Plant-Based Natural Dye-Stimulated Visible-Light Reduction of GO and Physicochemical Factors Influencing the Production of Oxidizing Species by a Synthesized (rGO)/TiO₂ Nanocomposite for Environmental Remediation

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ABSTRACT: Here, we report our findings related to the structural and photocatalytic considerations that influence the speed of electron−hole separation in semiconductor photocatalysis in the presence of reduced graphene oxide. A comparison of the exterior properties required for the degradation of the dye methylene blue and drug amoxicillin (C₁₆H₁₉N₃O₅S) as a probe by the synthesized photocatalyst reduced graphene oxide (rGO)/TiO₂ nanowire with graphene oxide and reduced graphene oxide; TiO₂ alone reveals that TiO₂ is significantly influenced by three factors: (1) rGO interactions with TiO₂ in terms of electron and hole transfer, (2) mode of reduction strategies adopted for reducing graphene oxide, and (3) production of OH• by the catalyst used. This work provides a thorough insight into the smooth, encouraging, and environment-friendly way developed for synthesizing reduced graphene oxide (rGO). The indigo dye-stimulated visible-light reduction methodology not only gives us an easy light-assisted reduction technique but also leads to new ways to get photoactive carbon-based titania semiconductor nanocomposites. Inspired by advances taking place in materials science as well as nanotechnology, we sought to develop improved photocatalytic materials by modifications to anatase TiO₂ through which opportunities to improve the performance of photocatalytic pollutant treatment may emerge.

1. INTRODUCTION

Since the discovery of TiO₂, it has been the center of attention of various photochemical as well as electrochemical investigations. Several studies have been conducted to assess the potential of TiO₂ as a photoactive catalyst for use in environmental sanitization such as water disinfection, air purification, the dissociation of water and solar energy conversion, and the degradation of textile effluents. When exposed to solar radiation, TiO₂ absorbs ultraviolet light from sunlight, resulting in the formation of an excited electron and a hole produced by the removal of the excited electron. The produced hole, upon forming on the particle’s surface, can interact with the adsorbed surface water and thereby form highly reactive hydroxyl radicals, which are electrically neutral, but highly reactive. TiO₂ has a band gap of only 3.2 eV, which allows it to be active in the UV range only. A 3.2 eV electronic band gap makes TiO₂ unfavorable for use under natural sunlight below a wavelength of ~380 nm. Apart from this, the quantum yield as well as the efficiency for photocatalytic reactions also decrease considerably because of the very high rate of electron and hole recombination. A number of schemes have been employed to solve these problems, such as doping with impurities in the form of metals and nonmetals (substitutional or/and interstitial), modification of the parent photocatalyst in terms of surface properties or nanocomposite formation with other supplementary materials (e.g., heterojunctions), pairing with different semiconductors of varying band gaps and packing noble metals, etc.

In particular, the amalgamation of TiO₂ nanomaterials with carbon-based nano raw materials such as graphene, graphite oxide, and carbon nanotubes has been proposed as a convenient method for enhancing the photocatalytic activity. Currently, graphene oxide (GO) and reduced graphene oxide (rGO) are utilized as the most effective support systems for enhancing photocatalytic activity as they possess unique physical as well as chemical properties, e.g., superior mechanical strength, high conductivity, extended specific surface area, etc. The overall effect of utilizing GO and...
rGO to synthesize a GO/rGO/TiO₂ nanocomposite is to enhance the photocatalytic activity of TiO₂ by reducing the excited electron and hole recombination, thereby increasing the light absorption range.¹³ The fusion of TiO₂ with rGO is one of the best methods to overcome the drawbacks of TiO₂.¹⁴ rGO has considerable utility in a wide range of areas. The rGO-dependent nanocomposites find uses as nanosensors for various biomolecules,¹⁵,¹⁶ photocatalysts for degradation of pollutants,¹⁷ methanol oxidation,¹⁸ lithium-ion batteries, etc.¹⁹ GO or rGO coupled with TiO₂ has been found to show significant electron-withdrawing as well as -storing ability.²⁰ Therefore, the nanocomposites of GO/TiO₂ or rGO/TiO₂ have received considerable attention from the scientific community in a large number of photofunctional applications such as purification of water and air photocatalytically, in water splitting for production of hydrogen as well as oxygen, in solar cells, and in bacterial inactivation.²¹

The function of graphite, graphene oxide, and reduced graphene oxide is proposed as follows. Under the irradiation of UV light of suitable frequency in titania, electrons excited from the conduction band (CB) migrate to the graphene oxide or reduced graphene oxide matrix, which has a more positive Fermi level and positively hinders the recombinattion of electrons and holes. However, the reverse of this process takes place upon excitation by visible light, where electrons transfer from the photoexcited state of graphene to CB of titania.²² The most commonly adopted method of synthesizing graphite oxide in the past was by the Hummers and Ophiman method. Here, graphite was treated with a mixture of sulfuric acid and potassium permanganate (a powerful oxidizer)²³ in the presence of sodium nitrate. When oxidizing agents react with graphite, graphene oxide is produced, which is a byproduct of this oxidation formed efficiently as oxidizing agents increase the intercalation interval between the layers of graphite. The completely oxidized compound can then disperse into the base material like water and graphene oxide is formed. Generally, carbon-based nanomaterials have been elaborately studied for various catalytic applications either as the catalyst by itself or by serving as an aiding matrix. Graphene is used to monitor and then enhance the electronic or photonic properties of the original catalyst of a particular electrochemical or photochemical reaction.²⁴ Unlike photonic and electronic applications, which are possible only with high-purity sp²-hybridized carbon-containing graphene that can only be produced by delicate approaches, it is expected that for solving our day-to-day energy or environment-related problems, we require methods that are cost-effective and produce large quantities easily and also help us to produce flawed single-layer or few-layer graphene with surface functionalization. Also, we need methods that can be quickly operated through the well-known Hummers’ process. Instead of giving us a single layer, graphene Hammer’s method gives us graphene oxide (GO). The resulting graphene oxide (GO) contains plenty of hydrophilic groups, namely, carboxyl, hydroxyl, and epoxy groups, which are bonded with carbon. In Hammer’s process, the synthesized graphene oxide has significantly distorted sp²-hybridized carbon with in-plane bonding that acts as scattering heads that adequately alter the surface conductivity and optoelectronic properties of graphene oxide, which otherwise possess low transparency, charge carrier mobility, and high resistivity. Graphene oxide on reduction and on rearrangements of the sp² aromatic structures results in the formation of reduced graphene oxide rGO with proficiency in charge shuttling and producing excellent catalytic sites. Reduction strategies using different reducing agents, namely, photochemical, hydrothermal, and chemical reagents like hydrazine, have been found to be useful for the preparation of reduced graphene oxide rGO.²⁵ Therefore, the need to find out an economically viable and fast process of chemically reducing graphene oxide without harming the environment is of utmost importance at this point in time. Here, we have used an adjusted Hummers’ method to fulfill our aim of synthesizing graphene oxide with enhanced electrical and chemical properties. By varying and optimizing the reaction parameters for fast synthesis of GO, we have used different reagents that are environmentally benign. Our green mode of chemical reduction utilizes natural dye as reducing agents for the synthesis of rGO from GO. Dye-stimulated visible-light reduction of GO in the absence of any reducing agents is a unique way to produce reduced graphene oxide. This work may provide a facile, encouraging, and environmentally friendly strategy to obtain graphene-based composite materials that can be used as photocatalysts for photodegradation of pollutants. Replacing toxic chemical dyes with natural dyes to reduce graphene oxide and then forming a nanocomposite with benign TiO₂, which is a chemically stable photocatalytic semiconducting material, we can achieve success in synthesizing interesting photocatalysts that can give us a wide opportunity to work in a natural environment to deal with pollutants.

The nanocomposite of reduced graphene oxide and TiO₂ (rGO/TiO₂) is found to have an enhanced photocatalytic effect.³¹ Compared to pure TiO₂, the improved photocatalytic effect of reduced graphene oxide/TiO₂ nanocomposites was largely attributed to three factors, which include the following:

1. High quantum efficiency with enhanced electron–hole pair separation.
2. Visible-light harvesting resulting from extended visible-light absorption.
3. High reaction possibility achieved by intensely enhanced reactant absorbability.³⁶

The rGO and TiO₂ heterojunction results in enhanced separation of the electron–hole pair in TiO₂, with the electron being transferred into reduced graphene oxide, which acts as an electron sink, prohibiting recombination of excited electrons, while the hole remaining in TiO₂ drives the oxidation process. This work elaborately describes a study, based on three primary substrates, viz., graphene, graphene oxide (GO), and reduced graphene oxide rGO. Here, their preparation and characterization, as well as the interaction of GO and rGO with titanium dioxide (TiO₂) affecting the properties of TiO₂ are studied. The photocatalytic properties of the produced reduced graphene oxide/titania nanowires (rGO/TiO₂ NWs) are reviewed using methylene blue (MB) as a probe for photodegradation. Photocatalytic properties of both graphene oxide and titania nanostructures were tested due to their diverse chemical structures. rGO contains oxygen functional groups as it is a graphene derivative and is therefore expected to promote a faster chemical interaction with TiO₂ nanoparticles.

This work provides a smooth, promising, and eco-friendly way to synthesize reduced graphene oxide and the preparation of graphene-centered nanocomposite materials with titania, which can function as an effective photocatalyst in degrading pollutants and dyes.
2. EXPERIMENTAL SECTION

2.1. Materials. Graphite flakes (99.99%), sulfuric acid (H$_2$SO$_4$), potassium manganese oxide (KMnO$_4$), hydrogen peroxide (H$_2$O$_2$), hydrochloric acid (HCl), and methylene blue dye were all procured from Merck. TiO$_2$ (P$_25$) nanoparticles were kindly provided by Sigma-Aldrich.

2.2. Synthesis of TiO$_2$ Nanowires (NWS). The hydrothermal method was used to synthesize crystalline anatase TiO$_2$ nanowires. In a distinctive preparation procedure that was initially carried out by Fan,$^{27}$ 3 g of the TiO$_2$ powder was added into 100 mL of an aqueous solution of 10 M KOH, and a homogeneous suspension was obtained by stirring for about 30 min. A 125 mL Teflon-lined autoclave was filled with the above suspension, filling up to 70% of the total volume. For 24 h, the autoclave was kept at 200 °C and then slowly allowed to cool to room temperature. With a dilute HCl aqueous solution, the obtained product was successively washed, along with deionized water and methanol, several times until a pH value of 7 was obtained. The wet product was baked at 70 °C for 6 h after recovery by vacuum filtration, and finally, a white-colored anatase TiO$_2$ nanowire powder was obtained.

2.3. Synthesis of Graphene Oxide.$^{28}$ Enlarged flake graphite was used for the preparation of graphene oxide. Using a modified Hummers’ method, graphene oxide was obtained by the oxidation of the enlarged graphite flakes. To 12 mL of concentrated H$_2$SO$_4$, we added 3 g of graphite flakes, 2.5 g of K$_2$S$_2$O$_8$, and 2.5 g of P$_2$O$_5$, and the mixture was stirred well, which progressively resulted in temperature changes of about 55–65 °C. Then, gradually, the combination was heated to 80 °C using a temperature-controlled water bath with constant stirring for about 5 h. As the reaction progressed, a paste was obtained from the above mixture. After 5 h, to stop the reaction, the paste was cooled slowly till it attained room temperature and 500 mL of deionized water was carefully added to it, thereby diluting the mixture. Re-oxidization was done by the slow addition of 2 g of KMnO$_4$ and another 500 mL of deionized water, followed by treatment of the mixture with a 30% H$_2$O$_2$ solution (10 mL). Addition of 30 wt % H$_2$O$_2$ results in the reduction of manganese ion to soluble manganese sulfate and manganese oxides. Thus, H$_2$O$_2$ converts the residual KMnO$_4$ into soluble manganese sulfate (MnSO$_4$) in an acidic medium, as described in the following reaction

\[
2\text{KMnO}_4 + \text{5H}_2\text{O} + \text{3H}_2\text{SO}_4 = 2\text{MnSO}_4 + \text{K}_2\text{SO}_4 + 8\text{H}_2\text{O} \text{ (steam)} + \text{SO}_2 \tag{1}
\]

On the addition of 30 wt % H$_2$O$_2$, bubbling occurred. This was followed by the formation of a bright yellow color product, indicating a high level of oxidation. By filtration through a thin Nylon film (of thickness 0.22 μm) and repeatedly washing the product with deionized water until the pH was neutral, we obtained graphite oxide. The product was dried in an oven at 60 °C for 2 h. Filtration and repeated washing removed the metal sulfate, and graphite oxide (GO) was separated by centrifugation at a speed of 4000 rpm for 2 h, and the supernatant was decanted away. A universal indicator was used to check the pH of the collected material. GO thus obtained was again stirred at 60 °C in distilled water for 6 h in a water bath. This process is called exfoliation.$^{27}$ Then, finally, the sonication of graphite oxide dispersion of 0.1 mg/mL in distilled water for 1 h resulted in beautifully exfoliated graphene oxide. After sonication, the graphene oxide (GO) powder was obtained by vacuum drying the sonicated product.

2.4. Synthesis of Reduced Graphene Oxide. Conversion of graphene oxide into graphene oxide turns out to be very detrimental to the individual graphene sheets, resulting in additional consequences after further reduction of the graphene oxide. The graphite to graphene oxide oxidation process already damages the platelets of discrete graphene, reducing its average size; therefore, further damage is unwanted. Graphene oxide contains flakes of monolayer and few layer graphene, interspersed with water and depending on the properties of the support media, the graphene platelet to platelet interactions can be weakened by varying the surface functionality.

Several methods can be used to convert graphite oxide into graphene oxide. Presently, GO is primed mostly by the method of Hummers and Offeman in 1958. Here, the oxidation of graphite to graphite oxide is carried out by reacting graphite with a nonaqueous mixture of sodium nitrate and potassium permanganate in concentrated sulfuric acid. A number of modifications have been proposed, and still the main tactic or strategy is unaltered. For this reason, a new term called modified Hummers’ method is in use.

The most common techniques proposed by Hummers and Offeman are either sonication or stirring or a blending of the two. Sonication is found to be the most effective way to exfoliate graphite oxide (up to almost the complete exfoliation level), but again, it results in severe damage to graphene flakes, leading to a decrease in the surface size from microns to nanometers.

The mode of reducing the parent compound graphene oxide is very crucial for the production of reduced graphene oxide (so far referred to as rGO), as ultimately, the quality of the rGO produced is solely dependent on the method that is followed. This in turn will control how the rGO will differ in terms of structure from the original graphene. Industrial applications such as fuel storage demand the use of large quantities of graphene and then rGO is the most obvious solution. Hence, the procedure adopted to reduce graphene plays an important role.

There are different ways to achieve reduction, based on physicochemical, thermogravimetric, or electrochemical means. In the past, rGO was produced by the treatment of GO with hydrazine hydrate using hydrogen plasma rGO, by strong pulse light produced by xenon flash stubs, and heating GO in distilled water at different degrees for different lengths, etc. The reduction methods generally used for reducing GO are reduction using hydrazine hydrate, by NaBH$_4$ solution, by hydrazine vapor thermal annealing at 900 °C and 1100 °C with Ar/H$_2$, and thermal annealing at 1100 °C and with vitamin C.$^{33}$ A number of these methods are capable of producing very superior-quality rGO, comparable to the original graphene, but they can be multifaceted or time-consuming.

The chemical reduction technique is a very precise and adaptable method for reducing graphene oxide. However, studies and experiments have shown that regrettably, the rGO formed is inferior in quality in terms of surface area and electronic conductivity. The reduction of GO at temperatures of 1000 °C or higher results in the formation of rGO with a very high surface area very close to the original graphene. Unfortunately, the platelets of graphene are damaged by heating and the pressure is released between the buildup and the carbon dioxide. Becerril et al.,$^{34}$ by thermal annealing at 1000 °C, reduced GO films, and, on quality vacuum at (<10$^{-5}$ Torr), recovered rGO. Microwave and photoreduction also
can be used for reducing graphite oxide powders in a commercial microwave oven, whereby, within 1 min in ambient conditions, rGO can be readily obtained. Electrochemical removal of oxygen functionalities is another promising method for obtaining reduced graphene oxide. However, unfortunately, all of these processes somehow cause only a substantial decrease in the GO mass (around 30%), which leads to severe structural deficiencies and also have an adverse effect on the mechanical strength of the rGO thus synthesized. Photochemical reduction of graphene oxide is a technique that has been found to yield superior-quality reduced graphene oxide, very nearly matching in terms of structure to perfect graphene. Natural dyes can be defined as colorants obtained from plants or animal matter. Many plant species contain natural coloring matter in their leaves, seeds, fruits, roots, or barks, suitable for use as dye in many industries. Hence, use of such natural dyes to reduce graphene oxide can lead to development of new facile techniques in graphene chemistry too (Schemes 1 and 2).

Natural dye collected from plants can be used as a stimulating agent to reduce graphene oxide. Plant-based dyes that show high absorption in the visible region of the solar spectrum act as visible-light-stimulating dyes. We have taken indigo dye for this purpose. The reduction of GO nanosheets was carried out by mixing GO and dye, thereby producing a suspension solution. In a typical synthesis, a dye solution is prepared by adding indigo plant dye powder to water under constant stirring at room temperature. After stirring for about half an hour, the dye solution is transferred to a GO solution with vigorous stirring for another 30 min, resulting in the formation of a consistent suspension solution. Nitrogen gas was then bubbled through the resultant suspension solution to eliminate the oxygen in the solution. The flow of nitrogen gas was continued for half an hour and then the (GO + dye) suspension solution was exposed to visible-light conditions for 60 min. The color of the suspension was anticipated to change from light yellow to black progressively with increasing irradiation time, suggesting the effective reduction of GO to rGO. After the realization of a black precipitate, the ensuing sample was recovered by filtration. Washing with distilled water, followed by drying at 60 °C gave the desired rGO nanopowders. A 100 W lamp furnished with visible light with \( \lambda \geq 400 \text{ nm} \) was the visible-light source used for the reduction (Scheme 3).

2.5. Synthesis of Reduced Graphene Oxide/TiO₂ Nanocomposites. To synthesize reduced graphene oxide/TiO₂ nanowire nanocomposites, we used the hydrothermal technique. To a solution of 90 mL of deionized water and 30
mL of ethanol, about 30 mg of rGO was mixed under sonication for almost 1 h to re-exfoliate the residual GO if present even slightly from top to bottom. Under constant sonication and stirring, 3 g of already prepared TiO2 nanowires were added to the rGO suspension until a homogeneous suspension was achieved. It finally displayed an unchanging light gray color. To synthesize the reduced graphene oxide TiO2 nanocomposite, finally, the suspension was then transferred into a 125 mL capacity Teflon-lined autoclave and it was maintained at 120 °C for 3 h. High-temperature treatment led to the formation of Ti—O—C bonding between TiO2 and rGO. On gradual cooling to room temperature, the product was formed; subsequent filtering and washing several times with deionized water, followed by drying under ambient conditions gave the final rGO/TiO2 nanocomposite. For comparison of the properties of mixed crystalline TiO2 with that of commercially available P25 anatase TiO2, the second sample of reduced graphene oxide titania (rGO TiO2) nanocomposite was also prepared according to the same procedure described above, in which the TiO2 nanowires were replaced with TiO2 P25 nanoparticles.

2.6. Characterizations. X-ray diffraction (XRD) patterns of the catalysts produced were collected at room temperature by means of Cu Kα radiation (wavelength λ = 1.54 Å) using a Philips analytical X-ray diffractometer at a scan rate of 1.2°/min. The diffraction intensity employed for the process was calculated in the 2θ range between 20 and 90°. To study surface properties, scanning electron microscopy (SEM) images of the prepared nanocatalysts were documented with a model JSM-6380 LA, a variable-pressure digital scanning electron microscope. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) patterns were done in a JEM-2100, a JEOL electron microscopy instrument. For the investigations, the samples were loaded on a TEM grid and secured to the equipment holder. The films were examined by a comprehensive view, i.e., positioning the specimen surface perpendicular to the electron beam. Fourier transform infrared (FTIR) spectra were obtained using a Bruker spectrometer. A Shimadzu, model-1800 UV-visible spectrophotometer was used to analyze the photocatalytic activity of the samples prepared can be quantitatively evaluated by equating the apparent reaction rate constants (k).

The photocatalytic degradation of methylene blue is a pseudo-first-order reaction, and its kinetics according to the Langmuir–Hinshelwood kinetic model (eq 4) can be expressed as follows37

\[
\ln(C_0/C_f) = k_t \cdot t
\]

where \(D_t\) is the degradation rate of dye after \(t\) minutes of reaction, \(C_0\) is the concentration of dye after \(t\) minutes of reaction, and \(C_f\) is the initial concentration. The photocatalytic activity of the samples prepared can be quantitatively evaluated by equating the apparent reaction rate constants (\(k\)). The photocatalytic degradation of methylene blue is a pseudo-first-order reaction, and its kinetics according to the Langmuir–Hinshelwood kinetic model (eq 4) can be expressed as follows37

\[
\ln(C_0/C_f) = k_t \cdot t
\]

where \(C_0\) and \(C_f\) are, respectively, the opening concentration and the reaction concentration of dye after time \(t\).

3. RESULTS AND DISCUSSION

The crystalline phase and phase identification were performed using the XRD pattern of the GO, rGO, TiO2, and rGO/TiO2 compositions as shown in Figures 1 and S1. The XRD spectra were calculated in a range of 2θ from −5° to 75° at a scan rate of 1.20/min. The distinguishing diffraction peak for rGO with (002) as (hkl) standards appears at the diffraction angle (2θ) of 26.1°, quantitatively matching the JCPDS file no. 00-0401. For the produced rGO, a peak connected to the periodic lamellar arrangement of graphite at 2θ = 26.1° conforming to the organized layer structure with an interlayer distance of 0.17
nm along the (002) alignment can be seen in diffractograms.\textsuperscript{38} For GO, a peak appears at 11°, conforming to the (001) plane with an interlayer spacing of 0.45 nm. The XRD of the synthesized rGO/TiO\textsubscript{2} shows all of the significant peaks of anatase titania. A comparison of the JCPDS (84-1286) with that of the 2θ value of the rGO/TiO\textsubscript{2} sample showed that the samples were anatase phase of titania. The peak position of rGO at 26.1° matching the (002) plane is merged by the plane at the (101) reflection of anatase TiO\textsubscript{2}. This is due to the assembling rGO sheet in the rGO/TiO\textsubscript{2} nanocomposite. Peaks at 2θ equal to 25.7, 38.2, 44.2, and 54.2 are assigned to (101), (004), (200), and (105) hkl planes, respectively, and these are in good agreement with the JCPD data file number 84-1286 (meant for lattice planes of the anatase TiO\textsubscript{2} phase). Therefore, the XRD pattern of rGO/TiO\textsubscript{2} indicates that this nanocomposite formed is a mixture of rGO and anatase TiO\textsubscript{2} phase, where GO’s characteristic diffraction peak in the XRD data beautifully displaces at around 2θ ∼ 11° corresponding to ∼7.81 Å basal spacing. The physical change demonstrating the conversion was the change in the brown color of GO to brownish black. The peak conforming to graphite is sharp and strong and appears at about 2θ = 26°. It can be seen in the figure that the peak for rGO appears in the 2θ angles ranging from 24 to 28° as a comprehensive peak, which has even low intensity in rGO produced by the thermal method. Normally, rGO with a few layers gives a broader and less intense peak in the XRD spectrum.

The FTIR spectra of the nanocomposite rGO/TiO\textsubscript{2} along with individual GO and rGO in the wavenumber range of 500−3800 cm\textsuperscript{-1} are presented in Figures 2 and S2. Large numbers of oxygen-based organic functional groups like carboxyl, hydroxyl, and epoxyl functional groups are recorded on the FTIR spectrum of GO. Three peaks at 1621, 1388, and 1100 cm\textsuperscript{-1} in Figure 2 can be correspondingly allocated to the carboxyl, hydroxyl, and epoxyl groups present on the surface of the GO sample, confirming the presence of oxygen encompassing functional groups formed after oxidation. The presence of the vibration band in the intermediate-frequency area can be attributed to the stretching of the Ti−O−C bond, due to vibrations of the C=O group of carboxylic acid and carboxyl groups present at the edges of GO, and can be seen at approximately 1055 cm\textsuperscript{-1} of rGO/TiO\textsubscript{2}. We can conclude from the FTIR data that 1622, 2468, 2973, and 3400 cm\textsuperscript{-1} corresponded to the C=O bond resulting from in-plane vibrations of the sp\textsuperscript{2}-hybridized carbon along with CO\textsubscript{2}, C−H, and C−OH vibrations, respectively. However, as expected, in as-prepared GO and rGO/TiO\textsubscript{2}, peaks from the region around 1590−1870 cm\textsuperscript{-1} conforming to C=O were not that intense, which proved the thermal reduction of GO into rGO (Table 1).

**Table 1. Absorption Peaks Corresponding to Various Oxygen Functional Groups**

| functional groups on rGO/TiO\textsubscript{2} | absorption peaks (cm\textsuperscript{-1}) |
|--------------------------------------------|--------------------------------------|
| water −OH stretching                       | 3410                                 |
| carboxylates or ketones C=O stretching     | 1734                                 |
| water −OH bending and C=C stretching       | 1629                                 |
| alcoholic C=O−H bending                    | 1420                                 |
| epoxide C=O−C or phenolic C=O−H stretching | 1227                                 |
| C=O stretching                             | 1055                                 |
| stretching vibration of Ti−O−Ti bonds in crystalline TiO\textsubscript{2} | 400−900 |

After exposure to visible light of the synthesized rGO/TiO\textsubscript{2} catalyst, the strength of absorption peaks matching with the oxygen-containing functional groups, viz., the C=O peak appearing at 1734 cm\textsuperscript{-1}, the alcoholic C=O−H peak at 1420 cm\textsuperscript{-1}, epoxide C=O−C or phenolic C=O−H stretching at 1227 cm\textsuperscript{-1}, and the C=O peak at 1055 cm\textsuperscript{-1}, has a substantial decrease in the resultant rGO/TiO\textsubscript{2} (Figure 2) compared with the GO (Figure S2, Supporting Information), indicating the active reduction of GO to rGO. The nonappearance of graphite and graphite oxide peaks or shifting of peaks is a solid signal of the formation of rGO. Throughout thermal reduction, these functional groups are either reduced or eradicated and then persist as exfoliated graphene layers. In rGO, minuscule bands extending from 3700 to 3000 cm\textsuperscript{-1} (O−H stretching vibration) can be detected in the FTIR spectra. This observation reveals that the rGO produced contains considerably fewer O−H groups. The O−H groups existing till now may relate perhaps to the structural OH groups or may be the physisorbed water from the air during the analysis, or it may be the exclusively reduced carboxylic groups to alcohols. However, it is sure that the nonpolar nature of rGO is not responsible for this water absorption. For rGO, all of the FTIR peak intensities of various functional groups are found to be relatively lower than that of GO, confirming that the reduction of GO takes place proficiently.

The morphologies of the synthesized GO and TiO\textsubscript{2} are characterized by SEM and an energy-dispersive X-ray (EDX) fluorescence spectrometer. Figure 3 shows the surface
topography and characteristics of GO (Figure 3a) and rGO/TiO$_2$ (Figure 3b) photographed at operational voltages of 20 and 15 kV, respectively. The SEM image of GO in Figure 3a showed exfoliated or expanded flakes with a kind of wavy architecture. It can be seen that a leaflike architecture is prominent for the individual GO sheets. This observation is in accordance with already published results. The SEM data implies that rGO facilitated the evolution of TiO$_2$ nanowires. The morphologies of the TiO$_2$ nanoparticles are like nanowires, as shown in Figure 3b. The rodlike TiO$_2$ nanoparticle has an average length of about 9 nm and a width of about 3.7 nm. The layers of rGO curled and the well-dispersed TiO$_2$ anchored on the rGO planes. This confirms that the TiO$_2$ was effectively loaded onto the rGO planes. As shown in Figure 3b, most of the TiO$_2$ nanoparticles are situated on the edge of GO sheets. It is evident that the morphology and crystalline pattern of TiO$_2$ are barely affected by rGO. The EDX of the rGO/TiO$_2$ nanocomposite is shown in Figure S3i, Supporting Information. The energy-dispersive spectrometry (EDS) spectrum (Figure S3i, Supporting Information) displays a strong carbon peak that is expected highly because of the high carbon percentage in rGO. EDS spectra also help to identify the peaks due to the other materials used or formed during the reduction process. Consequently, the effective synthesis and fundamental analysis of the rGO/TiO$_2$ nanostructure can be completed splendidly using an energy-dispersive X-ray (EDX) fluorescence spectrometer. The elemental composition of the rGO/TiO$_2$ nanocomposites is shown in Figure S3ii, Supporting Information, which permitted us to recognize the occurrence of carbon (C) along with oxygen (O) and titanium (Ti), which can all be attributed to the nanocomposites.

The low-resolution bright-field (a, b) and high-resolution (c, d) dark-field transmission electron microscopy images of rGO/TiO$_2$ nanocomposites are shown in Figure 4a–d. TEM images of rGO show a sheetlike arrangement with different pictures of the investigated area (Figure 4a). Typically, a wrinkled graphene nanostructure is observed due to its thin and more widespread sheetlike morphology, although the rGO/TiO$_2$ consists of numerous small nanoparticles with a size of 10–30 nm. The surface area of TiO$_2$ nanoparticles is enclosed by rGO nanosheets, leading to the creation of a unified network of rGO/TiO$_2$ nanocomposites. The pile arrangement of nanostructured graphene oxide layers along with some oxygen functional groups can be visualized from the dark areas. On the contrary, transparent areas indicate few layers of reduced graphene oxide with much thinner films resulting from exfoliation of the stacking/piled nanostructure. The sheets of graphene oxide could not undergo re-aggregation because of the powerful direct interaction between TiO$_2$ and the reduced graphene oxide sheet.
The multilayer structure of reduced graphene oxide is observed in the TEM image shown in Figure 4c,d, and the rGO sheet is detected in the dark-field TEM image depicted in Figure 4c.

Diffuse reflectance spectra (DRS) monitored in the range of 200–800 nm, respectively, of as-prepared GO, TiO2, and rGO/TiO2 materials are presented in Figures 5 and S4. The spectra show that GO and rGO affect the photosensitive properties of TiO2 considerably. Due to robust synergistic and intermolecular interactions concerning rGO and TiO2, considerable red shift is detected for rGO/TiO2.

For the rGO/TiO2 samples, light absorption in the direction of wavelengths greater than 400 nm was seen. Besides, the as-prepared TiO2 showed a smaller band gap of 3.00 eV, which is far less than the already researched and published values, for anatase, i.e., 3.2 eV. The influence of rGO in the TiO2 lattice can be seen by the enhancement of the electron transmission mechanism from anatase TiO2 to rGO resulting from newly formed intermediary energy stages just beneath the conduction band of TiO2. The dark gray color of the rGO TiO2 nanocomposite powders that we obtained supports our expectation that these rGO TiO2 nanocomposites will be photocatalytically active under visible radiation.

Thus, there was a decrease in the band gap from 2.98 in GO/TiO2 to 2.76 eV in rGO/TiO2. This reduction in the band gap of the rGO/TiO2 system played a vital role in the photodegradation of dye methylene blue together with UV and visible-light exposure by degrading dye methylene blue at room temperature. The assessment of dye concentration is carried out by observing the values of the maximum UV–vis absorbance peaks for 90 min. The photodegradation of MB was studied for each synthesized catalyst solution prepared using pure TiO2, GO, rGO, and rGO TiO2; the results obtained are plotted in Figures 7 and S6 resulting from the quick degradation of the dye within 60 min. Aqueous solutions of 10−5 M methylene blue dye were used to assess the photocatalytic activity of the prepared samples by the breaking down of the dye under UV radiation (at 677.5 nm). A 10−5 M methylene blue dye suspension is stirred, and successively, 0.05 g each of neat GO, rGO, and rGO TiO2 was added in this suspension for separate calculation and kept in the dark for 30 min to allow adsorption–desorption equilibration. The initial concentration (c) of the substrate is noted for omitting adsorption in the dark. All of these samples were taken in vials properly draped in aluminum foils. The initial concentration is noted after 30 min in the dark. According to the given results, it was confirmed that self-breakdown of the dye did not take place. The concentration of methylene blue dye is proportional

Figure 5. DRS of GO, rGO, and rGO/TiO2.

rGO/TiO2-treated GCE. By creating a potential difference to the electrodes, dopamine is readily converted to form dopamine quinone with an exchange of two electrons and two protons. These donated electrons at the electrode result in the production of a faradaic current. Compared to other electrodes, the rGO/TiO2-treated GCE exhibited better electro-oxidation activity toward dopamine. Enhanced electronic conductivity was possible by the combination of TiO2 and rGO, which promoted the electron-transfer frequency between the DA and electrodes present, and thereby produced a commendable synergistic outcome in the photocatalysis.

Thermogravimetric analysis (TGA) was applied as a complementary technique to assess the thermal behavior of GO/TiO2 and rGO/TiO2 nanocomposites. Figure S5 displays the TGA and differential thermogravimetry (DTG) plots of rGO/TiO2 and GO/TiO2. At 260 °C, rGO/TiO2 lost a mass, followed by GO/TiO2 at 100 °C. This results from the removal of the thermal component in the reduction process of GO and rGO. At 260 °C, adsorbed moisture in rGO/TiO2 is first lost. The pyrolysis of labile oxygenated moieties yielding CO, CO2, and steam is obtained at around 100 °C for GO.

3.1. Photocatalytic Activity of Catalysts in Aqueous Phase Photodegradation of Methylene Blue. The analysis of the photocatalytic activity of synthesized graphene oxide (GO), reduced graphene oxide rGO, and that of the rGO/TiO2 nanocomposite is studied under UV and visible-light exposure by degrading dye methylene blue at room temperature. The assessment of dye concentration is carried out by observing the values of the maximum UV–vis absorbance peaks for 90 min. The photodegradation of MB was studied for each synthesized catalyst solution prepared using pure TiO2, GO, rGO, and rGO TiO2; the results obtained are plotted in Figures 7 and S6 resulting from the quick degradation of the dye within 60 min. Aqueous solutions of 10−5 M methylene blue dye were used to assess the photocatalytic activity of the prepared samples by the breaking down of the dye under UV radiation (at 677.5 nm). A 10−5 M methylene blue dye suspension is stirred, and successively, 0.05 g each of neat GO, rGO, and rGO TiO2 was added in this suspension for separate calculation and kept in the dark for 30 min to allow adsorption–desorption equilibration. The initial concentration (c) of the substrate is noted for omitting adsorption in the dark. All of these samples were taken in vials properly draped in aluminum foils. The initial concentration is noted after 30 min in the dark. According to the given results, it was confirmed that self-breakdown of the dye did not take place. The concentration of methylene blue dye is proportional

Figure 6. CVs of GCE, rGO, TiO2, and rGO/TiO2.
complete saturation of the nanocomposites in the activity tests to study the adsorption process approving the schematized study was performed before the photocatalytic blue under irradiation of UV. The concentration of the dye after time, then assessed by measuring the absorbance (Equation 5)

\[ \ln(C_0/C_t) = kt \]

Here, \( C_0 \) and \( C_t \) are the initial concentration and reaction concentration of the dye after time, \( t \), respectively, and \( k \) is the rate constant. The photocatalytic activity of all catalysts was then assessed by measuring the absorbance \( (C_t) \) of methylene blue under irradiation of UV-visible light at 677.5 nm. A schematized study was performed before the photocatalytic activity tests to study the adsorption process approving the complete saturation of the nanocomposites in the first \( \approx \)10 min in the dark with the MB solution, under mechanical stirring. To ensure complete saturation of the nanocomposites with the dye, we kept the catalyst dye solution in the dark for about 30 min. Concerning the photocatalytic tests (Figure 7), substantial adsorption of MB dye onto the surface of the nanoparticles was detected during these 30 min, for nanocomposites with higher concentrations of GO and rGO. Moreover, rGO/TiO₂ nanocomposites showed higher adsorption of MB than the TiO₂/GO ones, and the superior adsorption of MB is predictable by the fact that MB is a cationic dye and therefore it is positively charged in solution. In turn, the electrostatic interaction between the dye and the catalyst surface is favored by the occurrence of carboxylic moieties on the GO surface.

3.2. Quenching Exploration for the Role of Oxidizing Species. A photocatalytic reaction is favored by how easily a photocatalyst can be excited to produce electron and hole pairs and how readily those \( e^-/h^+ \) couples can produce reactive oxygen species (ROS) by interacting with adsorbed water molecules from the atmosphere. *OH, \( \cdot H_2O_2 \), \( \cdot O_2 \), \( \cdot HO_2 \), and \( \cdot O_2^- \) are the major ROS species that are used to carry out the photocatalytic decomposition of organic pollutants or toxic chemicals under light exposure of suitable frequency. In the current study, GO, TiO₂, and rGO/TiO₂ were thoroughly studied as mediators for the photocatalytic degradation of MB under UV–vis irradiation. The dye solutions with 0.005 g of all catalysts were subjected to photocatalytic degradation in a photoreactor. The results (Figure S6, Supporting Information) show that the degradation of MB was maximum with the rGO/TiO₂ nanocomposite than that in pure TiO₂, or with GO or rGO alone. This alteration in the photoactivity of synthesized catalysts is primarily attributed to the extent of trapping of the \( \cdot O_2^- \) radicals, the \( OH^- \) radicals presented in the photocatalytic process. The degradation percentage of 43% by rGO/TiO₂ indicates that the reduced graphene oxide-modified TiO₂ sample showed higher photocatalytic activities than pure TiO₂ and commercial TiO₂. The conversion from graphite into graphene leads to an increase in surface area. Once again, the superior photocatalytic activity of the rGO/TiO₂ sample can be explained by the band gap as well as the coordination of Ti ions. The band gap values give us an idea about redox behavior. Thus, the higher the band gap values, the more powerful the redox capability. The oxidative decomposition of methylene blue by TiO₂ is said to be started by OH⁻ radicals. In the presence of \( O_2 \), the OH⁻ radicals are formed according to the following reactions

\[ TiO_2 \rightarrow h^+ + e^- \] (Equation 5)
\[ e^- + O_2 \rightarrow O_2^- \] (Equation 6)
\[ O_2^- + 2H^+ + e^- \rightarrow H_2O_2 \] (Equation 7)

Further, the synthesized nanomaterials are formed with an enhancement in surface area than pure rGO, or TiO₂. The surface area and the production of hydroxyl radicals are directly proportional to one another, and hence more will be photocatalytic decomposition for rGO/TiO₂. The joint effects make the substrate adsorption stronger. It is clear from Figure S6 (Supporting Information) that rGO/TiO₂ with higher surface area and smaller particle size had better photocatalytic activity. The gradual change in methylene blue concentration with rGO/TiO₂ is shown in Figure 8 for 90 min.

Figure 8. Change in the concentration of dye in the presence of rGO/TiO₂.

Figure 9 shows photodegradation of methylene blue as a function of catalyst based on first-order kinetics (Langmuir–Hinshelwood kinetic model).

The linear plots of \( \ln(C_0/C_t) \) vs light irradiation time for methylene blue ultimately show that photodegradation reactions occur along with pseudo-first-order reaction kinetics. The principle of the semiconductor photocatalytic reaction is quite simple. Upon absorption of photons of the incident radiation with energy significantly higher than the band gap of TiO₂, electrons are promoted from the valence band (VB) to the conduction band and this results in the formation of electron–hole pairs. As soon as they are formed, these charge carriers travel to the surface and begin to interact with the chemicals adsorbed on the surface of the photocatalyst and

\[ *OH, \cdot H_2O_2, \cdot O_2, \cdot HO_2, \cdot O_2^- \] radicals by the above-mentioned scavengers during a photocatalytic reaction. The degradation percentage of 43% by rGO/TiO₂ indicates that more number of \( O_2^- \) were trapped by rGO/TiO₂ when suitable light falls on it. The reduced graphene oxide-modified TiO₂ sample showed higher photocatalytic activities than pure TiO₂ and commercial TiO₂. The conversion from graphite into graphene leads to an increase in surface area. Once again, the superior photocatalytic activity of the rGO/TiO₂ sample can be explained by the band gap as well as the coordination of Ti ions. The band gap values give us an idea about redox behavior. Thus, the higher the band gap values, the more powerful the redox capability. The oxidative decomposition of methylene blue by TiO₂ is said to be started by OH⁻ radicals. In the presence of \( O_2 \), the OH⁻ radicals are formed according to the following reactions

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\[ O_2^- + 2H^+ + e^- \rightarrow H_2O_2 \] (Equation 7)
decompose these chemicals. Radicals or compounds like \( \cdot \text{OH}, \text{O}_2^- \), \( \text{H}_2\text{O}_2 \), or \( \text{O}_2 \) are usually involved in the photo-decomposition process and they play crucial roles in the photocatalytic reaction mechanisms. Titania photocatalyst, on exposure to light energy of suitable frequency, excites electrons from the ground state to the excited state. Subsequently, this is followed by the transfer of those excited electrons from the valence band into the conduction band of TiO\(_2\). The conduction band electrons are then transported to oxygen molecules adsorbed on the photocatalyst surface, thereby leading to the formation of reactive superoxide anions \( (\cdot \text{O}_2^-) \). These reactive superoxide anions are responsible for degradation of methylene blue on the TiO\(_2\) catalyst surface in a series of reaction events. When rGO is present, there is a change in the situation. This is because as rGO can competently trap electrons than the adsorbed oxygen species, this results in even more efficient migration and separation of conduction band electrons of TiO\(_2\) over the as-synthesized rGO/TiO\(_2\) photocatalyst than undoped TiO\(_2\). This creates surplus mobile holes in the hybridized valence band of the rGO/TiO\(_2\) photocatalyst at the same photoexcitation event. Thus, a probable mechanism for MB decomposition by the rGO/TiO\(_2\) comprises the plausible steps listed below. The superior photocatalytic activity of the rGO/TiO\(_2\) photocatalyst could result from the charge-transfer process between rGO and TiO\(_2\). When light of appropriate frequency falls on it, electron and hole pairs were produced on the conduction and valence bands of TiO\(_2\), respectively. When the TiO\(_2\) electrons have energy higher than the rGO, the electron in the conduction band (CB) of TiO\(_2\) is communicated to the CB of the rGO. The excited electrons on the rGO conduction band then react with adsorbed \( \text{O}_2 \) on the rGO surface and produce a superoxide radical \( (\cdot \text{O}_2^-) \) to oxidize MB. On the other hand, when the electrons from the valence band (VB) of TiO\(_2\) absorb the energy to compensate for the electronic vacancy in the VB of rGO, it produces a hole \( (\cdot \text{h}^+) \) in the VB of TiO\(_2\). The hole \( (\cdot \text{h}^+) \) generated in the VB of TiO\(_2\) reacts with the MB, producing an oxidized MB\( ^\cdot \) that in the presence of \( \text{O}_2 \) dissolved in water, and is reduced. Other \( (\cdot \text{h}^+) \) from VB of TiO\(_2\) breaks down water molecules \( \text{H}_2\text{O} \) to \( \cdot \text{OH} \) and \( \text{H}^+ \); simultaneously, the MB reaction with the \( \cdot \text{O}_2^- \) or \( \cdot \text{OH} \) or \( \cdot \text{H}^+ \) generated from other reactions to finally produces carbon dioxide and water.

Thus, a probable mechanism for MB decomposition by the rGO/TiO\(_2\) comprises the plausible steps listed below. The superior photocatalytic activity of the rGO/TiO\(_2\) photocatalyst could result from the charge-transfer process between rGO and TiO\(_2\). When light of appropriate frequency falls on it, electron and hole pairs were produced on the conduction and valence bands of TiO\(_2\), respectively. When the TiO\(_2\) electrons have energy higher than the rGO, the electron in the conduction band (CB) of TiO\(_2\) is communicated to the CB of the rGO. The excited electrons on the rGO conduction band then react with adsorbed \( \text{O}_2 \) on the rGO surface and produce a superoxide radical \( (\cdot \text{O}_2^-) \) to oxidize MB. On the other hand, when the electrons from the valence band (VB) of TiO\(_2\) absorb the energy to compensate for the electronic vacancy in the VB of rGO, it produces a hole \( (\cdot \text{h}^+) \) in the VB of TiO\(_2\). The hole \( (\cdot \text{h}^+) \) generated in the VB of TiO\(_2\) reacts with the MB, producing an oxidized MB\( ^\cdot \) that in the presence of \( \text{O}_2 \) dissolved in water, and is reduced. Other \( (\cdot \text{h}^+) \) from VB of TiO\(_2\) breaks down water molecules \( \text{H}_2\text{O} \) to \( \cdot \text{OH} \) and \( \text{H}^+ \); simultaneously, the MB reaction with the \( \cdot \text{O}_2^- \) or \( \cdot \text{OH} \) or \( \cdot \text{H}^+ \) generated from other reactions to finally produces carbon dioxide and water.

### Analysis of Hydroxyl (\( \cdot \text{OH} \)) Radicals

The rGO/TiO\(_2\) catalyst possesses more photocatalytic capability over GO or TiO\(_2\) or rGO under light irradiation. This was unreservedly due to the creation of more hydroxyl radicals in the case of the photocatalytic reaction carried out by means of rGO/TiO\(_2\). There has been a considerable reduction in the MB degradation rate for the catalytic agent rGO/TiO\(_2\) correspondingly. The superior degradation was attained mostly due to the existence of \( \cdot \text{OH} \) radicals and other reactive and highly responsive oxygen species like superoxide anion \( (\cdot \text{O}_2^-) \), hydrogen peroxide \( (\text{H}_2\text{O}_2) \), singlet oxygen \( (\text{O}_2) \), etc. The reactive oxygen species (ROS) label covers a sequence of very small and highly quick to respond molecules such as hydroxyl radical \( (\cdot \text{OH}) \), superoxide anion \( (\cdot \text{O}_2^-) \), hydrogen peroxide \( (\text{H}_2\text{O}_2) \), singlet oxygen \( (\text{O}_2) \), hydrochlorous acid, hypobromous acid, hydroperoxides, alkoxy radical \( (\cdot \text{RO}) \), peroxo radical \( (\cdot \text{ROO}) \), etc. produced under light irradiation. The nonfluorescent probe used 2',7'-dichlorodihydrofluorescein

\[
\text{TiO}_2/\text{rGO} + \text{light} \rightarrow \text{TiO}_2^+/\text{rGO} + \text{e}^- \quad (8)
\]
\[
\text{e}^- + \text{O}_2\cdot\text{O}_2^- \rightarrow 2\text{O}_2^- \quad (9)
\]
\[
\text{TiO}_2^+/\text{rGO} \rightarrow \text{TiO}_2/\text{rGO} + \text{h}^+ \quad (10)
\]
\[
\text{h}^+ + \text{H}_2\text{O}/\text{OH}^- \rightarrow \cdot \text{OH} \quad (11)
\]
\[
\text{methylene blue} + \cdot \text{OH} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \text{ (degraded products)} \quad (12)
\]
\[
\text{methylene blue} + \cdot \text{O}_2^- \rightarrow \text{CO}_2 + \text{H}_2\text{O} \text{ (degraded products)} \quad (13)
\]

Figure 9. (a) Degradation plot of methylene blue by the rGO/TiO\(_2\) nanocomposite, GO, and rGO, (b) creation of an electron–hole pair by light on the rGO/TiO\(_2\) nanocomposite, and (c) relative band gaps of Indigo, GO, rGO, TiO\(_2\), rGO/TiO\(_2\), and MB.
Lipophilic nonfluorescent DCFH2-DA de-acetylates to form another nonfluorescent molecule DCFH2, which then produces highly fluorescent DCF after reacting with the generated ROS. For photoluminescence observation of synthesized samples, they were placed under optical microscopy and ultraviolet irradiation. rGO/TiO2 is dark brown under usual light, while it appears yellow under UV irradiation. Light is scattered by nanoparticles in a colloid or in a suitable suspension, and can be represented diagrammatically as follows

\[
\text{rGO/TiO}_2 + \text{Light} \rightarrow \text{rGO/TiO}_2^* + e^-
\]

\[
e^* + O_2 \rightarrow 2O_2^-
\]

\[
\text{TiO}_2^* + \text{GO} \rightarrow \text{TiO}_2 + \text{GO}^* + e^-
\]

\[
h^- + H_2O \rightarrow \cdot OH
\]

\[
2,7'-\text{dichlorodihydrofluorescein} + \cdot OH \rightarrow 2,7'-\text{dichlorofluorescein}
\]

To have a thorough understanding of this photocatalysis, a theoretical approach of energetics involved can be developed for the nanomaterial synthesized (here rGO/TiO2 nanowires). Initially, indigo dye (ID) excited by visible light goes to a state of greater energy, and thus the lowest energy unoccupied molecular orbital (LUMO) of TiO2 is filled with an electron (eqs 14 and 15)

\[
\text{ID} + h\nu_{\text{visible}} \rightarrow \text{ID}^*\text{LUMO}
\]

\[
\text{ID} + h\nu_{\text{visible}} \rightarrow \text{IDLUMO}^*
\]

Also

\[
\text{IDLUMO}^* + \text{TiO}_2 \rightarrow \text{ID}^+ + \text{TiO}_2(e^-\text{CB})
\]

\[
\text{IDLUMO}^* + \text{TiO}_2 \rightarrow \text{ID}^+ + \text{TiO}_2(e\text{CB})^-
\]

The conduction band of TiO2 accepts this electron (eq 15). Here, both titanium ion (Ti\text{III}) and O behave as trapping agents for migrated electrons, and the recombination of electron and hole couple is hindered (eqs 16 and 17). Additionally, the photoinduced electron could be forwarded to GO also. 18The fate of the photoinduced electrons residing in CB, TiO2, or GO that can also be forwarded to an O2 molecule forming a superoxide anion O2** is shown in Equations 18–20

\[
\text{CB}(e^-) \rightarrow \text{Ti}^{2+}(e^-) + O_2 \rightarrow O_2^**
\]

\[
\text{CB}(e^-) \rightarrow O_2(e^-) + O_2 \rightarrow O_2^**
\]

and

\[
\text{CB}(e^-) \rightarrow \text{reduced (GO)} + O_2
\]

\[
\rightarrow \text{production of } O_2^**
\]

Generation of reactive oxygen species thus leads to the rapid degradation of pollutants as shown above (Supporting Information 7)

\[
O_2^** + H_2O \rightarrow \cdot OH
\]

3.4. Determination of Change of Chemical Oxygen Demand (COD) Using Photocatalytic rGO/TiO2 for the Water of Kolong River in Nagaon, Assam, India.

When rGO/TiO2 is exposed to a light source of suitable frequency, an electron from the valence band is promoted to the conduction band, leaving behind a positive hole in the valence band. The electron thus produced reaches the surface so that it could reduce any available species. On the other hand, the hole, upon migration to the surface, targets water adsorbed in the surface, converting them into hydroxyl radicals, which ultimately play a significant role in the degradation of pollutants by oxidizing them. Another essential component is the presence of molecular oxygen in the reaction media that acts as a scavenger of the photogenerated electrons, producing a superoxide radical ion. In the absence of oxygen, photocatalytic activity is almost completely suppressed and the dissolved oxygen concentration thus has a significant effect on the rate of photocatalyzed degradation of pollutant materials. Obviously, the chemical oxygen demand of a sample taken can be assessed simply by inspecting the alteration of the dissolved oxygen concentration under a photoinduced catalytic environment. The water samples inspected during this process were collected from Kolong River in Nagaon, Assam, India. With the help of an electrochemical dissolved oxygen sensor, first, the oxygen concentration in ppm was recorded. Then, the sample water was introduced into the Haber photocatalytic cell. When the UV lamp was turned on the concentration of 0.2 mg of rGO/TiO2, the slight yellowish color of the sample water gradually decreased till a constant white state was achieved in 20 min. In this state, again, the COD was recorded, which was a much smaller value than the previous one as expected. The
information provided by the sensor in the presence of rGO/TiO2 can be concluded as the utilization of an O2 molecule by the semiconductor.

\[
\begin{align*}
\text{rGO/TiO}_2 + \text{light} &= e^-\text{CB} + e^-\text{(Ti}^{\text{III}}+) \\
\text{rGO/TiO}_2 + \text{light} &= e^-\text{CB} + e^-\text{(Ti}^{\text{IV}}+) + O_2 \rightarrow O_2^* \\
\text{rGO/TiO}_2 + \text{light} &= 2e^-\text{CB} + O_2 \rightarrow O_2^-\text{CB}
\end{align*}
\]

Though all of the synthesized materials like GO, rGO, and TiO2 were used to see their effect on COD, it was found that only rGO/TiO2 produced the maximum change in COD even in the absence of any organic materials to degrade.

4. CONCLUSIONS
GO could be effectively reduced without using any reducing agents by a simple and ecologically safe methodology, which is based on the natural indigo dye-stimulated visible-light reduction mechanism. Taking into account the safe and potent method for the reduction of GO, our findings can provide a new understanding of the preparation and designing of diverse graphene-based nanomaterials for numerous potential uses. It has been found that GO and rGO modification of TiO2 improves the photo-induced reactions of the titania semiconducting catalyst significantly. The level of enhancement correlated with the reduction of GO, the strategy involved, and the nature of the reaction system (e.g., whether UV/vis or Vis light is used). Photocatalytic activities of modified TiO2 samples were superior to those of pure TiO2 or GO, or rGO alone. GO and rGO showed different influences on the photoreactivity, related to semiconductor support.

# ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04889.

Additional experimental results, namely, XRD, FTIR, DRS, TGA, and XPS studies (PDF)

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Notes
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