



Synthesis, Characterization and Applications of GO–TiO₂ Nanocomposites in Textile Dye Remediation

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Abstract

Textile azo dyes are used for coloring fabrics which are found to be potentially carcinogenic and mutagenic chemicals. It is disposed of as industrial effluents, causing major hazardous impacts on the aquatic ecosystem and getting deposited onto the soil for a prolonged period. Several conventional methods have been previously applied to eliminate these dyes but had low efficiency and high cost limitations. In order to overcome those issues, in this study, we have synthesized a GO–TiO₂ nanocomposite using the solvothermal method from graphene oxide (GO) nanoparticles and titanium dioxide (TiO₂) nanoparticles which were synthesized individually using modified Hummer's method and sol–gel method, respectively. The prepared TiO₂ nanoparticles and GO–TiO₂ nanocomposite were characterized using UV–visible spectrophotometry, FTIR spectroscopy, dynamic light scattering, zeta potential, XRD, scanning electron microscopy, and EDAX analysis. The textile azo dyes used were Crystal Violet, Brilliant Green, Malachite Green, and Rhodamine B, and their photocatalytic degradation was observed spectrophotometrically using TiO₂ nanoparticles and GO–TiO₂ nanocomposite. From the results obtained, we found that the GO–TiO₂ nanocomposite was successfully synthesized with TiO₂ doping and effectively reduced all the dyes used in this study compared to the standard photocatalyst TiO₂. On the other hand, the Brilliant Green and Malachite green have shown an increase in their color after TiO₂ treatment, which was diminished by using GO–TiO₂ nanocomposites. The biocompatibility of this GO–TiO₂ was studied using zebrafish embryos and the results demonstrated that the GO–TiO₂ nanocomposite was safe for the embryos without causing any delay in hatching or developmental abnormality. The outcome of this study yields a novel application of GO–TiO₂ nanocomposite in the reduction in azo dyes showing potential applications in wastewater remediation. Further studies are required to test the biocompatibility and efficacy of other dye removals.

Keywords Textile dyes removal · Wastewater remediation · Nanotechnology · Graphene oxide · Titanium dioxide

1 Introduction

In recent times, there is rapid industrialization and urbanization. The balance between environmental pollutants and the health of flora and fauna as well as humans have been at stake (Desai et al. 2021). Compared to all types of ecological pollutants the most severe problem is water pollution because the effluents from various dye industries meet the water bodies and contaminate them. Pigment manufacturing, food industries, cosmetic industries, textile industries, printing, leather industries, dyeing, etc., are all among the major contributors to wastewater pollution (Al-Musawi et al. 2022; Amini et al. 2008). It has been projected that 15% of the total used textile dyes remain

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unreacted and contribute directly to the effluents (Yaseen and Scholz 2019; Vedhantham et al. 2022). The synthetic textile dyes contribute to water and soil contamination as released from different sources (Nelson and Hites 1980). These dye contaminants cannot be removed by ordinary treatment processes and eventually stay in the environment for many years. Their presence affects the living beings of the ecosystem, severely causing skin irritation, nausea, liver and kidney damage, vomiting, gastrointestinal (GI) tract irritation, etc., in animals and humans. They can also inhibit germination of seeds, alter the length of root and shoot in plants, and inhibit microbial activity (Mittal et al. 2010; Senthilkumar et al. 2006).

For the management of discharge of azo dyes used in textile industries and allied industries into the soil and water bodies, many dye degradation processes have been proposed so far, which may harm the biota of the contaminated soil or water (Lellis et al. 2019). The use of nanoparticles is one of them which can ensure a sensitive way of textile dye reduction. For water decontamination, TiO_2 is utilized due to its photocatalytic property and advantages of being highly stable, low cost, efficient, and less toxic, whereas disadvantages are rapid recombination of excited electrons and holes, light absorption is limited within UV spectrum due to high bandgap. To overcome these limitations, several graphene-based carbon- TiO_2 nanocomposites were used because after exposure to UV–Visible light, the stability and photocatalytic reaction were enhanced many folds for such nanocomposites compared to only TiO_2 (Jeyasubramanian et al. 2019; Tayel et al. 2018). Graphene has become an interesting material in the research world with exceptional physiochemical, electrical, and optical properties that can be used in various applications, such as biosensors, catalysts, drug delivery systems, nanoelectronics, intercalating substance, polymer-based composites, for the production of hydrogen and storage (Obodo et al. 2019; Zindani and Kumar 2019; Elazab et al. 2019). TiO_2 is another highly studied nanoparticle for its efficient semiconductor photocatalytic activity. The environmental pollutants get degraded into fine organic chemicals using TiO_2 (Ram et al. 2012). Thus, both the TiO_2 and graphene were integrated into nanocomposite hybrids with outstanding properties for the development of novel applications. The earlier study confirmed the improved photocatalytic reactions of carbon-based TiO_2 composites of fullerenes, activated carbon, carbon nanotubes than only TiO_2 . Limitations were also present regarding the photocatalytic performance of TiO_2 along with poor synthesis methods that affected the recycling of the photocatalyst and lower capacity to capture light at the site of reaction. Therefore, the carbon allotrope graphene with increased surface area ($2600 \text{ m}^2/\text{g}$), electron mobility, and

transparency were highly sensible than combining other allotropes of carbon (Zhang et al. 2010a).

Metal oxide nanoparticles have been used in biomedical sciences like catalysis, biosensing, and degradation of amyloids, especially the zinc oxide nanoparticles and nanoflowers (Girigoswami et al. 2015, 2019; Akhtar et al. 2017). There is no available nanocomposite based on graphene oxide (GO) incorporated with a photocatalyst, which can degrade the textile dyes effectively and is biocompatible. In a previous study, graphene oxide has been successfully synthesized using agro wastes (Somanathan et al. 2015). In the present study, we have synthesized GO– TiO_2 nanocomposite and characterized them using different tools—UV–visible spectrophotometer, particle size analyzer (DLS), scanning electron microscope (SEM), Fourier-transform infrared spectroscopy (FTIR). The different azo dyes like crystal violet (CV), brilliant green (BG), malachite green (MG), and rhodamine B (RB) were studied for their reduction with the synthesized nanocomposite. Standard photocatalyst TiO_2 nanoparticles (NPs) were taken as a positive control. Compared to the standard photocatalyst, our synthesized nanocomposite exhibited superior remediation of textile dyes. Moreover, it was found that the synthesized nanocomposite was highly biocompatible as observed by the zebrafish embryo study.

2 Materials and Methods

2.1 Materials

Graphite powder was procured from Sigma Chemicals, ethanol, sulfuric acid, potassium permanganate, hydrogen peroxide, hydrochloric acid, isopropanol, acetic acid, titanium tetra isopropoxide were purchased from HiMedia.

2.2 Synthesis of Titanium Dioxide Nanoparticles

Titanium dioxide nanoparticles (TiO_2 NPs) were prepared according to Venkatachalam et al. (2007) with slight modifications. To prepare TiO_2 NPs, 5.2 ml of isopropanol and 2.5 ml of acetic acid were mixed, and stirred for 15 min using a magnetic stirrer in a 100-ml glass beaker covered with aluminum foil to avoid evaporation of solvents. 2.5 ml of titanium tetra isopropoxide was added dropwise and stirred for 10 min further followed by the addition of 1.75 ml of deionized water (DIW). This mixture was stirred for 10 min which led to the gel formation. The contents were transferred to a porcelain crucible and kept over the hot plate for drying. Due to the calcination, the gel was converted into a yellowish precipitate. The precipitate was then crushed with mortar pestle to produce TiO_2 NP powder and further calcinated at 200°C for 2 h.

2.3 Synthesis of Graphene Oxide (GO) from Graphite Powder

Graphene oxide (GO) nanosheets were prepared by modified Hummer's method from graphite powder as described by Zaaba et al. (2017) with slight modifications. 27 ml of sulfuric acid (H_2SO_4) and 3 ml of phosphoric acid (H_3PO_4) in a 9:1 ratio were mixed and stirred for several minutes in a 250-ml glass beaker kept on an ice bath. Then, 0.225 g of graphite powder was added into the mixing solution under stirring conditions. The solution was stirred further 10 min for proper mixing of the graphite powder and then 1.32 g of potassium permanganate (KMnO_4) was added very slowly into the solution. This mixture was stirred for 6 h until the solution became dark green. The elimination of the excess of KMnO_4 was done by adding 0.675 ml of hydrogen peroxide (H_2O_2) dropwise slowly and the solution was stirred for a further 10 min. The reaction was exothermic and was conducted on an ice bath. To wash the pellet, 10 ml of hydrochloric acid (HCl) and 30 ml of distilled water (DIW) were added and centrifuged at 8000 rpm for 10 min. Then the supernatant was decanted away, and the residue was rewashed with the only DIW 3 times using the same conditions of centrifugation. The washed GO solution was dried using a hot air oven at 90 °C for 24 h to produce the GO powder.

2.4 Synthesis of Graphene Oxide–Titanium Dioxide Nanocomposite (GO–TiO₂) Nanocomposite

The synthesized GO nanosheets were utilized to synthesize GO–TiO₂ nanocomposite according to Zhang et al. (2010a) with slight modification, where they have synthesized graphene–TiO₂, not GO–TiO₂. 0.450 g of GO as-synthesized was ultrasonicated in a 60 ml DIW and 30 ml of anhydrous ethanol solution to disperse it well, and 0.6 g of TiO₂ as-synthesized was added to the GO solution. The solution was stirred vigorously for 2 h to obtain a homogeneous suspension. Then, this suspension was autoclaved in a Teflon-coated autoclave and maintained at 120 °C for 24 h. The composite was recovered by filtration, washed with DIW 3 times at 8000 rpm for 10 min, and thoroughly dried at 60 °C in a hot air oven at 80 °C to get the final GO–TiO₂ nanocomposite.

2.5 Characterization of the Synthesized Nanostructures Using Different Photophysical Tools

The synthesized TiO₂ NPs, GO nanosheets and GO–TiO₂ nanocomposites were characterized using various tools.

The hydrodynamic diameter and stability in water of the synthesized GO nanosheets and GO–TiO₂ nanocomposites were measured using Malvern zeta sizer according to Girigoswami et al. (2015). Briefly, the samples were diluted in 3 ml DIW and sonicated two times for 15 min to measure the hydrodynamic diameter as well as zeta potential of the synthesized nanostructures. Fourier-transform infrared spectroscopy (FTIR) technique is utilized for obtaining an infrared (IR) spectrum when the IR light falls on the sample (solid, liquid, or gas) and either gets absorbed or transmitted. FTIR is used mainly to identify compounds and molecular groups of organic compounds because they have a wide range of functional groups, cross-links, and side chains involved. All these groups possess characteristic vibrational, stretching, and bending frequencies in the range of IR. The FTIR for GO nanosheets and GO–TiO₂ nanocomposite was conducted according to Girigoswami et al. (2015). The GO and GO–TiO₂ nanocomposites were made into pellets using KBr and the pellets were used to record the FTIR in transmittance mode. The absorption spectrum using Shimadzu UV–visible spectrophotometer was also recorded for the synthesized nanostructures according to Girigoswami et al. (2015), by diluting the samples in DIW, sonicate them, and recording the absorbance against appropriate blank solutions. High-resolution SEM (HR-SEM) is used for very high magnification visualization of the surface morphology of the synthesized nanostructures. SEM image was used for the structural confirmation and the chemical composition of the samples can be analyzed qualitatively and semi-quantitatively using SEM at a selected point using EDX. The SEM and EDX were done for the synthesized GO nanosheets and GO–TiO₂ nanocomposite according to Deepika et al. (2018). The samples were prepared for the SEM analysis by coating a thin layer (200 Å) of GO and GO–TiO₂ nanocomposite over a clean aluminum foil and dried in a vacuum and dirt-free environment. The surface was as such scanned for SEM and EDX analysis. The measurements were done at a 20 nm working distance with an accelerating voltage of 15 kV using a low energy secondary electron emitting FESEM (Su6600, Hitachi, Japan). XRD analysis was also done to find the crystalline structure of the synthesized nanostructures according to Girigoswami et al. (2015). The 2θ value was taken from 10° to 90°.

2.6 Textile Dye Reduction

The application of the synthesized nanocomposite (GO–TiO₂) toward textile dye remediation was also studied. The reduction in the textile dyes crystal violet (CV), brilliant green (BG), malachite green (MG), and rhodamine B (RB) was analyzed by the reduction in absorption at 588 nm for



CV, 624 nm for BG, 617 nm for MG and 553 nm for RB, respectively, using UV–visible spectrophotometer. The dye reduction was compared with standard dye reduction photocatalyst TiO₂ nanoparticles (NPs). The concentration and absorption maxima ($\lambda_{\max}$) of the dyes in water used are given in Table 1. The concentrations of the dyes were standardized to obtain an absorbance within 0.1.

For each type of dye used namely crystal violet (CV), brilliant green (BG), malachite green (MG), and rhodamine B (RB), three tubes were taken. To each tube, 5 ml dye was added at the concentrations given in Table 1. Then, to tube 1 nothing was added, tube 2 standard photocatalyst TiO₂ NPs were added, and tube 3 synthesized GO–TiO₂ nanocomposite was added. The amount of TiO₂ added was 0.01 g and GO–TiO₂ was 0.001 g which was standardized and used for all the dyes. The solution of dye and the respective nanostructures (TiO₂ and GO–TiO₂) were mixed using vortex and exposed to sunlight for 15 min. After sunlight exposure, tubes 2 and 3 were centrifuged at 8000 rpm for 15 min to remove the nanoparticles. The supernatant was decanted in two fresh tubes and the absorbance was measured at the respective absorption maxima for the dyes mentioned in Table 1.

2.7 Biocompatibility Assay Using Zebrafish Embryos

Zebrafishes, both male and female, were maintained in separate tanks, with the conditions described by Girigoswami et al. (2015). Standard flakes and blood worms were fed to the zebrafishes for maintaining them in healthy conditions with 12 h light–dark conditions in fish tanks with continuous bubbling of air. The embryos were produced by external spawning. The day before, two males and one female were kept in spawning tanks with grids at the bottom, so that the eggs could percolate and settle at the bottom of the tank. The next day early morning, the eggs were isolated, washed several times with distilled water, and with the help of a microscope, healthy embryos were selected for the experiments. Nearly 30 embryos were taken for each group of treatment for only TiO₂ and GO–TiO₂ at two doses; low dose (0.1%) and high dose (0.2%),

and the developmental stages were observed with time under an inverted microscope. The pictures were captured to find the physiological changes followed by cumulative hatchability to show the biocompatibility.

3 Results

3.1 Synthesis and Characterization of the Nanoparticles and Nanocomposite

The synthesized nanoparticles and nanocomposite were characterized using various tools. The hydrodynamic diameter of synthesized GO-nanosheet (Fig. 1a) and GO–TiO₂ (Fig. 1b) the nanocomposite was found to be 79 nm and 93 nm, respectively. The size has increased from GO nanosheet to GO–TiO₂ nanocomposite, confirming the incorporation of TiO₂ in GO. The zeta potential of synthesized TiO₂ nanoparticles (Fig. 1c), GO-nanosheet (Fig. 1d) and GO–TiO₂ nanocomposite (Fig. 1e) is found to be -29 mV, -20 mV, and -18 mV, respectively. The zeta potential of TiO₂ was highly stable after incorporation of TiO₂ in GO; the stability has decreased to -18 mV, which also represents a stable structure. The FTIR spectra for the synthesized nanocomposites showed typical characteristic bonds of C=C at 1634 cm^{-1} and O–H at 3312 cm^{-1} , respectively, for GO (Fig. 2a). After TiO₂ incorporation the C=C has shifted to 1646 cm^{-1} (Fig. 2b). The new peak below 1000 cm^{-1} represents the presence of Ti–O–Ti. The absorption spectra of TiO₂ and GO–TiO₂ nanocomposite are shown in Fig. 2c. We could see a typical shoulder peak of TiO₂ at 304 nm, whereas GO–TiO₂ nanocomposite has a small shoulder peak around 304 nm, confirming the incorporation of TiO₂ in the GO–TiO₂ nanocomposite. To confirm the crystalline structure of the synthesized TiO₂ nanoparticles and GO–TiO₂ nanocomposites, we have done XED analysis. The results (Fig. 2d) showed that the XRD peaks corresponding to the JCPDS pattern of TiO₂ anatase (JCPDS card no. 21-1272) were all present (Scarpelli et al. 2018; Awang and Talalah 2019). The TiO₂ XRD showed peaks at (101), (004), (200), (105), and (204), which matches with the JCPDS pattern for TiO₂ anatase. When GO was incorporated, the XRD peak intensity was found to be increased for each of these planes.

The surface morphology of the synthesized nanocomposite was visualized using SEM analysis. The typical nanosheet layered structure was observed for only GO (Fig. 3a). The incorporation of TiO₂ was visible over the GO nanosheets as seen in Fig. 3b. The size of TiO₂ NPs was found to be 20 nm. The EDX of GO–TiO₂ nanocomposite showed the incorporation of TiO₂ in the synthesized GO–TiO₂ nanocomposite with 1.2% incorporation by

Table 1 The concentration and $\lambda_{\max}$ of azo dyes used for the dye reduction study

Dye used	Concentration (μM)	$\lambda_{\max}$ for the dyes (nm)
Crystal Violet	6	588
Brilliant green	10	624
Malachite Green	25	617
Rhodamine B	10	553



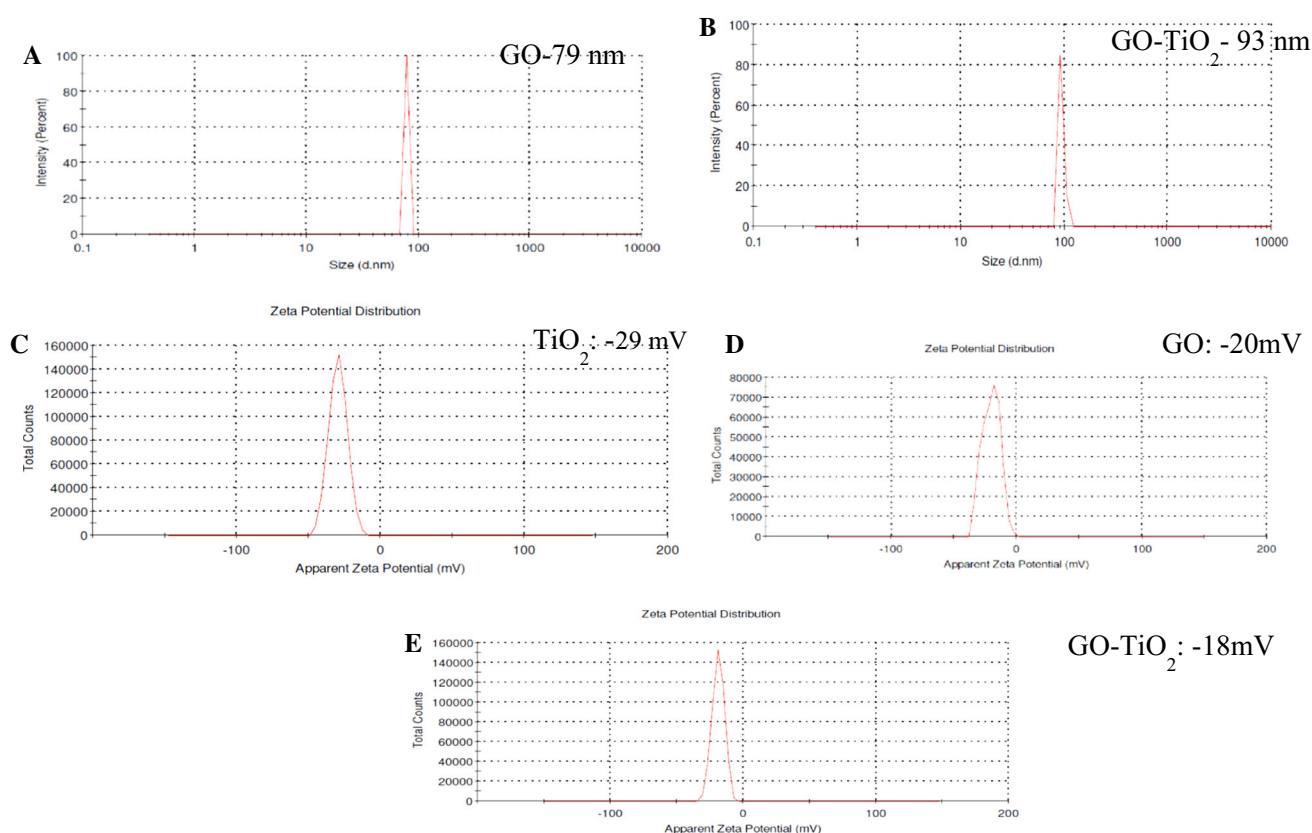


Fig. 1 The characterization of the synthesized GO-TiO₂ nanocomposite. The hydrodynamic diameter of synthesized **a** GO-nanosheet and **b** GO-TiO₂ nanocomposite, the zeta potential of synthesized

c TiO₂ nanoparticles (− 29 mV) **d** GO nanosheet (− 20 mV) and **e** GO-TiO₂ nanocomposite (− 18 mV)

weight as shown in Fig. 3c. The peaks denote the incorporation of TiO₂ in the nanocomposite.

3.2 Textile Dye Reduction by Synthesized GO-TiO₂ Nanocomposite

The reduction in the absorbance as observed spectrophotometrically for the dyes CV, BG, MG, and RB using TiO₂ NPs and GO-TiO₂ nanocomposites is shown in Fig. 4a, c, e, g, respectively. The change in the color of the dyes after the addition of TiO₂ NPs and GO-TiO₂ nanocomposites for CV, BG, MG, and RB is shown in Fig. 4b, d, f, and h, respectively. The absorption spectrum of the textile dyes without any catalyst and without any exposure to irradiation is shown in Fig. 4i. The spectrophotometric observation clearly showed that after treatment with GO-TiO₂ nanocomposites, all the CV, BG, MG, and RB dyes exhibited a complete reduction in the λ_{max} , respectively.

3.3 Biocompatibility Assay

The zebrafish embryos were taken as an *in vivo* model to study the biocompatibility of the synthesized

nanostructures. TiO₂ and GO-TiO₂ nanocomposite were compared, and the results are depicted in Fig. 5. The pictures were taken at 54 h post-fertilization (hpf) and the experiments were repeated thrice. The images showed that the control embryos had a transparent medium, and they were 100% hatched after 72 hpf (Fig. 6). In the TiO₂-treated zebrafishes, there was an aggregation of nanoparticles above the embryos, which may cause hindrance for the exchange of essential nutrients and gases required for their growth and development. This may be the reason for the delayed hatching of the embryos after treatment with the only TiO₂ at a high dose, and there was only 96% hatching compared to 100% observed in other treatments. The embryos treated with low as well as a high dose of GO-TiO₂ had some aggregation on the egg surface, but it was less pronounced compared to only TiO₂ nanoparticles. There was delayed hatching observed for GO-TiO₂ at a high dose, but the effect was lower compared to only TiO₂ treatment, and 100% hatching was observed for both low as well as a high dose of GO-TiO₂ treatment.

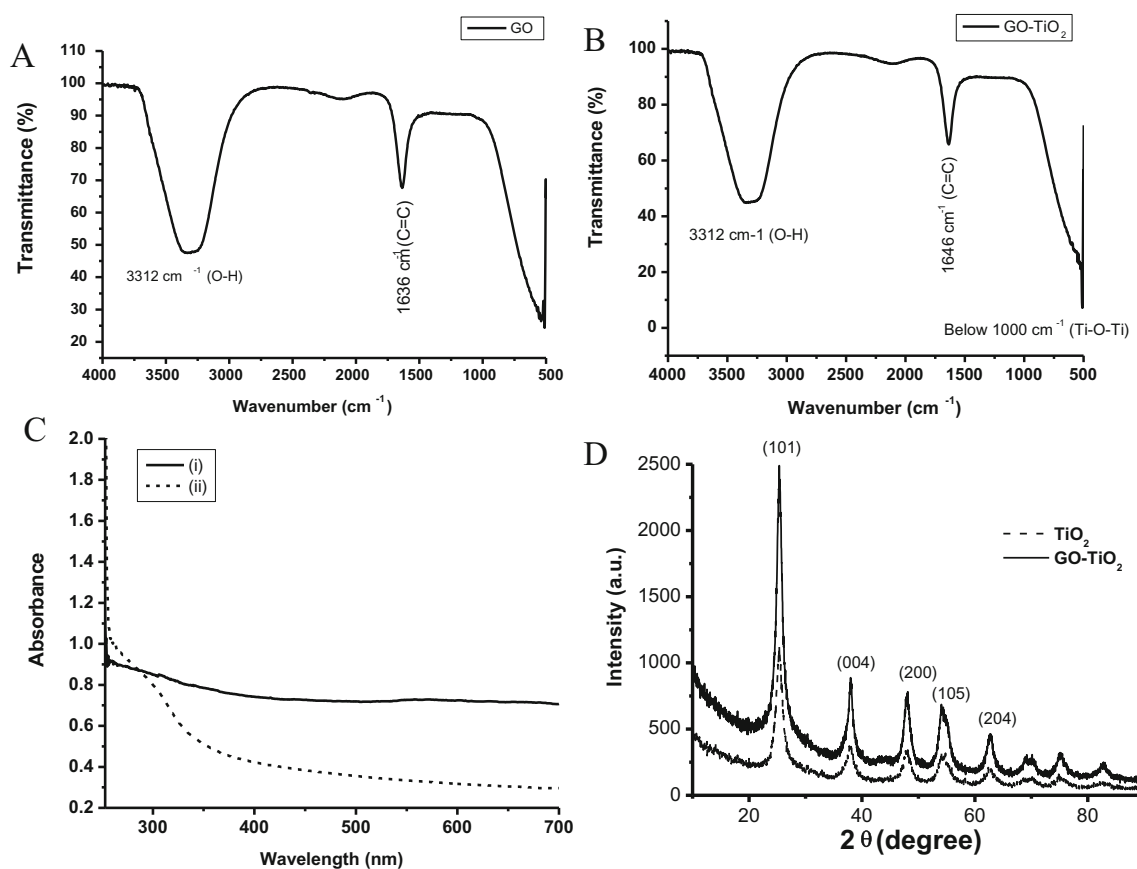


Fig. 2 The FTIR spectra of synthesized **a** GO nanosheet and **b** GO-TiO₂ nanocomposite. **c** The UV-visible absorption spectrum of (i) GO-TiO₂ nanocomposite (solid line) and (ii) TiO₂ nanoparticles

4 Discussion

Titanium dioxide nanoparticles (TiO₂) are a well-known widely used photocatalyst to reduce numerous pollutants and chemicals such as textile azo dyes into non-toxic residues. In recent studies, the two-dimensional Graphene oxide (GO) nanosheets exhibited astonishing properties mainly in visible light response and enhanced photocatalytic activity. Moreover, by doping TiO₂ nanoparticles onto the GO nanosheets forming Graphene oxide-Titanium dioxide (GO-TiO₂) nanocomposite, which was found to be a promising semiconductor photocatalyst under the visible light spectrum. The nanocomposite exhibited overall visible light response, enhanced bandgap reduction, surface plasmon resonance, electron mobility, and reduced electron-hole recombination. So far, the application of GO-TiO₂ nanocomposite was studied only for volatile aromatic pollutants (Zhang et al. 2010a), but its application in reducing toxic textile dyes has not been explored. We have successfully synthesized and characterized TiO₂ nanoparticles, GO nanosheets, and GO-TiO₂ nanocomposite. To achieve a maximum photocatalytic reduction in azo dyes

(dashed) **d** The XRD spectrum of (i) GO-TiO₂ nanocomposite (solid line) and (ii) TiO₂ nanoparticles (dashed)

such as Crystal Violet, Brilliant Green, Malachite Green, and Rhodamine B, the dyes were simulated with water, treated simultaneously with only TiO₂ nanoparticles, and GO-TiO₂ nanocomposite, and was monitored for their reduction. Previous studies exist for the application of TiO₂-graphene nanocomposites for the decontamination of wastewater (Tayel et al. 2018).

TiO₂ nanoparticles were synthesized successfully, using TTIP as a precursor through sol-gel method. The characterizations were executed after drying and calcination at 200 °C for 2 h. The particle size of the synthesized TiO₂ NPs was found to be around 20 nm (Fig. 3b) and was also very highly stable as observed from the zeta potential value of − 29 mV (Fig. 1c). The smaller the size, the activity of the nanoparticles is higher due to the very high surface area to volume ratio. The characteristic absorption spectrum with a typical shoulder peak was also observed for the synthesized TiO₂ NPs at 304 nm (Fig. 2c). Researchers have shown a similar kind of shoulder peak obtained after TiO₂ NP synthesis using the sol-gel method (Venkatchalam et al. 2007). These characterizations of TiO₂ NPs

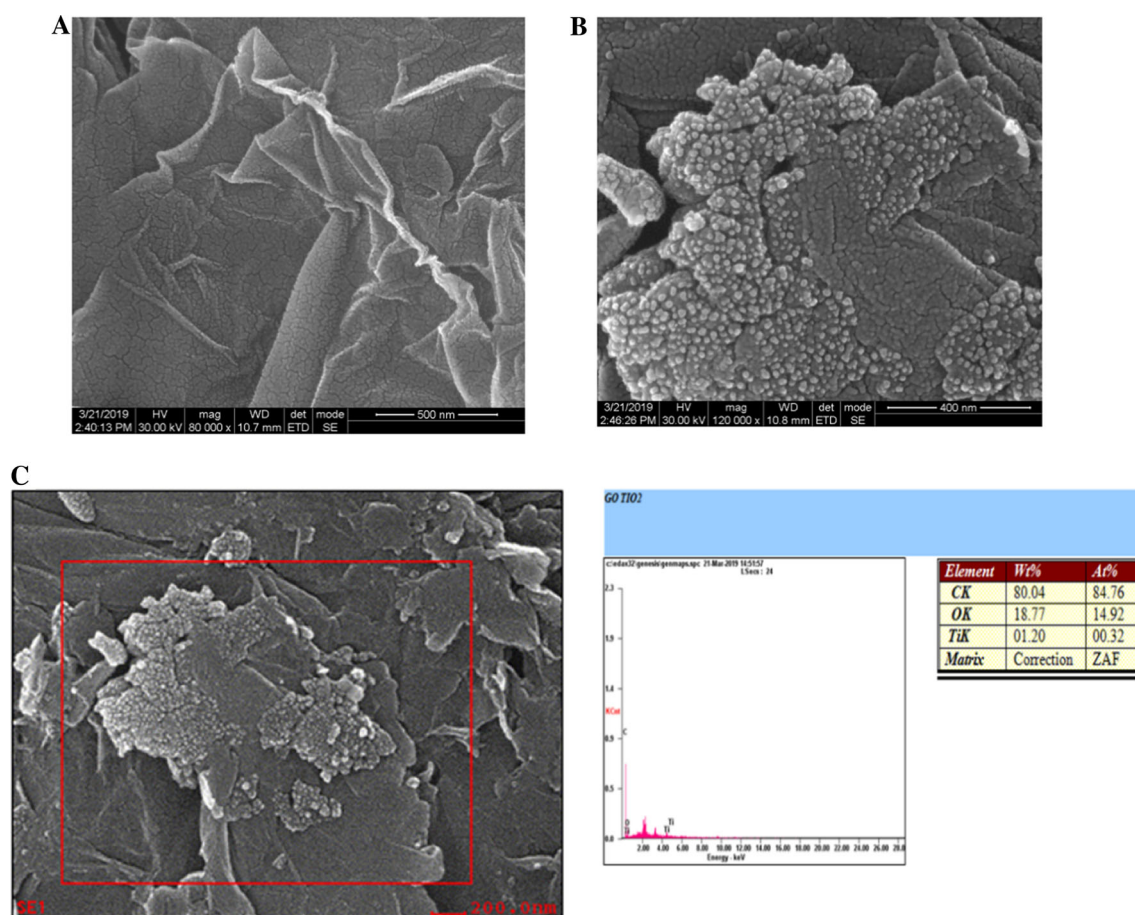


Fig. 3 The scanning electron microscope (SEM) images of **a** GO nanosheets and **b** GO-TiO₂ nanocomposite. This visualizes the GO sheet formation and further incorporation of TiO₂ into GO sheets.

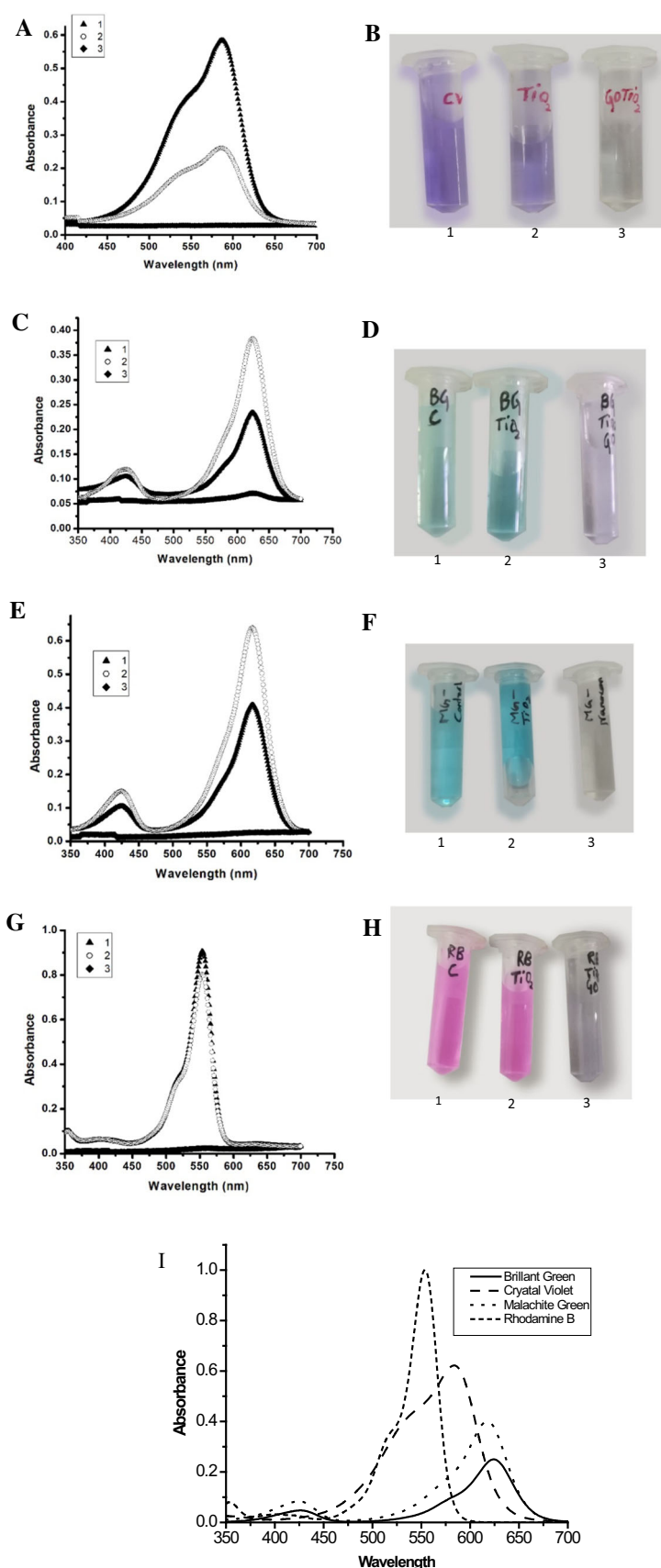
c The EDX analysis of GO-TiO₂ nanocomposite. This gives the exact composition of the GO-TiO₂ nanocomposite

showed that the synthesis was successful and the particles are highly stable in water.

To further proceed toward the nanocomposite synthesis, we have synthesized GO from graphene using modified Hummer's method. The GO was synthesized successfully as evidenced from the FTIR spectrum, which shows the characteristic bond vibrations for C=C at 1634 cm⁻¹ and O-H at 3312 cm⁻¹, respectively, for GO (Fig. 2a) as well as surface morphology visualized through SEM analysis (Fig. 3a). The typical layered structure of GO is observed in the SEM analysis. The synthesized GO was utilized to synthesize GO-TiO₂ nanocomposite using the hydrothermal method and characterized for the parameters. The FTIR spectroscopy showed that additional bands for Ti-O-Ti were incorporated in the spectrum apart from a shift in C=C to 1646 cm⁻¹ from 1632 cm⁻¹ (Fig. 2b). To further confirm the TiO₂ incorporation, SEM and EDX analysis was done. The SEM image clearly shows the incorporation of TiO₂ NPs on the surface of the GO sheets (Fig. 3b). Further, the EDX analysis (Fig. 3c) showed peaks corresponding to carbon, oxygen, and titanium. Thus, the

incorporation of TiO₂ NPs in the GO sheets has been confirmed. The XRD pattern of TiO₂ and GO-TiO₂ is shown in Fig. 2d. The graph shows that the nanoparticles were successfully synthesized, and the XRD peaks corroborate with the JCPDS pattern (card number 21-1272) for anatase TiO₂ nanoparticles. After GO incorporation, the intensity of each peak has increased. In previous study, researchers have shown that similar peaks were obtained for TiO₂ anatase (Scarpelli et al. 2018; Awang and Talalah 2019). It is known that if TiO₂ is incorporated in GO nanosheets, the photocatalytic activity will be enhanced. The improvement in photocatalytic activity is attributed to the following schemes: (i) the two-dimensional matt structure of GO will enhance the surface area of TiO₂ after the interaction. (ii) The π - π interaction between the aromatic contaminants and the network of aromatic groups of GO increases the adsorption of the contaminants to the nanocomposite facilitating the photocatalytic reduction and (iii) the nanocomposite decreases the recombination of the holes (positive) with the photogenerated electrons, because GO is a conductor of electrons and it acts as a sink for

Fig. 4 The textile dyes reduction by the GO–TiO₂ nanocomposite. The symbols used are: 1—only dye, 2—dye with TiO₂, 3—dye with GO–TiO₂ nanocomposite for all the graphs (a, c, e, g) and all the figures (b, d, f, h). The reduction in **a** Crystal Violet (CV), **c** Brilliant Green (BG), **e** Malachite Green (MG), and **g** Rhodamine B (RB), respectively, using GO–TiO₂ nanocomposite studied spectrophotometrically. The reduction in **b** CV, **d** BG, **f** MG, and **h** RB dye visible in the tubes. **i** The absorbance spectra of the dyes Crystal Violet (CV), Brilliant Green (BG), Malachite Green (MG), and Rhodamine B (RB) without the presence of any catalyst and without any sunlight exposure



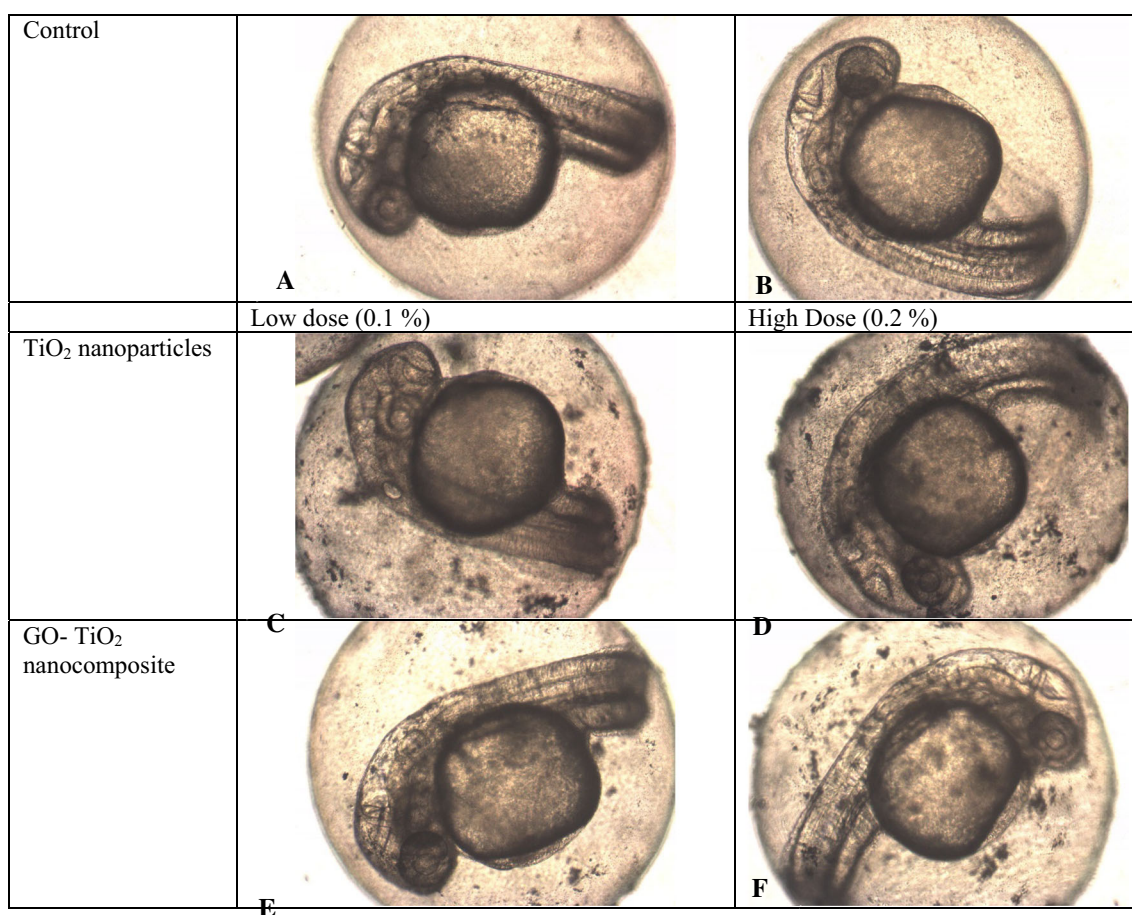


Fig. 5 The zebrafish embryos at 54 hpf in control (a) and (b), and after treatment with TiO₂ (0.1%) (c), TiO₂ (0.2%) (d), GO–TiO₂ (0.1%) (e) and GO–TiO₂ (0.2%) (f)

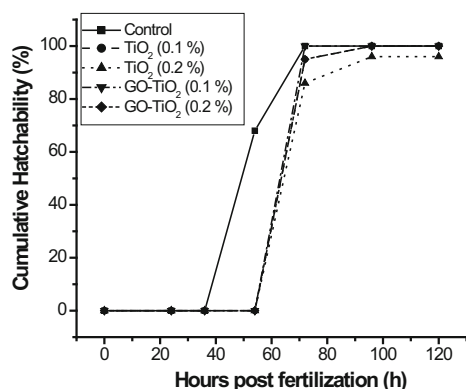


Fig. 6 Cumulative hatchability of zebrafish embryos at different hpf after treatment with TiO₂ and GO–TiO₂ nanoparticles

photogenerated electrons generated on the TiO₂ surface (Zhang et al. 2010b; Yoo et al. 2011; Liu et al. 2010; Leary and Westwood 2011).

The photocatalytic activity of the GO–TiO₂ nanocomposite was applied for the reduction in textile dyes—crystal violet (CV), brilliant green (BG), malachite green (MG),

and rhodamine B (RB). The reduction in CV was done using the nanocomposite as well as TiO₂ NPs. The effect in decolorization of CV was monitored spectrophotometrically using TiO₂ NPs (0.001 g) GO–TiO₂ (0.01 g) as shown in Fig. 4a and the percentage of reduction is shown in Table 2. The GO–TiO₂ nanocomposite could reduce 95% of the dye compared to the only TiO₂, which was 47%. Although there is no peak intensity observed at λ_{max} of CV (588 nm) after GO–TiO₂ nanocomposite treatment and the solution has also become colorless, showing complete dye remediation (Fig. 4b). GO–TiO₂ nanocomposite could reduce the BG dye completely as visible from the absence of any absorption peak at 624 nm (λ_{max} of BG) (Fig. 4c). TiO₂ was found to increase the intensity of the dye instead of reducing it. We got a similar finding for another green dye MG, which we will discuss next. The percentage of BG reduced by TiO₂ NPs and GO–TiO₂ nanocomposites is shown in Table 2. The percent reduction is negative (– 94%) for the standard photocatalytic agent TiO₂, whereas the GO–TiO₂ nanocomposite could reduce the dye to 81%. The color of the dye is completely reduced as shown in the picture (Fig. 4d).

Table 2 The percentage reduction in different textile dyes using TiO₂ nanoparticles and GO–TiO₂ nanocomposites

Dye used for reduction	% Reduction in dye using TiO ₂ nanoparticles	% Reduction in dye using GO–TiO ₂ nanocomposite
Crystal violet (CV)	47	95
Brilliant Green (BG)	– 94	81
Malachite Green (MG)	– 61	93
Rhodamine B (RB)	07	97

GO–TiO₂ nanocomposite could reduce the MG dye completely as visible from the absence of any absorption peak at 617 nm (λ_{max} of MG) (Fig. 4e). TiO₂ was found to increase the intensity of the dye instead of reducing it, similar to BG. The percentage of MG reduced by TiO₂ NPs and GO–TiO₂ nanocomposites is shown in Table 2. There was a negative reduction (– 61%) i.e., increase in color of MG with standard photocatalytic agent TiO₂, whereas GO–TiO₂ nanocomposite could reduce 93% of the dye. The absence of absorption peak at λ_{max} of MG showed that the dye is completely reduced by the synthesized nanocomposite which was also supported by the picture showing no color of the MG dye after GO–TiO₂ nanocomposite treatment (Fig. 4f). GO–TiO₂ nanocomposite could reduce the RB dye completely as visible from the absence of any absorption peak at 553 nm (λ_{max} of RB) (Fig. 4g). TiO₂ also reduced the dye but was not effective compared to GO–TiO₂ nanocomposite. The percentage of RB reduced by TiO₂ NPs, and GO–TiO₂ nanocomposites are shown in Table 2. There was minimal effect of standard photocatalyst TiO₂ on RB dye reduction (7%), whereas the synthesized nanocomposite could reduce 97% of the dye RB. The absence of any absorption peak at λ_{max} of RB after GO–TiO₂ nanocomposite treatment showed complete dye remediation which was also supported by the picture (Fig. 4h). The special mention requires for the dyes brilliant green (BG) and malachite green (MG), in which cases the standard photocatalytic agent TiO₂ increased the color intensity rather than decreasing it. Moreover, the use of synthesized GO–TiO₂ nanocomposite could reduce the colors of BG and MG effectively as visible from the loss of absorption peak for BG (Fig. 4c) and MB (Fig. 4e) spectrophotometrically. The absorption spectrum of the dyes crystal violet, Rhodamine B, Brilliant green, and Malachite green is shown in Fig. 4i without any catalyst and without any irradiation. The peak values show that there is no quenching of dye peaks before and after exposure to sunlight.

Methylene blue (MB) reduction has been demonstrated by other researchers using graphene–TiO₂ nanocomposite (Zhang et al. 2010a). Nitrogen doping with graphene TiO₂ nanocomposite was also shown to improve the

photocatalytic activity for the purpose of MB dye reduction (Shi et al. 2014). Researchers have extensively reviewed the recent progress in TiO₂ photocatalyst coupled with graphene materials, where the objective was to extend the absorption of light of TiO₂ from UV wavelengths toward the visible region. The review also focused on the current advances in the design as well as applications towards the degradation of synthetic dyes through photocatalysis (Giovannetti et al. 2017). Another review discussed the recent developments involved in the chemistry of TiO₂/G and TiO₂/GO nanocomposites. There was a detailed report on the mechanistic fundamentals, in short, of TiO₂ and TiO₂/G and TiO₂/GO photocatalysts along with the different synthesis strategies as well as characterization techniques applied to study TiO₂/G and TiO₂/GO nanocomposites. A brief description of the applications of nanocomposites for water decontamination was included. Wastewater treatment application was discussed for graphene–TiO₂ nanocomposite, not GO–TiO₂ nanocomposite which is a different material from the one we have synthesized in this study. Moreover, the different doping like N₂ gas, SiO₂, CNT addition to the G/TiO₂ is discussed. These doping make a different nanocomposite than what we have engineered (Tayel et al. 2018). In another study, the degradation of methyl orange (MO), an azo dye, was analyzed in simulated wastewater after treatment with the synthesized (GO–TiO₂–ZnO) nanocomposite (Raliya et al. 2017). Reports also exist on the photocatalytic degradation of structurally different azo dyes (amaranth, sunset yellow, and tartrazine) utilizing TiO₂–Pt nanoparticles (TPt), TiO₂–Pt/graphene oxide (TPt–GO), and TiO₂–Pt/reduced graphene oxide (TPt–rGO) composites in the presence of UV and natural sunlight irradiation (Rosu et al. 2017). In another study, graphene oxide (GO) flakes supported titanium dioxide nanoparticles, and SiO₂ insulated nano-sized magnetite aggregates were synthesized. The magnetically recyclable nanocomposite was made with SiO₂ assistance which was different from our nanocomposite (Linley et al. 2014). Thus, we propose that incorporating TiO₂ in GO might have facilitated the access to free electron, which participates in reducing the dye during photocatalysis. This

is the reason we believe that GO–TiO₂ is a superior photocatalyst compared to only TiO₂.

To understand the biocompatibility of the synthesized nanocomposites, we have executed an in vivo experiment with zebrafish embryos (Figs. 5 and 6). The embryos were treated with different doses of TiO₂ and GO–TiO₂ nanoparticles (0.1 and 0.2%), and their developmental stages were monitored along with their hatchability. There was an aggregation of nanoparticles observed for TiO₂-treated embryos at both low and high doses, and the embryos showed delayed hatching at high dose (0.2%) of TiO₂. Only 86% of embryos hatched after high dose treatment with TiO₂ after 72 h, whereas 96% hatched for GO–TiO₂ at the same time interval at high dose. After 96 h 100% hatching was observed for GO–TiO₂ at high dose, but there was only 96% hatching for high dose TiO₂ treatment. Thus, it was observed that TiO₂ at the high dose had delayed hatching as well as embryo killing effect (since 100% eggs did not hatch), and on the other hand, GO–TiO₂ at high dose showed 100% hatching.

The outcome of our study demonstrated that GO–TiO₂ nanocomposite was successfully synthesized and the nanocomposite was effective in reducing the textile dyes crystal violet (CV), brilliant green (BG), malachite green (MG), and rhodamine B (RB), although the effectiveness was different for different kinds of dyes. In the case of BG and MG, there was a complete reduction in the dyes using the nanocomposite, whereas the standard photocatalyst, TiO₂ NPs, alone could not reduce the dye intensity, instead enhanced it. The biocompatibility study using zebrafish embryos also showed that the synthesized GO–TiO₂ nanocomposite was non-toxic to the aquatic environment. However, there are previous reports on the toxicity of TiO₂ nanoparticles *Artemisia absinthium* L, which underwent salinity stress (Shariatzadeh Bami et al. 2021). In vivo reversal of TiO₂ toxicity in rat spermatozoa was also observed using vitamin A and E (Khanvirdiloo et al. 2021). Thus, the dose and exposure route of TiO₂ may pose some threat to the environment. Therefore, our synthesized GO–TiO₂ nanocomposite was very effective in reducing the dyes compared to the standard photocatalytic agent, TiO₂ NPs.

5 Conclusion

The profound use of nanomaterials in the field of bioremediation has been evident in recent years. We attempted to synthesize GO–TiO₂ nanocomposite by solvothermal method and applied it to reduce textile dye. As it is well known that textile dyes are not dissociated when used for dyeing purposes and the unused dyes are rejected as effluent in the water bodies. The engineered GO–TiO₂

nanocomposite could effectively reduce the textile dyes namely crystal violet (CV), brilliant green (BG), malachite green (MG), and rhodamine B (RB). The dyes like MG and BG were usually not reduced by known photocatalyst, TiO₂ NPs, but were completely reduced by our synthesized GO–TiO₂ nanocomposite. The nanocomposite was reducing CV, BG, MG, and RB completely as visible from the absence of color. Further studies for the biocompatibilities of the nanocomposite need to be explored. In the future, studies are warranted using different other types of water contaminants and other textile dyes.

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Availability of data and material All the authors declare that all data and materials support their published claims and comply with field standards.

Declarations

Conflict of Interest The authors have no relevant financial or non-financial interests to disclose. The authors have no conflicts of interest to declare that are relevant to the content of this article. All authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript. The authors have no financial or proprietary interests in any material discussed in this article.

Ethical Approval The manuscript is not to be submitted to more than one journal for simultaneous consideration. The submitted work is original and should not have been published elsewhere in any form or language (partially or in full). A single study is not split up into several parts to increase the quantity of submissions and submitted to various journals or to one journal over time (i.e., 'salami-slicing/publishing'). Results are presented clearly, honestly, and without fabrication, falsification or inappropriate data manipulation (including image-based manipulation). Authors have adhered to discipline-specific rules for acquiring, selecting and processing data. No data, text, or theories by others are presented as if they were the author's own ('plagiarism'). Proper acknowledgements to other works have been given.

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References

- Akhtar N, Metkar SK, Girigoswami A, Girigoswami K (2017) ZnO nanoflower based sensitive nano-biosensor for amyloid detection. *Mater Sci Eng C* 78:960–968
- Al-Musawi TJ, Arghavan SMA, Allahyari E et al (2022) Adsorption of malachite green dye onto almond peel waste: a study focusing on application of the ANN approach for optimization of the effect of environmental parameters. *Biomass Conv Bioref*. <https://doi.org/10.1007/s13399-021-02174-6>
- Amini M, Younesi H, Bahramifar N, Akbar A, Lorestani Z, Ghorbani F, Daneshi A, Sharifzadeh M (2008) Application of response surface methodology for optimization of lead biosorption in an aqueous solution by *Aspergillus niger*. *J Hazard Mater* 154:694–702
- Awang H, Talalah N (2019) Synthesis of reduced graphene oxide-titanium (rGO-TiO₂) composite using a solvothermal and hydrothermal methods and characterized via XRD and UV-Vis. *Nat Resour* 10:17–28. <https://doi.org/10.4236/nr.2019.102002>
- Deepika R, Girigoswami K, Murugesan R, Girigoswami A (2018) Influence of divalent cation on morphology and drug delivery efficiency of mixed polymer nanoparticles. *Curr Drug Deliv* 15(5):652–657
- Desai C, Jain KR, Boopathy R, van Hullebusch ED, Madamwar D (2021) Eco-sustainable bioremediation of textile dye wastewaters: innovative microbial treatment technologies and mechanistic insights of textile dye biodegradation. *Front Microbiol* 2021:12
- Elazab HA, Gadalla MA, Sadek MA, El-Idreesy TT (2019) Hydrothermal synthesis of graphene supported Pd/Fe₃O₄ nanoparticles as efficient magnetic catalysts for Suzuki Cross-Coupling. *Biointerface Res Appl Chem* 9(2):3906–3911. <https://doi.org/10.33263/BRIAC92.906911>
- Giovannetti R, Rommozzi E, Zannotti M, Anna D'Amato C (2017) Recent advances in graphene based TiO₂ nanocomposites (GTiO₂Ns) for photocatalytic degradation of synthetic dyes. *Catalysts* 7:305
- Girigoswami K, Viswanathan M, Murugesan R, Girigoswami A (2015) Studies on polymer-coated zinc oxide nanoparticles: UV-blocking efficacy and *in vivo* toxicity. *Mater Sci Eng C* 56:501–510
- Girigoswami A, Ramalakshmi M, Akhtar N, Metkar SK, Girigoswami K (2019) ZnO Nanoflower petals mediated amyloid degradation—an *in vitro* electrokinetic potential approach. *Mater Sci Eng C* 101:169–178
- Jeyasubramanian K, Muthuselvi M, Hikku GS, Muthusankar E (2019) Improving electrochemical performance of reduced graphene oxide by counteracting its aggregation through intercalation of nanoparticles. *J Colloids Interface Sci* 549:22–32
- Khanvirdiloo S, Ziamajidi N, Moradi A et al (2021) Effects of vitamins A and E on TiO₂ nanoparticles-induced spermatogenesis defects in male Wistar Rats. *Iran J Sci Technol Trans Sci* 45:1191–1200. <https://doi.org/10.1007/s40995-021-01114-3>
- Leary R, Westwood A (2011) Carbonaceous nanomaterials for the enhancement of TiO₂ photocatalysis. *Carbon* 49:741–772
- Lellis B, Fávoro-Polonio CZ, Pamphile JA, Polonio JC (2019) Effects of textile dyes on health and the environment and bioremediation potential of living organisms. *Biotechnol Res Innov* 3(2):275–290
- Linley S, Liu Y, Ptacek CJ, Blowes DW, Gu FX (2014) Recyclable graphene oxide-supported titanium dioxide photocatalysts with tunable properties. *ACS Appl Mater Interfaces* 6(7):4658–4668
- Liu J, Bai H, Wang Y, Liu Z, Zhang X, Sun DD (2010) Self-assembling TiO₂ nanorods on large graphene oxide sheets at a two-phase interface and their anti-recombination in photocatalytic applications. *Adv Funct Mater* 20:4175–4181
- Mittal A, Mittal J, Malviya A, Kaur D, Gupta VK (2010) Adsorption of hazardous crystal violet from waste water by waste materials. *J Colloid Interface Sci* 343:463–473
- Nelson CR, Hites RA (1980) Aromatic amines in and near the Buffalo River. *Environ Sci Technol* 14(9):1147–1149
- Obodo RM, Ahmad I, Ezema FI (2019) Introductory chapter: graphene and its applications. In: Ahmad I, Ezema FI (eds) *Graphene and its derivatives—synthesis and applications*. IntechOpen. <https://doi.org/10.5772/intechopen.86023>
- Raliya R, Avery C, Chakrabarti S, Biswas P (2017) Photocatalytic degradation of methyl orange dye by pristine titanium dioxide, zinc oxide, and graphene oxide nanostructures and their composites under visible light irradiation. *Appl Nanosci* 7(5):253–259
- Ram C, Pareek RK, Singh V (2012) Photocatalytic degradation of textile dye by using titanium dioxide nanocatalyst. *Int J Theor Appl Sci* 4(2):82–88
- Rosu M-C, Coros M, Pogacean F, Magerusan L, Socaci C, Turza A, Pruneanu S (2017) Azo dyes degradation using TiO₂-Pt/graphene oxide and TiO₂-Pt/reduced graphene oxide photocatalysts under UV and natural sunlight irradiation. *Solid State Sci*. <https://doi.org/10.1016/j.solidstatesciences.2017.05.013>
- Scarpelli F, Mastropietro TF, Poerio T, Godbert N (2018) Mesoporous TiO₂ thin films: state of the art. In: Yang D (ed) *Titanium dioxide—material for a sustainable environment*. IntechOpen. <https://doi.org/10.5772/intechopen.74244>. Available from: <https://www.intechopen.com/chapters/59572>
- Senthilkumar S, Kalaamani P, Subburaam CV (2006) Liquid phase adsorption of crystal violet onto activated carbons derived from male flowers of coconut tree. *J Hazard Mater* 136(3):800–808
- Shariatzadeh Bami S, Khavari-Nejad RA, Ahadi AM et al (2021) TiO₂ nanoparticles effects on morphology and physiology of *Artemisia absinthium* L. under salinity stress. *Iran J Sci Technol Trans Sci* 45:27–40. <https://doi.org/10.1007/s40995-020-00999-w>
- Shi J-W, Ai H-Y, Chen J-W, Cui H-J, Fu M-L (2014) The composite of nitrogen-doped anatase titania plates with exposed 001 facets/graphene nanosheets for enhanced visible-light photocatalytic activity. *J Colloid Interface Sci* 430:100–107
- Somanathan T, Prasad K, Ostrikov KK, Saravanan A, Krishna VM (2015) Graphene oxide synthesis from agro waste. *Nanomaterials (basel)* 5(2):826–834. <https://doi.org/10.3390/nano5020826>
- Tayel A, Ramadan AR, El Seoud OA (2018) Titanium dioxide/graphene and titanium dioxide/graphene oxide nanocomposites: synthesis, characterization and photocatalytic applications for water decontamination. *Catalysts* 8:491
- Vedhantham K, Girigoswami A, Harini A, Girigoswami K (2022) Waste water remediation using nanotechnology—a review. *Biointerface Res Appl Chem* 12(4):4476–4495
- Venkatachalam N, Palanichamy M, Murugesan V (2007) Sol-gel preparation and characterization of nanosize TiO₂: its photocatalytic performance. *Mater Chem Phys* 104:454–459
- Yaseen DA, Scholz M (2019) Textile dye wastewater characteristics and constituents of synthetic effluents: a critical review. *Int J Environ Sci Technol* 16:1193–1226. <https://doi.org/10.1007/s13762-018-2130-z>
- Yoo D-H, Cuong TV, Pham VH, Chung JS, Khoa NT, Kim EJ, Hahn SH (2011) Enhanced photocatalytic activity of graphene oxide decorated on TiO₂ films under UV and visible irradiation. *Curr Appl Phys* 11:805–808
- Zaaba NI, Foo KL, Hashim U, Tan SJ, Liu W-W, Voon CH (2017) Synthesis of graphene oxide using modified hummers method: solvent influence. *Proc Eng* 184:469–477



- Zhang Y, Tang Z-R, Fu X, Xu Y-J (2010a) TiO₂ graphene nanocomposites for gas phase photocatalytic degradation of volatile aromatic pollutant: is TiO₂ graphene truly different from other TiO₂ carbon composite materials? *ACS Nano* 4(12):7303–7314
- Zhang H, Lv X, Li Y, Wang Y, Li J (2010b) P25-graphene composite as a high performance photocatalyst. *ACS Nano* 4:380–386
- Zindani D, Kumar K (2019) Graphene-based polymeric nanocomposites: an introspection into functionalization, processing techniques and biomedical applications. *Biointerface Res Appl Chem* 9(3):3926–3933. <https://doi.org/10.33263/BRIAC93.926933>