Titanium Dioxide/Graphene and Titanium Dioxide/Graphene Oxide Nanocomposites: Synthesis, Characterization and Photocatalytic Applications for Water Decontamination

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Abstract: The use of titanium dioxide, TiO₂ as a photocatalyst in water decontamination has witnessed continuous interest due to its efficiency, stability, low toxicity and cost-effectiveness. TiO₂ use is limited by its large band gap energy leading to light absorbance in the UV region of the spectrum, and by the relatively fast rate of recombination of photogenerated electrons and positive holes. Both limitations can be mitigated by using carbon-TiO₂ nanocomposites, such as those based on graphene (G) and graphene oxide (GO). Relative to bare TiO₂, these nanocomposites have improved photocatalytic activity and stability under the UV–visible light, constituting a promising way forward for improved TiO₂ photocatalytic performance. This review focuses on the recent developments in the chemistry of TiO₂/G and TiO₂/GO nanocomposites. It addresses the mechanistic fundamentals, briefly, of TiO₂ and TiO₂/G and TiO₂/GO photocatalysts, the various synthesis strategies for preparing TiO₂/G and TiO₂/GO nanocomposites, and the different characterization techniques used to study TiO₂/G and TiO₂/GO nanocomposites. Some applications of the use of TiO₂/G and TiO₂/GO nanocomposites in water decontamination are included.

Keywords: TiO₂; graphene; graphene oxide; surface properties; photocatalytic applications; water decontamination

1. Introduction

Addressing environmental pollution is a top priority worldwide [1,2]. In this respect, the remediation of wastewater from organic contaminants presents an increasingly urgent need in order to address the associated environmental and public health negative impacts, and the surge in water reuse needs due to global water shortages. The textile dyeing and finishing industry is one of the most chemically intensive sectors and is ranked as number two polluter of clean water, after agriculture [3]. The potential magnitude of the environmental problems associated with wastewater from this industrial sector can be appreciated by considering the large number, 100,000, of commercially available dyes, with over $7 \times 10^5$ tons of dye-stuff produced annually [4]. This, coupled with the incomplete degradation of these dyes due to their chemical stability, contribute to the significance of this type of pollution. Thus, reactive azo dyes that constitute 65–70% of all dyes produced [5], are not totally degraded by conventional wastewater treatment processes that involve light, chemicals or activated sludge [6–8]. Additionally, a fraction of these dyes (estimated between 2% and 10%) is discharged directly into aqueous effluents or lost during the textile dyeing process [9].
Removal of these contaminants using efficient and environmentally-friendly methods is crucial [10,11]. Various strategies are utilized for wastewater treatment such as reverse osmosis, ultrafiltration, evaporation and solvent extraction. However, these techniques remove contaminants from water without converting them into harmless end-products [12]. Complete degradation can be readily achieved by oxidation, either chemically or photochemically [13]. The aim of any oxidative process is to produce and use hydroxyl free radical (HO•) as a strong oxidant to degrade pollutants. Hydrogen peroxide is used as an oxidant after activation, by metal ions for example as in Fenton reagent [6], or by UV radiation [14].

Photocatalytic processes, including oxidation, provide an attractive alternative because they rely on using the radiation energy to promote the required degradation. Examples of photocatalytic processes are dye decomposition [15], water/air purification [16,17], filtration [18] and self-cleaning applications [19]. Specifically, TiO₂ has been used as a photocatalyst in wastewater treatment of dyes [12,20–22], hormones [23], pharmaceuticals [24,25], industrial wastewater [26], and microbial disinfection [27–29].

Though anatase and rutile are the commonly used crystal phases of TiO₂ in photocatalytic reactions, amorphous TiO₂ has also been reported for enhanced photocatalytic activity as a result of surface defects leading to higher electron transfer [30–32]. This has also been reported for anatase [33–37]. The measured photocatalytic activity is found to depend not only on the crystal phases used, and the modifications carried out on the photocatalyst, but also the contaminant undergoing photocatalysis [38–40].

Rutile, the more thermodynamically stable polymorph, has a band gap value of ca. 3.0 eV. On the other hand, anatase has higher charge-carrier mobility and greater photocatalytic activity [41]. Its use is associated, however, with the rapid recombination between the positive holes on the TiO₂ surface and the photoinduced electrons, which reduces the overall photocatalytic efficiency. Moreover, its band gap is ca. 3.2 eV, meaning that it absorbs light radiation in the UV region of the solar spectrum, that represents 4% of the solar radiation [42–44]. Therefore, it is essential to decrease the energy of this band gap, leading to light absorption by TiO₂ in the visible region that represents 42% of solar radiation. This means a large enhancement in the light harvesting power of TiO₂-based material [45,46].

The photocatalytic activity of TiO₂ can be improved by doping with transition metals such as V, Ni and Cr, or with nonmetals such as N and S. Carbon-TiO₂ composites, including graphene (G) and graphene oxide (GO), provide enhanced photocatalytic activity and stability under UV light irradiation, relative to TiO₂ [47–49]. Although TiO₂ doping might lead to higher photocatalytic activity [50–55], increased surface area with improved contaminant adsorption are advantages of TiO₂/G and TiO₂/GO composites [56–59]. Furthermore, TiO₂/G and TiO₂/GO exhibit comparable photostability to doped TiO₂ [55,60–62].

Graphene is a carbon allotrope that exists of one atom thick layers arranged in a honeycomb two-dimensional (2D) crystal structure. It has shown remarkable optical, electrical, catalytic, thermal, and mechanical properties leading to numerous applications [63]. Graphene has very high electron mobility and a high surface area making it an attractive material for photocatalysis applications [64,65].

Graphene oxide is produced by oxidation of high purity graphite. It possesses unique properties that are different from those of G due to the existence of various oxygenated functional groups on the surface of GO sheets. These properties include attractive optical properties (GO is used as fluorescence labels [66]), high dispersibility in various polar solvents and the ability to attach diverse molecular structures on its surface, e.g., by hydrogen bonding. These properties facilitate the adsorption of various molecular structures on its surface, leading to a better control of the size, and the shape of the formed structures. In addition, the average cost of producing GO is smaller compared with those of G and several other nanomaterials. These remarkable properties are extremely beneficial in making TiO₂/GO nanocomposites. The relative hydrophilicity of GO, due to the highly oxygenated surface facilitates its interaction with aqueous dispersions of TiO₂, leading to the formation of strong,
chemically-bonded TiO$_2$/GO nanocomposites. This good dispersibility in aqueous solutions is not easily achievable with G without adding a dispersant [67,68].

Figure 1 shows the increase in the number of scientific publications and citations regarding TiO$_2$/G and TiO$_2$/GO nanocomposites during the past decade. The significant increase for the last five years is a clear evidence of the significance of the subject.

![Graph showing the increase in the number of publications and citations](image)

**Figure 1.** Total number of publications with the keywords “Titanium dioxide and graphene” and “Titanium dioxide and graphene oxide”, based on data from Web of Science database.

Figure 2 illustrates the main mechanistic steps for TiO$_2$ photocatalytic activity. The photo-reduction phase involves the excitation of electrons from the valence band (VB) to the conduction band (CB) with the formation of positive holes (h$^+$) after the absorption of light photons of proper energy. These photo-generated electrons and positive holes emerge to the TiO$_2$ surface and react with the adsorbed species. The photo-generated electrons react with the adsorbed oxygen to form hydroxyl radicals (OH*) and super-oxide radicals (O$_2$•$^-$). The formed radicals are highly reactive and represent the main intermediates in the oxidation of organic pollutants. Moreover, adsorbed hydroxyl ions and water molecules are oxidized by the positive holes formed in the CB to give hydroxyl radicals (OH*) which, in turn, degrade the organic pollutants to harmless end-products. This is known as the photo-oxidation phase [69,70].

![Diagram illustrating the main steps of TiO$_2$ photocatalysis](image)

**Figure 2.** Principles of TiO$_2$ photocatalysis.

The main steps involved in TiO$_2$ photocatalysis are summarized in Equations (1)–(6).

$$\text{TiO}_2 + \text{hv} \rightarrow \text{TiO}_2^* (e^- + h^+) \quad (1)$$
\[
\begin{align*}
\text{H}_2\text{O} + h^+ & \rightarrow \text{HO}^+ + \text{H}^+ \\ (2) \\
e^- + \text{O}_2 & \rightarrow \text{O}_2^{\bullet -} \\ (3) \\
\text{O}_2^{\bullet -} + \text{H}^+ & \rightarrow \text{HO}_2^* \\ (4) \\
\text{H}^+ + \text{O}_2^{\bullet -} + \text{HO}_2^* & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \\ (5) \\
\text{H}_2\text{O}_2 + h\nu & \rightarrow 2 \text{HO}^* \\ (6)
\end{align*}
\]

Recently, G and GO have been the subject of various studies where they were used to form composite materials with TiO\(_2\) with improved photocatalytic performance. This improvement is achieved by one or more of the following schemes: (1) Enhancement of the surface area of TiO\(_2\) due to its interaction with the two-dimensional matt structure of G and GO; (2) Enhancement of the adsorption of aromatic contaminants due to their strong \(\pi-\pi\) interactions with the aromatic network of G and GO; and (3) Decrease of the rate of re-combination between the positive holes and the photogenerated electrons due to the substantial electronic conductivity of G and GO that act as an electron sink for the photo-generated electrons on the surface of TiO\(_2\) [71–74].

The enhancement of the photocatalytic activity of TiO\(_2\) using G and GO is illustrated in Figures 3 and 4. In addition, some reports explained the role of G itself in the photodegradation of methylene blue (MB) using TiO\(_2\)/G nanocomposites through the formation of OH\(^\bullet\) using the photogenerated electrons on its surface [75,76].

Reviews on TiO\(_2\) photocatalysis have recently been published by Schneider [1], Xu [77], Dahl [78], and Fang [79] and on G-based photocatalysts by Chowdhury [70], Upadhyay [80], and Cao [81]. Comprehensive reviews on TiO\(_2\)/G and TiO\(_2\)/GO composites were presented by Tan [75], Torres [82], energy applications [83], and environmental applications [84]. Considering the significant increase in the number of publications on this topic, shown in Figure 1, together with the number of citations of these publications, we consider this updated review as timely and of wide interest.

In this respect, this review aims to update researchers in the field of TiO\(_2\)/G and TiO\(_2\)/GO nanocomposites with the most recent developments, as well as providing newcomers to this rapidly growing field with an up to date summary on TiO\(_2\)/G and TiO\(_2\)/GO nanocomposites synthesis, characterization, and applications. The detailed characterization section, which is unique to this review, aims at providing a guide to the different commonly used techniques for the elucidation of macroscopic and microscopic properties of TiO\(_2\)/G and TiO\(_2\)/GO nanocomposites. Additionally, some photocatalytic applications of TiO\(_2\)/G and TiO\(_2\)/GO nanocomposites in wastewater treatment are summarized, focusing on recent applications. A summary of the TiO\(_2\)/G and TiO\(_2\)/GO synthesis, characterization, and photocatalytic applications for the decomposition of water contaminants is given in Table S1 of supporting information.
The synthesis techniques used for the preparation of TiO\(_2\)/G and TiO\(_2\)/GO nanocomposites include hydrothermal (HT), solvothermal (ST), mechanical mixing with or without sonication, sol-gel techniques, deposition techniques of liquids (LPD), aerosol (AD), chemical vapor (CVD), spin coating, and electrospinning.

2. Synthesis of TiO\(_2\)/G and TiO\(_2\)/GO Nanocomposites

The synthesis techniques used for the preparation of TiO\(_2\)/G and TiO\(_2\)/GO nanocomposites include hydrothermal (HT), solvothermal (ST), mechanical mixing with or without sonication, sol-gel techniques, deposition techniques of liquids (LPD), aerosol (AD), chemical vapor (CVD), spin coating, and electrospinning.
and electrospinning. Unless otherwise specified, PTFE-lined autoclaves are employed for heating reaction mixtures above the boiling point of the solvent employed.

2.1. The Hydrothermal (HT) Method

The term hydrothermal synthesis refers to a technique for growing crystals from an aqueous solution in an autoclave at high temperature and pressure. The key steps in the HT preparation of TiO\(_2\)/G and TiO\(_2\)/GO nanocomposites are illustrated in Figure 5. Elevated pressures allow the use of low boiling point solvents, in particular, water. This use is beneficial as the majority of high boiling point solvents, such as dimethyl sulfoxide (DMSO), are either expensive or have some toxicity. The use of elevated temperatures produces high-quality crystals of the desired nanomaterial. HT synthesis allows the control of the composition and quality of the formed nanocrystals. However, the inability to monitor material crystal growth (in the autoclave) and the equipment cost are the main limitations associated with this method [85-88]. The HT reaction is used for the formation of the TiO\(_2\)/G nanocomposites and in the partial reduction of the GO into G [89].

![Figure 5. Schematic diagram of the HT synthesis of TiO\(_2\)/G nanocomposites, adapted with permission from reference [90]. Copyright 2014 Elsevier.](image)

The HT method uses TiO\(_2\) nanoparticles or nanowires as the source of TiO\(_2\) [91,92]. Other TiO\(_2\) precursors, such as TiCl\(_4\), TiF\(_4\), titanium nitride (TiN), (NH\(_4\))\(_2\)TiF\(_6\), tetrabutyl-titanate (TBT) or Ti (IV) isopropoxide, to produce TiO\(_2\) nanoparticles are other alternatives to produce TiO\(_2\)/G and TiO\(_2\)/GO nanocomposites [93]. TiCl\(_4\) and GO were used in one-step HT synthesis of TiO\(_2\)/G as the reduction of GO to G and the hydrolysis of TiCl\(_4\) to TiO\(_2\) nanoparticles were attained simultaneously. The formed TiO\(_2\) nanoparticles were bi-phasic; including both anatase and rutile phases. FTIR characterization confirmed the incomplete reduction of GO. The effect of different GO amounts in the formed nanocomposites was studied with the composite of 2 wt% GO showing the best photocatalytic activity in the degradation of rhodamine B dye. The presence of reduced GO in the formed TiO\(_2\)/G nanocomposites improved the photocatalytic activity by increasing the surface area, as confirmed using N\(_2\) Desorption Isotherms, giving more active sites, and producing more reactive species [89]. Similar results were reported by Li using different amounts of commercial TiO\(_2\) (P25) in aqueous dispersions of GO, followed by heating at 120 °C for 3 h in absence of reducing agents. The results showed that increasing the amount of G in the formed TiO\(_2\)/G nanocomposites is accompanied by an increase in the surface area and the adsorption capacity for dyes [94]. Uniform TiO\(_2\) nanoparticles distribution on the surface of G sheets was successfully achieved by Bai using the HT technique [93]. TiF\(_4\) was used as a TiO\(_2\) precursor, HI was used as a reducing agent for GO and morphology controlling agent. Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), FTIR and Raman spectroscopy were used to confirm the results. The formed TiO\(_2\)/G nanocomposites showed high stability under both visible (\(\lambda = 400 \text{ nm}\)) and UV (\(\lambda = 365 \text{ nm}\)) light irradiation. The improved photocatalytic activity of TiO\(_2\)/G nanocomposites compared to bare TiO\(_2\) was ascribed to the reduction in the electron-hole recombination rate in the formed nanocomposites. The effect of the medium pH on the photocatalytic activity of the formed nanocomposites was studied and found that increasing the pH value resulted in an increase in the photocatalytic degradation of bisphenol A (BPA). Optimum
degradation of BPA was at pH 11, where alkaline medium induces the production of more \( \text{HO}^* \) and improves the photocatalytic activity [93].

Nitrogen-doped anatase and G were used to synthesize N-doped TiO\(_2\)/G nanocomposites with enhanced photocatalytic activity by the HT method. The TiN solid powder served as the precursor of the N-doped TiO\(_2\) nanoparticles and GO was partially reduced during the HT reaction [95]. Gu reported the HT preparation of N-doped, N and V co-doped TiO\(_2\)/G and TiO\(_2\)/GO nanocomposites with higher visible light photocatalytic activity than bare TiO\(_2\) under visible light irradiation [90]. Amine-functionalized TiO\(_2\) nanoparticles with surface positive charges improved the interaction with GO sheets with surface negative charges. The wrapping of TiO\(_2\) with G and partial reduction of GO were achieved during the HT reaction [96,97]. Furthermore, amine-functionalized TiO\(_2\) nanoparticles, were used to prepare recyclable magnetic TiO\(_2\)/G nanocomposites using magnetic Fe\(_3\)O\(_4\) nanoparticles coating silica substrates. The recyclable magnetic TiO\(_2\)/G nanocomposites showed improved photocatalytic activity, due to the presence of G which acted as an electron sink for the photoinduced electrons. Nanocomposite recovery was achieved using a magnetic field [98].

The HT method was used by Ariffin to produce a photocatalytic filtration system for water treatment applications. TiO\(_2\)/G nanocomposites were deposited on a polypropylene porous filter. Titanium (IV) isopropoxide, as a TiO\(_2\) precursor, in triethanolamine (TEA) was added to GO suspension in aqueous ethanol and stirred at room temperature. It was then placed in contact with the polypropylene porous filter and heated to 120 °C for 24 h. The polypropylene filter thus modified with TiO\(_2\)/G exhibited high mechanical stability and improved photocatalytic activity, as measured by photodegradation of methylene blue and repeated for five cycles, as compared with the filter with TiO\(_2\) only [99].

Nguyen investigated the effect of temperature variation on the surface area and crystal phase during the HT synthesis of TiO\(_2\)/G flower-like nanocomposites. The results showed that lower temperatures resulted in amorphous samples with larger surface area. On the other hand, higher temperatures resulted in the formation of the TiO\(_2\) anatase crystalline phase with lower surface areas for the prepared nanocomposites. This conclusion was based on the results of x-ray diffraction (XRD), SEM, nitrogen adsorption, and Raman spectroscopy [100]. Flower-like TiO\(_2\)/G nanocomposites can be prepared using dropwise addition of acetic acid. The flower-like configuration improved the photodegradation of rhodamine B and trichloroethylene which was ascribed to the large increase in the surface area [101]. Furthermore, Zhang reported the importance of calcination of the hydrothermally prepared TiO\(_2\)/G nanocomposites to restore some surface oxygenated functional groups and improve TiO\(_2\) crystallinity. Calcined samples showed better photocatalytic activity in degradation of methyl orange dye and disinfection of \textit{E. coli}, compared to uncalcined TiO\(_2\)/G nanocomposites [102].

Facile, one-step HT reaction was used to prepare a TiO\(_2\)/G nanocomposites hydrogel with three-dimensional hierarchical inter-connected channels by Zhang. Compared with TiO\(_2\), the prepared hydrogel showed increased activity as a photocatalyst, as a dye-adsorbent, and as a supercapacitor. This was attributed to improved photocatalytic activity, enhanced adsorption capacity, and increased electrochemical capacitive performance [103]. Ascorbic acid can be used as reducing agent and crosslinker in the formation of three-dimensional TiO\(_2\)/G aerogels with high stability, recyclability, and improved photocatalytic activity, as reported by Li [104] recently, TiO\(_2\)/G nanocomposite foams were prepared using TBT and G foams in an HT process. The prepared foams exhibited larger surface area, photocatalytic activity and light absorption than TiO\(_2\) nanorods, as reported by Men [105].

An alkaline HT process, using NaOH, was used to transform commercial TiO\(_2\) (P90) to TiO\(_2\) nanotubes, and simultaneously reduce GO to G, giving TiO\(_2\) nanotube-G nanocomposites [91]. The same approach was used by Pan to obtain TiO\(_2\) nanowires-G nanocomposites. Aqueous solutions of KOH and commercial TiO\(_2\) (P25) were heated at 200 °C for 24 h. The produced TiO\(_2\) nanowires were added to GO aqueous suspension, and the mixture heated at 120 °C for 3 h. The TiO\(_2\) nanowires were more uniformly distributed on the G surface, with less aggregation than TiO\(_2\) nanoparticles, leading to
improved adsorption and photocatalytic activity [106]. Similar results were recently reported by other research groups [107,108].

The effect of glycerol during the HT synthesis of nanocomposites was studied by Shao. Glycerol inhibited the growth and agglomeration of TiO$_2$ in the solution and prevented the stacking of G sheets producing ultrafine TiO$_2$ nanoparticles of ca. 4 nm diameter homogeneously distributed on the G surface. This resulted in a large surface area, efficient charge separation, and high photocatalytic activity, towards rhodamine B and methylene blue degradation, for TiO$_2$/G nanocomposites prepared in the presence of glycerol [109].

Recently, graphene quantum dots (GQDs) were introduced as an excellent electron transfer agent that can improve the photocatalytic activity of TiO$_2$ effectively. Qu used the HT method to prepare TiO$_2$ nanotubes/GQDs nanocomposites with superior photocatalytic activity towards dye degradation, as methyl orange. The photocatalytic enhancement by GQDs was ascribed to three factors: efficient light absorption, improved photogenerated electron-pair separation, and photosensitization properties of GQDs [110]. TiO$_2$/GQDs nanocomposites exhibited superior photocatalytic activity in hydrogen evolution and photodegradation of dyes [111,112]. N-doped GQDs/TiO$_2$ nanocomposites were prepared hydrothermally using ethylenediamine and citric acid as N and C precursors. The prepared N-doped GQDs/TiO$_2$ nanocomposites showed excellent photocatalytic activity in the photocatalytic degradation of MB dye under UV light illumination [113]. N,S co-doped GQDs/G/TiO$_2$ nanocomposites were prepared by alkaline HT process and improved the photocatalytic degradation of methyl orange dye under visible light illumination [114].

2.2. The Solvothermal (ST) Method

Akin to the definition given in Section 2.1, the term solvothermal synthesis refers to a method for growing crystals from a non-aqueous solution using an autoclave at high temperature and pressure. As shown in Figure 6, The ST method of synthesis is similar to the HT counterpart, except that non-aqueous solvents are employed to yield the TiO$_2$/G nanocomposites. The ST method usually provides better control over the size distribution, shape and crystallinity of the prepared nanomaterials compared to the HT method, probably due to a combination of the solvent properties such as viscosity and polarity (relative to those of water) and higher temperatures used [86].

![Figure 6](image_url)

**Figure 6.** A schematic representation of the ST-based synthesis of TiO$_2$/G nanocomposites. Reprinted with permission from reference [115]. Copyright 2012 Elsevier.

Wang used a one-step ST method for the synthesis of G/CNTs (carbon nanotubes)/TiO$_2$ composites. They mixed GO, multi-wall carbon nanotubes (MWCNTs) and tetrabutyl titanate (TBT), as a TiO$_2$ precursor, in 2-propanol. The photodegradation of methylene blue dye and photo-reduction of Cr(VI) under UV light illumination were doubled compared to TiO$_2$/G nanocomposites. The photocatalytic activity of the prepared nanocomposites was dependent on the CNTs content, with 5 wt% CNTs as the optimal mass ratio. The addition of CNTs improved the photocatalytic efficiency by increasing the rate of HO$^\bullet$ formation, as confirmed using the fluorescence intensity of 2-hydroxyterephthalic acid [116].
In a study by Qian, N-doped TiO$_2$/G nanocomposites were prepared by heating a mixture of TBT, G, ammonium hydroxide in 2-propanol to 180 °C. Density functional theory (DFT) calculations were employed to explain the improvement in the photocatalytic activity after adding G to the N-doped TiO$_2$. It was suggested that N-doping generates empty states in the band gap of TiO$_2$ that lie beneath the Fermi energy levels of G. These states become filled with electrons when N-doped TiO$_2$ is in contact with G, causing ascending shift in the energy of TiO$_2$ bands, relative to G. This band position across the TiO$_2$/graphene hetero-junction results in energetically more favorable transfer of the photoexcited electrons, leading to a better photocatalytic activity [117].

Li used two TiO$_2$ precursors, TiCl$_4$ and titanium (IV) isopropoxide, with GO. Pluronic P123, a triblock copolymer based on poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) and a nonionic surfactant, was also used to prevent the agglomeration of TiO$_2$ nanoparticles and to increase the surface area of the prepared nanocomposites. This resulted in a sol that formed the required TiO$_2$/G nanocomposites upon ST treatment at 150 °C for 24 h. The formed nanocomposites exhibited high photocatalytic activity and stability under visible light and simulated sunlight illumination. This efficiency was ascribed to the improved textural properties, band gap narrowing and improved quantum efficiency of the produced nanocomposites [118].

Huang prepared chemically-bonded TiO$_2$/G nanocomposites prepared by dropwise addition of TBT ethanol solution to aqueous G dispersions containing known concentrations of G, followed by stirring and heating at 200 °C for 10 h. The resulting nanocomposites exhibited improved photocatalytic properties compared to the TiO$_2$/G nanocomposites prepared by mechanical mixing. The synergistic effect between TiO$_2$ and G through the formation of Ti–C chemical bonds increased the number of electron holes on the surface of TiO$_2$ and decreased the electron-hole pair recombination rates. This was confirmed by x-ray photoelectron spectroscopy (XPS) and photoluminescence (PL) spectroscopy [119].

Reduction of GO into G can be accomplished by adding glacial acetic acid during the ST process. Min added titanium (IV) isopropoxide to GO dispersion in acetic acid/ethanol solution. The mixture was stirred then heated at 120 °C for 24 h. The reduction of GO and deposition of TiO$_2$ onto G nanosheets were achieved during the ST process. The prepared TiO$_2$/G nanocomposites exhibited high photocatalytic activity under visible light illumination due to the formation of Ti–C and Ti–O–C chemical bonds at the hetero-junction as confirmed by XPS [120].

The morphology and shape of the formed TiO$_2$/G nanocomposites can be controlled using ethylene glycol as reported by Cai. Graphene nanosheets were sonicated with a TiCl$_4$ solution in this diol, and the mixture was heated at 180 °C for 12 h. The electrochemical behavior of the formed nanocomposites was investigated using coin-type cells against metallic lithium. High specific charge capacity was achieved, and the formed nanocomposites exhibited improved electrochemical performance [115]. Xie used glucose as a morphology controlling agent after addition to titanium (IV) isopropoxide/GO mixture in 2-propanol followed by H$_2$ reduction. The results showed that low glucose content can bridge chemically, through the surface hydroxyl groups, between GO surface and TiO$_2$ nanoparticles thus, results in well-dispersed TiO$_2$/G nanocomposites [121].

The morphology and shape of the prepared nanocomposites can also be controlled using HF as reported by Gu who synthesized TiO$_2$/G nanocomposites with exposed [001] facets through a one-step ST process. The nanocomposites were synthesized by adding TBT to GO suspension in 2-propanol followed by stirring. HF was added, followed by heating the mixture at 180 °C for 12 h. The trapping test, using ethylenediaminetetraacetic (EDTA) acid disodium salt as hole scavenger and tert-butanol as a radical scavenger, showed that the improvement in the photocatalytic activity was attributed mainly to the photogenerated holes in TiO$_2$ surface rather than the electrons transferred to G sheets [122].

2.3. Mechanical Mixing

This strategy is gaining attention due to its relative simplicity and the facile control of the reaction conditions. This method involves mixing dispersions of TiO$_2$ (either pristine or functionalized) and G or GO, possibly followed by sonication and stirring to provide maximum contact between
the nanocomposite starting materials [123], as illustrated in Figure 7. Gao prepared TiO2/GO nanocomposites by mixing TiO2 nanoparticles with GO dispersion in water, sonating and stirring, followed by centrifugation and vacuum drying to produce the TiO2/GO nanocomposites. The improvement in the photocatalytic activity was ascribed to the increase in the light absorption ability and effective electron-hole charge separation after mixing [124].

Figure 7. Schematic representation of the synthesis of TiO2/GO nanocomposites by mechanical mixing and sonication. Reprinted with permission from reference [17]. Copyright 2013 Elsevier.

Large-scale production of TiO2/GO nanocomposites (NRCs) was achieved by Liu using a two-phase system: GO dispersion in water and TiO2 nanorods dispersed in toluene. The oleic acid (dispersant)-capped TiO2 nanorods were synthesized by mixing tert-butylamine in water and titanium (IV) isopropoxide in oleic acid, followed by heating at 180 °C for 6 h. These nanorods were then added to GO aqueous dispersion with stirring at room temperature to ensure efficient co-ordination between GO and TiO2 nanorods (no sonication employed). The prepared TiO2/GO NRCs exhibited improved photocatalytic degradation of dyes and antibacterial activity compared to bare TiO2 nanorods and TiO2/GO nanoparticle composites, ascribed to the availability of more [101] facets and the effective electron-hole charge separation [125].

TiO2/GO nanocomposites were synthesized by mixing in water, followed by sonication for 90 min. The photocatalytic activity of these nanocomposites increased as a function of increasing the GO content up to 10 wt% [126], in accordance with other reported results [94]. Thermal exfoliation of GO followed by treatment with nitric and sulfuric acids under sonication, was used to prepare carboxy-functionalized G. The as-prepared carboxy-functionalized G was added to the TiO2 nanoparticles surface, as confirmed by FTIR, XRD, SEM, TEM, and Raman spectroscopy. The higher photocatalytic activity was attributed to the improved attachment of TiO2 on the functionalized surface of the G sheets [127].

The reduction of GO to G can be achieved using UV light irradiation, heat, or chemical reducing agents during the synthesis process. Ghasemi prepared TiO2/G nanocomposites by the simple mixing of TiO2 and GO suspensions with sonication followed by the reduction of GO to G using UV light irradiation. The reduction of GO to G and the formation of Ti–C bonds were confirmed by XPS. The TiO2/G nanocomposites were then doped with Pt and Pd and the Pt–TiO2–G nanocomposites showed the highest photocatalytic activity [17]. These results were corroborated with recent work conducted by Shengyan [128]. UV irradiation was also used to reduce GO to G in the synthesis of G-coated TiO2 nanocomposites. These led to an increase in photocatalytic hydrogen production, and photo-current generation, which was ascribed to the favorable interfacial charge transfer between TiO2 and G nanosheets [129]. The same reduction procedure was used to produce
TiO$_2$/G nanocomposite films by drop- and spin-casting onto fluorinated tin-oxide slides. The films exhibited better electron lifespan and improved photocurrent generation [130].

Thermal treatment of TiO$_2$/GO composites under inert atmosphere was reported to partially reduce the surface oxygenated groups of GO resulting in TiO$_2$/G nanocomposites with improved photocatalytic activity. The results showed that the charge separation in the TiO$_2$/G nanocomposites is more efficient relative to the TiO$_2$/GO nanocomposites. Additionally, increasing the GO content beyond 1.4 wt% reduced the photocatalytic performance, similar results were reported by Zhang [71,123].

2.4. Sol-Gel Methods

Sol-gel methods involve the synthesis of inorganic ceramics from solution by transforming the liquid precursor to a sol that gradually develops into a gel network structure [131]. The sol is a colloidal suspension that is formed by hydrolysis and condensation of the metal-alkoxide precursor. Sol-gel methods for TiO$_2$-based nanocomposites involve the hydrolysis of an appropriate TiO$_2$ precursor, usually a Ti alkoxide, followed by condensation in the presence of G or GO. An important advantage of sol-gel methods is the fact that elevated temperatures and pressures are not needed. Other advantages include reliability, controllability and low cost are reflected in sol-gel preparation of TiO$_2$/G nanocomposites [132]. The formation of Ti–O–C and Ti–O–Ti bonds is favored with low hydrolysis rate, low quantities of water, and the presence of excess Ti precursor [16,86]. The addition of TiO$_2$ precursors to the GO dispersions leads to the formation of relatively stable oxo- and hydroxo-bonds between TiO$_2$ and G surfaces leading to the formation of sols, then of gel-like network structures with the addition of more GO. These structures produce the desired nanocomposites upon drying and/or calcination as shown in Figure 8.

![Graphene sheets (GSs) to TiO$_2$/GSs (sol-gel preparation)](image_url)

**Figure 8.** Schematic diagram of the sol-gel preparation of TiO$_2$/GO nanocomposites. Reprinted with permission from reference [133]. Copyright 2010 Royal Society of Chemistry.

Štengl used TiO$_2$ peroxo-complexes as a precursor to prepare TiO$_2$/GO nanocomposites with varying GO contents using a one-step sol-gel method. NaOH and hydrogen peroxide were used to hydrolyze titanium oxysulfate (TiOSO$_4$) and produce a TiO$_2$ peroxo-complex [16]. In order to prepare TiO$_2$/G nanocomposites, Liu used titanium (IV) isopropoxide as the TiO$_2$ precursor, and reduced GO into G using hydrazine hydrate. The nanocomposites were formed by the dropwise addition of the Ti precursor into a mixture of G and the cationic surfactant cetyltrimethylammonium bromide in ethanol under stirring. Water was added to the mixture, and the suspension was stirred, dried and annealed at 500 °C for 5 min [134]. Titanium oxysulfate was used as a TiO$_2$ precursor by Park in a sol-gel process to prepare CdS-G-TiO$_2$ nanocomposites with improved photocatalytic activity under visible light illumination. The nanocomposites were synthesized by adding titanium oxysulfate precursor to CdS-G composites, previously prepared by mixing CdCl$_2$, Na$_2$S and GO, followed by drying and heating at 500 °C. CdS improved the photocatalytic degradation of methylene blue under visible light illumination, due to bandgap narrowing and enhanced visible light absorption [135].
2.5. Deposition Techniques: Liquid Phase Deposition (LPD), Aerosol Deposition (AD), Chemical Vapor Deposition (CVD), and Electrospinning

These techniques share the advantages of simplicity of the experimental procedure and formation of the nanocomposites at relatively low temperatures. The term liquid phase deposition, LPD, refers to the slow hydrolysis of a metal–fluoro complex \([\text{MF}_n]^{m-n}\) from an aqueous solution by addition of water to produce thin oxide films. Complexing agents are used to collect the liberated fluoride ions, e.g., boric acid or aluminum metal.

\[
\text{[TiF}_6^{2-} + n\text{H}_2\text{O} \iff \text{[TiF}_{6-n}\text{(OH)}_n]^{2-} + n\text{HF}}
\]  

While the addition of water causes the precipitation of the oxide, aluminum and boric acid act as fluoride scavengers that destabilize the fluoro complex and affect the oxide precipitation [136].

Pastrana-Martínez used LPD to deposit TiO\(_2\) on the surface of G nanosheets using ammonium hexafluorotitanate (IV), (NH\(_4\))\(_2\)TiF\(_6\), as the TiO\(_2\) precursor and G sheets produced by thermal reduction of GO. The hydrolysis of the TiO\(_2\) precursor and the production of the TiO\(_2\)/G nanocomposites stabilized by hydrogen-bonds occur simultaneously [137,138]. Similarly, Jiang used (NH\(_4\))\(_2\)TiF\(_6\) and G, prepared by thermal reduction of GO, to prepare TiO\(_2\)/G nanocomposites by LPD. The prepared nanocomposites have enhanced photocatalytic activity ascribed to improved adsorption capacity, electron transfer and larger surface area [139]. Recent work by Zhang used LPD and the same precursor, (NH\(_4\))\(_2\)TiF\(_6\), to prepare sandwich-like TiO\(_2\)/G nanocomposites with enhanced photocatalytic activity due to unique morphology with a consequent increase in surface area and photocatalytic activity [140].

Ultrafiltration membranes were prepared using LPD methods. The prepared membranes combine the photocatalytic degradation activity of TiO\(_2\)/G nanocomposites with the membrane filtration capacity. Athanasekou used the dip-coating process for the deposition of TiO\(_2\)/GO nanocomposites on the surface of ceramic membranes. These membranes included γ-alumina and silica single channel nanofiltration membranes with a pore size from 1 to 10 nm. The performance of the hybrid photocatalytic/ultrafiltration system exhibited improved pollutant removal efficiency compared to the reference membrane prepared by the same dip-coating technique using TiO\(_2\) without GO [18].

Antifouling hierarchical filtration membranes were prepared by filtering a dispersion of TiO\(_2\)/GO composite in ammonium hydroxide through polycarbonate filter membranes. This was followed by the deposition of a layer of TiO\(_2\) with a strong photocatalysis activity. The filtration capacity and photocatalytic degradation of direct red 80 and direct blue 15 dye solutions under UV-light illumination of these membranes, showed that the antifouling effect improves the water treatment ability [141].

Another deposition variety that results in porous films is aerosol deposition (AD) in which a high-speed gas jet is used to force the precursor powder to form a colloidal aerosol. These accelerated particles collide with the substrate at high speed, forming a condensed film at room temperature. This approach offers the advantage of continuous, single-step operation to produce tunable film structures with corresponding functionalities [142–144]. An example of this experiment for producing TiO\(_2\)/G film is shown in Figures 9 and 10. First TiO\(_2\)/G powder was obtained by the scheme shown in Figure 9:
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The obtained powder is then shaped into a film using the setup shown in Figure 10.

![Figure 9](image1.png)

Figure 9. Scheme employed to prepare TiO$_2$/G powder for the AD experiment. Reprinted with permission from reference [144]. Copyright 2014 Elsevier.

![Figure 10](image2.png)

Figure 10. Schematic diagram of the AD experiment and the results obtained. Part (a) shows the air gas tank, powder feeder, nozzle, vacuum chamber, and pumps, parts (b) and (c) show the SEM and TEM images of the TiO$_2$/G nanocomposite. Reprinted with permission from reference [144]. Copyright 2014 Elsevier.
Qin used a combination of techniques to prepare multilayer composites of G and TiO$_2$. A large-scale monolayer graphene film was synthesized by CVD on Cu foil deposited on SiO$_2$ wafer, by passing CH$_4$/H$_2$ mixture at 1000 °C, followed by cooling. A polymer support, poly(methyl methacrylate)(PMMA), was attached to the G film by spin-coating. The Cu and polymer layers were subsequently removed by treatments with ammonium persulfate (Cu) solution and acetone (PMMA), to yield G/SiO$_2$ chip. TiO$_2$ was deposited on this ship by AD to give G/TiO$_2$/SiO$_2$ chip, and the steps repeated to get G/TiO$_2$/G/SiO$_2$. The photocurrent performance of the formed nanocomposites was measured and evaluated for future applications in the production of photoelectric devices [145].

Wojtoniszak used CVD to prepare TiO$_2$/G nanocomposites with improved photocatalytic activity. TiO$_2$/G nanocomposites were prepared by adding pristine TiO$_2$ in a horizontal furnace with a quartz tube reactor. Acetylene was the carbon source for G and was heated at 400–500 °C in the presence of TiO$_2$. Higher production temperature and shorter CVD time led to the highest photocatalytic degradation activity among the prepared samples [146]. Gao used layer by layer (LBL) deposition for the preparation of a photocatalytic TiO$_2$/GO grafted filter membrane. They poured a TiO$_2$ suspension followed by a GO dispersion onto a polysulfone base membrane to obtain the composite membrane. The reduction of GO to G was achieved by UV irradiation. The efficiency of the LBL process in depositing TiO$_2$/GO onto the membrane was determined by the quartz crystal microbalance. The TiO$_2$/GO membranes showed improved photocatalytic activity under UV and simulated sunlight illumination [147].

Microwave-assisted one-step synthesis of TiO$_2$/G nanocomposites was reported by Yang. In this approach, the reduction of GO to G and the coating of TiO$_2$ on the G nanosheets occur concurrently. The TiO$_2$/G nanocomposites were produced by mixing a GO dispersion in water with commercial TiO$_2$ (P25), and the mixture was heated in a microwave equipment at 140 °C for 5 min. The TiO$_2$/G nanocomposites showed increased photocatalytic activity due to improved charge separation, light absorption, and dye adsorption capacity of the prepared nanocomposites [148]. A similar approach was used by Shanmugam to prepare TiO$_2$/G nanocomposites that exhibited almost 10-fold increase in the BET surface area compared to TiO$_2$ nanoparticles with an increase in the photocatalytic degradation activity under both UV and visible light illumination [149].

Self-cleaning applications of TiO$_2$/G nanocomposites were investigated by Anandan after preparing the TiO$_2$/G nanocomposites using spin-coating technique. They used titanium (IV) bis-ammonium lactate dihydroxide together with G sheets in the presence of glycerol to produce a homogeneous ceramic film on a glass substrate, which was calcinated at 400 °C before use. The prepared structure exhibited enhanced photoactivity and superhydrophilicity under UV light illumination [19].

Electro-spinning was used to prepare TiO$_2$/G nanocomposites with enhanced photocatalytic and photovoltaic properties. The TiO$_2$/G nanocomposites were prepared by dispersing G in N,N-dimethylacetamide containing polyvinyl acetate (PVAc) and TiO$_2$. This was followed by electrospinning and sintering at 450 °C for 1 h. The prepared TiO$_2$/G nanocomposites exhibited enhanced photocatalytic and photovoltaic properties, as compared with TiO$_2$ nanoparticles, for the photodegradation of azo dyes, and for use in dye-sensitized solar cells [150].

3. Characterization of TiO$_2$/G and TiO$_2$/GO Nanocomposites

The properties of TiO$_2$/G and TiO$_2$/GO nanocomposites, as well as their photocatalytic applications, depend mainly on the structure, morphology and the surface properties of the prepared nanocomposites. Therefore, various characterization techniques are employed for the characterization of TiO$_2$/G and TiO$_2$/GO nanocomposites used for photocatalytic applications. The most relevant of these techniques are reviewed below, using representative examples.
3.1. Structural and Elemental Analysis

3.1.1. X-ray Diffraction (XRD)

XRD is used for providing information about the crystal phase structure and phase purity of crystalline materials. In addition, the average particle size is calculated from the broadening of the appropriate peak in the XRD spectrum using Scherrer’s equation:

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

where, \( K \) is a dimensionless factor with a value close to unity, \( \lambda \) is the wavelength in Angströms (Å), \( \beta \) is the width at half height of the respective XRD peak, \( \theta \) is Bragg’s angle and \( D \) is the mean particle diameter in (Å).

Although XRD is widely used for structure determination of nanomaterials, it is of little use for amorphous materials as this technique requires highly ordered crystal lattice structure in order to provide useful information. In addition, mixtures of phases with low or no symmetry will produce a large number of diffraction points causing a poor differentiation between the multiple phases [151].

Bai used XRD to confirm that the formation process of TiO\(_2\)/G nanocomposites had no significant effect on the crystal phase of anatase. Additionally, the reduction of GO to G was confirmed by the disappearance of the GO peak at 2\( \theta \) = 13–14°, and the presence of a peak at 2\( \theta \) = 26.5° indicated that the stacking of G sheets is minimal as shown in Figure 11 [93]. However, the G peak at 2\( \theta \) = 26.5° could typically be masked in the TiO\(_2\)/G nanocomposites due to strong peak at 2\( \theta \) = 25.2° which is attributed to the anatase phase of TiO\(_2\) [127,148].

![Figure 11. XRD diffractogram of TiO\(_2\), TiO\(_2\)/reduced G (GR) nanocomposites and bare GR (inset). Reprinted with permission from reference [93]. Copyright 2014 Elsevier.](image)

3.1.2. Energy Dispersive X-ray Analysis (EDX)

EDX is used for the elemental analysis of different nanocomposites, see Figure 12. Hence it provides information about the ratio of the elements at the surface of the nanocomposite. However, poor resolution and spectral overlapping make EDX unreliable for quantitative analysis of elements [127]. Park used EDX to confirm the formation of Ti–C bonds in CdS-G/TiO\(_2\) nanocomposite due to the formation of surface complexes that include carbon atoms and TiO\(_2\). These surface complexes
were increased after treating the surface of the nanocomposites with nitric acid which improved the uniformity and homogeneity of TiO$_2$ distribution onto G sheets [135]. The O/Ti atom percentage using EDX was used to confirm the partial reduction of GO to G in accordance with IR results [152].

**Figure 12.** EDX spectrum of TiO$_2$/GO nanocomposite, showing the presence of C, O, and Ti elements. Reprinted with permission from reference [137]. Copyright 2012 Elsevier.

### 3.2. Size and Morphology Analysis

#### 3.2.1. Scanning Electron Microscopy (SEM)

SEM is a very useful technique for the examination of nanoscale materials because the three-dimensional images provide better information about the sample as a result of the significant depth of focus of SEM [153]. Nguyen used SEM to confirm the formation of the nanocomposites between TiO$_2$ and G sheets. Field emission SEM was used to show better “flower-like” structure of the formed TiO$_2$/G nanocomposites prepared by HT method under 120 °C. In addition, they reported the formation of nanoflakes on the surface of TiO$_2$/G nanocomposites with the increase in the preparation temperature. This was attributed to self-assembly of the nanorods and nanoflakes on the surface of the formed nanocomposites through van der Waals forces [100], as shown in Figures 13 and 14. Ni used SEM to confirm the wrapping of G on the TiO$_2$ nanoparticles. They reported that increasing the G load increases the wrapping of G nanosheets onto the TiO$_2$ surface. However, the excess G loading will decrease the photocatalytic activity of the prepared nanocomposites as G will interfere with the efficiency of light absorption by TiO$_2$ [97].

**Figure 13.** SEM images of TiO$_2$/G nanocomposites prepared by HT method at 120 °C (H120) and 160 °C (H160). Reprinted with permission from reference [100]. Copyright 2014 Elsevier.
3.2.2. Transmission Electron Microscopy (TEM)

Useful information about the surface structure, interface between the nanocomposite components, particle size and morphology of TiO$_2$/G nanocomposites can be obtained using TEM [154,155]. Gao employed this technique to confirm the spherical shape of the TiO$_2$ nanoparticles with high photocatalytic degradation activity and the formation of TiO$_2$/G nanocomposites [124], whereas Xu showed that TiO$_2$ nanoparticles are spread sporadically on the surface of GO due to low loading amount of TiO$_2$. This partial covering result in restacking of GO sheets into hierarchical membranes with TiO$_2$ nanoparticles trapped within as shown in Figure 15. These membranes have potential use in water purification [141].

Figure 14. SEM images of TiO$_2$/GO nanocomposites with different G loadings using magnification $\times 10,000$. Reprinted with permission from reference [97]. Copyright 2014 Elsevier.

Figure 15. TEM image of TiO$_2$/GO nanocomposite with low TiO$_2$ loading. Reprinted with permission from reference [141]. Copyright 2014 American Chemical Society.
3.2.3. Atomic Force Microscopy (AFM)

AFM is used to study the electrical properties, morphology and surface interactions of nanocomposites, and to probe the surface structural features of the scanned materials. However, the use of AFM to study the topographical and morphological properties of TiO$_2$/G and TiO$_2$/GO nanocomposites is uncommon due to the limited scan area and the possible fast deformation of the probe tip [151]. Li used AFM images and the associated height profile to show that the fabricated G is a single layer and that the formed TiO$_2$/G nanocomposites contain the TiO$_2$ nanoparticles uniformly distributed on the surface of the G nanosheets [118]. Additionally, Ghasemi used AFM to show that the average height of the G sheets is 0.85 nm while the average height of the formed TiO$_2$/G nanocomposites is 2.72–3.82 nm [17], as shown in Figure 16. Formation of three layers of GO and the stacking of G layers during formation of the TiO$_2$/G nanocomposites was also confirmed using AFM [122].

Figure 16. AFM images and height profiles of (a) GO and (b) TiO$_2$/G nanocomposites. Reprinted with permission from reference [17]. Copyright 2013 Elsevier.

3.3. Textural Analysis

Nitrogen Adsorption/Desorption Isotherms

Textural properties such as pore size distribution, pore volume, and specific surface area can be obtained using the nitrogen adsorption/desorption measurements. The surface area of the material examined ($S_{BET}$) is usually calculated using the Brunauer–Emmett–Teller (BET) equation:

$$S_{BET} = n A_m N$$

(10)

where, $n = V_m/22,414$ ($V_m$ is the monolayer capacity), $A_m$ is the molecular cross-sectional area occupied by the adsorbate monolayer per gram of adsorbent, and $N$ is Avogadro’s number [156,157]. The determination of $S_{BET}$ is important because the applications for the formed nanocomposites are greatly affected by their surface areas. Shi used the N$_2$ adsorption-desorption isotherms to
demonstrate the presence of mesopores and macropores in the prepared TiO2/G nanocomposites. They demonstrated that the specific surface area of the latter is larger than that of TiO2, with subsequent enhancement of the photocatalytic activity of the formed nanocomposites [95]. These findings are in agreement with the results of Yang who demonstrated an increase in the BET surface area, and the photocatalytic activity, with the increase in the G loading till 10 wt% in TiO2/G nanocomposites [148]. The higher surface area of TiO2/GO nanocomposites compared to their TiO2/G counterparts are attributed to the better assembly of TiO2 nanoparticles on the oxygenated surface of GO and better distribution of GO in the solution during the nanocomposite preparation [158]. On the other hand, increasing the HT treatment temperature during the formation of TiO2/G nanocomposites decreases the BET surface area because of the increase in pore size. This is ascribed to the change in the morphology and crystal structure by forming nanoflakes rather than the flower-like crystals as a result of the increase in the HT temperature, with a subsequent decrease in the specific surface area of the nanocomposites, as shown in Figure 17 [100].

![Figure 17](image_url)

**Figure 17.** Nitrogen adsorption-desorption isotherms and pore size distribution (inset) of TiO2/G nanocomposites prepared by HT at different temperatures. Reprinted with permission from reference [100]. Copyright 2014 Elsevier.

3.4. TiO2 Band Gap Energy Analysis

The band gap energy analysis and the study of the recombination rate, between the photoinduced electrons and the photogenerated positive holes on the surface of the TiO2 nanoparticles are crucial factors for the photocatalytic activity of TiO2/G nanocomposites. The band gap narrowing and decreased recombination rate that is associated with the addition of G to TiO2 nanoparticles can be calculated using different techniques, which are summarized hereafter [123].

3.4.1. UV–Visible (UV–Vis) Spectroscopy

UV–Vis Spectroscopy is the main technique used to measure the photocatalytic effect of TiO2/G and TiO2/GO nanocomposites on the degradation of environmental pollutants, such as polycyclic aromatic compounds and dyes. It was used to demonstrate the red shift in the absorption of N-doped TiO2, relative to the undoped sample [117]. Yang and Pastrana-Martinez reported a redshift using TiO2/G nanocomposites that results in narrowing the band gap and more efficient light harvesting
in the visible range. This redshift of ca. 50–60 nm was ascribed to the formation of Ti–O–C chemical bonds as reported for other carbon–TiO$_2$ nanocomposites [138,148].

On the other hand, diffuse reflectance UV–Vis spectroscopy (DRS-UV) is used to determine the band gap narrowing and the enhancement in visible light absorption. The sample reflectance is measured, converted into absorbance (using the Kubelka–Munk equation) [159], and the resultant spectrum is used to calculate the band gap energy between the conduction and valence bands of the formed TiO$_2$/G nanocomposites [119,158,160]. DRS-UV was also used to show that increasing the GO content in the TiO$_2$/GO nanocomposites increases light absorption in the visible region due to the increase in the availability of surface oxygenated groups that can react with the TiO$_2$ nanoparticles as shown in Figure 18 [123]. For TiO$_2$/G nanocomposites, an increase of the G content decreases the band gap energy, leading to a redshift and enhancement of the photocatalytic degradation of various environmental pollutants [94].

![Figure 18](image-url)

**Figure 18.** An example of the effect of the GO content on the UV–Vis absorption spectra (equivalent absorption Kubelka–Munk units) of TiO$_2$/GO nanocomposites, and calculated band gap (in eV). Part (a) shows the transformed spectra of bare TiO$_2$ (P25) and those of the synthesized nanocomposites as a function of increasing the GO content (1 to 6 wt%). Part (b) shows the relationship between the transformed Kubelka–Munk function and the energy of absorbed light. The effect of GO content on the band gap energy is shown in the inset. Reprinted with permission from reference [123]. Copyright 2013 Elsevier.
The effect of changing the preparation method of TiO$_2$/G nanocomposites on the band gap narrowing was studied by Fan using DRS-UV. The results showed that the sample prepared under HT conditions had the highest red shift and the largest band gap narrowing compared to the samples prepared by UV-assisted photoreduction, or by hydrazine chemical reduction. Furthermore, the effect of changing the mass ratio of TiO$_2$ to G was also studied by DRS-UV and the optimum ratio of TiO$_2$/G of 1/0.2 exhibited the highest photocatalytic activity [161]. The increased light absorption intensity of TiO$_2$/G nanocomposites compared to pure anatase TiO$_2$, resulted in an increase of the photocatalytic reduction of CO$_2$ under ambient conditions. This was supported by the decrease in band gap energy from 3.2 eV to 2.9 eV by the addition of G as measured by DRS-UV [162].

3.4.2. Electrochemical Impedance Spectroscopy (EIS)

EIS is used in the characterization of TiO$_2$/G and TiO$_2$/GO nanocomposites to measure the effect of the addition of G on the rate of the recombination between the photoinduced electrons and the positive holes generated on the surface of the TiO$_2$ nanoparticles. The addition of G to TiO$_2$ will give a smaller semicircle in the EIS plot indicating a decrease in the charge transfer resistance through the surface of the TiO$_2$/G nanocomposites, as presented in Figure 19. This effect is induced by the large surface area of G and its $sp^2$ network, which acts as electron transport medium from the conduction band of TiO$_2$ to G. Consequently, the presence of G in the nanocomposites will decrease the above-mentioned recombination rate. This leads to an increase in the lifetime of the charge carriers and improves the overall photodegradation process induced by the nanocomposites [90,93,119,163].

![Figure 19. EIS plots of TiO$_2$ nanoparticles (NP), TiO$_2$ nanoparticles/G (GNP), TiO$_2$ nanowires (NW), and TiO$_2$ nanowires/G (GNW). Reprinted from reference [92].](image-url)
TiO$_2$ nanoparticles (NP). In addition, the presence of G decreased the electron-hole recombination rate compared with their pure TiO$_2$ counterparts, as shown in Figure 19 [92]. The increase in the photocatalytic activity of TiO$_2$/G nanocomposites associated with the decrease in the electron-hole recombination rate can be measured by EIS as well as, photoluminescence (PL) spectroscopy [165].

3.4.3. Photoluminescence (PL) Spectroscopy

The recombination of photoinduced electrons and the positive holes after illumination with UV or visible light leads to the emission of photons that produce the characteristic PL peaks [127]. The introduction of G in the TiO$_2$/G nanocomposites is associated with substantial decline in the intensity of the PL spectrum of TiO$_2$ nanoparticles, as shown in Figure 20. This decrease in intensity is ascribed to the fact that G can transport the photogenerated electrons rapidly preventing the electron-hole pair recombination which is important in the enhancement of photocatalytic degradation [119,122,124,166]. Additionally, the increase in the G content increases the photocatalytic activity of the nanocomposites till an optimal content of G after which the photocatalytic activity decreases again [95,97].

Graphene quantum dots (GQDs), superior electron transfer agents and excellent photosensitizers, were used to prepare TiO$_2$/GQDs nanocomposites with enhanced photocatalytic activity. Hao used PL to demonstrate the electron transfer improvement in the formed nanocomposites associated with the PL peak decrease. In addition, the presence of GQDs caused an apparent red shift indicating the widening in the photosensitization band of TiO$_2$ and the formation of Ti–O–C chemical bonds coupled with significant improvement in the photocatalytic activity, as shown in Figure 21 [167].
3.5. Compositional Analysis

3.5.1. X-ray Photoelectron Spectroscopy (XPS)

For TiO$_2$/G and TiO$_2$/GO nanocomposites, XPS spectra are used to determine the efficiency of the GO reduction to G, the chemical states of Ti, O, and C species and characteristic bonding between TiO$_2$ and G/GO sheets through the formation of Ti–C and Ti–O–C bonds can also be confirmed by XPS. Using XPS, Huang studied the interaction between TiO$_2$ and G in TiO$_2$/G nanocomposites, prepared by the ST method, and by mechanical mixing. The presence of an additional peak in C 1s spectrum (at 281.2 eV) of the ST prepared sample was ascribed to the formation of Ti–C bonds. This was also confirmed by the analysis of Ti 2p core level in the XPS spectra, showing the presence of the two peaks at binding energies of 458.8 and 464.6 eV attributed to (Ti 2p$^{3/2}$) and (Ti 2p$^{1/2}$) respectively for anatase [119]. Furthermore, a shift in the Ti 2p and O 1s regions to higher binding energies after the formation of the TiO$_2$/G nanocomposites, was related to the perturbation of the Ti–O bonds at the surface after the addition of G sheets. In addition, the increase in the G amount was associated with a shift in the binding energies of the C-C and C-O bonds [118].

XPS is used to confirm the chemical reduction of GO to G. This determination is important because the presence of residual GO in the sample may affect the TiO$_2$/G nanocomposites properties, hence applications. The reduction of GO to G is confirmed by observing the decrease in C 1s and O 1s peaks that correspond to oxygenated species with a concomitant increase in the C–C peak intensity as shown in Figure 22 [122]. Additionally, the decrease in the intensity of C=O peaks, which are related to carbonyl groups at the edges of the reduced GO, was attributed to their more difficult reduction [158]. In the same context, XPS was used to confirm the reduction of GO to G after ethanol and UV-induced reduction [147], ST [122], and HT treatment [93,103]. Furthermore, XPS was used to study the photocatalytic degradation products of Bisphenol A by comparing the XPS spectra of the TiO$_2$/G nanocomposites before and after the compound photodegradation [93]. Consequently, XPS together with FTIR/Raman spectroscopy represent the most used techniques to trace the reduction of GO to G during the formation of TiO$_2$/G nanocomposites.

Figure 21. PL spectra of GQDs, TiO$_2$, and TiO$_2$/GQDs. Reprinted with permission from reference [167]. Copyright 2016 Elsevier.
3.5.2. Raman and FTIR Spectroscopy

These two complementary techniques are discussed together. Surface Enhanced Raman spectroscopy (SERS) is a powerful technique in studying the surfaces of composite materials [151,168,169]. For example, it can provide valuable information about the number and quality of the G layers, doping level, and crystal phase structure of TiO$_2$ [127]. Bai used Raman spectroscopy to confirm the presence of single layer G in the TiO$_2$/G nanocomposites and that TiO$_2$ (anatase) is the most prominent crystal phase in the prepared nanocomposites as shown in Figure 23 [93]. Raman spectroscopy is also used to evaluate the efficiency of chemical reduction of GO to G by observing the frequency shifts in the Raman G bands [158]. Thermal reduction of GO to G during HT treatment can also be detected using Raman spectroscopy [98,166]. Athanasekou used a micro-Raman spectrometer to evaluate the homogeneity of the distribution of TiO$_2$/G nanocomposites within an ultrafiltration membrane for water treatment where decreasing the pore size of the membrane lead to an inhomogeneous distribution of the TiO$_2$/G nanocomposites [18].

Figure 22. XPS spectra of C 1s for GO and TiO$_2$/RGO nanocomposites. From peak area, the reduction of GO was calculated as 76.5%. Reprinted with permission from reference [122]. Copyright 2013 American Chemical Society.
The reduction of GO to G and the formation of Ti–C and Ti–O–C chemical bonds in TiO$_2$/G and TiO$_2$/GO nanocomposites was also confirmed by FTIR. Efficient reduction of GO is verified by the decrease and/or disappearance of the bands of oxygenated functional groups at 3000–3500, 1720, 1350 and 1050 cm$^{-1}$ attributed to the transformation of GO to G, as shown in Figure 24. FTIR is typically used to confirm the reduction of GO to G [97,100,127,158,170]. Diffuse reflectance FTIR (DRIFT) has been employed for the same purpose [123].

![Figure 23. Raman spectra of TiO$_2$/GO nanocomposites with different GO amounts, adapted from reference [16].](image)

![Figure 24. FT-IR spectra for GO and G prepared by reduction of GO using glucose (GOG), hydrazine (GOH) and ascorbic acid (GOV). Reprinted with permission from reference [158]. Copyright 2014 Elsevier.](image)
3.5.3. Thermal Gravimetric Analysis (TGA)

TGA is used to analyze the amount of loaded G in TiO$_2$/G and GO in TiO$_2$/GO nanocomposites by subtracting the weight loss on heating bare TiO$_2$, usually in air flow conditions, from the weight loss obtained on heating the nanocomposites under the same conditions [122,141]. TGA curves of the TiO$_2$/G and TiO$_2$/GO nanocomposites involve three steps of weight loss. The first occurs below 100 °C and corresponds to the desorption of water molecules. The second step, at 200–300 °C, is due to the loss of functional groups with the release of CO$_x$ species. Finally, the destruction of the G carbon skeleton occurs above 450 °C [94]. Figure 25 shows the three main steps of weight loss of TiO$_2$/G nanocomposites under TGA conditions. In addition, the second step is used to evaluate the efficiency of reduction of GO to G, where more efficient reduction of GO to G leads to the presence of less oxygenated functional groups and consequently a weaker peak in the TGA plot. This is also confirmed by using the results of TGA and differential thermal analysis (DTA) [134]. Furthermore, the thermal stability of TiO$_2$/G and TiO$_2$/GO nanocomposites can be assessed by TGA and the results show that GO exhibits more weight loss, and is, therefore, less thermally stable than G at temperatures above 300 °C due to the loss of the oxygenated functionalities [158]. The same technique showed that the chemically bonded TiO$_2$/G nanocomposites prepared by the ST method had the onset of weight loss occurring at higher temperatures than that of mechanically mixed TiO$_2$/G nanocomposites, suggesting the formation of more thermally stable Ti–C chemical bonds [119,123].

![Figure 25](image-url)

**Figure 25.** TGA curves for TiO$_2$ (P25) and TiO$_2$/G nanocomposites with different amounts of G. Reprinted with permission from reference [94]. Copyright 2013 Elsevier.

3.5.4. Electron Spin Resonance (ESR)

As discussed above, the mechanism of the photocatalytic degradation by TiO$_2$/G and TiO$_2$/GO nanocomposites depends mainly on the formation of intermediate radicals such as •OH and O$_2$•−/HO$_2$•. The presence of these radicals can be evaluated using ESR. However, due to their short lifetimes and high reactivity, 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) is commonly used to trap these radicals forming a relatively stable species, as reflected in Figure 26. Experimental investigations demonstrated the presence of more intense signal for •OH under UV light irradiation during the photocatalytic process as compared with signals for O$_2$•−/HO$_2$•. These results were...
attributed to the conversion of the superoxide species $O_2^{•−}/HO_2^{•}$ to hydroxyl radicals $^{•}OH$ under UV light illumination increasing the intensity of the latter with a consequent increase in the photocatalytic activity [122,171].

![Figure 26. ESR spectra showing the formation of stable DMPO-based free radicals formed when doped TiO$_2$-GR is irradiated with visible light. Reprinted with permission from reference [171]. Copyright 2013 Elsevier.](image)

3.6. Microscopic Surface Properties

Determining the surface properties on the microscopic level of a catalytic material is relevant to its application because these surface properties have a significant impact on the adsorption/desorption processes on the catalyst surface, and on the physico-chemical processes taking place therein. In this respect, surface properties, such as the number, location, and strength of acidic and basic sites on the catalytic surface, as well as surface polarity and surface polarizability play a key role in the catalytic activity of the catalyst and hence its applications [172–174]. Surface free energy, determined by inverse gas chromatography, is used to determine the acidic and basic properties of solid surfaces accurately over a wide range of temperature [175,176]. This technique was used successfully to investigate the surface properties of G and GO [177]. However, very few techniques are used to systemically study these microscopic surface properties and their effect on the photocatalytic applications of TiO$_2$/G and TiO$_2$/GO nanocomposites; these are described below.

3.6.1. Point of Zero Charge (pH$_{PZC}$) Measurements

The point of zero charge (pH$_{PZC}$) is measured using a pH drift test where unbuffered solutions with variable pH values (2 to 12) are put into contact with the TiO$_2$/G and TiO$_2$/GO nanocomposites for some time, e.g., 24 h, and the final pH is recorded [158]. The pH$_{PZC}$ of TiO$_2$/GO nanocomposites decreases with the increase in the GO content. The decrease in the pH$_{PZC}$ indicates the increase in surface Brønsted acidity of the nanocomposites which is ascribed to the oxygenated functional groups on the surface of the GO. On the other hand, thermal treatment of the TiO$_2$/GO nanocomposites causes partial reduction of the surface acidic groups, which is confirmed by the increase in the value of pH$_{PZC}$ with increasing treatment temperature [123]. Furthermore, pH$_{PZC}$ is used to explain the higher photodegradation rate of methylene blue (MB) dye using TiO$_2$/GO nanocomposites relative to the photocatalytic degradation of methyl orange (MO) dye. The negative charge on the surface of the TiO$_2$/GO nanocomposites at pH values of 6 to 7.2, due to the dissociated surface groups, leads to efficient binding of cationic MB. This increases the photocatalytic efficiency. On the other hand,
the low pKa value of MO indicates weak adsorption of the negatively-charged species on TiO$_2$/GO nanocomposites [18].

3.6.2. Temperature Programmed Desorption (TPD)

TPD is used to calculate the amounts of different oxygenated surface functional groups that evolve as CO and CO$_2$ after heating the TiO$_2$/G and TiO$_2$/GO nanocomposites under an inert atmosphere, e.g., helium. The lower evolution of CO and CO$_2$ under TPD conditions for the G containing nanocomposites, compared to GO, is due to the lower number of oxygenated functionalities on the G surface. These findings are used as an effective method to evaluate the reduction efficiency of the GO using different reducing agents. For example, the amount of CO$_2$ released by TPD of GO was $5305 \, \mu$mol/g, and the amounts released by TPD of GO reduced by hydrazine, ascorbic acid, and glucose, were 957, 1215, and $1056 \, \mu$mol/g, respectively [158]. Furthermore, the deconvolution of the CO and CO$_2$ profiles is used to study the surface oxygenated functional groups in details. The CO$_2$–TPD profile deconvolution revealed that the surface of GO is covered with hydroxyl, epoxy, carboxylic acid, carboxylic anhydride, and lactone functional groups. On the other hand, the CO–TPD profiles of GO-containing composites include peaks that correspond to the presence of phenols, ethers, carbonyls, and quinones. Furthermore, the analysis of the TPD spectra for the G-containing composites shows that the reduction process affects mainly the hydroxyl and epoxy groups, as demonstrated in Figure 27 [158].

![Figure 27](image-url)
TPD is also commonly used to determine the number of the surface acidic and basic sites using the adsorption/desorption of NH$_3$ and CO$_2$ respectively. The use of NH$_3$-TPD method determines the overall surface acidity of solid materials, without distinction between Lewis acidity and Bronsted acidity [178]. Recently, NH$_3$-TPD was used to measure the overall surface acidity of TiO$_2$/G and TiO$_2$/GO nanocomposites. The overall surface acidity of TiO$_2$/GO nanocomposites was higher than the overall surface acidity of bare TiO$_2$ and TiO$_2$/G nanocomposites. This was ascribed to the presence of oxygenated functional groups on the surface of GO sheets [178].

4. TiO$_2$/G and TiO$_2$/GO Photocatalytic Applications for the Decomposition of Water Contaminants

Removal of environmental pollutants using photocatalysis is very promising for water treatment, filtration, self-cleaning and other various applications. As discussed above, the enhancement of TiO$_2$/G and TiO$_2$/GO nanocomposites as photocatalysts, relative to bare TiO$_2$ is attributed to a combination of: (i) inhibition of photoinduced electrons-hole pair recombination caused by G acting as electron sink for these photoinduced electrons; (ii) increase in the lifetime of the photogenerated electrons-hole pairs; (iii) narrowing of the band gap and red shift in light absorption that improves the photocatalytic activity of the formed nanocomposites; (iv) increase in the adsorption of the dye molecules on the surface of the nanocomposite relative to enhanced surface area and the strong $\pi$–$\pi$ interaction between the dye and the aromatic network of G [95].

Some applications of TiO$_2$/G and TiO$_2$/GO nanocomposites for the removal of environmental water pollutants are briefly presented below.

4.1. Photocatalytic Degradation of Dyes

MB dye is typically used as a model pollutant to study photocatalytic activity. This is due to the presence of large amounts of MB in industrial wastewater from paints, dye production and textiles manufacturers plus the difficulty in the removal of MB by usual degradation methods [95,179]. MB is considered by the international organization for standardization (ISO) as the standard test for photocatalytic film activity [180]. The photocatalytic degradation of MB under UV–Vis light irradiation is usually described by pseudo-first order kinetics [95,160].

Shi prepared N-doped TiO$_2$/G nanocomposites (NTS/G), where TiO$_2$ were in the form of anatase plates with exposed {001} facets using one-pot HT method. The prepared NTS/G nanocomposites exhibited higher degradation rate for MB in comparison to the NTS without G. This enhanced photodegradation (measured at $\lambda$ >420 nm) confirmed that the presence of G in the nanocomposites is responsible for this improvement. The nanocomposite samples prepared by adding 6 mL of GO aqueous solution during the HT preparation, showed a better photodegradation of MB than the samples prepared by adding 2, 4, 8 and 10 mL of GO aqueous solution, respectively. This implied that increasing the amount of G had a competing effect between enhancing the photocatalytic degradation rate of MB and decreasing the light absorption of the photocatalyst itself, as shown in Figure 28. An optimal amount of G in the nanocomposites gives a maximum photocatalytic activity for the degradation of MB dye [95].
manufacturers plus the difficulty in the removal of MB by usual degradation methods [95,179]. MB is considered by the international organization for standardization (ISO) as the standard test for photocatalytic film activity [180]. The photocatalytic degradation of MB under UV–Vis light irradiation is usually described by pseudo-first order kinetics [95,160].

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Recyclable magnetic TiO$_2$/G nanocomposites are produced using GO loaded with TiO$_2$ nanoparticles and SiO$_2$ insulated magnetite aggregates followed by HT treatment to reduce GO to G. The prepared nanocomposites enhanced the photodegradation rate of MB by 20%, relative to commercial TiO$_2$ (P25). Although the enhancement is modest, catalyst recovery is simply achieved by exposing the used nanocomposites to a magnetic field for ca. 1 min, to collect the nanocomposites, followed by UV treatment for an extended time to remove any remaining organic contaminants [98].

The addition of CNTs to the TiO$_2$/G nanocomposites improves the photodegradation of MB by a 2.2-fold. This was ascribed to the decrease in the recombination of photoinduced electron-hole pairs caused by both G and CNTs which is confirmed by the increase in the number of formed hydroxyl radicals in presence of CNTs [116].

The addition of G can improve the photodegradation of MB by a photothermal effect (PTE) which contributed ~38% to dye degradation. This new mechanism of photocatalytic enhancement caused by G was proposed by Gan. TiO$_2$/G nanocomposites were prepared by an HT method with different
amounts of G. The 5 wt% sample showed the highest photocatalytic effect. The PTE was induced using near-infrared (NIR) radiation, representing a significant part of sunlight radiation. This work implies that the role of PTE of solar radiation in the photodegradation process is enhanced by the addition of G [181]. TiO$_2$/G nanocomposites prepared using microwave-assisted synthesis with deposited TiO$_2$ nanoparticles on the G sheets, have improved visible light absorption. This was ascribed to the formation of Ti–O–C bonds as compared to the nanocomposites prepared by mechanical mixing. The higher photocatalytic performance under xenon lamp irradiation of the former compared to the latter is confirmed using the photodegradation of MB. The microwave-assisted sample decomposed MB from an original concentration of 10 mg/L to ca. 0.5 mg/L in 5 h. The mechanically mixed sample, on the other hand, resulted in a final concentration of ca. 4 mg/L [148].

TiO$_2$/G nanocomposites containing strongly wrapped G onto TiO$_2$ nanoparticles were prepared by Ni. They mixed amine-functionalized TiO$_2$ nanoparticles with different amounts of GO aqueous dispersions under vigorous stirring, followed by HT treatment to reduce GO to G. Compared to the nanocomposites prepared without amine functionalization, the amine-functionalized TiO$_2$/G nanocomposites exhibited higher photodegradation of MB of about 7-fold increase in MB degradation after 120 min. The higher photocatalytic activity was a result of the strong interaction between G and TiO$_2$ after wrapping. This interaction decreased the band gap in these samples. The researchers also reported that increasing the amount of added G increased the photocatalytic activity till a content of 2 wt% G, followed by a subsequent reduction in the photocatalytic activity with further increase of G due to the interference with the light absorption [97]. Zhang prepared multifunctional TiO$_2$/G hydrogels using a one-pot HT method. The formed TiO$_2$/G hydrogels had better photocatalytic degradation of MB compared to pristine TiO$_2$ nanoparticles [103]. The effect of the presence of different oxidants on the photodegradation of MB by TiO$_2$/G nanocomposites was investigated by Sun. They reported better photodegradation of MB under visible light compared to UV irradiation. In addition, the effect of hydrogen peroxide (H$_2$O$_2$) as an oxidizing agent on the photodegradation of MB was superior to other oxidants such as peroxymonosulfate and peroxydisulfate. The improved effect of H$_2$O$_2$ was attributed to a lower quenching effect and higher trapping of the photoinduced electrons [160]. Photodegradation of both cationic MB, and anionic Congo red, dyes was achieved using biphasic TiO$_2$/G nanocomposites prepared by HT method. Compared to UV-filtered light, natural sunlight improved the photodegradation of both dyes which implies the importance of the UV part of natural sunlight [182].

The photodegradation of reactive black-5 dye (RBK-5) was evaluated using TiO$_2$/G nanocomposites prepared from P25 TiO$_2$ with different amounts of G ranging from 1 to 10 wt% in an HT process. The degradation removal efficiency for RBK-5 for the TiO$_2$/G nanocomposites was improved compared to the P25, reaching more than 90% under UV radiation. However, the change in G content showed no significant variation in the degradation removal efficiency [94]. On the other hand, acid orange 7 (AO7), a common dye used in textile industry, was fully degraded using TiO$_2$/G nanocomposite under UV light irradiation within 20 min. This improved photodegradation was ascribed to the formation of the strongly oxidizing (•OH), as a result of the favorable effect of G on the separation between the photoinduced electrons and positive holes [124]. In addition, the improved AO7 photodegradation using N-doped, N and V co-doped TiO$_2$/G and TiO$_2$/GO nanocomposites under visible light irradiation was attributed to the enhancement of dye adsorption and light absorption, extended photogenerated pairs lifetime, and photosensitizing effect of G on the doped nanocomposites [90].

TiO$_2$/G nanocomposites showed improved photodegradation of rhodamine B dye under visible light irradiation due to the strong chemical interaction between the OH groups on the surface of TiO$_2$/G nanocomposites and the COOH group of the dye molecule. The presence of P123 nonionic surfactant, a triblock copolymer, during the nanocomposite formation decreased TiO$_2$ nanoparticles aggregation and increased the surface area and this combined effect further improved the photodegradation of rhodamine B and increased the catalytic stability of the formed nanocomposites [118]. The presence of
GO in TiO$_2$/GO nanocomposites prepared by two-step HT synthesis, improved the photodegradation of rhodamine B by a three-fold increase over P25. During the HT synthesis ethanol/water mixed solvent and sulfuric acid were used to enhance the growth of TiO$_2$ on the GO sheets and decrease the growth of free TiO$_2$ nanoparticles in the solution [183].

4.2. Photocatalytic Degradation of Chemicals and Pharmaceuticals

Groundwater contaminated by domestic wastewater is likely to contain small amounts of chemicals that are clearly of anthropogenic origin, e.g., caffeine and pharmaceuticals, calling for new methods of decontamination. The use of TiO$_2$/G and TiO$_2$/GO nanocomposites as photocatalysts for the degradation of pharmaceuticals has increased in the recent years. Recyclable magnetic TiO$_2$/G nanocomposites exhibited improved photodegradation of caffeine and carbamazepine, an anti-epileptic drug [98]. Carbamazepine was efficiently removed from water using TiO$_2$/G nanocomposites prepared by the microwave-hydrothermal method under UV-A light irradiation [184] and by TiO$_2$/G aerogels prepared by HT method [185]. Photodegradation of three aromatic pharmaceuticals, carbamazepine, sulfamethoxazole antibacterial and ibuprofen anti-inflammatory, using TiO$_2$/G and TiO$_2$/Fe nanocomposites under both visible and UV light irradiation. TiO$_2$/G nanocomposites showed higher photocatalytic activity under UV light irradiation ascribed to the decreased rate of recombination between electron-hole pairs. On the other hand, TiO$_2$/Fe nanocomposites exhibited higher photodegradation under visible light irradiation attributed to efficient band gap narrowing [51]. Moreover, the immobilization of TiO$_2$/G nanocomposites on optical fibers improved the photocatalytic degradation of these three aromatic pharmaceuticals in aqueous solutions [186].

Diphenhydramine (DP) is one of the most widely used anti-histaminic drugs and the third most detected healthcare product in the liver of fish collected from different locations in the United States. The low biodegradation and high toxicity of DP prompted Pastrana-Martínez to study the photodegradation of DP using TiO$_2$/G and TiO$_2$/GO nanocomposites. The results showed that TiO$_2$/GO nanocomposites had a higher DP photodegradation rate compared to TiO$_2$/G nanocomposites under both UV–Vis and visible light irradiation. The improved photoactivity was attributed to the more efficient distribution of TiO$_2$ on GO sheets [158]. Moreover, the photodegradation of DP using TiO$_2$/G nanocomposites is achieved using direct oxidation by the photoinduced holes rather than reduction by the photogenerated electrons as reported in another work by the same group [138]. In this context, the effect of different treatment temperatures on the photodegradation of DP using TiO$_2$/G nanocomposites was also studied [123].

TiO$_2$/GO nanocomposites prepared by LPD, achieved improved photocatalytic degradation of four priority pesticide residues: alachlor, atrazine, diuron and isoproturon in both ultrapure and natural water samples [187]. Li investigated the effect of different G contents in TiO$_2$/G nanocomposites on the photodegradation of aldicarb pesticide, and norfloxacin antibiotic. G content of 0.86 wt% exhibited the best photocatalytic performance [118]. The thickness of the TiO$_2$ layer in TiO$_2$/Fe$_3$O$_4$/G nanocomposites affected the photodegradation rate of enrofloxacin antibiotic and the optimum thickness was 17 nm ascribed to a maximum balance between effective photogeneration and transport of electrons [188]. The effect of the synthesis method was studied by Gholamvande for the photodegradation of famotidine, an anti-ulcer drug, as a model water pollutant. TiO$_2$/G nanocomposites, prepared by sol-gel method exhibited 90% decrease in the initial famotidine concentration after 45 min compared to 50% and 30% decrease for the TiO$_2$/G mechanically mixed and pure TiO$_2$ powder, respectively [189]. Antipsychotic, risperidone, was successfully removed from different water samples, including distilled, tap, river and lake water. TiO$_2$/G nanocomposites enhanced the photodegradation of risperidone, compared to TiO$_2$ nanoparticles, in all tested samples and the effect was directly proportional to the G amount till 20%, as reported by Calza [190]. Chlortetracycline, a persistent antibiotic in aquatic environments, was successfully removed using TiO$_2$/GO nanocomposites prepared by mixing TBT and GO dispersions in ethanol/water.
mixture. The effect of pH was studied and weakly acidic conditions, pH 4, exhibited the highest photodegradation rate [191].

The herbicide 2,4-dichlorophenoxy acetic acid is used worldwide in agriculture and is present in large amounts in wastewater. It was efficiently removed using TiO$_2$/G nanocomposites doped with noble metals as Platinum (Pt) under UV–Vis light due to the large surface area and the decrease in the electron-hole recombination in addition to the high photonic efficiency caused by the noble metal [17]. Acetic acid photooxidation using TiO$_2$/G nanocomposites under visible light irradiation was studied by Morawski [192]. The photodegradation of bisphenol A, an environmental pollutant, was evaluated using TiO$_2$/G nanocomposites with uniform TiO$_2$ nanoparticles distribution and enhanced photocatalytic activity under UV and visible light irradiation. The degradation resulted in all carbon atoms of bisphenol A converting to CO$_2$ [93]. Hydrothermally prepared TiO$_2$/GO nanocomposites were used by Fu to study the photocatalytic degradation of phenol. Cost analysis of the prepared nanocomposites showed the economic feasibility of using TiO$_2$/GO nanocomposites in removing phenolic compounds from water. The photodegradation rate constant is almost doubled for the formed nanocomposites compared to other photocatalysts, as Cu-TiO$_2$ [193].

Naphthenic acids, produced by extraction of bitumen, represents a challenge in wastewater treatment due to the complex chemical structure. TiO$_2$/G nanocomposites prepared by ST method represent a promising solution, due to the efficient charge separation and increased surface area, naphthenic acid photodegradation showed promising results at pH 3. The study of the reactive species, involved in the photodegradation process, revealed that positive holes and HO$^\bullet$ are the most prominent, as confirmed using ethylenediaminetetraacetic (EDTA) acid disodium salt as hole scavenger and isopropanol as radical scavenger [194].

4.3. Other Applications for Water Decontamination

Combining photocatalysis and filtration processes are beneficial to synergistically improve water decontamination from different pollutants. A hybrid photocatalytic/ultrafiltration system was produced using TiO$_2$/G nanocomposites deposited into the pores of monolith filters using a dip-coating technique. The prepared membranes were tested for the elimination of MB and MO dyes under UV and visible light irradiation. The effect of the pore size of the monoliths filters was studied and the elimination of both dyes using the novel hybrid membrane was better than the standard nanofiltration process [18]. In addition, the anti fouling effect of TiO$_2$/GO hierarchical filtration membrane under UV irradiation was demonstrated by the effective removal of organic dyes (Direct Red 80 and Direct Blue 15) [141]. A Polypropylene filter modified with TiO$_2$/G, exhibited a higher rate of elimination of MB under halogen lamp irradiation as compared with the TiO$_2$-modified filter [99].

Gao used the layer by layer methodology to deposit TiO$_2$/GO nanocomposites on the surface of polysulfone base membrane. The prepared membrane increased the elimination of MB, as a model contaminant, under both UV and sunlight irradiation with higher efficiency under sunlight irradiation of ca. four-fold more than the TiO$_2$ modified membrane, without G. The prepared membrane showed also a three-fold increase in the membrane flux under UV light, this was ascribed to the membrane hydrophilicity due to TiO$_2$ and GO and the photoinduced contaminant degradation [147]. Another variation involved the use of the dip-coating technique to prepare hydrophilic polyacrylic acid coating with antibacterial and self-cleaning properties using TiO$_2$/G nanocomposites. High photocatalytic activity, stability, and hydrophilicity render this coating as a potential enhancement in antibacterial coatings [195].

Other environmental photocatalytic applications of TiO$_2$/G and TiO$_2$/GO nanocomposites include the photocatalytic removal of fulvic acid, a natural organic matter that increases the level of heavy metals and adsorbed organic pollutants in drinking water. The improved adsorption and photodegradation of fulvic acid by TiO$_2$/G nanocomposites under UV light irradiation were attributed to the presence of G sheets in the formed nanocomposites [196]. The photoreduction of Cr(VI) to Cr(III) under UV light irradiation using TiO$_2$/G/CNTs composites was evaluated. The results showed that
the photoreduction of Cr(VI) was dependent on the released electrons from the valence band of TiO$_2$ to G, where CNTs enhances this transfer by acting as a charge transmitting path, rather than the formation of positive holes that affect the oxidation of dyes as MB [116]. Liu reported the increase in surface area enhanced the photoreduction of Cr(VI) under visible light irradiation [56]. Photocatalytic removal of radioactive uranium (VI) from aqueous solutions was achieved using TiO$_2$/Fe$_3$O$_4$/G nanocomposites. The presence of G improved the photocatalytic efficiency as well as decreased the photo dissolution of Fe$_3$O$_4$ compared to TiO$_2$/Fe$_3$O$_4$ composites. The prepared nanoparticles were easily recovered by exposure to magnetic fields, thus the recyclability of the nanocomposites was achieved [197].

Photodecomposition of the bromate, a carcinogenic contaminant found in drinking water, into bromide ion using TiO$_2$/G nanocomposites under UV light illumination was studied by Huang. The best photocatalytic performance was found for 1%wt content G at pH 6.8. The decrease in bromate concentration with concomitant increase in bromide level, at nearly the same amount of total bromine content, proved that the photodecomposition of bromate is primarily due to photoreduction rather than adsorption [166]. The disinfection of Escherichia coli (E. coli) using TiO$_2$/GO nanocomposites in solar light was attributed to the strong oxidant activity of hydroxyl radicals (•OH) generated from the interaction of dissolved oxygen and water molecules with the positive holes on the surface of the nanocomposites [124].

5. Conclusions

Nanocomposites of TiO$_2$ with G and GO are obtained, inter alia, by thermal methods, sol-gel process, mechanical mixing with or without sonicating, and deposition either in the liquid phase, gas phase, or as a film. Compared to bare TiO$_2$, the produced nanocomposites have smaller bandgap energies, slower rates of recombination between the photoinduced electrons and the holes on the TiO$_2$ surface, and larger surface areas. The latter, leading to enhanced contaminant adsorption, represents a primary advantage of TiO$_2$ nanocomposites with G and GO relative to doped TiO$_2$ which could possibly exhibit higher photocatalytic activity. These changes in the physicochemical properties of TiO$_2$/G and TiO$_2$/GO are determined by an array of techniques, based on diffraction (X-ray), spectroscopy (UV–Vis, FTIR, Raman, EPR), microscopy (SEM and TEM), adsorption/desorption of gases (BET) etc.

The decrease in the band gap energy leads to absorbance in the visible region of the spectrum, i.e., it turns photo-oxidation by sunlight feasible, in contrast to using UV radiation with bare TiO$_2$. The catalytic efficiency is further enhanced by the concomitant increase in the lifetime of the charge carriers, and catalyst surface area. This leads to higher adsorption of aromatic pollutants, e.g., azo dyes, due to their strong π–π interactions with the aromatic network of G and GO. We hope that this review contributes to increasing the interest in the development of efficient photocatalysts, and their application to solving some pressing global problems, especially water pollution.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2073-4344/8/11/491/s1, Table S1: Synthesis, characterization, and applications of TiO$_2$/G and TiO$_2$/GO nanocomposites in the literature.

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**Conflicts of Interest:** The authors declare no conflict of interest.
| Abbreviation | Full Form |
|--------------|-----------|
| AD           | Aerosol deposition |
| AFM          | atomic force microscopy |
| AO7          | acid orange 7 |
| BET          | Brunauer–Emmett–Teller |
| BPA          | bisphenol A |
| CB           | conduction band |
| CNTs         | carbon nanotubes |
| CVD          | chemical vapor deposition |
| DFT          | density functional theory |
| DMPO         | 5,5-Dimethyl-1-pyrroline-N-oxide |
| DMSO         | dimethylsulfoxide |
| DP           | diphenhydramine |
| DRIFT        | diffuse reflectance Fourier transform infrared spectroscopy |
| DRS-UV       | diffuse reflectance UV–Vis spectroscopy |
| DTA          | differential thermal analysis |
| E. coli      | Escherichia coli |
| EDTA         | ethylenediaminetetraacetic acid |
| EDX          | energy dispersive X-ray analysis |
| EIS          | electrochemical impedance spectroscopy |
| ESR          | electron spin resonance |
| FTIR         | Fourier transform infrared spectroscopy |
| G            | graphene |
| GO           | graphene oxide |
| GQDs         | graphene quantum dots |
| H$_2$O$_2$   | Hydrogen peroxide |
| HT           | hydrothermal |
| ISO          | international organization of standardization |
| LBL          | layer by layer |
| LPD          | liquid phase deposition |
| MB           | methylene blue |
| MO           | methyl orange |
| MWCNTs       | multi-wall carbon nanotubes |
| N,V$_2$TiO$_2$–G | Nitrogen and Vanadium co-doped TiO$_2$/G nanocomposites |
| NIR          | near-infrared |
| NTS/G        | Nitrogen-doped TiO$_2$/graphene nanocomposites |
| P123         | triblock copolymer of poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) |
| pHZPC        | the point zero of charge |
| PL           | photoluminescence spectroscopy |
| PMMA         | poly(methyl methacrylate) |
| PTE          | photothermal effect |
| PTFE         | polytetrafluoroethylene |
| PVAc         | polyvinyl acetate |
| RBK-5        | reactive black-5 |
| SEM          | scanning electron microscopy |
| SERS         | surface enhanced Raman spectroscopy |
| ST           | solvothermal |
| TBT          | tetrabutyl-titanate |
| TEA          | triethanolamine |
| TEM          | transmission electron microscopy |
| TGA          | thermal gravimetric analysis |
Ni, Titanium nitride
TiO$_2$/GO NRCs, TiO$_2$/GO nanorods composites
TiOSO$_4$, Titanium oxysulfate
TPD, temperature programmed desorption
VB, valence band
XPS, X-ray photoelectron spectroscopy
XRD, X-ray diffraction

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