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Graphene- and Graphene Oxide-Bounded Metal Nanocomposite for Remediation of Organic Pollutants

Brajesh Kumar

Abstract

Nanotechnology is one of the most interesting areas concerned with consumer products including cosmetics, household appliances, electronics, textiles, and food production as well as in medical products. Environmentally benign, economical, practical, and efficient processes for the synthesis of graphene (rGO)-/graphene oxide (GO)-bounded metal nanoparticles and their use for the remediation of organic pollutants (dyes, pharmaceutical wastes, pesticides, etc.) have been increasingly important goals in the chemical community from economic, safety, and environmental points of view. In this chapter, various strategies have successfully demonstrated the synthesis of graphene-/graphene oxide-bounded metal nanoparticles using various natural sources (plant extracts, biomolecules, polysaccharide, alcohols, etc.) and their applications in environmental remediation.

Keywords: green synthesis, graphene, graphene oxide, organic dye, XRD, adsorption, photocatalytic effect, ecofriendly

1. Introduction

In 1959 American theoretical physicist Richard P. Feynman popularization through his lecture "There is a plenty of room at the bottom," revolutionize a new era technology, where manipulation of the properties of a device is possible at atomic, molecular and macromolecular scales called nanotechnology [1]. Nanoparticles, having particle sizes ranging between 1 and 100 nanometers, have a very surprising history, their synthesis is not limited to a modern laboratory, they have existed in nature for a long time, and their use can be traced to ancient times; for example, the application of metal nanoparticles as color pigments in luster and glass appeared in Mesopotamia during the ninth century. Nanosized metal particles have unique chemical and physical properties that are significantly different from those of the bulk equivalents [2]. Now, the deliberate manipulation of the matter at the aforementioned scale allows the creation of materials with unique (and unusual) optical, chemical, photoelectrochemical, electronic, and biological properties that can be applied in catalysis, biosensing, imaging, medicine, and other important fields [3, 4].

Eco-friendly methods for nanoparticle synthesis using plants or plant extracts, fruits, agricultural wastes, microorganisms, enzymes, fungi, starch, sucrose, and

maltose have been suggested as possible alternatives to chemical and physical methods, and biological approaches to the synthesis of nanoparticles are attracting research attention. Biological molecules can undergo highly controlled, hierarchical assembly, which makes them suitable for the development of reliable and eco-friendly processes for metal nanoparticle synthesis. Furthermore, these methods are cheap and rapid and efficiently produce single atoms or molecules with a wide variety of shapes (spheres, prisms, or plates) in the nanoscale level [4, 5]. Phytosynthesis of metallic nanostructures has become a more suitable alternative technique than physical and chemical methods because they are simple, nontoxic, rapid, cost-effective, eco-friendly, and sustainable. In the other hand, it has been widely recognized that carbon-based nanomaterials such as carbon nanotubes, carbon nanofibers, active carbon, and graphene can be used in a lot of important applications like sensing, catalysis, conversion, energy storage, polymer composites, and pollution prevention; all these properties are strongly coupled to carbon's structural conformation and, thus, its hybridization state [6].

In the past few years, carbonaceous and carbon-based nanomaterials have been attracting a significant research interest because of their exclusive characteristics, including good biocompatibility, nontoxicity, high mechanical/thermal properties, and relative ease of functionalization [7]. Among other nanomaterials, graphene has become a rising star in condensed matter physics and material research due to its exclusive mechanical, physical, and chemical features. The term "graphene" was proposed in 1986 to define single atomic layers of graphite. Since its discovery as important allotropes of carbon, graphene has become one of the most advanced carbon nanomaterials. It is a two-dimensional single sheet sp^2 hybridized of carbon atoms arranged in a hexagonal close-packed honeycomb like a crystal lattice through σ- and π-bonds, and it also has high specific surface area (2,630 $m^2\,g^{-1}$) [8]. Specifically, the chemical oxidation-exfoliation-reduction of graphene to obtain graphene oxide (GO), which has abundant oxygen-containing functional groups (epoxy, carbonyl, carboxyl, hydroxyl, etc.), allows the creation of the perfect surface to anchor organic nanoparticles for enhancement of wider applications (**Figure 1**) [9]. Because of its novel and unique properties, tremendous fundamental and technological studies have been stimulated. Graphene has a unique band structure in which the conduction band and valence band just touch each other, forming an exactly zero bandgap semiconductor (also known as a semimetal) [10]. Since the first successful production in 2004 by Andre Geim and his coworkers at
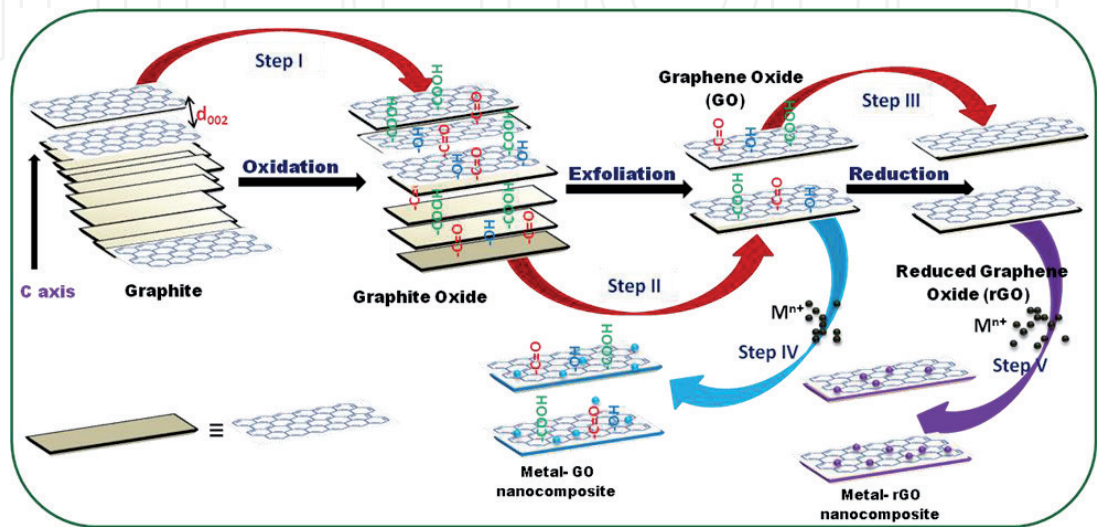
Figure 1.
Schematic representation for the synthesis of graphene oxide, graphene (rGO), and its metal nanocomposite.

Manchester University, graphene have become a "rising star" material thanks to its unique properties such as large theoretical specific surface area, high thermal conductivity, good biocompatibility, optical transmittance, good electrical conductivity, high elasticity, chemical and electrochemical inertness, and easy surface modification; for these reasons graphene can be used in field effect transistors, sensors, transparent conductive films, clean energy storage, conversion devices, catalysis, photocatalysis, nanocomposites, solar cells, drug delivery, etc. [11].

In the last few decades, a vast number of synthetic organic compounds, including textile dyes, pharmaceutical compounds, and pesticides, have been found in wastewater and surface/groundwater due to wastewater discharged from various industries and domestic households. Most of the pharmaceutical compounds and dyes are highly polar, of low volatility, and extremely resistant to biodegrading processes; these constitute a potential risk for the aquatic and terrestrial organism and also a collateral generation of microbial resistance. For this reason, the need of the improvement of the decontamination efficiency of organic pollutants using eco-friendly techniques is increasing with time [12, 13]. Ozonization, photo-fenton, biodegrading processes, and photocatalysis have been widely used techniques for organic compound degradation; all these methods show a high rate of effectiveness [14]. Semiconductor and noble metal nanoclusters in nanometer size display a lot of interesting optical, electronic, chemical, and biological size−/shape-dependent properties; in terms of pollutant degradation, the noble metal nanoparticles exhibit increased photochemical activity because of their unusual electronic properties and high surface [15].

Over the last years, nanotechnologies have been implemented in almost all branches of human activities, including wastewater treatment. Numerous nanomaterials are utilized to eliminate inorganic and organic species from wastewater effluents, in many cases even more efficiently than the conventional adsorbents. These include nanoparticles of metals, metal oxides, carbon nanotubes, graphite, fullerenes, carbon-based nanocomposites, etc. [16]. On the other hand, graphene oxide enhances the possibilities for the construction of graphene-involved catalyst and graphene-based hybrid nanocomposites with inorganic species, such as noble metal nanoparticles in order to photodegrade pollutants (**Figure 1**). The photodegrade activity is promoted by the high specific surface area ($2,630 \ \text{m}^2 \ \text{g}^{-1}$), enhanced active sites, large delocalized π-electron systems, good chemical stability, unique electronic properties of graphene-based materials, and excellent transparency; this means it is an excellent adsorbent for organic and inorganic pollutants [17]. For example, graphene/graphene oxide could be used in combination with common photocatalysts (TiO_2, ZnO), leading to the enhancement of absorptivity of pollutants. This means a new generation of photocatalyst systems used as an adsorbent for wastewater handling purposes [18].

2. Graphene oxide and graphene synthesis

The trend to produce graphene and graphene nanoplatelets in bulk quantities centers on chemical exfoliation of graphite, which is more advantageous than other methods. Ideally, the graphene material should have just one layer, but recently graphene with two or more layers are being investigated with the same interest. One of the most developed techniques to obtain graphene with high yields single layer powder following a modified Hammers method, which consists of the initial oxidation of graphite to water dispersible graphite oxide, which results in an increase in the interlayer spacing between the oxygen-containing graphene layers. The oxygen-containing functional groups make GO sheets highly hydrophilic and render them prone to swelling quickly and therefore easy to be dispersed in water [19].

This process must be followed by mechanical or chemical exfoliation of graphite oxide to graphene oxide sheets and the final reduction to graphene (**Figure 1**) [4, 20]. Also, the reduction of graphite oxide, using thermal or chemical procedures, to obtain graphene, appropriately named reduced graphene oxide, has been a challenging research area. For a long time, hazardous, toxic, and explosive reducing agents have been used, as in the synthesis of metallic nanoparticles [21]. In order to avoid the use of these chemicals, some authors recommend the use of biomolecules such as ascorbic acid, reducing sugars, casein, and plant extracts; generally they contain a lot of polyphenols which are converted to their corresponding oxidized quinone forms with the power to reduce graphene oxide [22].

3. Graphene oxide and graphene-metal nanocomposite synthesis

Graphene and graphene oxide have a plate-like structure with a large specific area and fantastic properties, making the sense to use these kinds of materials as a substrate for the deposition of inorganic nanoparticles like silver, gold, copper, palladium, iron, cobalt, zinc, tin, etc. Several techniques which are used to decorate graphene and graphene oxide are employed, for example, a solution-based method, electrodeposition, thermal evaporation, photochemical, and solventless bulk synthesis, among others; in any case, the type of solvent, nature and concentration of metal precursor, the presence of a dispersing and/or reducing agent, time, and temperature are factors that must be controlled to obtain a narrow particle size distribution [23, 24]. The hydrophilicity and exfoliation of graphene oxide have offered exciting opportunities to build nanocomposites and to form strong physical interactions with small molecules and polymers [24].

Nanoparticles have been produced by chemical strategies for a long time; in this process harsh, toxic, and expensive chemicals (e.g., hydrazine, sodium borohydride, dimethylformamide, and ethylene glycol) could be used as non-environmental friendly reducing agents; for this reason, the goal of the green chemistry is to foster the use of eco-friendly solvent medium and reducing and stabilizing agents [25]. Current research in phytosynthesis using plant extracts have shown that they are a good alternative for fast and nontoxic production of nanoparticles; this is thanks to the antioxidant activity of several plants which have a high content of polyphenols (e.g., flavonoids, flavones), carotenoids, reducing sugars, terpenoids, glutathiones, and metallothioneins, among other molecules, that could act as reducing and capping agents in the nanoparticle formation and replace toxic chemicals [26]. The phytosynthesis of metallic nanoparticles involves three main steps: (i) selection of the solvent medium, (ii) selection of environmentally benign reducing agent, and (iii) selection of nontoxic substances for nanoparticle stability [27].

Nanocatalysis is a recent field of research in nanoscience; most of the studies involve the use of spherical or undefined-shape nanoparticles with a small size, as an alternative to conventional materials [28]. The combination of graphene or graphene oxide with metallic nanoparticles has opened a new field in environmental remediation through the increase of photocatalytic degradation activity against organic pollutants due the ability to absorb light and enhance heterogeneous catalysis [4, 29]. The organic pollutants discharged by industries can remain in the environment because they have high solubility in water and high stability to light, temperature, and biological degradation. Recently, biogenic synthesis of graphene- or graphene oxide-bounded metallic nanocomposite for the photodegradation of organic compounds in wastewater, such as dyes, pharmaceutical and personal care products (PPCPs), and pesticides (**Figure 2**), has received much attention due to the toxicity thereof to human beings and the environment.
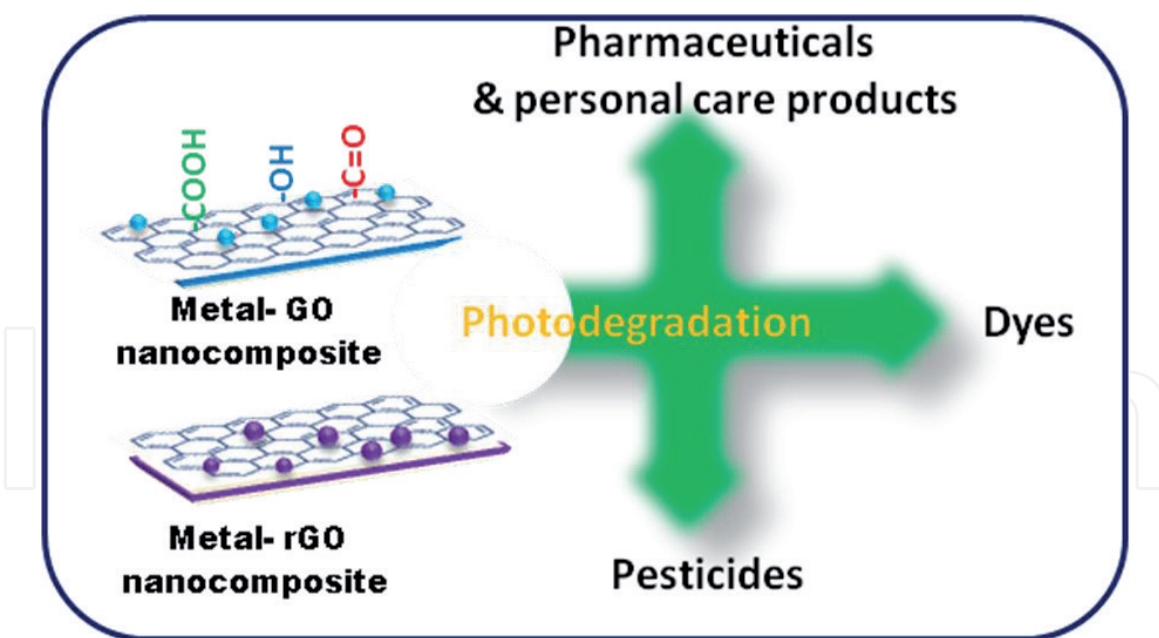
Figure 2.
Utilization of graphene oxide/graphene-metal nanocomposite for the photodegradation of various categories of organic pollutants.

## 4. Photocatalytic degradation mechanism for organic pollutants

Recently, in order to degrade organic dye compounds, many researchers around the world have studied on the photocatalyst material which is usually a wide bandgap semiconductor in the presence of solar energy. For practical applications, development of efficient, reproducible, and cost-effective visible light-induced photocatalyst is desirable for the large-scale production of catalyst. Recently, many research papers are dedicated to the plasmonic photocatalysis by using noble metals as silver [30], carbonaceous-based (nanotubes, fullerenes, graphene, etc.) [31], and semiconductor-carbonaceous composite based photocatalysts [32] and their structure (to include size, shape, crystallinity, porosity, contact form, etc.). The principals behind the heterogeneous photocatalysis are based on a complex sequence of reactions which create electron–hole pairs under photo-illumination. Briefly photocatalyst absorbs UV and/or visible light irradiation from sunlight, which is abundantly available as natural irradiation energy or an illuminated light source as shown in **Figure 3**. The electrons (e^-) in the valence band (VB) of the photocatalyst are excited to the conduction band (CB), while the holes are left in the valence band. This, therefore, creates the missing negative charges/negative (e^-) and positive electron–hole (h^+) pairs. This stage is referred to the semiconductor's "photoexcited" state, and the energy difference between the valence band and the conduction band is known as the "bandgap." This must correspond to the wavelength of the light for it to be effectively absorbed by the photocatalyst. The electron–hole pairs that are generated in this way migrate toward the surface where they can initiate redox reactions with adsorbates. Photogenerated reactions with the positive holes are linked to oxidation of hydroxyl groups or water molecules to produce hydroxyl ($\bullet OH$) radicals and reactions with electrons to dissolved oxygen to reduce superoxide radical anion ($\bullet O_2^-$), which then reacts with H^+ to form $\bullet HO_2$ and H_2O_2, followed by rapid decomposition to $\bullet OH$. Degradation/disinfection of toxic pollutants operates through the formation of $\bullet OH$, which have very low reaction selectivity. These $\bullet OH$ radicals drive the oxidation of pollutants to complete mineralization, i.e., less reactive pollutants [28, 33].

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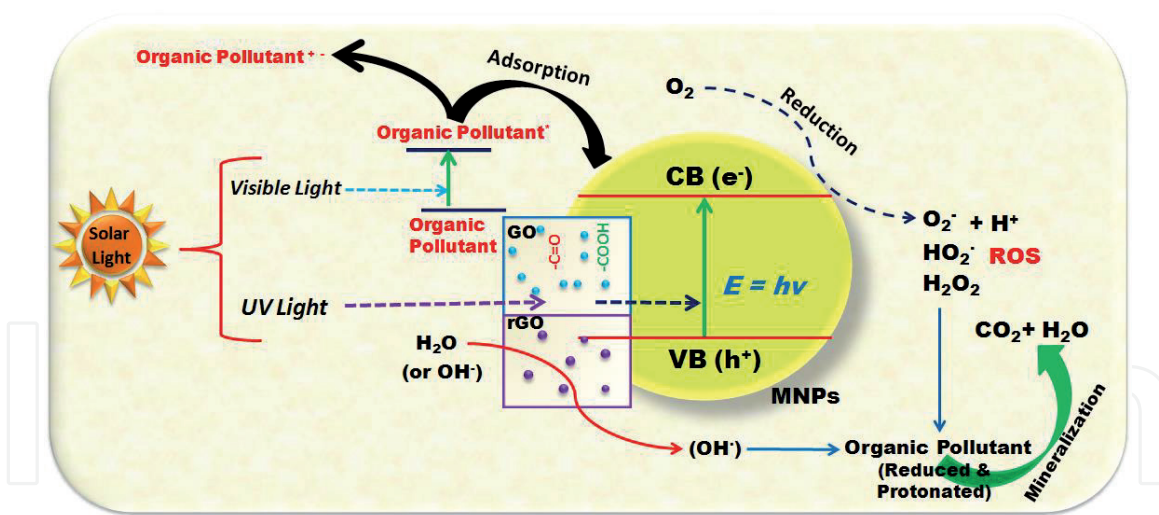
Figure 3.
Mechanism for the photocatalytic degradation of organic pollutants.

5. Photocatalytic degradation of dyes

Over the recent decades, graphene- or graphene oxide-bounded metallic nanocomposite-based photocatalysts have attracted great attention in water purification because of their high photosensitivity, environmental friendliness, stability, nontoxic nature, and low cost. Carbonaceous material is well known as an effective adsorbent due to hydrophobic interaction, π-π interactions, hydrogen-bonding interactions, and electrostatic and dispersion interactions, and it has large specific surface area and also acts as electron scavengers due to their large electron storage capacity. **Figure 4** shows the structural formula for the salts of different toxic organic dyes. Vizuete et al. reported on the formation of a silver-graphene (Ag-G) nanocomposite through the reduction of Ag^+ and graphene oxide using berry extract of Mortiño (*Vaccinium floribundum* Kunth). The as-prepared Ag-G nanocomposite showed an enhanced photocatalytic activity for the degradation of methylene blue (k = 0.0163283 min^{-1}) and methylene orange (k = 0.0140985 min^{-1}) in an aqueous medium under sunlight irradiation [34]. Chandu et al. reported in
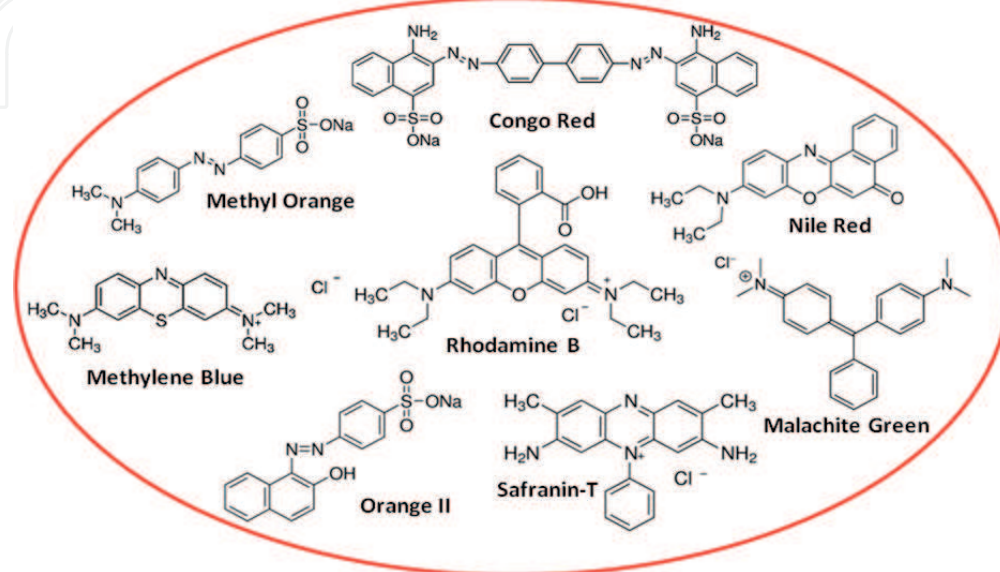
Figure 4.
The structural formula of salt for different toxic organic dyes.

situ synthesis of a nanocomposite of silver decorated on reduced graphene oxide sheets using betel leaf extract as a stabilizing and reducing agent. The sheet structure of reduced graphene oxide and uniformly distributed 28 nm silver nanoparticles exhibited good photocatalytic efficiency (95% in 2 h) against methylene blue in sunlight [35]. In another paper, Chandu et al. efficiently synthesized graphene oxide sheets decorated with silver nanoparticles (CRG-Ag nanocomposite) in 12 h using custard apple leaf extract, and as-synthesized CRG-Ag nanocomposite showed excellent photocatalytic efficiency of 96% in 2 h under sunlight using methylene blue (5 mg/L) as a model pollutant [36]. Maryami et al. used *Abutilon hirtum* leaf extract as a reducing and capping agent for the synthesis of silver supported on the reduced graphene oxide (Ag/RGO). The crystalline nature of the Ag/RGO nanocomposite was identified using XRD analysis and employed as a catalyst for the reduction of organic dyes such as 4-nitrophenol (4-NP), Congo red (CR), and rhodamine B in the shortest possible time in water at mild conditions [37].

Chandra et al. explained that the photodegradation of eosin, methylene blue, and rhodamine B is almost 80% in the presence of graphene-Mn_2O_3 nanocomposite [38]. In other hand, Benjwal et al. elaborated the enhanced photocatalytic degradation of methylene blue by reduced graphene oxide-metal oxide (TiO_2/Fe_3O_4)-based nanocomposites with efficiency (~100% within 5 min) [39]. Nenavathu et al. has synthesized functionalized graphene oxide (FGS)/ZnO nanocomposites with enhanced photocatalytic activity toward the photodegradation of the safranin T dye in aqueous solution via an economical, facile, and simple solution route, followed by calcination under environmental conditions [40]. Xiong et al. investigated the effect of modification of reduced graphene oxide with crystalline copper species. The copper species acted as an electronic relay, passing the excited electrons from the reduced graphene oxide to the adsorbed oxygen. The continuously generated reactive oxygen species led to the degradation of rhodamine B under visible light irradiation [41]. Fu and co-workers prepared a magnetically separable $ZnFe_2O_4$/graphene nanocomposite photocatalyst by a facile one-step hydrothermal method. The photocatalyst exhibited 88% of methylene blue degradation by adding H_2O_2 at 5 min and reached up to 99% at 90 min after irradiation of visible light. It serves a dual function as a photoelectrochemical degrader and a generator of hydroxyl radicals via photoelectrochemical decomposition of H_2O_2 [42].

Lui et al. synthesized hierarchical TiO_2 nanoflowers using a solvothermal reaction. The graphene-wrapped hierarchical TiO_2 nanoflowers showed improved performance of degradation of methylene blue under UV irradiation. This enhanced photodegradation is attributed to the excellent ability of transport of the charge, that is, electron as graphene has excellent conductivity which in turn suppresses the recombination of the electron-hole pair and provides more preferential adsorption sites for methylene blue which in turn enhances the degradation of methylene blue [43]. Lv et al. reported a quick and facile microwave-assisted synthesis method to produce ZnO-reduced graphene oxide hybrid composites and studied the photocatalytic performance in the degradation of methylene blue. The results showed that reduced graphene oxide plays an important role in the enhancement of photocatalytic performance. It was shown that the ZnO-rGO composite with 1.1% wt rGO achieved a maximum degradation efficiency of 88% in a neutral solution under UV light as compared to pure ZnO (68%) due to increased light absorption and reduced charge recombination [44]. Thangavel et al. first reported the synthesis and photocatalytic behavior of β-tin tungstate-reduced graphene oxide (β-SnWO₄-rGO) nanocomposites. The degradation efficiency of 55 and 60% were achieved by β-SnWO₄ alone, whereas in the presence of rGO, the photocatalytic degradation efficiency was found to be increased up to 90 and 91% in methylene orange and rhodamine B, respectively [45].

Ternary nanocomposites comprising Ag-Cu_2O supported by glucose-reduced graphene oxide with enhanced stability and visible light photocatalytic activity were synthesized by Sharma et al. via a facile and green approach using Benedict's solution and glucose solution at room temperature. The resulting Ag-Cu_2O/rGO nanocomposites showed excellent photocatalytic efficiency for the photodegradation of methyl orange, and the degradation rate was higher than the pristine Cu_2O and Cu_2O/rGO NCs. [46]. Xiong et al. reported an excellent visible light photocatalytic performance for graphene modified with gold nanoparticles in degrading non-biodegradable dyes like rhodamine B, methylene blue, and orange II in the water. The rate constants were calculated to be about 8.7×10^{-3} min^{-1}, 4.1×10^{-2} min^{-1}, and 9.4×10^{-4} min^{-1} for rhodamine B, methylene blue, and orange II, respectively. It confirmed that graphene modified with gold photocatalyst has four important features in comparison to the TiO_2: (1) high adsorption ability toward organic dyes, (2) strong p-p interaction with dye chromophores, (3) efficient photosensitized electron injection, and (4) slow electron recombination. These features make the graphene modified with gold composite a good candidate for photo-assisted degradation of dye pollutants in water [47].

Palladium-decorated ZnS/rGO nanocomposites prepared by a coprecipitation method showed significant visible light-induced photocatalytic activity toward the degradation of indigo carmine dye. The highest photocatalytic activity was 1.0% Pd-ZnS/rGO sample for degradation of 20 ppm indigo carmine ($k = 2.19 \times 10^{-2}$ min^{-1}) [48]. Kurt et al. prepared platinum and palladium-decorated reduced graphene nanosheet having antioxidant activity; IC_{50} values are 46.1 and 90.2 μg/mL, respectively, based on the ABTS method and 80.2 and 143.7 μg/mL according to the DPPH method. It also showed photocatalytic elimination of fuchsine and indigo carmine dyes under light irradiation [49]. Isari et al. prepared a ternary nanocomposite of Fe-doped TiO_2 decorated on reduced graphene oxide using simple sol-gel method. The DRS results of the photocatalysts showed a narrowing bandgap by the introduction of Fe ions to the titania framework. The maximum removal of rhodamine B is 91% after 120 min under solar illumination by using 0.6 g Fe-doped TiO_2/rGO nanocomposite containing 3% Fe and 5% rGO, with an initial pH of 6 [50]. El-Shafai et al. fabricated two nanocomposites, namely, graphene oxide-iron oxide (GO-Fe_3O_4) and graphene oxide-iron oxide-zirconium oxide (GO-Fe_3O_4@ZrO_2), and characterized their identity by using different spectroscopic techniques. It was observed that newly fabricated GO-Fe_3O_4 (3.66 eV) and GO-Fe_3O_4@ZrO_2 (3.20 eV) nanocomposites have the advantage of smaller bandgaps than GO (4.00 eV), which result in increased adsorption capacity and photocatalytic effects. Results confirmed that RhB is efficiently adsorbed over the surface of graphene oxide (~93%) and has a significant inhibitory effect against *E. coli* bacteria [51].

The hydrothermal synthesis and photocatalytic activity of SnS-reduced graphene oxide nanocomposites for the photodegradation of malachite green in water were being investigated by Wang et al.. The experimental results indicated that the as-synthesized nanocomposites showed excellent sunlight-excited photocatalytic activity of malachite green in water with quasi-kinetic rate constant in the range of ~0.32–0.69 h^{-1} and it increased to ~0.60–1.82 h^{-1} by using H_2O_2 synthetically [52]. Ye et al. prepared CdS-graphene and CdS-carbon nanotube nanocomposites by a hydrothermal method and studied them as photocatalysts for the evolution of hydrogen and the degradation of methyl orange under visible light irradiation. The incorporation of graphene or carbon nanotube into CdS significantly enhanced the photocatalytic activities for both reactions. It confirmed that the rate of photodegradation of methylene orange was the highest for the CdS-graphene and it is 7.9 times higher than that of CdS alone and 1.8 times higher than that of

the CdS-carbon nanotube composite [53]. Recently, Ansari et al. for the first time fabricated cobalt hexaferrite nanoparticles using natural reducing agents (carbohydrates and pigments) by the sol-gel method and compared photocatalytic activities with their carbon-based nanocomposites including graphene and carbon nanotube. It was found that the degradation order of methylene orange under UV irradiation is arranged as graphene-based nanocomposite > CNT-based nanocomposite > pure nanoparticles. It may be due to the unique structure and a specific surface area of graphene (2D) and maybe CNT (1D). Kinetics studies showed that photocatalytic reactions in the presence of pure nanoparticles and CNT-based nanocomposites followed by pseudo-first-order, but in presence of graphene-based nanocomposites followed by zero-order indicates saturation of graphene surface with MO as an organic pollutant through physical absorption [54]. Till date, very few works has been done related to phytochemical-mediated synthesis of metal-/metal oxide-bounded graphene oxide/reduced graphene oxide nanostructures for the degradation of organic pollutants.

6. Photocatalytic degradation of pharmaceutical and personal care products

During the past few decades, the focus of environmental research has been more toward nonbiodegradable pharmaceuticals and personal care products because of its possible direct damages to living organisms and agriculture. PPCP can be further classified as antibiotics, anticonvulsants, contrast agents, hormones, nonsteroidal anti-inflammatory drugs (NSAIDs), β-blockers, lipid regulators, painkillers, preservatives, disinfectants, insect repellants, fungicides, soaps and detergents, fragrances, and sunscreen UV filters [55]. **Figure 5** shows the structural formula for different pharmaceutical and personal care products. Adsorption, photocatalysis, and a combination of these two are considered to be promising technologies for the removal of antibiotics from wastewater. The adsorption method has the advantages of easy operation, low cost, high efficiency, strong reproducibility, and availability of different adsorbents. Whereas photocatalysis, as the best advanced oxidation process (AOPs), is an economic, efficient, and green technology for degrading antibiotics using sunlight and ambient conditions [56]. Although graphene-based photocatalyst have the high potential for the photocatalytic degradation of antibiotics due to the interaction of the aromatic ring of antibiotics with graphene oxide/reduced graphene oxide mainly via π-π bond interaction.
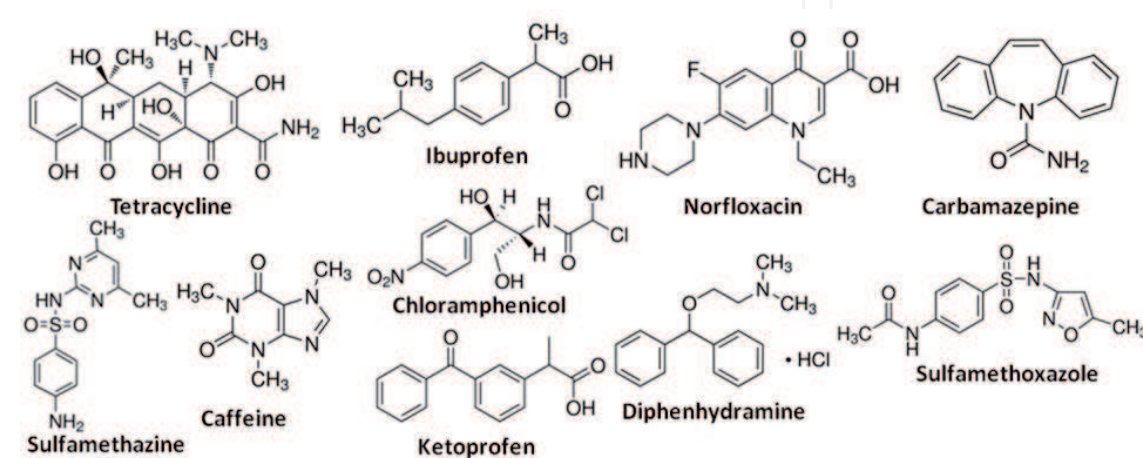
Figure 5.
The structural formula for different pharmaceutical and personal care products.

Tetracycline, the second most widely used antibiotics worldwide, has been extensively used as human medicine, as a veterinary drug, and as a growth promoter in animal cultivation. It is poorly metabolized and absorbed by humans and animals; thus large fractions are excreted via urine and feces. Therefore, it has been frequently detected in soil, surface waters, and even drinking water. Looking at this issue, Song et al. prepared MnO_2/graphene nanocomposite by an in situ hydrothermal method, and it successfully removed up to 99.4% of the tetracycline residue in pharmaceutical wastewater [57]. On the other hand, Shanavas et al. studied the degradation of ibuprofen and tetracycline molecules efficiently under visible light irradiation within 90 min using ternary $Cu/Bi_2Ti_2O_7$/rGO composite. The analysis of the obtained results suggested that the Cu nanoparticles and the rGO sheets play a major role in the photocatalytic ability of $Cu/Bi_2Ti_2O_7$/rGO photocatalysts by acting as charge carrier trappers and the suppression of e^--h^+ pair recombination [58]. A novel nitrogen-modified reduced graphene oxide nanocomposite with the function of adsorption and catalytic degradation of norfloxacin and ketoprofen in water was successfully explained by Peng et al. A complete removal of norfloxacin (20 mg/L) was achieved within 210 min with the addition of 10 mmol/L $S_2O_8^{2-}$ and 100 mg/L of as-prepared nanocomposite, and the removal efficiency of total organic carbon (TOC) was 89% [59].

The enhanced photocatalytic activities of graphene-TiO_2 composites make them an ideal material for remediating PPCP. However, one of the major obstacles to using nanoscale catalysts in water treatment is the difficulty in separating and recovering the catalysts. Lin et al. synthesized a series of TiO_2-reduced graphene oxide-coated side-glowing optical fibers (SOFs) by polymer-assisted hydrothermal deposition method. Photocatalytic performance of the synthesized nanocomposites exhibited significantly higher photocatalytic activities than pure TiO_2. The highest catalytic activity was observed by 2.7% reduced graphene oxide, resulting in 54% degradation for carbamazepine, 81% for ibuprofen, and 92% for sulfamethoxazole after 180 min high-pressure UV irradiation; the mineralization rates of the pharmaceuticals were similar between 52 and 59% [60]. Pastrana-Martínez et al. synthesized a graphene oxide-modified TiO_2 composite through liquid phase deposition and employed it to photocatalytically degrade diphenhydramine under ultraviolet and visible light irradiation. It was noted that the total degradation and significant mineralization of diphenhydramine pollutant (in less than 60 min) was achieved under near-UV/Vis irradiation for the optimum 3.3–4.0% wt GO in as-synthesized composites [61]. 3D porous rGO-TiO_2 aerogel was shown to remove carbamazepine (10 ppm) by more than 99% within 90 min in aqueous solution. The macroporous 3D structure of the aerogel resulted in abundant surface sites, effective charge separation, improved mass transport of contaminants, and easy separation [62].

A family of titanium-derived cobalt nanoparticles (Co_3O_4/TiO_2) and amine-functionalized titania Co_3O_4/TiO_2 graphene oxide nanocomposite synthesized via sol-gel and hydrothermal routes exhibit excellent performance for the photocatalytic degradation of oxytetracycline under solar and visible irradiation. Heterojunction formation between a low concentration of discrete Co_3O_4 nanoparticles and anatase titania strongly promoted the photocatalytic oxidative degradation of oxytetracycline, which was further enhanced upon trace GO addition. Amine functionalized 2% wt Co_3O_4/TiO_2/GO exhibits excellent rates and stability toward oxytetracycline photodegradation under visible light irradiation [63]. Fe_3O_4/Mn_3O_4-rGO nanocomposite was also used for a comprehensive photocatalytic degradation of the aqueous sulfamethazine solution. The results revealed 99% sulfamethazine degradation efficiency at optimum conditions of 0.07 mm/L sulfamethazine concentration, 0.5 g/L of Fe_3O_4/Mn_3O_4-rGO nanocomposites, 35°C, pH 3, and hydrogen peroxide concentration of 6 mM [64]. Karthik et al. fabricated

a nanocomposite consisting of graphene oxide-decorated cerium molybdate nanocubes (Ce $(MoO_4)_2$/GO)) and utilized it in the photocatalytic degradation of chloramphenicol under visible light irradiation. The Ce $(MoO_4)_2$/GO composite displayed excellent photodegradation potential against the drug and showed higher degradation efficiency (99% within 50 min) than the pure Ce $(MoO_4)_2$ nanocubes. The impressive performance of the composites was assigned to the excellent separation of the photogenerated electrons and holes [65]. A magnetically recyclable GO-TiO$_2$ composite showed up to 99% removal of carbamazepine and caffeine within 60 min under UV irradiation, and this composite was fully recoverable and reusable by magnetic separation. The added benefit is that the GO-TiO$_2$ composite is fully recoverable, reusable, and easy to produce [66]. The electrospun one-dimensional graphene oxide-nanofiber TiO$_2$ composite was prepared by using polyvinyl-pyrrolidone (PVP) as a fiberizing carrier. It showed a higher photodegradation rate of 4-chlorophenol under visible light irradiation relative to pristine TiO$_2$ due to the enhanced separation efficiency of photogenerated electron-hole pairs [67].

7. Photocatalytic degradation of pesticides

Pesticides are naturally derived or synthetically produced chemicals meant to control and destroy the pests and weeds. It includes bactericides, fungicides, herbicides, and insecticides. The excessive use of pesticides comes with various environmental apprehensions and harms living organisms due to their carcinogenic effects. So, there is an urgent need to develop a technology which can detect and degrade these hazardous pesticides efficiently without harming the environment with low cost. Nanoscience and nanotechnology is the emerging field which can serve this purpose [68]. Graphene-based composite materials hold great potential as adsorbent and photocatalyst for pesticide remediation from wastewater. A strong π-π interaction of the organic contaminant with the aromatic ring of graphene is the mechanism behind the strong adsorption behavior of GO toward different pesticides [68]. **Figure 6** shows the list of some pesticides normally used in the agricultural field. Boruah et al. prepared nanocomposite with Fe$_3$O$_4$ NPs and reduced GO (rGO) for the removal of triazine pesticides. The electrostatic interaction between the nanocomposite and the pesticide helped in efficient adsorption and removal of the pesticide. The nanocomposite exhibited 93.61% adsorption efficiency for the pesticides. Easy recovery of these magnetic nanocomposites from the reaction mixtures by applying an external magnetic field was an added advantage
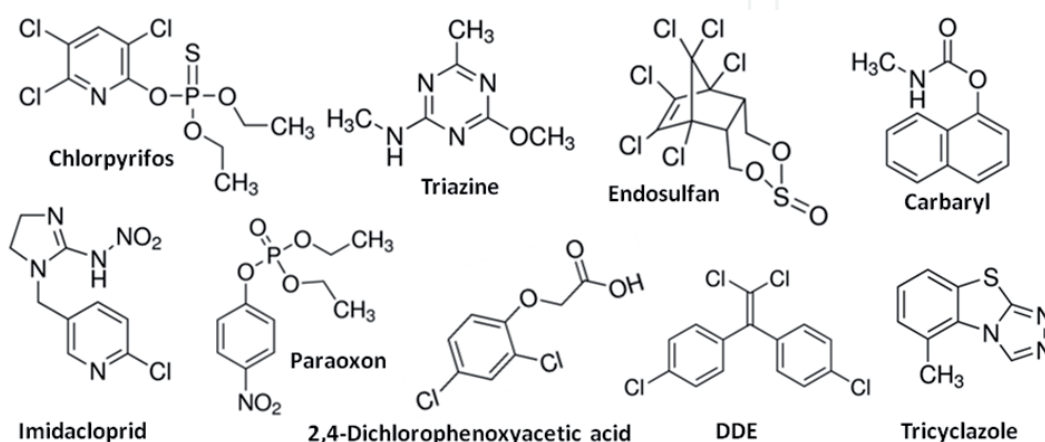
Figure 6.
The structural formula for different pesticides.

over their large and specific surface area [69]. The graphene-coated silica (GCS) nanocomposite was employed as a highly efficient adsorbent for removal of several organophosphorus pesticides from the contaminated water. The efficient adsorption was attributed to the electron-donating effects of N, S, and P atoms and the strong π-bonding network of benzene rings in the pesticides [70]. In another study, nanocomposite of rGO and silver nanoparticles has been used for the degradation and removal of organochlorine pesticides including dichlorodiphenyldichloroethylene (DDE), chlorpyrifos, and endosulfan. Silver nanoparticle-induced dehalogenation of pesticides, followed by adsorption of the degraded products on rGO, was the basic two-step mechanism behind the degradation and removal of these pesticides. The high reusability and adsorption capacity exhibited by this nanocomposite support its utilization for the remediation of different pesticides present in water and soil [71]. Cata et al. established a simple and cost-effective method of dispersing 15 nm silver nanoparticles on the surface rGO nanosheets uniformly using a one-pot hydrothermal process with the presence of polyvinylpyrrolidone as both the surfactant and reducing agent. The results indicated that the as-prepared rGO-Ag nanocomposites exhibit the highest surface-enhanced Raman spectroscopy (SERS) efficiency and good sensitivity with tricyclazole pesticide. These can be explained by the electron interactions between silver nanoparticles and graphene oxide, which make unique material advantages for the highly effective detection of pollutant molecules in the environmental monitoring applications [72].

Gupta et al. proposed the use of $CoFe_2O_4@ TiO_2$-rGO nanocomposites for the removal of an organophosphate insecticide, chlorpyrifos, from wastewater. The photocatalytic degradation of chlorpyrifos followed the pseudo-first-order kinetic model. The $CoFe_2O_4$ magnetic nanoparticles have already been proven as efficient photocatalysts for the degradation of environmental pollutants and could be easily separated by applying the external magnetic field [73]. Keihan et al. demonstrated the first time photodegradation of organophosphorus pesticide, paraoxon, using a nanocomposite. They prepared Ag nanoparticle and graphene co-loaded TiO_2 with various contents of Ag and graphene via a facile surfactant-free solvothermal method with a mixture of water and ethanol. It showed the best photocatalytic activity for the degradation of paraoxon containing nanocomposite with 6% wt Ag and 1% wt graphene under visible light irradiation. Further, complete photodegradation of paraoxon is confirmed by gas chromatography–mass spectrometry, and it produces 4-nitrophenol, diethylphosphate, mono-ethylphosphate, hydroquinone, and hydroxyhydroquinone as major intermediates, and subsequent photodegradation of these results in complete mineralization of paraoxon [74]. In another study, rGO has been utilized to fabricate nanocomposite with β-cyclodextrin/iron oxide for the removal of organochlorine pesticides from honey. The mechanism behind the removal of pesticide involved its adsorption on the nanocomposite based on magnetic solid-phase extraction. The prepared nanocomposite helped to detect very low concentrations of pesticides up to ppt and sub-ppt levels [75]. Improper discharge of chemical pesticides and herbicides into water bodies causes harmful effects on both the environment and human health. Ebrahimi et al. investigated the photocatalytic degradation of 2, 4-dichlorophenoxyacetic acid (2,4-D) using Mn-doped zinc oxide/graphene nanocomposite under light-emitting diode (LED) radiation in aqueous media. The results showed that 66.2% of 2,4-D could be photocatalytically degraded using Mn-doped zinc oxide/graphene nanocomposite under LED radiation at optimal conditions (pH 5, initial Zn concentration of 10 mg L^{-1}, nanocomposite concentration of 2 g L^{-1}, contact time of 120 min) [76]. Graphene oxide-titanium dioxide (GO@TiO_2) nanocomposite with mean diameter size of 14 nm has been fabricated by El-Shafai et al. and further used as photocatalyst for enhanced degradation of carbaryl and imidacloprid. It was found that

the photocatalytic degradation efficiency of carbaryl and imidacloprid was 22 and 92.6% in the presence of $GO@TiO_2$ whereas 7 and 56.6% in the presence of TiO_2 alone. It suggests the superiority of $GO@TiO_2$ nanocomposite over TiO_2NPs for degradation of the examined toxic insecticides [77].

8. Conclusion

In conclusion, graphene oxide- and graphene-bounded metal nanocomposites have become more and more employed for wastewater treatment purposes and allow the design of next-generation photocatalyst systems. These nanocomposites may be good alternatives to the other materials such as TiO_2, CNT and fullerenes, or supported matrix. We reviewed the current advances in the fabrication and applications of the new nanocomposite materials for the remediation of toxic organic pollutants, dyes, pharmaceutical and personal care products, and pesticides. It also suggested the low cost, simple, and ecofriendly technique development to solve the pure water crisis in the coming years. The most common systems reported in the literature are based on the dispersion of metallic nanoparticles on the surface of the GO/rGO. As we know, the properties of photocatalysts are highly dependent on the surface structure of materials. On looking the benefits of plant materials for the synthesis of nanoparticles, various plant materials are also reported for in situ reduction of graphene oxide and metallic salts to fabricate graphene-bounded metallic nanocomposite, efficiently. It showed the role of GO/rGO as the sensitizer to metallic nanoparticles and enhances the catalytic effect in solar light. In this regard, this book chapter highlights the importance environment-friendly GO-/rGO-bounded metal nanocomposite and renewable energy for the environmental protection by following the concept "nature purification by natural materials."

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