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REVIEW

Exploring graphene and its derivatives for various applications: photocatalysis

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Abstract

There has been a significant concern in treating industrial wastewater for the removal of pollutants, organic and inorganic both. The degradation of contaminants is the most challenging part of the treatment, and thus, various methods are utilized and implemented for the same. But of all the processes, photocatalysis is the most effective and leads toward a greener degradation approach. Different elements exhibit the properties of semiconductors and thus make their way into the photocatalysis process. Carbon in its nanoform has gained much attention from all the conventional compounds used for photocatalysis. Graphene and its compounds, such as graphene oxide and reduced graphene oxide (rGO), possess versatile properties such as high surface area, good thermal stability, enhanced mechanical strength, chemical inertness, and biocompatibility which make them suitable for various applications that are spread in almost every field. Whether it be corrosion or friction resistance, in the medical field, or environmental application, graphene-based compounds have shown favorable results. When these nanomaterials are combined with conventional photocatalysts, they offer enhanced degradation of the pollutants present in the wastewater and modified rGO composites exhibits better results in terms of reduction in concentration and time during the photodegradation process. This review depicts the various preparation methods of graphene nano-photocatalyst with its applications and the multiple compounds combined with reduced graphene oxide. It also discusses the gaps and the applications with prospects.

Keywords Graphene-based compounds · Photocatalysis · Applications of graphene oxide · Reduced graphene oxide · Nanocomposites

Introduction

The mechanism of photocatalysis involves the process that is governed by light. As we split the term photocatalysis, it can be understood it consists of two words, photon and catalyst. These materials are responsible for altering the reaction rate when exposed to light, and thus, phenomenon is known as photocatalysis (Ameta et al. 2018). Various methods are available for the degradation of organic pollutants, but among all the methods, photocatalytic degradation by photocatalysts is a promising technique as this technique is widely used because organic pollutants are entirely degraded to generate reactive oxygen species into harmless products such as CO_2 and H_2O with energy sources such as visible light and UV light (Nasir et al. 2021, Yao et al. 2021) .This technique induces some chemical reactions and decomposes if optimum conditions are fulfilled (Salim et al. 2019). All photocatalysts are semiconductors that absorb light and acts as a catalyst, when the light falls on the surface of the photocatalyst, an electron–hole pair is generated. There are two types of photocatalytic reactions, homogeneous, where semiconductor and reactant are in the same phase, and heterogeneous, where semiconductor and reactant are in different phases (Ameta et al. 2018).

When the photocatalysts are exposed to sunlight or an artificial light source, photons are irradiated from the semiconductors with energy equal to or greater than their band gap. The electrons in the valence band agitate, which

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is followed by the movement of electrons in the conduction band, and this results in the generation of holes in the valence band (Purabgola et al. 2022). The advantage of semiconductor photocatalysis is that it utilizes solar energy as a substitute for another conventional energy source (Berberidou et al. 2019). The photocatalytic performance of pure semiconductor photocatalysts is relatively low as they are inefficient in utilizing light energy, resulting in the combination of photogenerated charge carriers (Suresh et al. 2020). Sunlight has been considered the primary energy source since the inception of human civilization. The development of various photocatalytic processes found its place in the quest for using sunlight as a source of energy generation. Photocatalysis is a process driven by sunlight which is freely available, and at the same time, it is environmentally friendly method as there is no generation of hazardous secondary waste (Mishra and Acharya 2021). Much emphasis is levied upon the usage of visible light as 43% of the total available sunlight is occupied by the visible light spectrum that provides the necessary heat and energy for photocatalytic activity. In addition to this, the low cost of visible light-driven photocatalysis is looked upon as an alternative for the treatment of wastewater (Ma et al. 2022) owing to some factors that govern the efficiency of photocatalysts, such as crystal structure, surface area, morphology, particle size, band gap, and co-catalyst selection (Ma et al. 2020).

Much attention has been drawn toward nanoparticle use in wastewater treatment because of tiny particle sizes, nanoparticles are responsible for improved physical and chemical properties. The other essential properties, such as optical, magnetic, etc., are entirely different than that of conventional materials. Applications of nanomaterials in catalysis, pharmaceutical, and water remediation are noticeable (Joshi and Gururani 2022). The magnetic nanomaterials are used as adsorbents. Some materials, such as MnFe2O4, NiFe2O4, and FeO4, are widely used in water treatment due to their high dispersibility in water and hydrophilic nature (Katubi et al. 2021). The wastewater treatment process is commonly assisted by nanomaterials incorporated AOP systems (advanced oxidation process) that generate OH radicals that enhance the treatment of wastewater owing to its high reactivity. Specific characteristics of nanomaterials, such as direct band gap, high optical absorption factor, and layered structure, make them apt as photocatalysts in wastewater purification, removing certain pollutants (Ahmed et al. 2022). The most crucial aspect that a nanomaterial is supposed to possess is sustainability. The recent advances in nanomaterials focus on the way of its utilization, prospects, and its limitations. The limitations of the macro-sized conventional adsorbents are overcome by using nanosized adsorbents that enhance the degradation of organic pollutants and thus treat wastewater (Abbo et al. 2021).

Over the past few years, many researchers have tried to develop new nanomaterials comprising carbon nanotubes and graphene. Carbon-based materials have gained much attention owing to their properties of chemical, mechanical, and physical stability (Sonawane et al. 2021). With the emergence of carbon-based nanomaterials such as carbon nanotubes, the other materials that have graphene as their parent structure also show antibacterial properties for the treatment of wastewater (Liu et al. 2011). Carbon; containing nanoparticles, when utilized as a medium for the treatment of wastewater, the carbon molecules get attached by covalent bonds. The hydrophobic effect adsorbs the pollutant molecule by these nanomaterials (Khan et al. 2022). Nanostructures possess a smaller size that enhances the effective surface area and functionalism; therefore, it is widely used in the preparation of catalysts that are used for the treatment of wastewater and its purification. These nanomaterials are very effective in removing several organic and inorganic pollutants and pathogens that cause diseases from wastewater (Jain et al. 2021). Some pollutants are classified under POP (persistent organic pollutants) that do not degrade quickly. But the nanomaterials that are active in biodegradation must be developed and implemented into the system (Gusain et al. 2020). The design and development of catalytic materials is trial and error, and so, many experiments must be conducted, and the developed catalyst must characterize under extreme conditions for stability, activity, and renewability (Mandade 2021). The new catalyst designed or developed must fulfill the criteria of having a lower band gap than the conventional photocatalysts (Byrne et al. 2018).

Much emphasis is put on the discharge of wastewater from industries that contain contaminants, some toxic too. Various techniques such as chemical oxidation, physical adsorption, photocatalysis, and nanofiltration help overcome the problems of harmful and hazardous pollutants from water. Photocatalysis finds its foremost place in these techniques, looking for greenness, affordability, and efficiency (Yao et al. 2021a). The treatment techniques used to remove contaminants from wastewater have a threat of producing the second pollutants. Hence, there is a requirement to devise an environmentally friendly catalyst that makes no harmful second products (Yao et al. 2021a). Also, the end products of the photocatalysis are H_2O and CO_2 with the elimination of the secondary treatment. Photocatalysis is cost-effective and green for the degradation of dyes (Bibi et al. 2021). Various adsorbents, such as silica gel, activated carbon, zeolites, etc., made their way to remove dyes from wastewater but were not efficient as expected. Photocatalytic nanomaterials, when used as adsorbents, were found to be efficient owing to their efficiency and other properties (Karthik et al. 2020). The scientific and engineering community pays much attention to the dream material known as graphene as it possesses a single-atom-thick sheet composed of sp2 hybridized carbon and fabricated through mechanical exfoliation. Graphene has a unique 2D honeycomb lattice structure and is considered the thinnest and strongest material in the universe. It also possesses several excellent chemical and physical properties (Li et al. 2016). In modern nanomaterial technology, graphene discovery has found its place as it differs in properties other than graphite. Graphene finds its applications in various fields such as sensors, photovoltaics, energy storage, and electronics (Rasheed et al. 2021). Graphene-based compounds are widely utilized in sensors and biosensors because of their properties of high surface area, good thermal conductivity that results in their performance of showing accuracy, selectivity, and sensitivity along with long-term stability (Riahi et al. 2020).

Graphene is widely used in photocatalysis owing to its characteristics such as good conductivity, large specific surface area, and high electron mobility. It acts as a platform for the migration of carriers. The properties of graphene are tailored to make it suitable for photocatalysis, as the regular arrangements of carbon atoms pose a limitation to graphene (Bie et al. 2021). Graphene is found to have minimum dissolution, and it is inert for various practical uses, and so, it needs to be chemically modified (Vasseghian et al. 2022). It possesses some intrinsic properties that make it suitable as the support of many semiconductors with low band gaps (Appavu et al. 2018). There was an excellent need for synthesizing graphene-based semiconductors such as graphene oxide (GO) based on high yield, abundant surface functional groups, and flexible solution processability. The role of GO in photocatalysis is found to be diverse, attributing to the unique features of surface chemistry. GO acts as a macromolecular surfactant to promote the dispersion of insoluble materials. A two-dimensional structure allows GO to be one of the inducers of the growth template of composite materials with varied morphology (Lu et al. 2021) that contains plenty of oxygenated functional groups, making it flexible and accessible (Zhang et al. 2015a, b).

GO offers excellent dispersibility in polar solvents to aid composites synthesis due to the presence of oxygen-containing surface groups. GO acts as an electron acceptor, which hinders electron–hole recombination; it increases the adsorption of organic pollutants through π-π bonds between the sp^2 region of graphene and can create oxygen vacancies, thus improving photocatalytic efficiency (Costa et al. 2021). The functional groups such as epoxy, carboxyl, and hydroxyl are attached by a covalent bond in the graphene base plane, making it hydrophilic and dispersible in water. GO is preferred because its surface structure consists of hydroxyl and carboxyl groups used for composite synthesis. GO can also be synthesized through biological route. Figure 1 (Yaqoob et al. 2021) shows SEM images of lignin-based GO (L-GO), ZnO, and the complex L-GO-ZnO. The increase in surface area of the active surface is clearly visible in complex L-GO-ZnO. The GO structure shows clear sheet-like arrangement, and the complex L-GO-ZnO depicts sharp edges with holes and also the presence of some elements (Yaqoob et al. 2021).

GO accelerates the electron mobility at the interface and, thus, increases the adsorption rate of the pollutants. GO is an altered form of graphene that contains functional groups at the base and the edges of the planar structure. This makes it easier to functionalize GO chemically by forming inorganic complexes through nanoparticle immobilization. The presence of oxygen on the surface of GO acts as an anchor. The GO sheets tend to aggregate themselves when the dispersed solutions are dried, thus to prevent the aggregation of GO layers, metal oxide nanoparticles are distributed evenly over the surface, which acts as a stabilizer.

The synergic effects are exhibited with the combination of GO sheets and metal oxides (Kamalam et al. 2021). During the exfoliation of graphite to convert it into graphene oxide, the enlarged layer distance allows the delamination of graphite oxide into graphene oxide under ultrasonication. As mentioned earlier, graphene oxide's base and edges contain oxygen. This oxygen partially breaks sp^2-sp^2 bonds

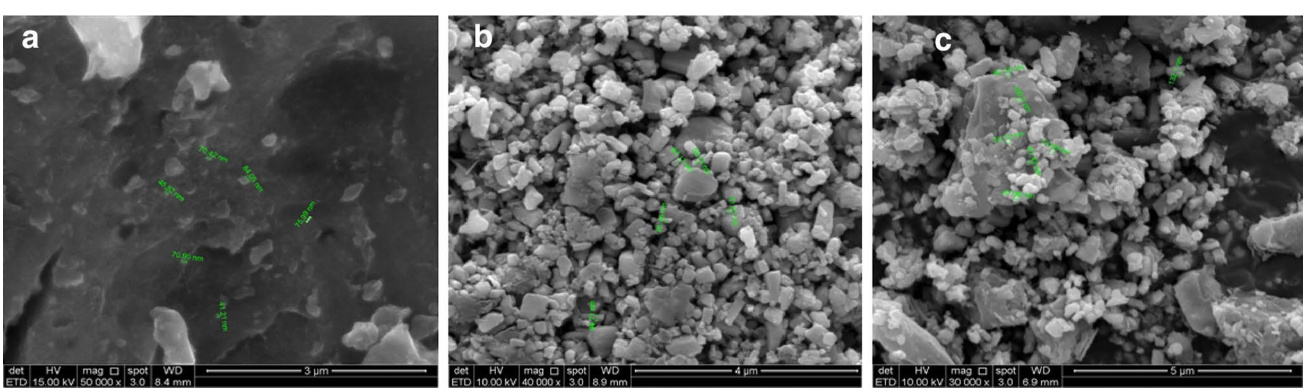

Fig. 1 SEM micrograph of as-prepared biomaterial-based **a** L-GO, **b** ZnO, and **c** L-GO–ZnO (Reproduced from Yaqoob et al. 2021, with kind permission of the copyright holder, Springer Nature)

into sp^3-sp^3 bonds making GO a good insulator. Hence to restore the π-conjugated structure and conductivity, GO is transformed into reduced graphene oxide (rGO). As rGO contains low oxygen, the properties of graphene are recovered to some extent making it an excellent electrical and thermal conductor (Liu and Speranza 2021). GO can widely be used as a filtration medium where the harmful gas can be filtered from liquid as it is permeable to liquid (Priyadarsini et al. 2018).

From the various literature available, rGO is chosen as one of the benchmark materials for semiconductor nanoparticle performance improvement as it enhances the separation of the photogenerated charge carriers, thereby improving the photocatalytic performance. The defects in rGO play a vital role in the photocatalytic activity of the nanocomposites (Mondal et al. 2021). The photogenerated electrons are easily separated due to the higher electron mobility of rGO. As a result, the interaction of rGO with dye molecules increases and with an increase in photodegradation (Khan et al. 2020). As mentioned in the work carried out by (Zhao et al. 2022), it is found that the introduction of rGO in the composites inhibits aggregation and improves the conductivity of the catalyst. The composite TiO_2-rGO shows enhanced photochemical activity imparting higher current density in one such case of water splitting (Tayebi et al. 2019).

rGO composites with Gd and V_2O_5 exhibited enhanced optical response in the visible region with decreased band gap values as compared with Gd-doped V_2O_5(Chaudhary et al. 2021a). rGO composites with ZnO have shown enhanced photocatalytic activity with 100% efficiency in degradation of dyes under visible light in 90 min (Khurshid et al. 2019).

Synthesis of GO, rGO, doped, and composites

The final quality of GO depends on the carbon source apart from the chemical synthesis. The availability of various types of graphite and the varied synthesis methods affects the properties of GO exhibiting modified structure and properties. The lateral size of the flake and the number of layers with the disorder are the physical characteristics involved that show that the final properties of GO are attributed to the parent material and method of synthesis, making every structure suitable for specific applications (Costa et al. 2021). A British researcher Benjamin Broodie carried out the first-ever synthesis of GO by oxidizing graphene with potassium chloride ($KClO_3$) and fuming nitric acid. The product obtained was named graphic acid by Broodie as it consisted of carbon, hydrogen, and oxygen. After around 40 years of this invention, Staudenmaier modified the process used by Broodie. His method consisted of slow mixing of potassium chloride with a solution of sulfuric acid and concentrated nitric acid with graphite. The mixture was agitated for 1 week in a calm environment.

The result obtained was modified properties of graphite with an increase in oxidation rate. Hundred years later, scientists Hummers and Offeman devised a new method for synthesizing graphite oxide, eliminating the explosion risk with reduced reaction time. In the improved method, sulfuric acid, sodium nitrate, and potassium permanganate with graphite were mixed and heated at 45 °C for 2 hours. The mixture was washed with water and treated with H_2O_2 for higher oxidation. The method which improves the route and method proposed by Hummers is known as the modified Hummer's method. The tour group then presented a modification in the Hummers method in 2010. They substituted sodium nitrate with phosphoric acid in the sulfuric acid solution in the ratio of 9:1 with an increased quantity of $KMnO_4$. This prevented the generation of harmful gases such as NO_2 and ClO_2 with easy temperature control and improved degree of oxidation. The free water oxidation method was proposed by Sun and Fugestu in 2013. They used expanded graphite and potassium permanganate. Potassium permanganate acted as an oxidizing agent and intercalating agent. The intercalation of potassium permanganate between graphite layers occurred in a sulfuric acid medium.

Recently, a more advanced method of synthesizing GO is proposed. The researchers prepared ultrawide GO using a swelling crystal strategy using oxidation monolithic crystal swelling that can convert graphite into ultrawide GO. This minimizes GO reduction by preventing gelling so that graphite oxide can easily be purified (Rhazouani et al. 2021). The standard methods for preparing rGO involve reducing GO by thermal, chemical, or electrical processes. When GO undergoes chemical reduction, it is deoxygenated with a reducing agent, and rGO is synthesized. The other ways to produce rGO are less adopted as the chemical route gives the structure stability. At times, the chemicals used for the reduction may cause toxicity which can be replaced by green chemicals as per the requirements (Dash et al. 2021). The GO was dispersed and treated with ammonia and N_2H_4 for exfoliation and heated to 90 °C, allowing the flakes of rGO to appear in the solution (K. Chaudhary et al. 2021b). The most distinguished materials widely used for photocatalysis to treat wastewater are ZnO and TiO_2. Over the years, ZnO has exhibited exceptional features such as being cost-effective, having strong oxidation capacity, extraordinary photosensitivity, and high chemical stability (Amate et al. 2020) with pyroelectric and piezoelectric characteristics (Lee et al. 2016). It possesses a wide band gap of around 3.37 eV that is required for the reaction and faster recombination of electron–hole pairs. ZnO has found its place in performance using strategies including metal loading, doping, composite loading, and improved structural design. GO becomes the suitable option for ZnO-based photocatalysts due to its functionality of hydroxyl and carboxyl groups that possess charge separation properties. Figure 2 Nisar et al. 2022 depicts the TEM images of the prepared rGO and ZnO-rGO nanocomposite. The thin sheets are clearly visible in the TEM image of rGO which is indication of high exfoliation during synthesis process where as the other image ZnO-rGO shows independent and homogeneous distribution of spherical ZnO particles.

Along with ZnO, TiO_2 is also a prominent material as a photocatalyst. The studies over the same show its effectiveness to be used extensively for degrading organic pollutants and air cleaning. The advantages of using TiO_2 are its low cost, low toxicity, high chemical stability, and improved chemical stability compared to other semiconducting materials. When TiO_2 makes a composite structure with GO, it prevents accumulation and helps prevent greater surface area and more active sites for the degradation of pollutants. The efficiency of this composite reduces the usage quantity. Table 1 depicts the synthesis method of various graphene-based nanomaterials. Figure 3 (Shaheer et al. 2021) depicts the SEM images of various dopants that were involved in formation of nanocomposites such as TiO_2, indium, and tungstate in various compositions. It can be seen that when rGO is added, there is uniform distribution over the surface of the catalyst. Figure 4a–e (Vinodhkumar et al. 2020) exhibits FESEM images of rGO/Fe3O4 nanocomposites of varying compositions of the dopant Fe_3O_4 over the surface of rGO. The images depict the tight attachment of Fe_3O_4 over the sheet of rGO, Fig. 5a and b (Fatima et al. 2021) illustrates the SEM images of the prepared dopant AgO.CuO.WO_3 and AgO.CuO.WO_3/rGO. The globules of dopants and the nanocomposite of the dopant over the surface of rGO are clearly visible in the micrographs. In Fig. 5a, the voids between the globules are visible, and the same spaces are then occupied when rGO is added into the composite of various metal oxides.

Properties of graphene-based materials

The properties of graphene vary drastically from graphite, and that leads to its application in the fields of sensors, photovoltaics, and energy storage (Tahernejad-Javazmi et al. 2019). It possesses high density, two-dimensional transparent structure. The primary constituent material of graphene is carbon; its shape resembles a honeycomb. It maintains elasticity which makes it a suitable material for industrial purposes. The chemical exfoliation method is the one that is widely used to prepare graphene. To achieve the desired mechanical strength properties, graphite is converted to GO by Hummer's method (Rasheed et al. 2021). GO possesses unique surface features and structures that play a vital role in heterogenous photocatalysis. It acts as a macromolecular surfactant that promotes the dispersion of insoluble materials. The two-dimensional form of GO serves as the growth template in preparing various composite structures. GO can be used directly as a photocatalyst if it possesses a suitable degree of oxidation. The properties such as electrical conductivity, surface chemistry, dispersibility, and semiconductor properties make GO work as a photocatalyst (Lu et al. 2021).

The GO nanoparticles are widely used as antifouling materials to prepare membranes that are used to remove microorganisms in ultrafiltration and nanofiltration (El-Shafai et al. 2021). When GO undergoes chemical reduction, the electrical conductivity properties are restored. The evolved reduced product obtained is rGO. This rGO contains a particular set of functional groups that enhance its properties of dispersibility and solubility. The flexible composites of GO and rGO have varied and multifunctional properties of energy storage, water purification, photocatalysis, and robotics (Khan et al. 2016). The properties of graphene and rGO do not provide promising performance; hence, the composites are developed to improve

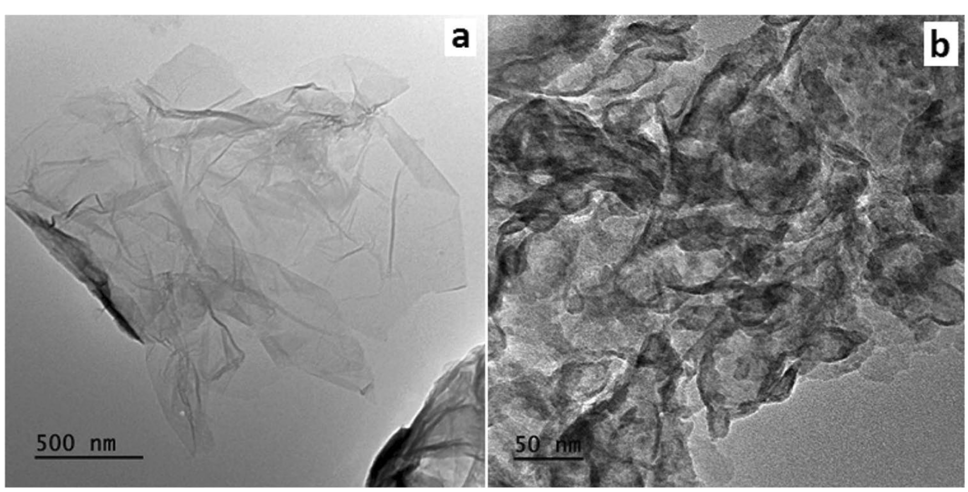

Fig. 2 Transmission electron micrographs (TEM) of **a** prepared rGO and **b** ZnO-rGO (Reproduced from Nisar et al. 2022, with kind permission of the copyright holder, Springer Nature)

Table 1 Synthesis methods of various graphene-based nanocomposites

Sample	Synthesis method/ doping method	Reaction temperature (°C)	Reaction time (h)	Solvent	Structure	Dopant	Referencess
AgO.CuO.WO_3 with rGO	Acid co-precipitation	–	2	DI water	Layered	Sodium tungstate, copper sulfate pentahydrate, and silver nitrate	(Fatima et al. 2021)
ZnO-rGO	In situ hydrothermal	140	24	DI water	Layered	$Zn(CH_3COO)_2·2H_2O$	(Tuan et al. 2020)
Cu-rGO	In situ hydrothermal	200	24	DI water	Layered	Copper acetate	(Ikram et al. 2020)
RGO-Ag/ZnO	Single-pot synthesis approach	80C	12	L-Methionine	Layered	Zinc acetate dihydrate and silver nitrate	(Belachew et al. 2020)
rGO/Fe_3O_4	Solvothermal process	180	10	Ethylene glycol	Layered	$FeCl_3$•$6H_2O$	(Vinodhkumar et al. 2020)
ZnO-rGO	–	90	4	DI water	Layered	Zinc acetate	(Nisar et al. 2022)
rGO/CuS	Modified precipitation method	80	2	Dimethylformamide	–	Copper acetate and thiourea	(El-Hout et al. 2020)
TiO2/In0.5WO_3/rGO	Wet impregnation method	450	2	NaOH solution	–	Sodium tungstate, indium chloride, and TTIP	(Shaheer et al. 2021)
$ZnFe_2O_4$@rGO	Hydrothermal method	200	10	DI water	Layered	$Zn(NO_3)_2.6H_2O$, $Fe(NO_3)_3.9H_2O$	(Baynosa et al. 2020)
$ZnCr_2O_4$-rGO	Chemical process	80	3	DI water	Sheet type	Zinc sulfate and chromium nitrate	(Tantubay et al. 2021)
Ag-ZnO-rGO	In situ synthesis	140	2	DI water	Sheet type	Zinc nitrate hexahydrate and silver nitrate	(Abdulhusain et al. 2022)
NiO/rGO	Hydrothermal method	Room Temp	24	Water	Layered	$NiCl_2$	(Fatimah et al. 2023)
Ag-$FeCo_2O_4$@rGO	–	80	12	DI water	Sheet type	Ferrous chloride, cobalt chloride, and silver nitrate	(Naghani et al. 2023)

their properties, making them conductive (Razaq et al. 2022) (Table 2).

Applications of graphene-based compounds

Owing to the versatile properties of graphene and the derived compounds, the use of these compounds has noticeably increased in almost every field. The applications are not limited to a single domain; it is widely spread in nearly every area and has shown promising results. Some of the applications are as follows:

Corrosion

The coatings of various polymers can prevent corrosion over the surface of the metal. But these polymers show permeability toward many chemicals that contain chlorides, sulfides, water, and other chemicals that corrode the substrate (Smith et al. 2019). But graphene and its derivatives are found to resist penetration, at times even passivating the surface by the oxide film. Compared to rGO obtained by exfoliation of GO, GO was found to be more corrosion resistant than rGO for steel substrate (Ghauri et al. 2017). Graphene and its derivatives, such as GO and rGO, are reported to exhibit anticorrosive properties (Zhang et al. 2015a, b). When mixed with epoxy resins, rGO was found to reduce corrosion rates by four times, Young's modulus was increased 200 times, and there was a reduction in the plasticity index by 27% for the rGO-epoxy mixture. When PANI nanofibers were deposited on GO sheets, they showed that GO was compatible with epoxy resin and exhibited improved thermal stability, barrier, and protection properties. The modification over the surface of GO when the elements such as Zn and Ce are attached to the surface through a layer-by-layer method proved to exhibit promising results as anticorrosive agents forming a protective film over the metal surface. Through the process, zinc acts as a sacrificial anode and the metal surface as a cathode, thus, creating protection over the metal surface and protecting it against corrosion (Ding et al. 2018).

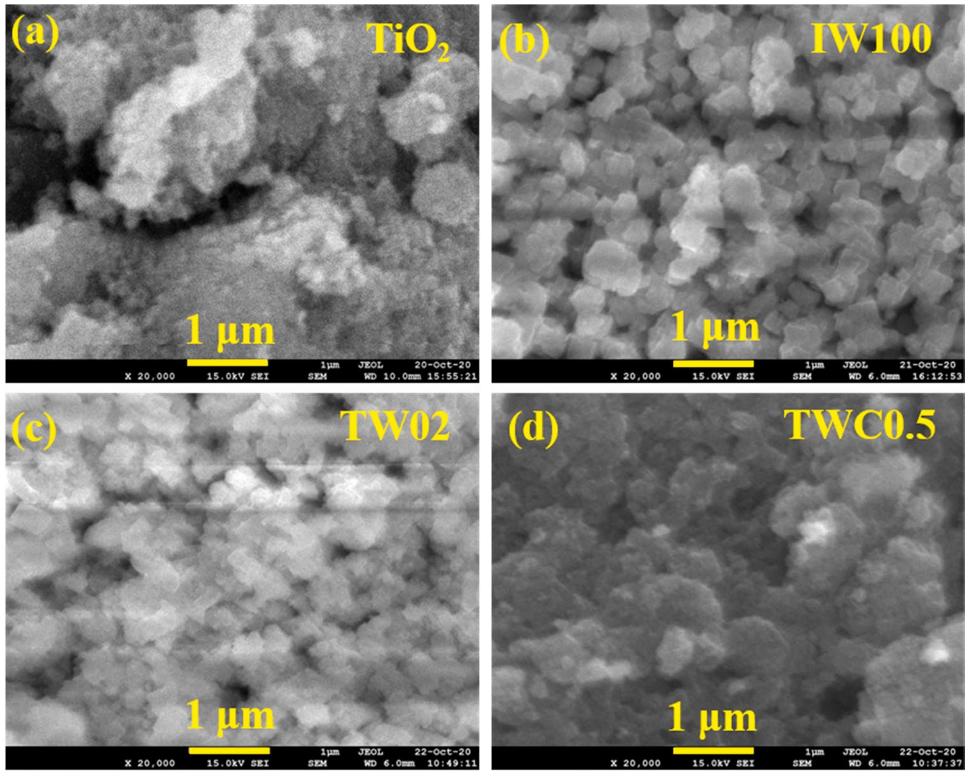

Fig. 3 **a–d** FESEM images of the dopants for photocatalyst (Reproduced from Shaheer et al. 2021, with kind permission of the copyright holder, Elsevier)

With new materials being derived, fluorinated graphene is considered a material for protecting metal surfaces. Fluorinated graphene has a low surface energy that makes it apt as a material used to prepare hydrophobic coatings and forms a barrier for corrosion. The flake-like structure of fluorinated graphene causes a labyrinth effect that causes extension in diffusion paths, making it corrosion-resistant. The robust hydrophobicity makes the dispersion of fluorinated graphene complex. Dispersibility is a vital factor that is required for practical purposes. To make fluorinated graphene dispersible, many researchers explored the ways and found that the addition of alkali in fluorinated graphene and co-modifying it with oxygen, making it dispersible. Compared to conventional dispersants, cerium, a rare earth element, is a versatile corrosion-resistant reagent (Smith et al. 2019). The inhibitive properties of cerium were observed by researchers when the appropriate amount of cerium phosphate was mixed with epoxy. Better protection from corrosion was reported as compared to other conventional materials (Morozov et al. 2019).

A coating was always needed to protect against corrosion that had self-repairing properties. Dopamine and polydopamine are the materials that include catechol and amine groups. These materials can be used to modify the surfaces. Polydopamine, when modified on the surface of graphene oxide, with epoxy resin as its primary material, coating showed improved properties of inhibition from corrosion. This happens due to the action of catechol–Fe ions that inhibit corrosion by coordinating bonding. Another material that is looked upon for corrosion inhibition is benzenetriazole. An effort has been made to create a nanocomposite that solves the corrosion problem by enhancing interface incompatibility. Loading benzenetriazole into mesoporous polydopamine over GO surface resulted in a nanocomposite structure. Polydopamine and released benzenetriazole formed adsorption layers over the damaged areas, thereby protecting the metal surface (Kar Editor, n.d.).

Epoxy resins have found their place in coatings preventing the metal surface from corrosion. But its characteristics to crack and become brittle make epoxy as ineffective as a coating for corrosion inhibitor. Thus, a need arose for certain materials that overcome these limitations and form a protective barrier to a corrosive environment. Studies have found applications of GO and rGO as the layered structure provided the vital force of attraction with oxygen-containing groups, thus passivating the surface. Graphene and rGO have strong mechanical properties, high surface area, good thermal conductivity, and stability. Nano-TiO_2 particles are non-toxic, anti-aging, and cheap raw materials. Researchers synthesized GO-TiO_2 to improve dispersion results (Ahmad et al. 2020; Liu et al. 2019). As compared to the individual components, GO and TiO_2, the dispersion ability of GO-TiO_2 in epoxy resin was improved, the state of the surface was found to be hydrophobic from hydrophilic, and the anti-corrosion ability of the coating was reported to increase (Zhu et al. 2022).

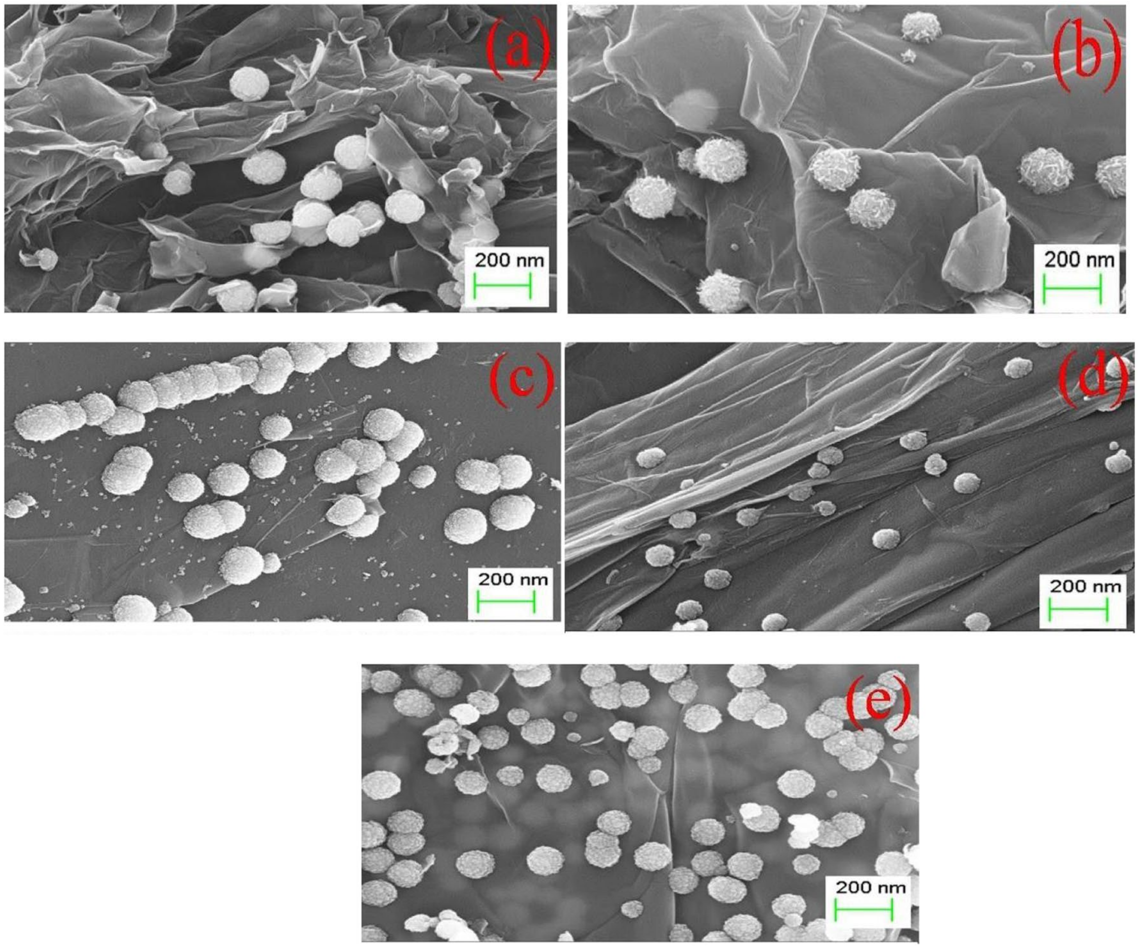

Fig. 4 FESEM images of **a** GF1:1, **b** GF1.5:1, **c** GF2:1, **d** GF1:1.5, and **e** GF1:2 nanocomposites (Reproduced from Vinodhkumar et al. 2020, with kind permission of the copyright holder, Elsevier)

Medical field

Graphene and graphene-based compounds possess diversified properties that make them suitable for varied applications. One such field is the medical field. The composite structure has enhanced electronic, biological, mechanical, and optical properties that suit the area of medicine domain. Researchers have studied and are trying to develop various biosensors for detecting the early onset of various fatal diseases. One of the essential applications of these graphene-based compounds is in the early detection of tumor growth in the colon, breast, lungs, and other vital organs of the human body (Priyadarsini et al. 2018). Graphene is also essential in developing a stem cell culture that helps diagnose various autoimmune and genetic disorders. The various applications are observed in gene delivery, drug delivery, biosensing and bioimaging, cancer treatment, substrates for antibacterial effects, differentiation of stem cells, biomedical implantation, photothermal therapy, and mass spectroscopy (Wang et al. 2011; Akhavan and Ghaderi 2010).

Graphene and rGO have straightforward functionalism, biocompatible nature, and good physical stability, making it an excellent transducer material. When rGO is prepared by green method, it disperses in water, emanating high electrical conductivity. Conjugation of folic acid with rGO using N-hydroxysuccinimide and establishes polymeric linkage. Compared to other sensors, these types of sensors of this type find their application in sensing cancer. It detects body fluids and thereby feels the early stages of cancer onset (Bai et al. 2021).

Fire prevention

There has been a significant boom in the textile industry for the development of intelligent textiles, taking into consideration health, sport, automotive, and military (Grancarić et al. 2018). This led to an increase in the production of conductive fabrics, which resulted in risking of combustion of the garments. Thus, there came into existence the functional textiles that are used are garments for firefighters and various

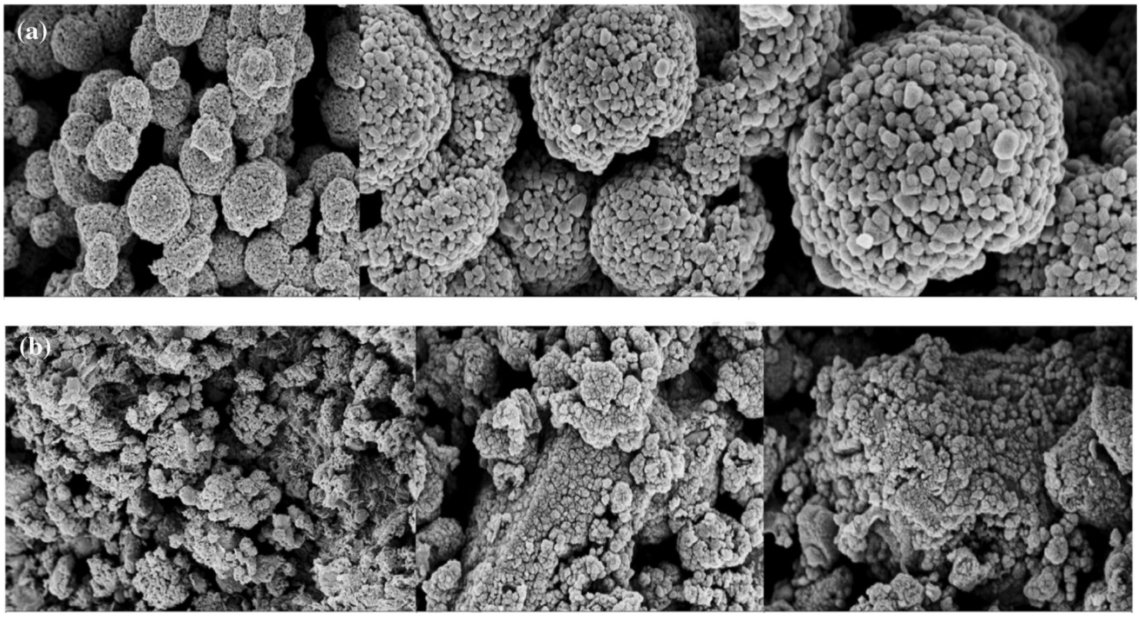

Fig. 5 **a** Micrographs of hetero-metallic oxides AgO.CuO.WO3 at various magnifications and **b** micrographs of AgO.CuO.WO3/rGO nanocomposite at various magnifications (Reproduced from Fatima et al. 2021, with kind permission of the copyright holder, Elsevier)

Table 2 Physical properties of graphene-based nanocomposites

Sample	Synthesis method	Surface area (m^2/g)	Pore volume (cm^3/g)	Avg. particle size (nm)	References
FAH-rGO/CD	Hydrothermal and ex situ polymerization process	145.35	0.287	11–14	(Priya et al. 2020)
FAH-rGO/SA-4	Hydrothermal and ex-situ polymerization process	151.3542	0.2846	6–8	(Nithya Priya et al. 2021)
TiO_2/rGO	–	110.549		4–25	(Trinh et al. 2021)
Fe−ZnO/rGO	Hydrothermal method	48.2	0.061	–	(Guo et al. 2019)
rGO-PDTC/Fe_3O_4	–	194.8	0.33	–	(Fu and Huang 2018)
ZrO_2-rGO	Dispersion	390	0.196		(Kaur and Pal 2016)
C@Co_3O_4/rGO	Precipitation	118	–	–	(Aadil et al. 2020)
Ag-TiO_2/rGO	Facile one-pot solvothermal method	184.5	0.56	–	(Zhang et al. 2017)
SnO_2 NPs/rGO	Hydrothermal method	128.52	0.14	4.39	(Niavol and Moghaddam 2021)
MnO_2-graphite/RGO		79.8	0.17	5.3	(Yao et al. , 2021b)
NiO/rGO	Hydrothermal method			10-30	(Fatimah et al. 2023)
$ZnAl_2O_4$/rGO	Hydrothermal method	241.2	0.16	4.70	(Miroliaee et al. 2019)
ZnS/rGO	Precipitation	80.1	0.091	–	(Agorku et al. 2015)
rGO–CuO	Hydrothermal reduction	128.9	0.707	–	(Gusain et al. 2016)
RGO/Al_2O_3	Dry sol–gel method	242.4	0.1753	4	(Jastrzębska et al. 2015)
Mn_3O_4 / rGO	Physical mixing method	34.25	0.16	18	(Anilkumar et al. 2017)
MnBDC@75% rGO	Dispersion-ultrasonication	28.359	0.064	–	(Wahab et al. 2020)

flame retardants. The aim was to maintain the thermal stability of cotton/polyester, silk, and wool fabrics. GO, a derivative of graphene, contains polar groups that bind with the fabric surfaces and is water dispersible, and the conductive fabric was prepared using rGO. A cotton fabric where a sheet of GO is dispersed is reported to have increased resistance which ultimately shows that the fire retardancy capacity of the fabric can be increased with the dispersion of GO sheet (Gu et al. 2010). Additionally, GO with other materials offers improved flame retardancy. Researchers have shown that GO and phosphorus flame retardant were used to modify the cotton/polyester fabric for their flame-retardant properties (Zhao et al. 2020).

Graphene-based fire retardants are adequate as they can maintain the effect on flame retardance of the polymers causing physical barriers (Huang et al. 2012). The van der Waals force between the π-π interactions causes graphene to restack. This inhibits the dispersibility of graphene in the polymer matrix. This is overcome by the use of metal oxides along with GO, modifying the surface. One of the rare earth metals, cerium, is a versatile element that has excellent catalytic properties (Guler et al. 2017). CeO_2 is a fire retardant and effective in epoxy resins and polyethylene. These results inspired researchers to use CeO_2 combined with rGO to improve the fire safety of thermoplastic polyurethane (TPU). It was found that a char layer was formed that prevented heat and mass transfer between the polymer and fire (S. Wang et al. 2019).

One of the essential thermosetting plastic, epoxy resins, is widely used in industries for various purposes. But this material has a significant risk of flammability and emission of toxic smoke on burning. Certain flame retardants such as phosphorus or nitrogen-containing compounds are used along with metal–organic compounds and inorganic fillers to reduce the fire hazards in the industry for epoxy resins. The phosphonates are embedded in their sheets with graphene-based derivatives such as GO and rGO. Metal–organic zinc N–N piperazine with high thermal stability was synthesized to functionalize rGO. The results showed enhanced fire resistance and thermal stability of the modified epoxy resin (Wang and Wang 2021).

Application for mechanical wear/friction

As observed in daily life, the regulations of environmental conservation are becoming stringent. There has been a need to develop a lubricant that would reduce friction substantially, improve fuel efficiency, and lower emissions. The lubricant properties of graphene have not been studied much. Though graphene did not show any reduction in friction due to its layered structure, rGO assembled on a silicon substrate through covalent linkage showed a decrease in friction. The lubrication properties of rGO result from its covalent bonding that reduces the shear resistance owing to its structure. Even studies have shown that graphene forms a nanolubricant that easily disperses stably in the lube medium, providing wear resistance (Mungse and Khatri 2014). Solid lubricants in the micro/nanoscale have gained attention owing to their tendency to reduce friction and increase the lifespan of the devices. Graphene is one of the materials with some unusual tribological properties that impart a lubricating effect and extends the devices' life. When applied to macrosystems, it was observed that 4–5 layers of graphene could reduce friction and thus wear in a significant magnitude. Graphene could also sustain in highly humid and dry environments (Berman et al. 2014). One such material, silicon rubber, is widely used in various applications because of its exceptional properties to resist chemical attacks, thermal stability, electrical insulation, and biocompatibility (Myshkin et al. 2005). Despite all these favorable properties, silicon has a low modulus that makes it prone to deformation when exposed to little stress. Many fillers are added to increase its modulus. rGO was studied as a material that could be used as a filler material to form a nanocomposite with silicone rubber to enhance its modulus and thus increase the wear and friction resistance properties. The results depicted that the addition of rGO to silicon rubber increased the modulus of the nanocomposite. The material loading was reduced as rGO offered a high surface area providing significant contact points in the matrix of silicon rubber (Penkov et al. 2014). The presence of rGO reduced the contact between the metal and the material as it acted as a lubricant. Even the various properties such as thermal stability and wear resistance were found to be improved in the nanocomposite containing rGO (Sarath et al. 2021).

Lubrication is the critical aspect that one looks for when concerned about energy loss due to friction and wear of machines and various devices. The additives with different functionalities and desired properties are added to achieve efficient lubrication. Carbon-containing nanomaterials have shown properties of enhanced friction and wear resistance. The use of these materials was effective in abrasion caused by the moving parts of the devices. Graphene and its derivatives have been proven as suitable additives that have extra smoothness and ease of shearing. When TiO_2/F-rGO (fluorinated rGO) is added to the base oil, the properties such as mechanical strength and resistance to friction are found to increase. The results showed that a protective layer was formed that provided resistance to shear and increased load-bearing capacity. The tribological behavior of the base oil was modified to suit the application of resistance to friction and wear (Zhao and Ci 2020).

Applications in water decontamination

The expanding industrialization has brought concern for the environment. Various industries are responsible for damaging the natural water matrix by contaminating it with organic and inorganic pollutants that become the prime reason for people's health. The emissions in the natural water bodies of some organic materials, such as antibiotics, make the human population resist antibiotics. Other elements that are discharged, such as arsenic, lead, and chromium, are responsible for causing chronic health problems, including anemia, heart diseases, and hepatic and renal failures. Some of the compounds of arsenic are the leading cause of cancer. Thus, water sources must be maintained in quality so that humans, animals, and the environment are protected. Many water treatment technologies are developed and implemented for water decontamination. The advanced oxidation processes are the ones that are widely employed for water treatment to remove contaminants and disinfect water. The efficiency of these methods can be increased with the use of nanomaterials. Graphene and hybrid graphene compounds have gained much attention for their exclusive properties such as high surface area and enhanced physical and chemical properties in water treatment technologies (Sepúlveda et al. 2022).

GO is obtained from the oxidation of graphite and is used to remove various pollutants from water. It has a high surface area, abundant functional groups, and extraordinary mechanical strength, making it suitable for water treatment. The edges of the planar surface have a negative charge; thus, adsorption and removing contaminants become easier with various mechanisms (Abubshait et al. 2021). GO, when doped with metal oxides, increases the properties, and the removal efficiency of the modified catalyst increases. When Fe_3O_4 is mixed with GO in the proportion of 9:1, the elimination of lead-containing contaminants increases to 30% concerning GO, whereas Fe_3O_4-GO in the proportion of 5:1 was capable of removing 10.3% contaminant lead in comparison with GO (Yoo et al. 2020).

The application of reduced graphene oxide is observed in the removal of colored dye (neutral red) and a colorless compound, ciprofloxacin, from the wastewater through photocatalysis, for this manganese dioxide, nanorods over rGO nanosheets were used as a nanocatalyst. The photocatalytic activity of the hybrid composite MnO_2-rGO showed a significant increase in removal efficiency from 50 to 94% of neutral red dye. It was also observed that the degradation of ciprofloxacin was enhanced from 49 to 74% through photocatalysis. The nanocatalysts were effective for four cycles when they were used for neutral red dye and ciprofloxacin (Chhabra et al. 2019). With the rate at which pollution is increasing daily, environmental protection has become a threat with challenges to overcome, and one of the major reasons behind this is growing industrialization. Toxic materials are added to the ecosystem via air or water, causing pollution of the system as a whole. GO, with its nanostructure, is effective in controlling air pollution as a multilayered structure is capable of adsorbing gases and thus reducing the concentration of pollutants in the air. Certain gases such as CO, H_2S, and NH_3 are efficiently adsorbed on the surface of GO. The application of GO is also observed in disinfecting the water and making it free from bacteria that are responsible for causing diseases. The edges of GO nanosheets act as a cutter that destroys the membrane, thus damaging the cell membrane of bacteria and ultimately killing them (Sajjad et al. 2017).

GO has a high surface area, good planar properties, and biocompatibility that makes it apt to carry an antibacterial active substance. The application of GO for light-driven processes to exhibit its activity is low as its reactive oxidative species (ROS) is low. In a few cases, the preparation of nano-antibacterial materials modified with anthraquinone has shown hyper-oxide generation in a photo-induced disinfection system. Sodium anthraquinone-2 sulfonate was used to alter GO to gain AQS-GO composite (anthraquinone-2-sodium sulfonate), GO ultimately imparted properties such as high surface area, thermal and mechanical stability, enhanced strength, and a suitable carrier for the antibacterial component. When implemented in the real system, the composite's antibacterial properties were higher than that of GO (Zhang et al. 2020).

GO is reduced using chemical reductants such as hydrazine, which produces reduced graphene oxide nanosheets. But hydrazine is harmful to both human health and the environment. The explosive nature and corrosive nature of hydrazine makes it unsuitable. Even the doping of materials causes a problem when hydrazine is used as a reductant. It alters the electronic properties of GO. Sometimes GO sheets agglomerate, which is irreversible. The addition of stabilizers such as porphyrins or polyamines can prevent this. Thus, to overcome these problems, a green approach to reduction is employed using chemically stable materials that do not hinder human health and the environment. Reducing agents such as microbes and polyextracts are used. These natural products and many others were harmless and ultimately a greener approach in synthesizing the rGO. Natural products such as glucose, sugar, and vitamin C were investigated for the cost-effective and green approach. Another material that is gaining attention is bagasse which has lignin and cellulose and becomes a polymeric template for the synthesis of nanomaterials. The rGO obtained is potentially active to be used for the adsorption process, specifically in wastewater treatment. The bagasse-based rGO was tested to reduce the concentration of dyes. The observed values of removal were promising, giving 92% efficiency imparting large surface area because of the porous structure (Gan et al. 2019). Table 3 shows the various degradation data using photocatalysis process.

Types of GO nanostructures

When we refer to the nanoscale, one of the dimensions of the material is less than 100 nm. The entity with at least one nanosized functional group and exhibits physical, chemical, and biological properties that characterize nanoscale is known as a nanostructure. When looking for nanomaterials,

Table 3 Various degradation details of graphene-based nanocomposites

Component	Pollutant degraded	Degradation time (min)	Source of light	Band gap (eV)	References
GO	Phenoxazin-3 one dye	40	UV	3.26	(Krishnamoorthy et al. 2011)
rGO	Methylene Blue	210	Visible	3.97	(Mazarji et al. 2022)
ZnO/GO	Methylene Blue	90	Visible	3.01	(Chaudhary et al. , 2021b)
ZnO/rGO	Methylene Blue	90	Visible	2.6	(Chaudhary et al. 2021a)
Cu/rGO	Rhodamine B	60	UV	2.85	(Safajou et al. 2021)
Cu/rGO	Methylene Blue	60	UV	2.85	(Safajou et al. 2021)
rGO.Fe_3O_4/TiO_2	Malechite Green	55	UV		(Bibi et al. 2021)
rGO/TiO_2	BPA	60	Visible	2.69	(Ramesh et al. 2021)
TiO_2-rGO	Methylene Blue	90	UV	–	(Yu et al. 2022)
TiO_2-rGO	Rhodamine B	90	UV	–	(Yu et al. 2022)
TiO_2-rGO	Methyl orange	90	UV	–	(Yu et al. 2022)
CuO-rGO	Methylene Blue	90	100W Xe lamp	–	(Sagadevan et al. 2021)
CuO-rGO	Congo Red	90	100W Xe lamp	–	(Sagadevan et al. 2021)
AgNP-rGO	Chlorpyrifos	105	Visible	–	(Chinnappa and Joseph 2022)
GO-TiO_2-ZSM5	Cyanide	180	High-pressure mercury lamp	3.2	(Pan et al. 2022)

carbon nanotubes, and graphene find their recognition as nanostructures that exhibit varied properties suitable for several applications worldwide (Sechi et al. 2014). A single-layered atomic structure of graphite is known as graphene. Graphene has gained much attention due to its versatile physical properties in various applications. GO, one of the derivatives of graphene, is a two-dimensional carbon sheet structure suitable for chemical modification. The researchers have investigated their properties and utilized these nanostructures to synthesize nanoparticles with desired properties. One such study showed the synthesis of the pure hexagonal closed pack (hcp) structure of Au sheets on GO. The structure contains the unique arrangement of the Au atoms. This hcp structure transforms into a face-centered cubic (fcc) structure. Studies reveal that the fcc structure is more stable for noble elements such as Ag and Au. Concentrating on Au, ultrathin Au square sheet exhibits a similar dimensional effect, and the hcp phase is preferred, but when tested, it is also transformed to the fcc phase. The synthesis generally shows an hcp phase with unique surface characteristics and stability under ambient conditions (Huang et al. 2011).

One of the applications of carbonaceous nanomaterials is in supercapacitors. Graphene and its derivatives are widely used in such applications owing to their properties such as high electrical conductivity, thermal stability, and mechanical flexibility. The increased surface area of graphene-based materials is the regulating factor that helps to control the morphology of electrochemically active nanomaterials. The composite structure of GO and CuO has shown the highest capacitance and good electrochemical performance that is useful for CuO molecules to participate in redox reactions. The CuO nanostructures on GO were examined for their electrochemical processes. The resulting composites exhibit high electrical conductivity that is suitable for supercapacitors. This hybrid composite showed enhanced energy storage capacity, high-energy density, and recycling stability (Islam et al. 2018). The vibrant shapes of graphene and its derivatives, such as GO, have drawn much attention due to the varied properties at the nanoscale. The shaped edges of nanoflakes and nanorods exhibit distinct electronic and magnetic properties. There are variations in the origin and band gaps in every shape edge. The graphene quantum dots result from graphene or graphene oxide with size less than 10 nm and possesses different band gaps that depict other low toxicity properties, biocompatibility, and photoluminescence. A single-step method for GO with PLA (pulse laser ablation) gives various shapes such as nano-squares, nano-rectangles, nano-triangles, nano-hexagons, and nanodisks. The GO sheets are converted to nanoribbons and nanoflakes (the various nano-shapes mentioned above) (Lin et al. 2015).

Many strategies are employed to improve the performances of carbon nanomaterial-reinforced matrices. The composite matrix of graphene and carbon fibers exhibited an assisted magnetic field and enhanced electrical and mechanical properties. Carbon does not show ferromagnetism; thus, to increase the magnetic, the composite is decorated with Ni, Fe, and other ferrites. A freeze-drying method in combination with molecular level mixing, a reduction process was carried out to prepare GO-CNT nanostructures decorated Ni nanoparticles. These nanostructures were successfully implemented to prevent the expansion of the epoxy matrix. This makes epoxy material find its place in aerospace, aviation, and automobile manufacturing (Hu et al. 2022).

Problems encountered with GO/modified GO in photocatalysis applications

Over a while, graphene and its compounds have become research hotspots. These materials possess unique surface properties exhibiting high surface area, thermal stability, mechanical strength, and excellent electron acceptor. Due to the strong van der Waals force of attraction, graphene sheets are agglomerated, and thus, loss in accessible surface area is noticed in adsorbates. With innumerable advantages, the drawback is a synthesis of adsorbent that is way too time-consuming (Pyrzynska 2023). Photocatalytic technology has been widely used because of its low-cost processing and environmentally friendly method for removing environmental pollutants. GO and rGO are the materials that are employed as photocatalysts owing to their versatile properties. These graphene-based compounds are even modified by adding metal oxide that increases the functional group in the structure and enhances their activities. But in the process of photocatalysis of dyes, GO is inefficient in reducing the concentration of dyes due to the wide band gap and recombination of photogenerated particles (Prakash 2022).

The combination of GO with TiO_2 compound exhibiting semiconductor properties made a nanocomposite that showed enhanced photocatalytic activity. The band gap for alone TiO_2 for the photocatalysis was observed to be 3.10 eV, but when TiO_2 was combined with GO, the band gap reduced to 2.60 eV. This is because of the presence of various functional groups in the structure that provides high surface area. The problem with using these nanocomposites is that they agglomerate and reduce the available surface area, thereby decreasing the photodegradation process (Kong et al. 2022). The surface of GO is chemically active, which allows the organic molecule to attach to it. This will cause modification in the electronic properties of the structure. Also, the addition of metal oxide enhances its properties as a photocatalyst, but the aggregation of particles becomes a concern (Yadav et al. 2022).

Conclusion and future scope

This review explores a versatile carbonaceous nanomaterial, graphene, and its derivatives. The extensive properties of graphene-based compounds include high surface area, good thermal stability, excellent mechanical strength, and the capability to combine with other metal oxides and form composite structures suitable for various applications. The synthesis methods of graphene base compounds are also discussed at length. One of the major applications that are discussed here is photocatalysis. The degradation of pollutants in the wastewater, organic and inorganic, both through a greener approach with various metal oxides, is discussed in case studies. This review describes all the properties and applications of graphene derivatives. A brief insight into different GO nanostructures is also described in this literature.

Along with all the advantages, a few areas have remained untouched. During photodegradation, agglomeration of GO nanocomposites occurs, reducing the composite's effective surface area. This reduces the rate of photodegradation. Another area that needs attention is the real system comprising varied concentrations of pollutants. The concentration of the pollutants keeps varying with changes in pH and temperature. The further exploration of the prevention of agglomeration and application in a real system, GO-based catalysts need extensive study and experimentation.

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