

Review

# Application and Prospect of Graphene and Its Composites in Wastewater Treatment

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Received: 12 November 2019

Accepted: 29 January 2020

## Abstract

Graphene has received extensive attention due to its excellent properties, and is considered to have broad application prospects in the fields of material processing, energy, biomedicine and drug delivery. Recently, graphene and its composite materials have been gradually applied to wastewater treatment. Here, different graphene composites and their properties are outlined. The application of graphene and its composites as adsorbents and catalysts in typical wastewater treatment (such as dye wastewater, heavy-metal wastewater, oily wastewater, refractory organic wastewater) is reviewed. The treatment efficiency and treatment mechanism of different graphene composites are summarized and analyzed. Finally, reasonable comments and suggestions are raised about the existing problems in wastewater treatment applications. And the outlook for and the future development of graphene and its composites were discussed.

**Keywords:** graphene, graphene composites, wastewater treatment, adsorption, catalysis

## Introduction

Graphene successfully stripped for the first time by Ander K. Geimhe and Konstantin S. Novoselov of the University of Manchester in 2004, is a two-dimensional layered novel carbon nanomaterial with hexagonal honeycomb crystal lattice formed by sp<sup>2</sup> hybrid orbital [1]. Following zero-dimensional fullerene, one-dimensional carbon nanotubes, three-dimensional

diamond, graphene fills the gap of two-dimensional carbon materials [2]. Graphene has a unique structure and excellent electrical, optical, thermal and mechanical properties [3, 4]. It is considered to be a new strategically important material and has received extensive attention in the fields of electronics, medicine, energy and so on [5-8]. Also, graphene has special properties, such as permeability to protons and specific surface area of up to 2630 m<sup>2</sup>·g<sup>-1</sup> and has been widely used in the field of environmental pollution control [9, 10].

However, the extremely strong  $\pi$ - $\pi$  stacking and van der Waals forces between the graphene layers cause

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graphene to agglomerate easily in water [11]. This will result in a lower specific surface area than the theoretical value, which will greatly reduce the active sites involved in the catalytic reaction, affecting the adsorption effect and catalytic efficiency [12]. Besides, graphene is often produced as a powder, which makes it difficult to separate, easy to remain in the water, and will cause certain harm to aquatic ecosystems [9, 13]. In order to solve these problems, graphene was modified. It was prepared as composite materials such as a gel, a magnetic material, or was supported on a skeleton material such as a sponge, a ceramsite or a metal material. Graphene oxide is an important graphene derivative having a sheet structure similar to graphene. The traditional methods for preparing graphene oxide include Brodie method, Staudenmaier method and Hummers method [14]. The carbon atoms in graphene oxide are modified by a large number of oxygen-containing groups, which makes graphene oxide have good dispersibility and reaction activity. These oxygen-containing groups provide active sites for the graphene oxide to be further modified by the introduction of new functional groups [15]. Therefore, it has been widely used in energy storage materials, catalysis, pollutant removal, sensors and other fields, showing an excellent prospect. A large number of studies have shown that due to the special structural characteristics of graphene and graphene oxide, they can effectively remove organic and inorganic pollutants such as heavy metals, antibiotics, dyes, etc. in water as adsorbents and catalyst carriers and good treatment effects have been achieved [16-18]. The application and principle of graphene and its composites in water treatment are simply illustrated in Fig. 1.

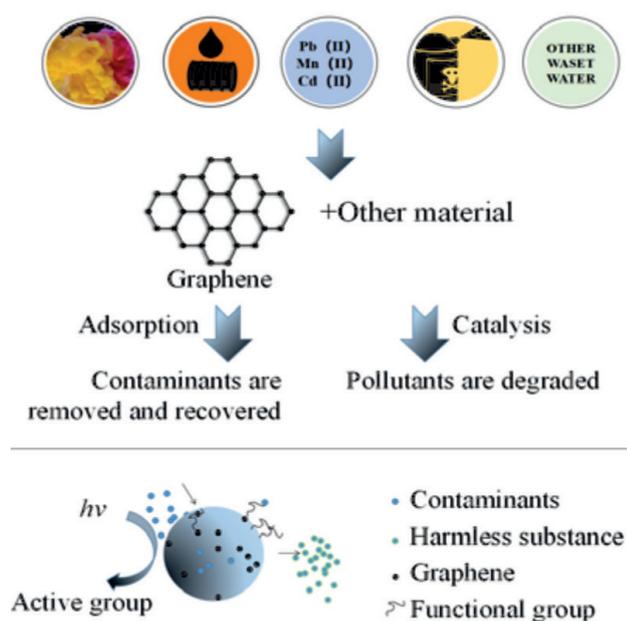


Fig. 1. Application of graphene and its composites in wastewater treatment.

## Application of Graphene and Its Composites as Adsorbents in Wastewater Treatment

Adsorption with the advantages of simple operation, high efficiency, no secondary pollution, low investment cost, and so on, is one of the widely used methods in the field of sewage treatment. The good effects have been achieved in the pollution control of organic matter, heavy metals, radioactive and other pollution in water [19]. The mechanisms include exchange adsorption, physical adsorption and chemical adsorption [20]. Graphene and its composite materials have a large specific surface area, so they are widely used as adsorbents to treat dyes, oils and heavy metal's wastewater. Table 1 summarizes the preparation methods and properties of graphene and its composites as adsorbents.

### Dye Wastewater

Dye is widely used in industrial production of cosmetics, textiles, leather, etc. And dyes are used in large quantities and wide varieties. About 10% to 20% of the dyes are discharged with production wastewater during use [21]. Dye wastewater has the characteristics of complex composition, deep color, low biodegradability and biologic toxicity. Currently, commonly used dye wastewater treatment methods include biological treatment, chemical oxidation, photocatalytic degradation, and adsorption [22]. The treatment of dye wastewater by adsorption has become the focus of research because of its many advantages.

At present, the macroscopic of nano-materials is currently the trend of nanotechnology development, and also promotes the effective separation and practical application of nano-adsorbed materials in water. Graphene aerogel (GA) is a three-dimensional porous network structure mainly composed of graphene. It has the nano-properties of graphene and the macrostructure of aerogel [23]. GA not only has the excellent properties of graphene but also solves the problem that graphene is easy to agglomerate and improves the adsorption performance of graphene. Long Chen et al. [24] first prepared agar/graphene oxide (AGO) composite aerogel using a vacuum freeze-drying method as an adsorbent to treat methylene blue (MB) dye wastewater, and the adsorption capacity can reach  $578 \text{ mg}\cdot\text{g}^{-1}$ . Studies have shown that AGO has excellent regeneration property after repetitious adsorption and desorption. Moreover, AGO has large adsorption capacity and is easy to be separated, which is an important direction for the development of graphene composites.

Polysaccharide materials are excellent adsorbents with rich hydroxymethyl, hydroxy and carboxyl groups. Natural polysaccharides k-carrageenan and tragacanth have certain adsorption capacity and high biodegradability, which are non-toxic and low cost. Meiling Yang et al. [25] prepared k-carrageenan/graphene oxide gel beads (k-Car/GO GBs) using

Table I. Graphene and its composite as adsorbents.

Adsorption Materials	Preparation	Contaminant	Adsorption capacity	Ref
Agar/ Graphene oxide (GO) composite aerogel	Vacuum freeze-drying method	Methylene blue	578 mg·g <sup>-1</sup>	[24]
k-carrageenan/GO gel beads	Simple dropping method	Methylene blue	628.93 mg·g <sup>-1</sup>	[25]
New magnetic hydrogel beads biosorbent	Gelation method	Crystal purple	94.0 mg·g <sup>-1</sup>	[28]
		Congo red	101.74 mg·g <sup>-1</sup>	
Additive-free three-dimensional graphene aerogel	Directional-freezing method	Various oils and organic solvents	120 to 200 times of its own mass	[30]
Melamine sponge (MS)/Reduced graphene oxide (RGO)	Skeleton of sponge substrates coated with uniform graphene	Crude oil	About 1500 mg(a)	[31]
Modified cellulose / graphene aerogel	Chemical vapor deposition of CGAs	Various oils and organic solvents	80 to 197 times of its own mass	[33]
Poly (sodium acrylate)-GO double-network hydrogel	Sodium acrylate, methylene bis acrylamide, ammonium persulfate and GO are heated in deionized water	Cd (II)	238.3 mg·g <sup>-1</sup>	[35]
		Mn (II)	165.5 mg·g <sup>-1</sup>	
Tetraethylenetetramine/polypyrrole/GO aerogel	Hydrothermal self-assembly and freeze-drying technique	Cr (VI)	408.48 mg·g <sup>-1</sup>	[36]
Spongy polysiloxane-GO gel	Sol-gel method	Pb (II)	256.41 mg·g <sup>-1</sup>	[37]
		Cd (II)	136.98 mg·g <sup>-1</sup>	
Sodium alginate/GO aerogel	<i>In-situ</i> crosslinking and freeze-drying methods	Cu (II)	98.0 mg·g <sup>-1</sup>	[39]
		Pb (II)	267.4 mg·g <sup>-1</sup>	
New magnetic biosorbent	Gelation method	Cu (II)	66.67 mg·g <sup>-1</sup>	[28]
		Pb (II)	98.0 mg·g <sup>-1</sup>	
GO/alginate composite membrane	Material liquid is spread on a glass plate	Pb (II)	320.51 mg·g <sup>-1</sup>	[40]
Sulfonated magnetic GO complex	Reaction of aryl diazonium salt of sulfanilic acid with magnetic GO	Cu (II)	62.73 mg·g <sup>-1</sup>	[41]
Functionalized magnetic GO	Mechanically agitating the mixture of mGO and EDTA dispersions	Cu (II)	301.2 mg·g <sup>-1</sup>	[42]
		Pb (II)	508.4 mg·g <sup>-1</sup>	
		Hg (II)	268.4 mg·g <sup>-1</sup>	
Layered GO film	Induce directional flow method	Cu (II)	72.6 mg·g <sup>-1</sup>	[43]
		Cd (II)	83.8 mg·g <sup>-1</sup>	
		Ni (II)	62.3 mg·g <sup>-1</sup>	
Aminated GO nanosheet	Combine GO with the aromatic diazonium salt	Co (II)	116.35 mg·g <sup>-1</sup>	[44]
Sulfuric acid-doped diaminopyridine polymer	Mutual oxidation-reduction technique	Cr (VI)	609.76 mg·g <sup>-1</sup>	[45]

(a) Acities of the MS@RGO monolith (1.91 cm×1.82 cm×1.82 cm) oil absorption. The oil temperature was 95°C.

a simple dropping method. Scanning Electron Microscope (SEM) showed that the k-Car/GO GBs prepared by this method had more surface wrinkles and pores. The MB has a negatively charged sulfate group, and k-carrageenan is rich in hydroxymethyl and hydroxyl groups, which causes hydrogen bonds and electrostatic interactions to exist between them [26]. At the same time, there is a  $\pi$ - $\pi$  stacking interaction between MB molecules and GO [27]. Therefore, the adsorption capacity is significantly higher than that of the pure  $\kappa$ -carrageenan gel beads ( $\kappa$ -Car GBs), which can be as high as 628.93 mg·g<sup>-1</sup>.  $\kappa$ -Car/GO GBs has good regenerability and is easily separated from water,

making it an ideal adsorbent material.

Razieh Sahraei et al. [28] prepared a new magnetic biosorbent hydrogel bead using modified biopolymer tragacanth (GT), polyvinyl alcohol (PVA) and GO in boric acid and acetone solution. The maximum adsorption capacities of cationic dye crystal purple (CV) and anionic dye congo red (CR) can reach 94.0 and 101.74 mg·g<sup>-1</sup> respectively. SEM images showed that the composite material after adding GO has a rougher surface than pure GT. Simultaneously, the addition of GO also enhanced the mechanical strength and swelling of GT. The composite has a good regeneration performance.

## Oily Wastewater

For oily wastewater, the ideal treatment effect is to adsorb the oil without water absorption and to recycle the adsorbed oil [29]. Usually, the oil is removed from the adsorbent by extrusion, which requires the adsorbents to have the hydrophobicity properties, easy separation and anti-extrusion mechanical properties [30-32]. In most cases, the fragile characteristic of graphene aerogels limited their use in the treatment of oily wastewater [30].

To increase the compressive performance of graphene aerogel, Tao Liu et al. prepared an anisotropic, porous structure, highly compressible, additive-free three-dimensional graphene aerogel (AGA) by using anisotropically grown ice crystals as a template to orient the frozen graphene hydrogel [30]. AGA can quickly absorb oil from the water surface for porous structure and hydrophobic properties. The absorption capacity can reach 120 to 200 times of AGA's mass. After absorbing organic liquid, AGA can be regenerated by combustion, distillation, and extrusion. The results show that AGA also has a good adsorption effect on other organic compounds such as ethanol, acetone, n-heptane and n-hexane. At the same time, AGA has the excellent compressive capacity and enables AGA to be used in the wider range of fields.

Cellulose, as a wood derivative, is a low-cost material with a wide range of sources, but the cellulose aerogels usually cannot be regenerated in a dry condition after extrusion. Mi Hao-Yang et al. [33] prepared cellulose/graphene aerogel (CGAs) by bi-directional freeze-drying to produce a special anisotropic aligned porous structure, giving them high compressibility and elasticity. After simple silylation of CGAs by chemical vapor deposition (CVD), the modified cellulose/graphene aerogel (MCGA) with super-hydrophobicity properties was obtained, and the adsorption capacity of MCGA for oil was 80 to 197 times of its mass. 85% of the oil could be recovered by mechanical compression for secondary use.

Jing Ge et al. [31] used Joule-heated graphene wrapped sponge (GWS) to process the leaked crude oil in seawater at high speed, and the graphene was uniformly wrapped as a skeleton sponge by centrifugal assisted dip coating. Because of the hydrophobicity of graphene, crude oil can be selectively absorbed into the pores of GWS. At the same time, A voltage was applied to GWS to cause the current to flow through the graphene to generate Joule heat. And the surrounding crude oil was heated to reduce its viscosity, which increases the diffusion coefficient of crude oil in the GWS so that the crude oil in water can be adsorbed quickly, and the crude oil after adsorption can be recycled.

These composite materials of graphene not only have a good effect on wastewater treatment but also do not require high temperature and inert gas protection in the preparation process. Because of their simple preparation

process and low cost, these composite materials have broad application prospects in many fields.

## Heavy Metal Wastewater

In the production process of machinery manufacturing, mining, metallurgy, chemical industry, etc. wastewater containing heavy metals will be produced. With the development of industry, heavy metal pollution is becoming more and more serious in water [34]. Heavy metals not only damage the aquatic ecosystems but also seriously harm to the human health. So heavy-metal wastewater treatment has become a hot issue.

Rui Xu et al. [35] prepared a poly(sodium acrylate)-graphene oxide (PSA-GO) double-network hydrogel adsorbent for the adsorption of Cd(II) and Mn(II) in water with a maximum adsorption capacity of 238.3 mg·g<sup>-1</sup> and 165.5 mg·g<sup>-1</sup>. PSA-GO gel has extraordinary mechanical strength and good reproducibility. Electrostatic adsorption and surface complexation play an important role in the adsorption process. Qianwei Liang et al. [36] obtained a novel nitrogen-doped ultra-light graphene oxide aerogel with three-dimensional (3D) network structure, tetraethylenetetramine/polypyrrole/GO aerogel (TPGA). Polypyrrole and TEPA acted as crosslinkers and provided amino functional groups when TPGA is used to remove Cr (VI) ions from water. The adsorption capacity of TPGA for Cr (VI) ions was up to 408.48 mg·g<sup>-1</sup> at a pH of 2.0. The aerogel showed good regenerability and satisfactory recovery of Cr (VI) ions in actual water samples. A spongy polysiloxane-graphene oxide (PS-GO) gel adsorbent was made by sol-gel method for removing lead and cadmium in wastewater [37]. The maximum adsorption capacity reached 256.41 mg·g<sup>-1</sup> and 136.98 mg·g<sup>-1</sup>, respectively. Moreover, the PS-GO gel adsorbent has remarkable mechanical strength and excellent reproducibility. In the static treatment process, after five cycles, it still maintained a removal efficiency of over 99%. Among the above gel materials, graphene became the main body for adsorption because of the large specific surface area and abundant functional groups. Other materials act as cross-linking agents, making graphene macroscopically avoiding agglomeration of graphene, to make its performance can be fully exerted [38]. Also, the introduction of new functional groups provides more active sites and enhances the adsorption properties of the materials.

In recent years, biopolymers such as sodium alginate have received more and more attention because of their rich functional groups, strong environmental compatibility, good biodegradability and low cost. However, a single biological aerogel has some defects, such as weak mechanical strength and uneven structure. To solve the structural problems, it has become the focus of research adding the fillers to enhance the mechanical strength. Graphene oxide has excellent mechanical

properties and high adhesion, making it an ideal reinforced filler. Chenlu Jiao et al. [39] prepared ordered porous sodium alginate/graphene oxide (SAGO) aerogel by *in-situ* crosslinking and freeze-drying methods. Compared with pure sodium alginate aerogel (SA), the SAGO has excellent mechanical strength and elasticity, and its adsorption property is greatly improved. The maximum adsorption capacity for Cu (II) and Pb (II) can reach 98.0 mg·g<sup>-1</sup> and 267.4 mg·g<sup>-1</sup>, respectively, which is mainly attributed to the interconnected porous structure and abundant functional groups of SAGO.

In addition to aerogels, graphene oxide can also be prepared into composite membranes for use as adsorbent materials. The maximum adsorption capacity of GO/sodium alginate composite membrane for lead (II) is 320.51 mg·g<sup>-1</sup>, and the main mechanism of action is physical adsorption [40]. The novel magnetic biosorbent hydrogel bead with a good adsorption effect was prepared by Razieh Sahraei et al. using a wide range of inexpensive biopolymer and graphene oxide with high specific surface area [28]. The maximum adsorption capacities for Pb (II) and Cu (II) can reach 81.78 mg·g<sup>-1</sup> and 66.67 mg·g<sup>-1</sup>, respectively.

Adsorb ability of the adsorbent to metal depends on the number and type of functional groups for binding heavy metals. In order to enhance the adsorption performance, it is necessary to introduce some stable functional groups with specific orientation. The sulfonic acid group (-SO<sub>3</sub>H) is a functional group having excellent adsorption performance, and can form a stable complex with various metal ions. Xinjiang Hu et al. [41] synthesized sulfonated magnetic graphene oxide complex (SMGO) using p-aminobenzenesulfonic acid. SMGO has good adsorption properties for Cu(II) and can be easily separated by magnetic separation technique. The research has shown that the functionalized magnetic graphene oxide has good adsorption properties for Pb(II), Hg(II) and Cu(II), and the magnetic separation can be completed in only 25 seconds [42].

Ping Tan et al. [43] prepared a novel layered graphene oxide film with a large interlayer spacing by inducing directional flow, which has a good adsorption effect on Cu(II), Cd (II) and Ni(II). Fang Fang et al. [44] prepared aminated graphene oxide nanosheet (GO-NH<sub>2</sub>) by combining graphene oxide with aromatic diazonium salt. The GO-NH<sub>2</sub> has a specific surface area of up to 320 m<sup>2</sup>·g<sup>-1</sup> and excellent adsorption performance. The removal rate of Co (II) exceeded 98% when the cobalt-containing wastewater is treated with a membrane made of this material. The adsorption process of the new layered graphene oxide film and GO-NH<sub>2</sub> conforms to the pseudo-second-order kinetics equation, which indicates that chemical adsorption is the main process for controlling the adsorption rate. A variety of groups in the material interact strongly with the adsorbed metal ions through electrostatic and chemical interaction.

The sulfuric acid-doped diaminopyridine polymer was synthesized *in situ* on the surface of graphene

oxide by mutual oxidation–reduction technique, using its large and porous surface as an adsorbent to remove high-concentration Cr(VI) from water [45]. The removal rate decreases with increasing pH, but the removal rate can still reach 46% at pH 9. At lower pH value, the main removal mechanism is the reduction reaction of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>. At higher pH value, anion exchange between dopant SO<sub>4</sub><sup>2-</sup> and CrO<sub>4</sub><sup>2-</sup>/Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> was the main removal mechanism. The high concentration of 500 mg·L<sup>-1</sup> Cr(VI) wastewater can be purified in just 100 mins. And the composite has good regenerability.

In summary, the composite materials with the distinct internal structures were prepared using different materials by diverse processes, so that their application ranges and adsorption characteristics were also significantly different. Some graphene composites can achieve satisfactory pollution treatment effects under special conditions, which limited the scope of application of these materials. Some graphene composites have good removal effects on multiple heavy metals or pollutants. Therefore, the application fields and scope of these composites will be wider. And an in-depth study of their structure and properties will be more meaningful.

### Application of Graphene and Its Composites as Catalyst in Water Treatment

Due to the unique physicochemical properties of graphene and its composites, they have been used as high-efficiency catalysts for the removal and degradation of environmental pollutants [46, 47]. In the general catalytic process, the surface atoms of the catalyst often play a decisive role in the catalytic reaction, while the internal atoms do not participate in the catalytic reaction [48]. However, in the graphene-based catalyst, the catalytic atoms were completely exposed, which greatly increased the contact between the catalytic atoms and the substrates, thereby maximizing the catalytic effect [49]. The Table 2 summarizes the basic information of graphene and its composites as catalysts.

Adsorption is the initial step of heterogeneous catalysis. Studies had shown that when graphene was used as the wall of carbon nanotubes [50]. The carbon nanotubes showed ultra-strong association with polycyclic aromatic hydrocarbons (PAHs) and metal because graphene is flatter and more ductile. In photocatalysis, the pollutant molecules were transferred from the solution to the surface of graphene and its composites. By the strong  $\pi$ - $\pi$  interaction between the molecules and graphene, the photoexcited electrons react rapidly with the O<sub>2</sub> adsorbed on the materials to generate free radicals under illumination, so that more electrons and holes can be produced on the surface of the composites, thereby effectively improving the photocatalytic efficiency [51, 52]. Also, in the presence of heteroatoms, such as nitrogen, boron, etc. the  $\pi$  electron cloud of graphene and its composite materials

Table 2. Graphene and its composite as catalysts.

Materials	Preparation	Contaminant	Degradation ratio/rate	Ref
Three-dimensional grapheme foam	Loading nZVI on porous	Azo dye orange IV	94.50%	[58]
Reduced GO/polyethyleneimine/Ag nanocomposite gel	Preparation of hydrogel using polyethylene imine	Rhodamine B	Up to 100%	[59]
		Methylene blue	Up to 100%	
GO TiO <sub>2</sub> photocatalysts	Liquid phase deposition method	Mixture of diuron, alachlor, isoproturon and atrazine	$8.2 \times 10^{-3} \text{ mol} \cdot \text{min}^{-1} \cdot \text{g}^{-1}$	[66]
Reduced GO-silver nanocomposites	Adding an appropriate amount of AgNO <sub>3</sub> to the reduced GO dispersion system	Pesticides and halocarbon compounds	Up to 100%	[67]
Ag <sub>3</sub> PO <sub>4</sub> -GO composite	Electrostatically driven method	2,4-Dichlorophenol (2,4-DCP)	55.91%	[68]
GO/Fe <sub>3</sub> O <sub>4</sub> -horseradish peroxidase binary enzyme catalyst catalyzes	Ultrasonic-assisted reverse co-precipitation method(GO/Fe <sub>3</sub> O <sub>4</sub> )	2,4-DCP	93%	[69]
2D $\gamma$ -MnO <sub>2</sub> /2D rGO nano-hybrid	Hydrothermal method	4-Nitrophenol	Up to 100%	[70]
TiO <sub>2</sub> -graphene composite	Hydrothermal method	Bromate	99%	[73]
TiO <sub>2</sub> nanowires / Fe <sub>2</sub> O <sub>3</sub> nanoparticles/ GO sheets	Hydrothermal, colloidal blending, and vacuum filtration method	Humic acid	98%	[76]

would be distorted, resulting in empty or additional orbitals to enhance catalyst performance [53, 54].

### Degradation of Dye Wastewater

Organic dyes cannot be completely degraded, so they can cause pollution to be discharged into the environment with the wastewater. It has been the focus of many researchers on the efficient treatment of such pollutants and the recovery of catalysts in water.

Graphene and its derivatives have a strong  $\pi$ - $\pi$  stacked porous structure and excellent mechanical strength, which makes them ideal carriers for immobilizing various nanoparticles and provides ideal water/solid interface. And interconnecting porous structure enables the materials to be in full contact with organic dyes [52, 55]. Among the many nanomaterials, nano-zero-valent iron (nZVI) has a larger specific surface area and higher reaction efficiency. However, nZVI has a high saturation magnetization, making it prone to aggregate. Loading nZVI on graphene and its composites not only solves the problem of easy aggregation, also protecting nZVI from rapid oxidation and facilitates the recovery of materials in water [56, 57]. Wei Wang et al. [58] prepared 3DG-Fe by loading nZVI on porous three-dimensional grapheme (3DG) foam. Because 3DG has a strong adsorption effect on the azo dye orange IV, when nZVI was supported on it, the effective collision between the active site of nZVI and the dye molecules can be significantly improved. The degradation rate of the azo dye orange IV can reach 94.5%, while the removal rate by pure nZVI was only 70.5%.

Tifeng Jiao et al. [59] used 3D graphene coagulation in the presence of polyethyleneimine (PEI) to reduce

GO. And silver acetate simultaneously in the hydrogel matrix were to prepare an RGO/PEI/Ag nanocomposite gel based on reduced graphene oxide (RGO). On the RGO/PEI/Ag nanocomposite gel, Ag was uniformly distributed on the RGO lamellae as the active site of photocatalysis, and the organic dyes methylene blue (MB) and rhodamine B (RhB) have nearly 100% degradation effect under ultraviolet irradiation condition. It also has a catalytic effect in the dark, but the efficiency is reduced.

### Degradation of Persistent Organic Pollutants

TiO<sub>2</sub> nanofibers have the large specific surface area and high porosity, which provide more active sites for the adsorption, resulting in a more effective photocatalytic process [60]. Many studies have demonstrated that GO-TiO<sub>2</sub> composites have excellent catalytic performance [61-65]. Marta Cruz et al. [66] prepared a graphene-based GO-TiO<sub>2</sub> composite catalyst. Studies have shown that under visible light conditions, the catalyst has great degradation effect for the mixture of diuron, alachlor, isoproturon and atrazine, and the degradation rate can reach  $8.2 \times 10^{-3} \text{ mol} \cdot \text{min}^{-1} \cdot \text{g}^{-1}$ . In addition, the degradation of pollutants can still achieve the desired results in natural water. A novel reduced graphene oxide-silver nanocomposites (RGO@Ag) can first degrade the pesticides and halocarbon compounds in water by Ag nanoparticles, and then adsorb the reaction products onto the RGO plate through  $\pi$ - $\pi$  interaction to achieve the desired treatment effect of the target contaminants [67]. Moreover, the composite material has good regeneration performance and opens up a new direction for removing persistent organic pollutants in water.

$\text{Ag}_3\text{PO}_4$  is a photocatalyst with excellent performance. To solve the slight solubility of  $\text{Ag}_3\text{PO}_4$  in solution and the photo-induced corrosion caused by the band structure, Xiaojuan Chen et al. [68] prepared  $\text{Ag}_3\text{PO}_4$ -GO composite photocatalyst to degrade 2,4-dichlorophenol (2,4-DCP). And the specific surface area of  $\text{Ag}_3\text{PO}_4$ -GO composite photocatalyst increases with the increase of GO addition. The  $\text{O}_2$  adsorbed on GO generates free radicals under the action of photogenerated electrons, and the electron transport speed is very fast because of the good conductivity of GO, which makes the composite exhibit excellent visible-light photocatalytic activity and stability compared with pure  $\text{Ag}_3\text{PO}_4$ . About 55.91% of the 2, 4-DCP or intermediates were mineralized under 60 minutes of irradiation. Jia Huang et al. [69] prepared a composite of artificially simulated enzyme-like catalysts (GO/ $\text{Fe}_3\text{O}_4$ ) using graphene oxide and nano- $\text{Fe}_3\text{O}_4$ . Combining artificial simulated enzyme-like catalyst with the natural enzyme horseradish peroxidase (HRP) as a binary enzyme catalyst catalyzes the oxidation 2,4-DCP with a removal rate of 93%. The removal rate was higher than that of 2, 4-DCP using HRP or GO/ $\text{Fe}_3\text{O}_4$  alone. The binary enzyme catalyst showed good catalytic stability. Research showed that strong electrostatic interaction and hydrogen bond were the main interaction forces between the oxygen-containing functional groups of GO and the surface amino acid residues of HRP, which was also the key to improving the catalytic performance.

Yuxian Wang et al. [70] synthesized 2D  $\gamma\text{-MnO}_2$ /2D rGO nano-hybrid ( $\text{MnO}_2$ /rGO) using two-dimensional reduced graphene oxide (2D rGO) hydrothermal method, and 2D/2D hybrid materials were applied to catalytic ozonation of 4-nitrophenol for the first time. The catalytic efficiency of  $\text{MnO}_2$ /rGO was much higher than that of  $\text{MnO}_2$  or rGO alone. Among them, rGO was considered to promote the transfer of electrons. The quenching test showed that oxygen radicals  $\text{O}_2\cdot^-$  and  $\text{IO}_2\cdot$  play a major role in the degradation of 4-nitrophenol. Moreover, 2D  $\text{MnO}_2$ /rGO catalyst has good stability.

### Other Applications

Bromate ( $\text{BrO}_3^-$ ), which has carcinogenicity and genotoxicity, was an inevitable toxic by-product in the process of ozone disinfection in drinking water, which is carcinogenic and genotoxic [71, 72]. Xin Huang et al. [73] prepared  $\text{TiO}_2$ -graphene composite (P25-GR) photocatalyst for the degradation of  $\text{BrO}_3^-$ . The excited photogenerated electrons rapidly flowed to graphene, effectively separating electron-holes pairs and preventing charge recombination, thereby improving the catalytic efficiency of  $\text{TiO}_2$ . The test results of photoluminescence spectra (PL) also support this conclusion. The highest degradation rate of  $\text{BrO}_3^-$  by P25-GR photocatalyst was 99%, which was significantly higher than that of P25 alone [74].

Membrane fouling caused by natural organic compounds such as humic acid is one of the main obstacles to the wide application of membrane technology in water treatment [75]. A composite membrane composed of  $\text{TiO}_2$  nanowires/ $\text{Fe}_2\text{O}_3$  nanoparticles/GO sheets was used to remove humic acid with a removal rate of up to 98% [76]. In natural water,  $\text{TiO}_2$  is negatively charged or neutral, so it cannot adsorb the same negatively charged humic acid, resulting in a lack of effective contact, and the photocatalytic effect were greatly reduced. Nano- $\text{Fe}_2\text{O}_3$  has a strong adsorption effect on humic acid, which enhanced the effective contact between the adsorbent and the adsorbate. The promotion of charge separation by GO film solved the problem of electron-hole pair recombination in  $\text{TiO}_2$ . Therefore, the  $\text{Fe}_2\text{O}_3$  nanoparticle and GO film together enhanced the photocatalytic activity of the film. The appearance of this film has promoted the practical application of the future photocatalytic film in water treatment.

### Conclusions

Graphene's excellent properties make it widely used in water treatment. However, the use of graphene alone has a toxic effect on organisms due to its fineness and difficulty in separating it from the water. To solve those problems, through modifying and compounding graphene with other materials, researchers have prepared more excellent materials, such as aerogels, magnetic materials, etc. by modifying graphene or combining with other materials. These materials were widely used in the treatment of heavy metal wastewater, persistent organic pollutants, dye wastewater, oily wastewater and other wastewater as adsorbents and catalysts.

These novel water treatment materials with good pollution treatment effect, regeneration performance and stability have wide application and development value in the future. Although graphene and its composite materials have a large adsorption capacity, the adsorption process often required harsh conditions such as ultraviolet light irradiation, specific pH to achieve the desired effects. Besides, in the natural water, the same catalytic efficiency as laboratory experiments cannot be achieved. The resolution of those problems in the future will enable this new type of materials to obtain a wider range of application and scope.

### Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 41501514), The Fundamental Research Funds for the Central Universities (No. N172304046; N182303031); The Natural Science Foundation of Hebei Province, China (No. D2019501004; B2014501053); the Opening

Foundation of Ministry of Education Key Laboratory of Pollution Processes and Environmental Criteria (No. 201903); Key research and development program of Hebei Province, China (No. 19224204D).

### Conflict of Interest

The authors declare no conflict of interest.

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