed in an ice bath. Subsequently, 3 g of $KMnO_4$ was cautiously added to the solution to prevent excessive heating, with continuous stirring over a 3-h (the ice bath was removed after the first 20 min). After the 3-h reaction, 50 mL of distilled water was gradually introduced into the mixture. The change in color to brown indicated the successful formation of graphene oxide. An additional 100 mL of water was added to the mixture to ensure the complete oxidation of graphite. To eliminate excess $KMnO_4$, 5 mL of H_2O_2 was incorporated. The synthesized GO was then collected through centrifugation and underwent multiple rinses with H_2O. Finally, the GO nanosheets were dried in an oven at 90 °C for 24 h.

Synthesis of TiO$_2$ Anatase Nanorods

TiO$_2$ nanorods were synthesized using 2 g of commercially available TiO$_2$ anatase powder with a particle size of 325 mesh. Initially, a 10 M NaOH solution was added to the TiO$_2$ powder, and the mixture was stirred for one hour to achieve a uniformly dispersed suspension. Subsequently, the resulting mixture was transferred into a Teflon-lined stainless steel autoclave with a 50 mL capacity. This autoclave was then placed in a preheated oven at a temperature of 180 °C and left to react for 24 h. Afterwards, the mixture was allowed to cool naturally to room temperature, forming a white powder product. To isolate the solid product, centrifugation was employed. The obtained solid was then washed repeatedly with water and a 0.1 M HCl solution until the pH of the product was adjusted to approximately 7. The resulting product was dried overnight in an oven set at 60 °C to yield the TiO$_2$ nanorods.

Synthesis of TiO$_2$ Decorated GO Nanosheets [TiO$_2$@ GOn]

The preparation of TiO$_2$-decorated GO nanosheets involved the utilization of the impregnation method. Initially, 100 mg of GO nanosheets were dispersed in 20 mL of water, and this resulting solution underwent sonication in an ultrasonicator for 1 h to ensure complete exfoliation of the nanosheets. Subsequently, 10 mg of TiO$_2$ nanorods were introduced into the mixture, followed by another round of sonication for an additional hour. The resulting mixture was refluxed for 8 h at a temperature of 80 °C. Upon completion of the reaction, the product was collected via centrifugation, washed with water, and subsequently dried in an oven. This process yielded the TiO$_2$-decorated GO nanosheets, referred to as TiO$_2$@GOn.

Initial Degradation Studies (Adsorption Efficiency Assessment):

Before the introduction of the photocatalyst, preliminary degradation experiments were conducted under both dark and light conditions to assess the adsorption efficiency of the catalyst. Adsorption is critical, as it provides insight into how much dye the catalyst can adsorb from the solution before actual photocatalytic activity is initiated. A dye solution with a concentration of 25 ppm was used, and the solution was allowed to reach adsorption equilibrium by being left in the dark for 30 min. This step ensures that any observed changes in dye concentration are due to adsorption and not degradation by light. After 30 min, 3 mL of the solution was extracted for UV–Vis spectroscopic analysis to quantify the amount of dye adsorbed onto the catalyst surface. The blank (without the catalyst) and the test sample (with the catalyst) were analysed to differentiate between natural degradation and adsorption phenomena. The experiment was conducted using 0.5 mg of the TiO$_2$@GOn catalyst, and the sample was then exposed to a solar simulator to initiate degradation.

Calibration Curve Establishment

To ensure accuracy in quantifying dye concentration during the degradation process, a calibration curve was established by preparing dye solutions with known concentrations ranging from 5 to 25 ppm. UV–Vis spectroscopy was used to measure absorbance at specific wavelengths for each concentration. This calibration curve is vital for translating

absorbance readings into concentration values during photocatalytic degradation experiments.

Effect of Catalyst on the Degradation of Neutral Red Dye:

The role of the catalyst in the degradation efficiency was examined by varying the amount of TiO_2@GOn catalyst from 0.5 mg to 3 mg. This investigation sought to identify the optimal catalyst amount for maximum dye degradation. The degradation efficiency was measured using UV–Vis spectroscopy, which tracks the reduction in absorbance over time. An increase in catalyst concentration is expected to enhance photocatalytic degradation, although, beyond a certain point, an excess of the catalyst may cause agglomeration, which can reduce the effective surface area and impede light penetration, thereby diminishing degradation efficiency.

Determination of Catalyst Efficiency:

Degradation efficiency was further studied using dye solutions with concentrations ranging from 25 to 100 ppm. In each case, 1.5 mg of the TiO_2@GOn catalyst was employed to ensure consistency across the tests. By taking periodic UV–Vis spectra, the degradation process was closely monitored until complete dye degradation was observed. The efficiency of the catalyst was quantified based on the percentage reduction in dye concentration over time. This step ensures that the catalyst's performance is assessed across a broad range of dye concentrations, which can help simulate real-world scenarios where dye concentrations vary.

Effect of pH on the Degradation Pattern:

pH has a significant influence on the photocatalytic degradation of dyes, as it can affect the surface charge of the catalyst, the ionization state of the dye, and the generation of reactive oxygen species (ROS) during photocatalysis. Three solutions with different pH levels (acidic, neutral, and basic; pH 3, 7, and 10) were prepared using HCl and NaOH. The degradation behavior at each pH level was investigated in the same manner as the earlier experiments, using UV–Vis spectroscopy to monitor absorbance changes over time. Acidic conditions may favor the adsorption of positively charged dyes due to electrostatic attraction between the negatively charged catalyst surface and the dye. Conversely, basic conditions may enhance the formation of hydroxyl radicals (•OH), which are key agents in the photocatalytic degradation process. Therefore, this study provides insights into the optimal pH range for the most efficient dye degradation.

Results and Discussion

Graphene oxide (GO) is a remarkably versatile material known for its high surface area and thermal stability. What makes GO particularly intriguing is the presence of carboxyl (–COOH) and hydroxyl (–OH) functional groups on its two-dimensional layers. These functional groups create accessible sites for easy functionalization with various catalytically active materials. Leveraging these advantages, we prepared a composite material, TiO_2-incorporated GO nanosheets, using the impregnation method. In the initial stages of this process, TiO_2 was synthesized in the form of nanorods. This was achieved by treating commercially available TiO_2 anatase powder with a concentrated NaOH solution. These TiO_2 nanorods were subsequently incorporated into the GO nanosheets, giving rise to the composite material known as TiO_2@GOn. A comprehensive array of spectroscopic and analytical techniques was employed to ensure the successful synthesis and characterize the resulting materials. These techniques included Fourier-transform infrared spectroscopy (FT-IR), powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and transmission electron microscopy (TEM), among others. Through these analyses, we gained valuable insights into the composition and structure of the GO nanosheets, TiO_2 nanorods, and the TiO_2@GOn composite, allowing for a thorough understanding of their properties and potential applications.

Structural Validation

The Fourier-transform infrared spectroscopy (FT-IR) analysis played a crucial role in characterizing the synthesized materials, and the resulting spectra provided valuable insights into their composition and structural features. In the FT-IR spectra of the material (as shown in Fig. 1), all the characteristic peaks of graphene oxide (GO) were evident. Notably, the peak observed at 1718 cm^{-1} corresponds to the presence of the C=O group within the GO nanosheet. Additionally, distinct peaks at 1641, 1375, and 1048 cm^{-1} were attributed to specific structural elements of the GO nanosheet. The peak at 1641 cm^{-1} is associated with the sp2 hybridized C=C in-plane vibration, while the one at 1375 cm^{-1} corresponds to the C–O–C vibration. Furthermore, the peak observed at 1048 cm^{-1} can be attributed to the –COOH functional group present on the GO nanosheet. These findings collectively confirm the successful transformation of graphite into GO nanosheets, consistent with prior research findings (Bera et al. 2018).

Moving on to the TiO_2 component, its FT-IR spectrum exhibited a prominent peak at 664 cm^{-1}, indicative of the Ti–O interaction. A smaller peak at 1634 cm^{-1} was also

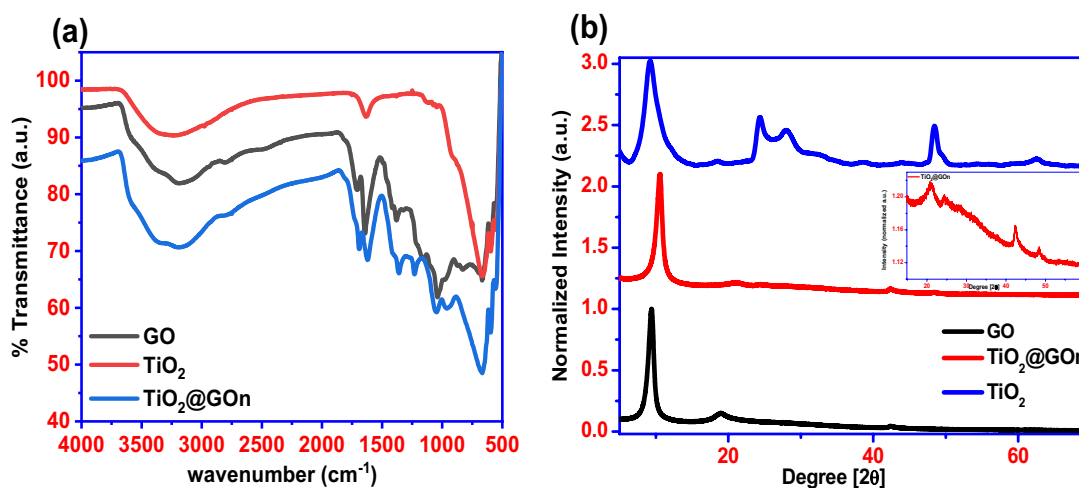**Fig. 1** (**a**) FT-IR spectra of GO, TiO_2 and TiO_2@GOn; (**b**) Powder XRD pattern of GO, TiO_2 and TiO_2@GOn

observed, attributed to the Ti–OH interaction. This specific peak is associated with the TiO_2 nanorods' composition (Sharma et al. 2011; Shi et al. 2015; Verma et al. 2012). Subsequently, after synthesizing the TiO_2@GOn composite from the respective starting materials, the FT-IR spectra of the resulting material were examined. Importantly, all the pertinent peaks in neat GO and TiO_2 FT-IR spectra were discernible in the TiO_2@GOn complex. This observation is strong evidence for successfully incorporating TiO_2 nanorods into the GO nanosheets, effectively forming the TiO_2@GOn composite.

Powder X-ray diffraction (PXRD) analysis is a powerful technique used to study the crystalline structure of materials. PXRD was used to analyze the structure of graphene oxide (GO), titanium dioxide (TiO_2), and a TiO_2@GOn nanocomposite. The PXRD pattern of GO exhibits a prominent peak at 2θ 9.38° (JCPDS card No. 892482). This peak corresponds to the characteristic peak of graphene oxide nanosheets. This suggests that the GO material has a well-defined crystalline structure, and this peak serves as a fingerprint for identifying GO. The PXRD pattern of TiO_2 shows peaks at various 2θ values, specifically at 9.04, 24.18, 28.02, and 48.30 (JCPDS Card No. 78–2486-crystallographic planes of anatase). Peaks at 2θ values of 24.18, 28.02, and 48.30 indicate the TiO_2 anatase crystal structure (Waterhouse et al. 2013; Jahani et al. 2023). Anatase is one of the common crystalline phases of TiO_2. The peak at 2θ 9.04 corresponds to the H-titanate structure, indicating the presence of H-titanate in the TiO_2 nanostructure. The coexistence of TiO_2 and H-titanate in the sample is significant as it suggests that both materials are present and contribute to the overall composition. This combination may have implications for the synthesis process and the resulting material's properties, particularly in the formation and stabilization of nanowires.

The PXRD pattern of the TiO_2@GOn nanocomposite displays peaks that correspond to the neat GO and TiO_2 nanowires. These peaks indicate that the nanocomposite contains both GO and TiO_2 components, confirming the successful formation of the composite material. Additionally, it's noted that the concentration of TiO_2 in the nanocomposite is only 10 wt% of the GO weight. This suggests that the TiO_2 nanowires are a minor component within the composite. The inset picture of the zoomed PXRD pattern likely highlights the peaks specific to the TiO_2 nanowires, helping to distinguish and analyze their contribution within the composite. The PXRD analysis revealed valuable information about the crystalline structures present in the investigated materials. It confirmed the presence of GO, identified different phases of TiO_2 (anatase and H-titanate), and demonstrated the successful formation of the TiO_2@GOn nanocomposite. This information is essential for understanding the composition and structure of these materials, which can have implications for their properties and potential applications.

Thermogravimetric analysis (TGA) was conducted to explore the impact of temperature on the thermal stability of the synthesized nanocomposite. In the case of graphene oxide (GO), an intriguing observation emerged as the TGA pattern exhibited a sharp decline in mass at 168 °C (Yagub et al. 2014; Zhang et al. 2020), a distinctive characteristic associated with GO nanosheets. This abrupt drop in mass during TGA analysis is typically linked to materials with a significantly high surface area, a hallmark of GO nanosheets. Moving on to titanium dioxide (TiO_2), it displayed an overall 16% reduction in weight during the analysis, primarily attributed to the release of occluded water molecules from its structure. In contrast, the TiO_2@GOn nanocomposite exhibited a more complex three-stage degradation pattern in the TGA spectra. This intricate TGA pattern corresponded to
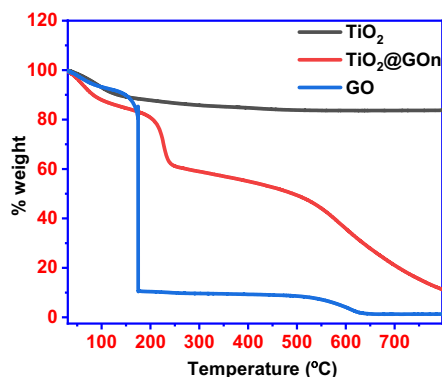
Fig. 2 Thermogravimetric analysis pattern of GO, TiO_2 and $TiO_2@$GOn

the sequential processes of desorbing surface-adsorbed water molecules, decomposition of organic functional groups, and finally, the vaporization of carbon as carbon dioxide (CO_2). This comprehensive TGA investigation provides valuable insights into the thermal behaviour of the nanocomposite, shedding light on its composition and the various thermal processes it undergoes with changing temperatures.

The complex thermal gravimetric analysis (TGA) pattern (Fig. 2) observed for the $TiO_2@$GOn nanocomposite signifies a series of successive processes during heating. Initially, the weight loss corresponds to the desorption of surface-adsorbed water molecules. Subsequently, the TGA profile reflects the decomposition of organic functional groups present in the graphene oxide component. These functional groups include oxygen-containing moieties such as epoxy groups (C–O–C), hydroxyl groups (C–OH), and carboxyl groups (COOH). The final stage of the TGA curve indicates the vaporization of carbon, primarily in the form of carbon dioxide (CO_2), suggesting the thermal degradation of carbonaceous structures within the nanocomposite. The identification of specific degraded organic functional groups could be further elucidated through complementary techniques like Fourier-transform infrared spectroscopy (FTIR) or X-ray photoelectron spectroscopy (XPS), offering a more detailed chemical analysis of the $TiO_2@$GOn nanocomposite's composition and thermal stability.

Transmission electron microscopy (TEM) analyses were conducted on graphene oxide (GOn), titanium dioxide (TiO_2) nanorods, and the $TiO_2@$GOn nanocomposite to gain deeper insights into their surface morphologies. The structural examination of GOn unveiled its characteristic sheet-like structure, a typical feature of GO nanosheets. The TEM images of GOn further highlighted a high degree of exfoliation within the nanosheet structure, indicating the successful separation of individual layers. Turning to the TEM analysis of TiO_2 nanorods, a visually stunning structure emerged. The nanorods displayed an average length of 50–80 nm and

a thickness of approximately 8 nm. The excellent exfoliation of GO nanosheets and the well-defined structure of TiO_2 nanorods converged to form the $TiO_2@$GOn nanocomposite. This amalgamation was confirmed through TEM imaging, where the TEM image of $TiO_2@$GOn showcased the successful incorporation of TiO_2 nanorods onto the surface of the GO nanosheets. This detailed TEM analysis provided (Fig. 3) valuable visual evidence of the nanocomposite's structure, reaffirming the integration of TiO_2 nanorods with the GO nanosheet substrate, which holds promise for various applications due to its unique structure and properties.

Photocatalytic Degradation of Neutral Red Dye Using $TiO_2@$GOn

The combination of high surface area graphene oxide (GO) nanosheets and photo-catalytically active titanium dioxide (TiO_2) nanorods holds promise for enhancing photocatalytic degradation, particularly in synthetic dyes. In this study, the $TiO_2@$GOn nanocomposite was employed as a photocatalyst for degrading the neutral red dye. Initially, a comprehensive evaluation was conducted to assess the individual contributions of neat GO, TiO_2 nanorods, and the $TiO_2@$GOn nanocomposite towards the degradation of the dye. The initial degradation studies with GOn alone and TiO_2 alone, and both showed no significant dye degradation. Furthermore, the study aimed to distinguish between adsorption and degradation processes, thus conducting reactions in the presence and absence of light when using the $TiO_2@$GOn catalyst.

In the absence of light, it was observed that there was a significant adsorption capacity of approximately 20%, which occurred over an extended period. Conversely, in the presence of light, the $TiO_2@$GOn catalyst initiated the degradation of the neutral red dye (Fig. 4). This observation demonstrates the photocatalytic activity of TiO_2 nanorods as they respond to light energy to drive the degradation process. Importantly, TiO_2 and GO in the same nanocomposite synergistically enhance the catalytic activity. This cooperative effect likely arises from the combination of GO's efficient adsorption properties and photocatalytic activity of TiO_2, ensuring the effective degradation of the dye molecules when exposed to light. Overall, these findings illustrate the potential of the $TiO_2@$GOn nanocomposite as an effective photocatalyst for the degradation of synthetic dyes, with its components working in tandem to enhance the catalytic process.

This study systematically investigated the impact of varying the catalyst concentration on its catalytic activity. Four different quantities of catalyst were tested, ranging from 0.5 mg to 3 mg, to understand how the amount of catalyst affects the degradation of a target compound, likely the neutral red dye. The results demonstrated a clear relationship

Fig. 3 (**a**, **b**) TEM images of GO nanosheets, (**c**, **d**) TEM images of TiO_2 nanorods, and (**e**, **f**) TEM images of TiO_2@GOn nanocomposite
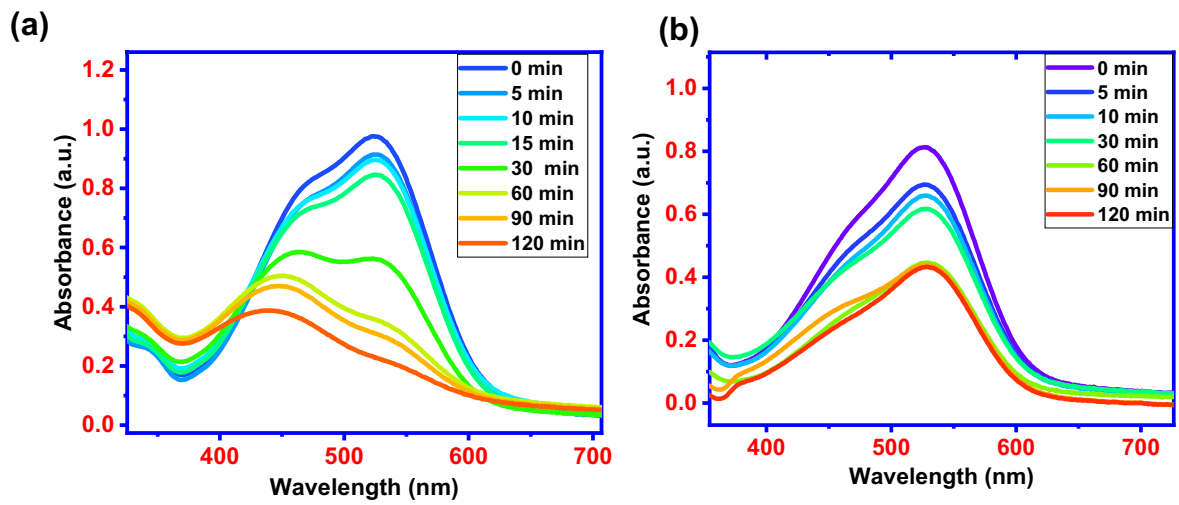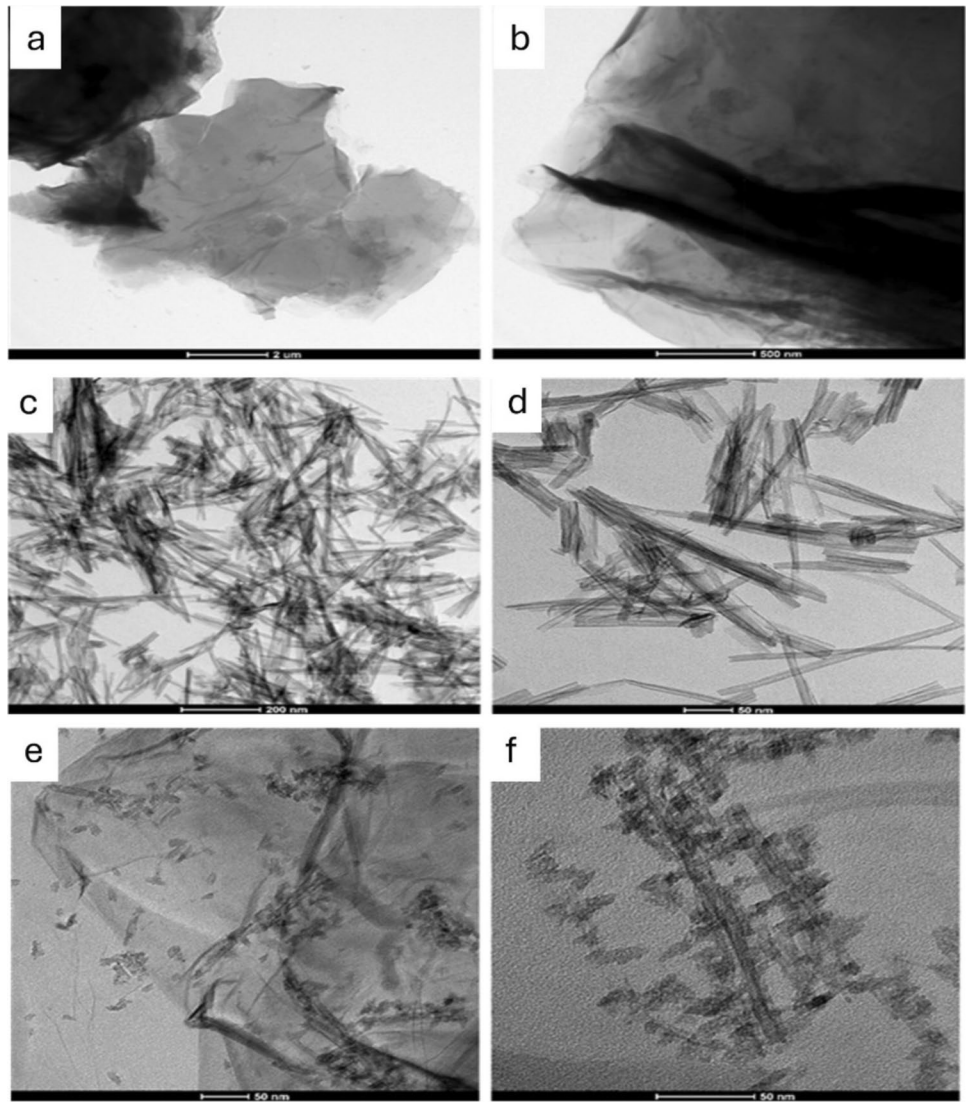

Fig. 4 Photocatalytic neutral red dye degradation by TiO_2@GOn catalyst for (**a**) 50 ppm neutral red dye solution; (**b**) 100 ppm neutral red dye solution

between catalyst concentration and degradation efficiency. Starting with 0.5 mg of the catalyst, a significant degradation of approximately 78% was achieved within 4 h. As the catalyst amount was increased to 1 mg, the degradation efficiency improved, reaching 85% degradation within a shorter time frame of 3 h. Further increasing the catalyst amount to 1.5 mg and 3 mg resulted in even faster degradation times, reduced to 2 h and 1 h, respectively, and higher degrees of degradation at 92% and 95%, respectively. These findings suggest that a slight increase in the catalyst amount, from 0.5 mg to 3 mg, led to a noticeable improvement in the degradation efficiency, highlighting the catalyst's catalytic activity's sensitivity to concentration changes.

It's worth noting that all these reactions were conducted at room temperature and a neutral pH of 7. Additionally, the study hints at the possibility of conducting similar reactions under basic pH conditions, expanding the scope of potential applications for this catalyst. These findings provide valuable insights into optimizing the catalyst concentration for efficient degradation processes, offering a potential pathway to enhance the catalyst's performance for various catalytic applications.

In order to establish the efficacy and versatility of the TiO_2@GO catalyst, the photodegradation of the neutral red dye was carried out in both acidic and basic environments (Fig. 5). Absorbance versus wavelength plots were recorded to assess the catalyst's degradation performance under varying pH conditions. The results demonstrated the catalyst's ability to degrade the dye in both acidic and basic mediums effectively. In the acidic medium, the TiO_2@GO catalyst demonstrated a significant degradation of the neutral red dye. The absorbance versus wavelength plots revealed that the catalyst effectively facilitated the photocatalytic degradation process. The achievement of approximately 50%

degradation within a short timeframe of 2 h indicates the catalyst's ability to efficiently degrade the dye even under acidic conditions. This performance suggests that the TiO_2@GO catalyst is robust and effective in an acidic environment, showcasing its adaptability for potential applications in scenarios where acidity is a concern, such as certain types of wastewater.

The TiO_2@GO catalyst exhibited even more remarkable performance in a basic medium with a pH of 10. The absorbance versus wavelength plots showed an impressive degradation rate of approximately 90% under these conditions. This signifies that the catalyst is highly efficient in degrading the neutral red dye in a basic environment, emphasizing its versatility and adaptability. The catalyst's outstanding performance in basic conditions highlights its potential for applications in alkaline environments, making it a promising candidate for use in wastewater treatment processes where elevated pH levels may be encountered. The results from both acidic and basic mediums collectively confirm the TiO_2@GO catalyst's versatility. It effectively degrades neutral red dye in neutral and basic environments, showcasing its adaptability to a wide range of pH conditions. This versatility is a crucial factor that positions the TiO_2@GO catalyst as a valuable tool for various environmental applications, particularly in wastewater treatment and environmental remediation. The TiO_2@GO catalyst has demonstrated robust performance across different pH levels, making it a promising candidate for addressing challenges in diverse environmental conditions.

To assess the impact of dye concentration on the degradation efficiency of the TiO_2@GO catalyst, a series of dye solutions were prepared at concentrations ranging from 25 to 100 ppm. These solutions were subjected to photodegradation experiments (Fig. 6) in the presence of 1.5 mg of the
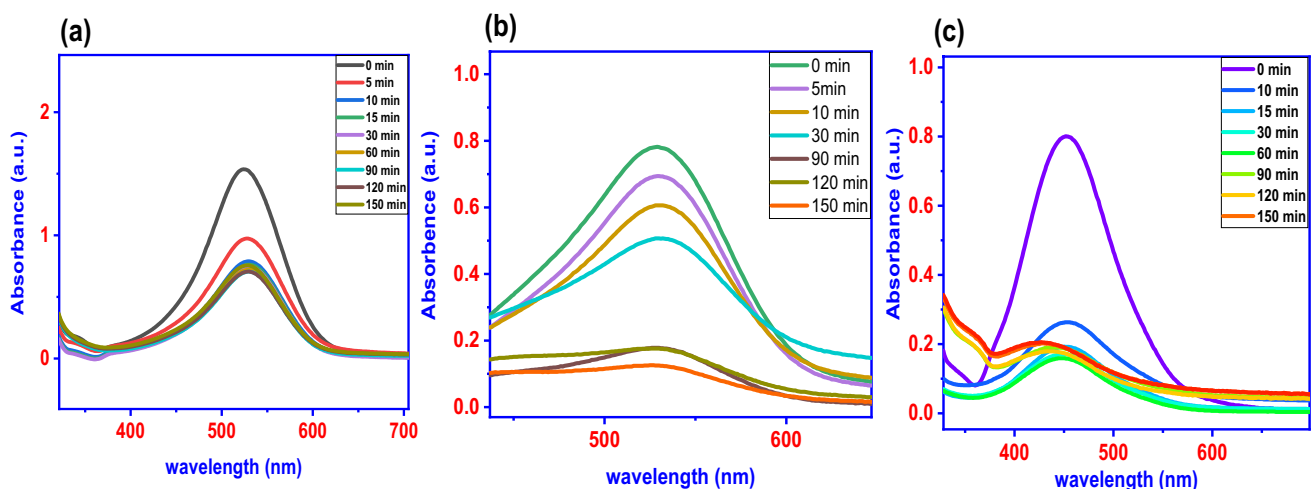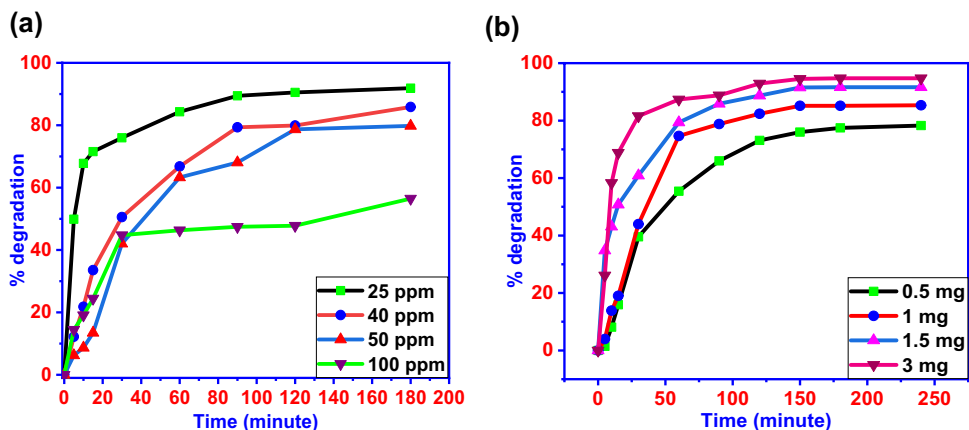

Fig. 5 Photocatalytic neutral red dye degradation by TiO_2@GOn catalyst in the (**a**) acidic medium of pH 3, (**b**) neutral medium of pH 7, and (**c**) basic medium of pH 10

Fig. 6 Photo catalytic degradation ability of TiO$_2$@GOn (**a**) in different concentrations of dye and (**b**) different amounts of catalyst for 25 ppm concentration neutral red dye solution


catalyst, and their degradation patterns were monitored using a UV–Vis spectrophotometer. The results provided insights into how the initial concentration of the dye affected its degradation by the catalyst. Starting with a 25 ppm dye solution, an impressive degradation rate of approximately 95% was achieved, indicating the catalyst's remarkable efficiency in degrading the dye at lower concentrations. As the dye concentration increased to 40 ppm and 50 ppm, the degradation percentages remained relatively high, at around 80%. This suggests that the catalyst continued to exhibit substantial effectiveness even at higher dye concentrations, although the degradation rate showed a slight decrease compared to the lower concentration.

The degradation efficiency was still notable in a 100 ppm dye solution, with approximately 60% degradation achieved. This result indicates that the catalyst could effectively degrade a significant portion of the dye even when the initial concentration was relatively high. Overall, these findings demonstrate that the TiO$_2$@GO catalyst is capable of efficiently degrading the neutral red dye across a range of concentrations, making it versatile for potential applications in treating wastewater with varying dye concentrations. This

versatility is a valuable feature for environmental remediation and water treatment processes.

In investigating adsorption degradation kinetics, data collected at various catalyst concentrations (Fig. 7) were analyzed using two kinetic models: the pseudo-first-order and pseudo-second-order models. These models are commonly used to describe adsorption processes. The pseudo-first-order equation ($\log(q_e-q_t) = \log(q_e) - k_1 \times t/2.303$) and pseudo-second-order equation ($t/q_e = 1/k_2 q_e^2 + t/q_e$) were applied, where q_t and q_e represent the adsorbed amount of neutral dye at time t and equilibrium, respectively, and k_1 and k_2 are the rate constants for the respective kinetic models. The results indicated that the pseudo-second-order kinetic model best fit the experimental data, as evidenced by the highest K_2 value of 0.373 g/mg·min. This significant K_2 value suggests a strong affinity between the TiO$_2$@GO catalyst and the dye molecule, leading to efficient adsorption and degradation. The findings not only elucidate the kinetics of the degradation process but also underscore the catalyst's effectiveness in degrading dye molecules, which has important implications for wastewater treatment and environmental remediation applications.

Fig. 7 Linear fit data for the degradation of neutral red dye in different amounts of catalyst for (**a**) pseudo 1st order kinetic model and (**b**) pseudo 2nd order kinetic model
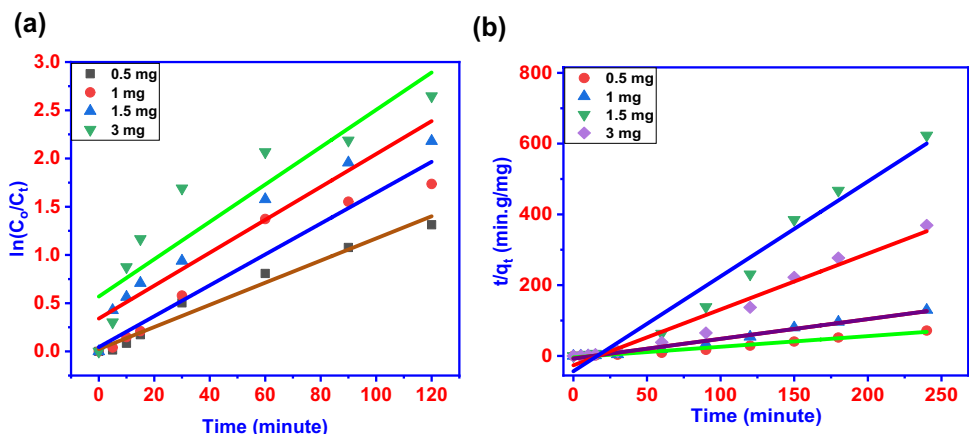
Incorporating graphene oxide (GO) nanosheets alongside titanium dioxide (TiO_2) nanorods in the TiO_2@GOn nanocomposite plays a pivotal role in the adsorption and photodegradation of neutral red dye. This synergy is achieved through several key mechanisms. Firstly, functional groups such as –COOH and –OH on the GO nanosheets enhance ionic and electronic interactions, significantly improving the adsorption capacity for neutral red dye compared to TiO_2 nanorods alone. GO's remarkable adsorption ability in the visible light region and its small band gap further contribute to lowering the energy required for degradation within the TiO_2@GOn nanocomposite. Moreover, GO can act as an electron conductor and acceptor, facilitating the interfacial electron transfer process from TiO_2.

Additionally, GO effectively prevents the recombination of charge carriers, thus enhancing the photocatalytic activity of the overall TiO_2@GOn nanocomposite. As a result, the TiO_2@GOn catalyst exhibits a powerful synergistic effect between adsorption and photocatalysis, leading to highly efficient degradation of neutral red. This combination of properties makes the nanocomposite an excellent candidate for environmental remediation and wastewater treatment applications where removing dye pollutants is crucial.

The photocatalytic efficiency and the impact of the high surface area of graphene oxide (GO) in enhancing the photocatalytic degradation of various dyes by titanium dioxide (TiO_2) nanorods were rigorously demonstrated through selectivity studies using Azocarmine G2 dye as a test case. This study subjected a 25 ppm solution of Azocarmine G2 dye (Fig. 8) to photocatalytic degradation using three different catalysts: TiO_2@GOn, GO alone, and TiO_2 alone. The results revealed the remarkable effectiveness of TiO_2@GOn as a catalyst. With just 1.5 mg of TiO_2@GOn, complete degradation of the Azocarmine G2 dye was achieved within a relatively short period of 1.5 h. This outstanding performance underscores the exceptional photocatalytic
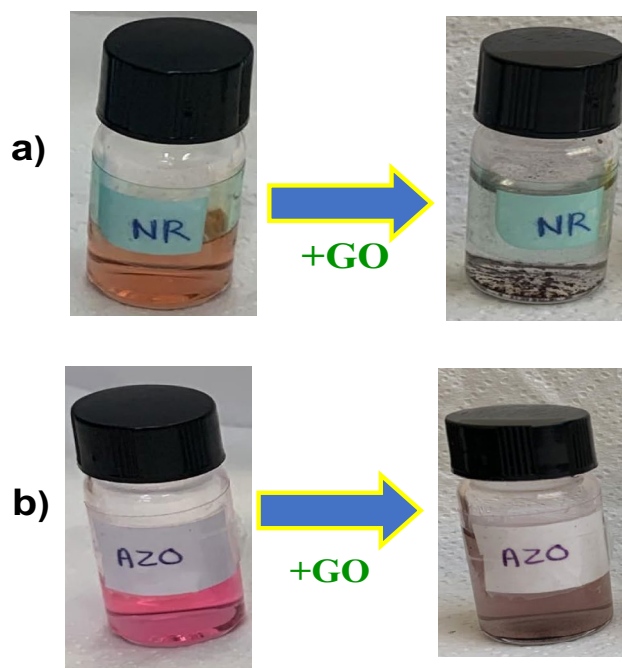

Fig. 9 Photocatalytic (**a**) neutral red and (**b**) azocarmine G2 dye degradation by GO catalyst

capabilities of the TiO_2@GOn nanocomposite. This study not only confirms the excellent photocatalytic efficiency of the TiO_2@GOn catalyst but also highlights the crucial role played by the high surface area of GO in enhancing the degradation of various dyes. These findings have significant implications for removing dye pollutants from wastewater and environmental remediation, where a versatile and efficient catalyst like TiO_2@GOn can play a pivotal role in addressing pollution challenges.

A comparison of the efficiency of graphene oxide (GO) in the degradation of two different dyes, neutral red and

Fig. 8 Photocatalytic Azocarmine G2 dye degradation by TiO_2@GOn (GT1) catalyst
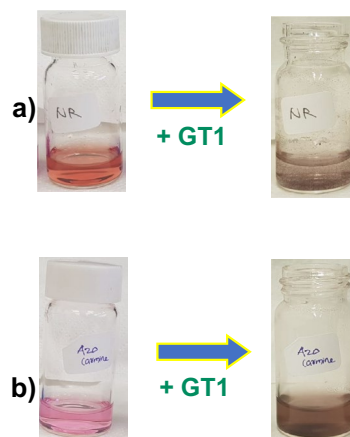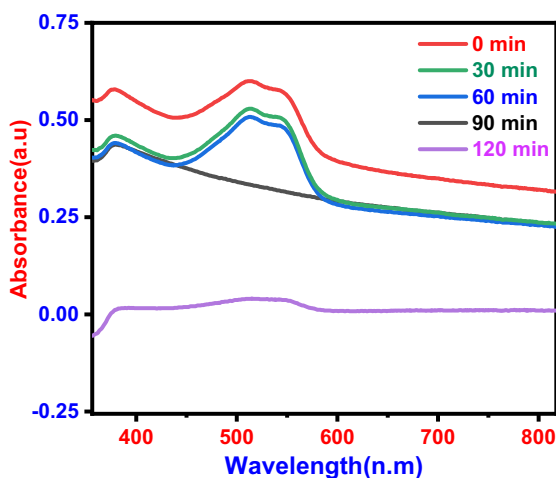
Azocarmine G2, reveals contrasting results. GO demonstrates effectiveness in the degradation of neutral red but is not suitable for Azocarmine G2 degradation, as depicted in Fig. 9. In the case of neutral red degradation, GO proves to be a successful catalyst, likely due to its high surface area and the presence of functional groups that enhance ionic and electronic interactions. These characteristics enable GO to efficiently adsorb and facilitate the degradation of neutral red dye, leading to its effective removal. Conversely, when it comes to Azocarmine G2, GO does not exhibit the same efficiency level. This variation in performance could be attributed to the specific chemical properties and structural characteristics of Azocarmine G2, which may not interact favourably with GO or require different catalytic conditions for degradation.

We observed an impressive degradation efficiency of approximately 95% for the dye in neutral and basic mediums. This outcome underscores the potential of the $TiO_2@$ GOn nanocomposite as an efficient catalyst for removing this persistent dye pollutant from industrial wastewater streams. This research has contributed to developing a highly effective and promising catalyst, the TiO_2-incorporated graphene oxide nanocomposite, for the efficient degradation of dyes. This advancement holds great potential for addressing dye pollution in wastewater, emphasizing the importance of such innovative solutions in the broader context of sustainable environmental management.

These findings underscore the importance of catalyst selectivity and the need for tailored approaches when addressing diverse dye pollutants. While GO may be effective for certain dyes like neutral red, its suitability for other dyes, such as Azocarmine G2, may be limited. Therefore, a comprehensive understanding of the catalyst's capabilities and its compatibility with specific dye molecules is crucial for designing effective wastewater treatment strategies and environmental remediation processes.

The results of comparing the efficiency of titanium dioxide (TiO_2) in the degradation of two different dyes, neutral red and Azocarmine G2, reveal that TiO_2 is not an effective catalyst for the degradation of either dyes, as depicted in Fig. 10. For the degradation of neutral red, TiO_2 does not exhibit significant efficiency. This could be due to various factors, such as the specific chemical properties of neutral red, the reaction conditions, or the inherent limitations of TiO_2 as a photocatalyst for this particular dye. Similarly, in the case of Azocarmine G2 degradation, TiO_2 also demonstrates inefficacy. This suggests that TiO_2 may not have the necessary catalytic properties to interact with and degrade Azocarmine G2 under experimental conditions effectively.

These findings emphasize that TiO_2, a commonly used photocatalyst for various applications, may not be universally effective for degrading all dye pollutants. The selectivity of a catalyst is crucial, and its suitability for a particular dye may depend on the specific dye's chemical structure and reactivity. Therefore, it's essential to carefully choose or tailor catalysts based on the characteristics of the target pollutants in wastewater treatment and environmental remediation efforts.

The catalytic degradation of neutral red dye using the $TiO_2@$GOn nanocomposite involves a complex mechanism that capitalizes on the distinct properties of titanium dioxide (TiO_2) nanorods and graphene oxide (GO) nanosheets. This process unfolds in several stages, encompassing adsorption, light activation, and the generation of reactive species that facilitate degradation.

Mechanism of Catalytic Degradation

Adsorption Phase

The initial step in the catalytic degradation of neutral red dye using the $TiO_2@$GOn nanocomposite involves the adsorption of dye molecules onto the surface of graphene oxide (GO) nanosheets. This process is crucial for enhancing the overall degradation efficiency. GO's high surface area significantly contributes to its ability to adsorb a large number of dye molecules, providing ample sites for interaction. Additionally, the presence of functional groups such as carboxyl (–COOH) and hydroxyl (–OH) on the GO surface facilitates ionic and hydrogen bonding with the dye. These interactions increase the adsorption capacity compared to TiO_2 alone,
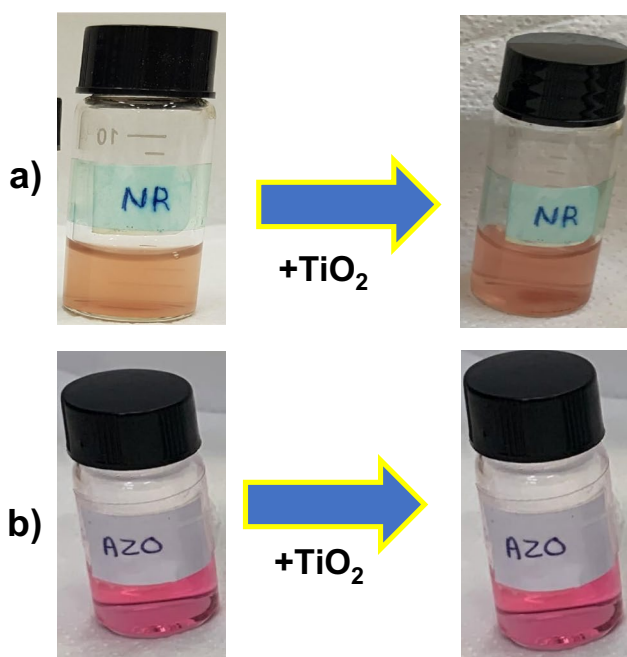

Fig. 10 Photocatalytic (**a**) neutral red and (**b**) azocarmine G2 dye degradation by TiO_2 catalyst

which lacks such extensive functionalization. Furthermore, the hydrophobic nature of the aromatic structure of the neutral red dye promotes additional hydrophobic interactions with the GO surface, leading to more efficient adsorption. As a result, this initial adsorption phase is critical in positioning the dye molecules in close proximity to the catalyst, setting the stage for effective degradation.

Light Activation and Charge Generation

Once the dye is adsorbed, the next phase involves the activation of the TiO_2 catalyst through light exposure. Upon illumination, TiO_2 absorbs photons, which provides enough energy to excite electrons from the valence band to the conduction band, resulting in the formation of electron–hole pairs (e^-/h^+). This charge generation is a vital step in the photocatalytic process. The effective separation of these charges is crucial, as it allows for a higher availability of active species for the degradation reactions. The generated holes remain in the valence band, while the conduction band electrons are free to migrate. This separation of charges is essential for minimizing recombination events, which would otherwise reduce the efficiency of the photocatalytic reaction. By sustaining the availability of charge carriers, the TiO_2 catalyst can effectively contribute to the degradation of the neutral red dye.

Electron Transfer to GO

In this catalytic system, the generated electrons play a significant role in enhancing the degradation process. After being excited, the conduction band electrons transfer from TiO_2 to the GO nanosheets. GO acts as an electron conductor, facilitating this transfer and helping to prevent recombination of the electron–hole pairs. This effective electron transfer is pivotal, as it ensures that the majority of charge carriers remain active and available for subsequent reactions. The interaction between the TiO_2 and GO allows for a synergistic effect that boosts the overall photocatalytic activity. By efficiently channeling electrons away from TiO_2, GO enhances the catalyst's performance, thereby promoting the degradation of the dye molecules adsorbed on its surface.

Formation of Reactive Oxygen Species (ROS)

The generated holes and electrons initiate a series of reactions that lead to the formation of reactive oxygen species (ROS), which are key players in the degradation of neutral red dye. The holes can react with water molecules, producing hydroxyl radicals ($\bullet OH$) through the following reaction:

$$h + + H_2O \rightarrow \bullet OH + H+$$
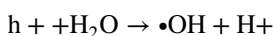
Hydroxyl radicals are highly reactive and can oxidize organic compounds, including the neutral red dye, leading to its degradation. Concurrently, the conduction band electrons can react with molecular oxygen (O_2), generating superoxide anions ($O_2 \bullet^-$):

$$e - + O_2 \rightarrow O_2 \bullet -$$
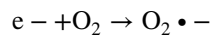
These reactive species—hydroxyl radicals and superoxide anions—are crucial for attacking the dye molecules, leading to oxidative breakdown of their complex structures. The presence of these ROS not only initiates the degradation process but also enhances the overall efficiency.

Degradation of Neutral Red Dye

As a result of the interactions with ROS, the neutral red dye undergoes a series of oxidative reactions that break down its molecular structure. Hydroxyl radicals, in particular, play a significant role in this degradation process. They can attack various functional groups within the dye, cleaving chemical bonds and leading to the formation of smaller, less harmful by-products. This degradation pathway typically results in mineralization, where the dye is ultimately converted into non-toxic by-products, such as carbon dioxide (CO_2) and water (H_2O). The ability of the TiO_2@GOn nanocomposite to effectively degrade the neutral red dye under different conditions, such as varying light intensity and dye concentration, demonstrates its robustness as a photocatalyst.

Effect of Environmental Conditions

The versatility of the TiO_2@GOn nanocomposite is further highlighted by its performance across various pH levels. Experimental studies indicate that the catalyst can effectively degrade neutral red dye in both acidic and basic environments. In acidic conditions, the catalyst maintains a significant degradation rate, demonstrating its robustness even when the pH is low. In contrast, the catalyst exhibits even higher degradation efficiency in basic environments, which can be attributed to the enhanced reactivity of the available reactive species under these conditions. The adaptability of the TiO_2@GOn system across different pH levels underscores its potential applicability in diverse environmental settings, particularly in the treatment of wastewater with varying chemical characteristics.

Kinetic Studies

Kinetic studies provide additional insights into the degradation process of neutral red dye using the TiO_2@GOn nanocomposite. By analyzing the data collected at various catalyst concentrations, researchers applied both

pseudo-first-order and pseudo-second-order kinetic models to describe the adsorption dynamics. The results indicated that the pseudo-second-order model best fit the experimental data, suggesting a strong affinity between the TiO$_2$@GOn catalyst and the dye molecules. This strong affinity implies that the rate of degradation is dependent on the availability of active sites on the catalyst rather than just the concentration of the dye. The significant rate constant derived from the pseudo-second-order model indicates that the TiO$_2$@GOn catalyst is highly effective in facilitating the degradation process, thereby reinforcing its potential application in wastewater treatment and environmental remediation.

Conclusion

This study introduces an innovative synthesis method for the TiO2@GOn nanocomposite, which effectively combines titanium dioxide (TiO2) nanorods with graphene oxide (GO) nanosheets, demonstrating a simple and efficient approach. Importantly, our research proposes a hypothesis regarding the enhanced photocatalytic performance of TiO2@GOn. The nanocomposite exhibits an impressive 95% removal rate in the degradation of neutral red dye under both neutral and basic conditions, significantly outperforming traditional materials. A notable innovation of this work is the focus on the structural analysis of the nanocomposite, highlighting its high surface area, which is essential for improving the photocatalytic degradation process. The remarkable synergy between GO and TiO2 within the nanocomposite is crucial, facilitating the rapid degradation of neutral red dye and achieving a 95% removal rate in just 1.5 h—representing a significant advancement compared to existing studies. Our research enhances the field by performing a thorough comparative analysis involving TiO2@GOn, GO alone, and TiO2 alone in the degradation of multiple dyes. This analysis reveals the substantial role of GO's high surface area in boosting the photocatalytic degradation efficiency of TiO2 nanorods. In contrast, both GO and TiO2 alone demonstrated limited effectiveness in degrading the dyes, highlighting the distinct advantages of the TiO2@GOn nanocomposite. These findings signify a major advancement, indicating the potential of TiO2@GOn for tackling difficult dye degradation challenges and paving the way for innovative applications in advanced wastewater treatment and environmental remediation.

Author contribution Shabi Abbas Zaidi: Conceptualization, Methodology, Writing – review & editing. Bagmita Bhattacharyya, Hayarunissa Anwar: Data curation, Methodology, Writing – original draft. Maimoona Mohamed, Hanan Sheikh, Sarya Muhannad Alfarwati, Rouzait Anwar Jarrar: Visualization, Investigation. Mithra Geetha: Validation. Kishor Kumar Sadasuvuni: Supervision.

Declarations

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