Visible-Light-Driven Carbon-Doped TiO₂-Based Nanocatalysts for Enhanced Activity toward Microbes and Removal of Dye

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ABSTRACT: Solar-driven photocatalytic approach is an attractive, clean, and effective way for decontamination of water. In this work, visible-light-activated TiO₂ nanoflakes (TNFs) and carbon-doped TiO₂ nanoflakes (C-TNFs) were synthesized via a facile hydrothermal route using different carbon sources. The as-synthesized nanostructures were successfully characterized by powder X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM), critically disclosing the anatase nature containing titanium–oxygen having flake/platelet-like morphology with ~32 nm in size, respectively. The photocatalytic activity was characterized via the degradation of methylene blue (MB) and bacterial inactivation of Escherichia coli (Gram-negative) and Staphylococcus aureus (Gram-positive). The experimental results showed that C-TNFs significantly enhanced photocatalytic activity compared to bare TNFs. It was found that TNF nanocatalysts exhibited superior photocatalytic activity against photodegradation of MB (92.7%) and antibacterial activity (85.6%) under sunlight irradiation. In addition, reduced graphene oxide (RGO)-TNFs have a good recycling ability and are expected to be a promising candidate for photocatalytic applications under sunlight. Consequentially, the higher activity of RGO-TNF nanocatalysts under sunlight irradiation for organic degradation and bacterial inactivation implies that hydrothermal synthesis allows for the preparation of efficient and low-cost carbon-doped photocatalysts for the photodegradation of a wide range of environmental pollutants.

1. INTRODUCTION

Environmental and energy issues attracted great attention owing to fast-growing population and increased economic development.¹ One of the major concerns is the safety of our most precious natural resource, water. Water is so vital to our survival that we cannot even imagine our existence without it.² Surface water quality is constantly deteriorating as a result of the addition of enormous amounts of industrial effluents, agricultural, domestic waste, and waste runoff into water resources, rendering it unfit for human consumption and causing water pollution.³ Various agents like pathogenic bacteria, minerals, and other toxic organic substances that are present in drinking water have adversely affected human health.⁴ Currently, researchers are focusing on developing new energy and pollution-control technologies that utilize light energy to remove pollutants in a cost-effective, reproducible, and nontoxic manner.⁵ In recent years, tremendous progress has been made in the oxidative decomposition of organic pollutants immersed or diffused in aquatic environments.⁶ Among “advanced oxidation processes”, photocatalysis has evolved as a novel destructive mechanism that results in the complete mineralization of the majority of organic pollutants.⁷ Photocatalysis has several advantages over competing processes, including (i) complete mineralization, (ii) no water disposal problem, (iii) inexpensive costs, and (iv) only mild temperature and pressure requirements.⁸ An ideal photocatalyst should be photoactive, physiologically and chemically inert, nontoxic, and economically feasible. The majority of the photocatalyst absorbs UV radiation, which accounts for only a small portion of solar energy (about 3–4%).⁹ In past decades, many researchers have made significant efforts to use TiO₂ and modified TiO₂ for their photocatalytic activity under UV/visible light illumination.¹⁰ The modification of TiO₂ with carbon materials to improve photocatalytic activity has become a growing topic in recent years.¹¹ Notably, carbon doping into TiO₂ lattice substituting a Ti or O atom to form a Ti–C or C–O–Ti bond produces a hybrid orbital just above the valence band of TiO₂ confers a significant
enhancement in visible-light-driven photocatalytic activity.\textsuperscript{12} The introduction of carbon enhances TiO\textsubscript{2} conductivity by facilitating charge transfer from the bulk of the TiO\textsubscript{2} structure to the oxidation reaction surface area.\textsuperscript{13} Moreover, carbon can provide a high surface area for the absorption of pollutants, which is a fundamental principle of pollutant decomposition, thus enhancing the photocactivity of the obtained materials.\textsuperscript{14} In addition, carbon can be prepared from environmentally friendly and low-cost raw materials and has advantages of stability compared with other materials.\textsuperscript{15} To date, various allotropes of carbon including activated carbon,\textsuperscript{16} carbon nanofibers,\textsuperscript{17} carbon nanotubes,\textsuperscript{18} carbon spheres,\textsuperscript{19} carbon quantum dots\textsuperscript{20} fullerene,\textsuperscript{21} graphene,\textsuperscript{22} etc. have been widely investigated as support materials for photocatalyst and greatly improves their photocatalytic performance. Taking all of the above aspects into consideration, combining carbon and TiO\textsubscript{2} is a promising way to obtain photocatalysts with enhanced photocatalytic activity in environmental, energy, and biomedical fields.

In the present study, we demonstrated a facile hydrothermal fabrication method to synthesize carbon-doped TiO\textsubscript{2} nanocatalysts using graphene oxide (GO) and reduced graphene oxide (RGO), carbon, and TiO\textsubscript{2}. The morphology of TiO\textsubscript{2} plays a crucial role in photocatalysis because it includes photoreactions happening at the surface of TNFs because their nanoscale nature offers a high surface-to-volume ratio for effective photocatalytic applications. Therefore, we have incorporated TNFs with GO and RGO for the first time to further enhance its photocatalytic activity. The synthesized nanocatalysts were characterized using the following analytical techniques: powder X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) spectroscopy, and UV–visible spectroscopy. The photocatalytic activity was screened against selected pollutants including MB, Gram-negative \textit{Escherichia coli}, and Gram-positive \textit{Staphylococcus aureus} in aqueous suspension.

2. RESULTS AND DISCUSSION

2.1. Structural Analysis. Powder XRD analysis was used to determine the crystalline phase and crystallite size of the synthesized nanocatalysts. Figure 1 depicts the XRD patterns of samples TNFs, GO-TNFs, and RGO-TNFs. The characteristic peaks in the XRD pattern of TNFs assembled as 2\(\theta\) values of 25.8, 37.2, 47.9, 53.1, 54.8, and 62.5 are assigned to the planes of anatase (101), (004), (200), (105), (211), and (213), respectively, confirming anatase phase (JCPDS No. 21-1272).\textsuperscript{23} The XRD pattern of GO-TNFs and RGO-TNFs shows diffraction peaks attributed to the anatase phase. Furthermore, a very small diffraction peak at 2\(\theta\) = 10.7\textdegree\textsuperscript{2} is detected in the XRD patterns that belongs to the (002) crystal plane of GO confirming the incorporation of GO with TNFs in the composite.\textsuperscript{24} However, no diffraction peak relating to RGO was observed in the XRD pattern of RGO-TNFs. This may be attributed to the small amount, which results in a low diffraction intensity of RGO (below the detection limit of the XRD instrument). A related finding was also reported in ref.\textsuperscript{25} The average crystallite sizes of the synthesized material were determined from the XRD pattern using the Debye–Scherrer equation,\textsuperscript{26} as seen below.

\[
D = \frac{k\lambda}{\beta\cos \theta}
\]

where \(D\) is the crystallite size in nm, \(k\) (0.9) is the Scherrer constant related to crystallite structure, \(\lambda\) is the wavelength of associated radiations, \(\theta\) is Bragg’s angle, and \(\beta\) is the full width at half-maximum of the diffraction peak. The average crystalline sizes of TNFs, GO-TNFs, and RGO-TNFs calculated using eq 1 are shown in Table 1. It can be seen that fabricated material has exhibited different crystallite sizes that may be due to the addition of different carbon contents. Therefore, the average crystallite size of TNFs increased from 32.31 to 35.18 nm but is still in good agreement with each other.

The surface functionalities of synthesized TNFs and carbon-doped TNFs were confirmed by FT-IR analysis. Figure 2 displays the FT-IR spectra of TNFs and their composites GO-TNFs and RGO-TNFs. The FT-IR spectrum of TNF depicts two broad peaks at 3420 and 1630 cm\textsuperscript{-1} corresponding to symmetrical and asymmetrical –OH groups, and bands at 2917, 2842, and 1386 cm\textsuperscript{-1} reveal stretching and bending modes of C–H bonds caused by the presence of isopropanol used for the synthesis of TNFs. The strong band positioned at 496 cm\textsuperscript{-1} is attributed to the stretching vibration of Ti–O and

![Figure 1](https://doi.org/10.1021/acsomega.1c06112)  
**Figure 1.** XRD pattern of TNFs (black—), GO-TNFs (red—), and RGO-TNFs (blue—).

![Figure 2](https://doi.org/10.1021/acsomega.1c06112)  
**Figure 2.** FTIR pattern of TNFs (black—), GO-TNFs (red—), and RGO-TNFs (blue—).
which suggested the structure of TiO$_2$. However, in the FT-IR spectra of GO-TNFs and RGO-TNFs nanocomposites, there are bands characterizing the vibrations of oxygen-containing bonds, such as bands positioned at 1050, 1612, and 1743 cm$^{-1}$ attributed to the stretching vibrations due to C–O–C bonds of alkoxy group and the C=C and C=O bonds of the carboxyl group, respectively. The intensity of absorption peaks of these oxygenated functional groups is reduced in composites, indicating that TiO$_2$ preferentially binds to GO and RGO at these sites. Additionally, FT-IR spectra of both nanocomposites show a broad peak due to the stretching vibration mode of hydroxyl present in carboxyl and adsorbed H$_2$O. The adsorbed water plays an important role in enhancing the photocatalytic activity of the nanomaterial. Under light illumination, these surface hydroxyl groups are trapped by holes to form hydroxyl radicals, suppress the electron–hole recombination, and increase the photocatalytic efficiency.

Furthermore, a broad band below 1000 cm$^{-1}$ can also be seen in the nanocomposites indicating vibration of Ti–O–Ti and Ti–O–C bonds formed due to residual carboxyl groups of GO and RGO with TNFs in the composites during hydrothermal treatment. All of these vibrational modes show a strong chemical interaction of TNFs with GO and RGO in their nanocomposites.

The band gap of synthesized nanocatalysts was determined using UV–visible absorption spectroscopy. The calculated band gaps for TNFs, GO-TNFs, and RGO-TNFs were 3.00, 2.75, and 2.62 eV, respectively. It has been demonstrated that doping GO and RGO with TNFs decreases their band gap. These findings are consistent with reported values, which range from 3.18 to 2.66 eV when TiO$_2$ was doped with different carbons. Furthermore, various studies explained that the decreased band gap is caused by the interaction of GO and RGO with TiO$_2$, which produces intermediate states near the valence band of TiO$_2$, allowing photogeneration of electrons from lower-energy states.

2.2. Morphological Analysis. SEM was used to analyze the shape features of the prepared TNFs and carbon-doped TNFs. A typical SEM image, shown in Figure 3a, reveals the flake-like morphology of TNFs, which is very uniform and quite clean. However, TNFs can be seen well distributed across the wrinkled two-dimensional layers GO and RGO in Figure 3b,c, forming a unified composite. Furthermore, TEM was employed to evaluate the effect of carbon content on the in situ growth of TNFs. Figure 4a illustrates a TEM image of TNFs, which shows the flakes stacking together and having a semisquare or irregular shape. The synthesized TNFs with crystalline platelets flakes can be observed with a thickness of around 5–10 nm and a length of 30–50 nm. Although similar morphology has been described previously in the literature, this method is more convenient and economical. Figure 4b,c shows the TEM images of GO-TNFs and RGO-TNFs.
composite, respectively, demonstrating that most of TNFs are widely distributed and only a small number of particles aggregate. These TNFs can be seen adhering evenly to the surface of the GO and RGO sheet, with no aggregation.

2.3. Photocatalytic Performance. The photocatalytic performance of as-synthesized TNF, GO-TNF, and RGO-TNF nanocatalysts was monitored by the photodegradation of MB dye in aqueous solution under sunlight irradiation. It was observed that the MB does not self-degrade in the presence or absence of sunlight, suggesting dye stabilization. Figure 5a–c shows the gradual decrease in the absorption intensity of the MB in aqueous solution under sunlight irradiation with TNF, GO-TNF, and RGO-TNF nanocatalysts. As the time was extended from 10 to 60 min, significant differences in peak reduction were observed. The photodegradation percentages of TNFs, GO-TNFs, and RGO-TNFs are illustrated in Figure 6a. No photodegradation was observed for TNF, GO-TNF, and RGO-TNF nanocatalysts in the dark. For TNFs, only 58.4% MB was found to degrade after 60 min of sunlight illumination. However, a greater photodegradation percentage of MB was observed with GO-TNF and RGO-TNF nanocatalysts. As the time was extended from 10 to 60 min, significant differences in peak reduction were observed. The photodegradation percentages of TNFs, GO-TNFs, and RGO-TNFs are illustrated in Figure 6a. No photodegradation was observed for TNF, GO-TNF, and RGO-TNF nanocatalysts in the dark. For TNFs, only 58.4% MB was found to degrade after 60 min of sunlight illumination. However, a greater photodegradation percentage of MB was observed with GO-TNF and RGO-TNF nanocatalysts after the same illumination time. Comparatively, RGO-TNFs show the best activity with 92.7% photodegradation after 60 min exposure to sunlight, which may be attributed to the lower oxygen content functional groups over RGO sheets than GO, which may facilitate efficient charge transfer through its conjugated structure and hence suppress photogenerated electron–hole pair recombination. Furthermore, RGO can readily form stable aqueous dispersion through electrostatic stabilization, which can provide larger adsorptive centers due to its π–π interactions, greater surface area, higher hydrophobicity, and more defect sites. The findings show that the carbon doping increases the photocatalytic activity of TNFs, which is attributed to the enhanced adsorption capacity of carbon over the TNF surface. This synergistic effect of carbon and TNFs is generally accepted. The reusability and stability of a photocatalyst are essential considerations for determining the commercial and practical applications. In this regard, the reusability experiment was carried out to determine the degradation efficiency of GO-TNF and RGO-TNF nanocatalysts for repeated five cycles (Figure 6b). After the successful photodegradation of MB, the nanocatalyst was taken out from the reaction mixture by centrifugation and filtration, followed by several washes with DI water and ethanol. The separated nanocatalyst was dried in vacuum at 80 °C and used for the photodegradation of MB following the same protocol. The slight decrease in photocatalytic performance was monitored from 92 to 75% after five cycles, so the nanocatalysts are quite stable and recoverable.

2.4. Photocatalytic Antibacterial Activity. To demonstrate the photocatalytic antibacterial efficiency of TNFs, GO-
TNFs, and RGO-TNFs, experiments were carried out in the dark and under sunlight irradiation. The samples were evaluated in relation to two different bacterial strains (E. coli and S. aureus). Figure 7a,b shows images of bacterial colonies grown on the agar plate after 40 min exposure to sunlight and dark with TNF, GO-TNF, and RGO-TNF nanocatalysts. The control test (without the photocatalyst) was performed, and the growth of the bacterial strain was observed under both dark and sunlight environments. However, the bacterial strain with nanocatalysts (1 mg/L) when exposed to sunlight and dark conditions yielded different results. The obtained results are shown in Figure 8a,b. There was no significant difference in the number of bacteria in the dark atmosphere. While the number of bacteria decreased within 40 min of sunlight irradiation, a greater bacterial reduction (85.6%) was achieved with RGO-TNF nanocatalysts, and the reduction % is shown in Figure 9.

It should be observed that GO-TNFs and RGO-TNFs were found to be more effective at inactivating bacteria than TNFs. The higher antibacterial activity was attributed to the presence of carbon content as an electron trap for effective charge separation to enhance bacterial inactivation kinetics in the presence of sunlight.\textsuperscript{37a-d,39} None of the test samples showed any bactericidal activity in a dark environment. Hence, the bacterial cell proliferation is photoinduced inactivation rather than chemotoxic cell death.

3. MATERIALS AND METHODS

The chemicals used in the analysis were extremely pure and of analytical grade, collected from commercial sources, and used without any additional treatment. Commercial titanias (\textit{TiO}_2), graphene oxide (GO), and reduced graphene oxide (RGO) for
doping were purchased from Merck. All of the other chemicals were purchased from Sigma-Aldrich, which included ethyl alcohol (CH₃CH₂OH), isopropanol ((CH₃)₂CHOH), hydrochloric acid (HCl), sodium hydroxide (NaOH), and methylene blue (C₁₆H₁₈N₃SCl₃H₂O). The glasswares were washed and autoclaved at 121 °C for 15 min. During the experiment, ultrapure water (Milli-Q water purification system; Millipore Co.) was used.

3.1. Fabrication of Titania Nanoflakes and Carbon-Based Nanostructure Composites. In the first step, titania nanoflakes (TNFs) were successfully synthesized in accordance with the reported facile and one-pot liquid-phase deposition method and then processed to fabricate GO- and RGO-based composite materials. The composites of TNFs with GO and RGO were synthesized via a hydrothermal method following the dispersion of 0.0248 g of GO and 0.487 g of TNFs in a solvent mixture containing 40 mL of DI and 20 mL of ethanol by a magnetic stirrer for 1 h at room temperature. The obtained gray-colored homogeneous suspension was transferred into a Teflon-lined stainless autoclave and heated at 160 °C for 4 h. The resulting product was cooled down to room temperature, and the synthesized composite was recovered by filtration, washed with DI water and ethanol, and subsequently dried overnight at 60 °C. The same procedure was repeated with RGO, and the synthesized nanocatalysts were named GO-TNFs and RGO-TNFs (Figure 10).

3.2. Instrumentations. To characterize the synthesized material multiple techniques were used to avoid any sort of error in the process. Initially, the functionalities present in nanocatalysts were determined by employing an FTIR spectrophotometer (Thermo Nicolet 5700) in the range of 4000–500 cm⁻¹. The crystalline phase was confirmed on a powder XRD diffractometer (D/max-IIIB, Rigaku) with a Cu Kα (λ = 1.5406 nm) operating at a tube voltage of 40 kV and current of 20 mA. The morphology, structure, and composition of the samples were observed with scanning electron microscopy (FE-SEM J SM 7800F) and transmission electron microscopy (TEM, Tecnai, G2 F30), while the catalytic tests were monitored using a UV–visible absorption spectrophotometer (Biochrom Libra S-22).

3.3. Photocatalytic Dye Degradation. The photocatalytic dye degradation of the TNFs and carbon-doped TNFs was determined by monitoring the photodegradation of methylene blue (MB) in an aqueous solution in the presence of sunlight. The nanocatalysts (TNFs, GO-TNFs, and RGO-TNFs) (10 mg) were mixed into 50 mL of MB solution (10 mg/L). Prior to being exposed to sunlight, the mixture was sonicated for 30 min in the dark to achieve dye adsorption/desorption equilibrium. After that, the mixture was exposed to sunlight periodically, 4 mL of the solution was withdrawn at certain time intervals, and the nanocatalyst was separated by centrifugation. The absorbance of the clear solution was determined at 665 nm using a UV–Vis spectrophotometer. The screening was performed from 11:00 to 14:00 on a sunny day (35–40 °C). Using the below equation, the percent degradation was calculated during the experimental study by observing the change in the MB absorption profile.

\[
\% \text{ degradation} = \left( \frac{X_i - X_f}{X_i} \right) \times 100
\]  

where \(X_i\) and \(X_f\) represent the initial and final absorbances of dye, respectively.

3.4. Photocatalytic Antimicrobial Activity. The glassware autoclaved at 121 °C for 1 h was used during the photocatalytic experiment. To investigate the antibacterial activity of synthesized TNF and carbon-doped TNF nanocatalysts, Gram-negative E. coli and Gram-positive S. aureus were chosen as target bacteria. The bacterial cells were cultivated in a conventional manner using a nutrient broth culture medium prepared by dissolving 18 g of nutrient broth no. 2 in 1 L of distilled water and sterilizing it at 121 °C. To standardize the culture (maintaining the initial bacterial concentration of \(10^2–10^5\) CFU/mL), the strains were inoculated in 5 mL of the sterilized nutrient broth and incubated at 37 °C for 24 h. The Petri dishes were poured with 20 mL of Mueller-Hinton Agar (38 g/L), allowed to solidify, and then incubated for 24 h. To make the working solution of \(10^5\) CFU/mL (colony-forming unit/mL), a fixed volume of the

Figure 9. Reduction of TNF, GO-TNF, and RGO-TNF nanocatalysts against E. coli and S. aureus bacterial strains.

Figure 10. Schematic illustration of the fabrication process of carbon-doped TNFs.
grown culture was transferred to the cylindrical glass vessel. The nanocatalyst concentration was fixed at 1 mg/mL. The reaction mixture containing 250 μL of bacterial solution and 250 μL of nanocatalyst solution was kept under sunlight for 40 min. The reaction mixture (10 μL) was taken out after a regular time interval of 10 min and spread over agar plates. Finally, the plates were incubated at 37 °C for 24 h. A control assay in the absence of nanocatalyst material was also conducted in parallel for testing the disinfection efficiency. The same set of samples were tested simultaneously under dark conditions. The antibacterial efficiency from CFU/mL for each sample was calculated by the following equation

\[
\text{% reduction} = \left(\frac{A - B}{A}\right) \times 100
\]

where \(A\) is the initial number of bacterial colonies and \(B\) is the number of bacterial colonies at any time \(t\).

4. CONCLUSIONS

In summary, visible-light-driven TiO2 nanoflakes (TNFs) and carbon-doped TNFs were synthesized using a simple hydrothermal process. For the fabrication of TNFs, graphene oxide and reduced graphene oxide were used as carbon sources. Under dark and sunlight irradiation, the photocatalytic performance and antibacterial activity of TNFs and carbon-doped TNFs were examined against MB dye, E. coli, and S. aureus bacteria. In comparison to bare TNFs, carbon-doped TNFs demonstrated a substantial increase in sunlight-induced degradation and bacterial inactivation, which was due to the inclusion of carbon as an "electron and hole trap" that enables effective charge separation, which is advantageous for photocatalysis. As a result, simple carbon modification allowed the preparation of novel GO-TNF and RGO-TNF nanocatalysts that have new insights into enhancing the TiO2 photocatalytic performance and have a broad range of environmental applications.

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Notes

The authors declare no competing financial interest.

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