

Review

Preparation and Application of Graphene–Based Materials for Heavy Metal Removal in Tobacco Industry: A Review

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Abstract: Heavy metals are nondegradable in the natural environment and harmful to the ecological system and human beings, causing an increased environmental pollution problem. It is required to remove heavy metals from wastewater urgently. Up until now, various methods have been involved in the heavy metal removals, such as chemical precipitation, chemical reduction, electrochemical, membrane separation, ion exchange, biological, and adsorption methods. Among them, adsorption by graphene–based materials has attracted much more attentions for the removal of heavy metals from wastewater systems in recent years, arising due to their large specific surface area, high adsorption capacity, high removal efficiency, and good recyclability. Therefore, it is quite important to review the heavy metal removal with the graphene–based material. In this review, we have summarized the physicochemical property and preparation methods of graphene and their adsorption property to heavy metals. The influencing parameters for the removal of heavy metals by graphene–based materials have been discussed. In addition, the modification of graphene–based materials to enhance their adsorption capability for heavy metal removal is also reviewed. The heavy metal removal by modified graphene–based materials in the tobacco industry has been especially described in detail. Finally, the future trend for graphene–based materials in the field of heavy metal wastewater treatment is proposed. This knowledge will have great impacts on the field and facilitate the researchers to seek the new functionalization method for graphene–based materials with high adsorption capacity to heavy metals in the tobacco industry in the future.

Keywords: graphene; functionalization; heavy metal removal; adsorption; tobacco industry



Citation: Xu, X.; Zeng, J.; Wu, Y.; Wang, Q.; Wu, S.; Gu, H. Preparation and Application of Graphene–Based Materials for Heavy Metal Removal in Tobacco Industry: A Review. *Separations* **2022**, *9*, 401. <https://doi.org/10.3390/separations9120401>

Academic Editor: Gavino Sanna

Received: 22 October 2022

Accepted: 23 November 2022

Published: 1 December 2022

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1. Introduction

Generally, heavy metals are metals with a density higher than 4.5 g/cm³, including chromium (Cr), cadmium (Cd), arsenic (As), mercury (Hg), lead (Pb), and so on [1]. Heavy metals are difficult to be degraded in the natural environment [2,3]. Nowadays, a large amount of heavy metal wastewater in mining, metallurgy, machinery manufacturing, chemical industry, electronics, and other industries is directly discharged into the natural environment without treatment, causing severe harm to the ecological environment and human health [4,5]. Heavy metal pollution is becoming a significant global environmental problem so far [6]. Therefore, it is urgent to remove heavy metals from wastewater [7]. In the past few decades, many methods have been developed for the treatment of heavy metals, such as chemical precipitation, chemical reduction, electrochemical, membrane separation, ion exchange, biological, and adsorption methods [8–11]. These methods are relatively mature and play an important role in the field of water pollution control [12]. Among these methods, adsorption is one of the most effective methods because of simple

operation and low cost [13,14], which exhibits a great potential application for heavy metal removal [15].

Normally, the removal efficiency of the adsorption method mainly depends on the type of adsorbent. Recently, various low-cost adsorbents developed from agricultural wastes, industrial by-products, or natural polymer materials have been widely used in the treatment of heavy metal wastewater [16]. However, it is difficult for these common adsorbents to reduce the concentration of heavy metals in wastewater to ppb level. In addition, their subsequent recovery and reuse are also difficult. Therefore, the research and development of new adsorbents are currently a research hotspot in the field of heavy metal wastewater treatment [17].

Carbon nanomaterials possess at least one dimension less than 100 nm. They have the advantages of small size, large pore volume, large specific surface area, high adsorption efficiency, low operation process, and low production cost [18]. These characteristics make them have broad prospects in the field of heavy metal wastewater treatment [19]. At present, common adsorbents, such as lignin, molecular sieve, zeolite, activated carbon, and mesoporous silica, which are widely used in heavy metal wastewater treatment [20], have difficulty in reducing the concentration of heavy metal in wastewater to ppb level. Moreover, the long adsorption time and poor selectivity also limit their applications for heavy metal removal. By contrast, the use of new carbon nanomaterials as adsorbents can solve these problems very well. The new carbon nanomaterial adsorbents mainly include carbon nanotubes, graphene, and other nano-adsorbents with carbon as the main element and sp^2 as the main hybrid form [21]. With the unique structure and pore size distribution of these materials, the new carbon nanomaterial adsorbents have very large specific surface areas, high electron transfer rates, outstanding physical properties, and good thermal conductivity [22]. The new carbon nanomaterial adsorbent has outstanding advantages to adsorb heavy metals, such as strong adsorption capacity, high removal efficiency, fast equilibrium speed, low price, no secondary pollution, and good recyclability [23].

Graphene is a two-dimensional carbon material [24,25]. Its crystal lattice has a hexagonal lattice structure with a single layer of crystalline carbon atoms inside. It can combine three adjacent carbon atoms through sp^2 hybridization, and the remaining valence electron can form a delocalized large π bond [26]. The discovery of graphene in 2004 by Geim et al. [27] overturned the classical theory that “thermodynamic expansion does not allow two-dimensional crystals to exist freely at a limited temperature” and shocked the entire physics community, which set off a research boom in the field of graphene. As depicted in Figure 1, graphene is the mother for building graphitic materials of all dimensionalities. For example, it can be wrapped into zero-dimensional (0D) fullerene, rolled into the one-dimensional (1D) carbon nanotubes, or stacked into three-dimensional (3D) graphite as well. Currently, graphene is receiving extensive attention in the field of heavy metal wastewater treatment due to its large specific surface area and huge adsorption flux [28,29].

Even though there are some reviews on graphene for heavy metal removal, they mostly focus on the organo-functionalized magnetic graphene oxide nanocomposites [30], graphene oxide and its composites [31], hybrid graphene materials [32], and graphene-based materials for heavy metal removal in the electroplating process [33]. Particularly, Xu et al. [34] reviewed the modification of graphene-based materials and their adsorption efficacy on the heavy metals and radionuclides from wastewater. They also discussed the detailed adsorption mechanism, adsorption dynamics, and isotherms. The work by Kong et al. [35] mostly focused on the improvement of adsorption capacities to heavy metals for graphene-based materials. They indicated three strategies, such as surface functionalization regulation, morphology and structure control, and material composite, to enhance the heavy metal adsorption capacities of graphene-based materials. Unfortunately, the details on the physicochemical properties of graphene and fabrications of graphene-based materials are rarely summarized for heavy metal removal [36]. In addition, the graphene-based materials for heavy metal removal in the tobacco industry have not been

summarized yet. Therefore, in this review, we discuss in detail the physicochemical properties and fabrication methods of graphene as well as the modification of graphene to improve their heavy metal removal ability. We also discuss the effect parameters on heavy metal removal, especially in regard to its use in heavy metal removal in the tobacco industry, as well as proposed future perspectives in this field.

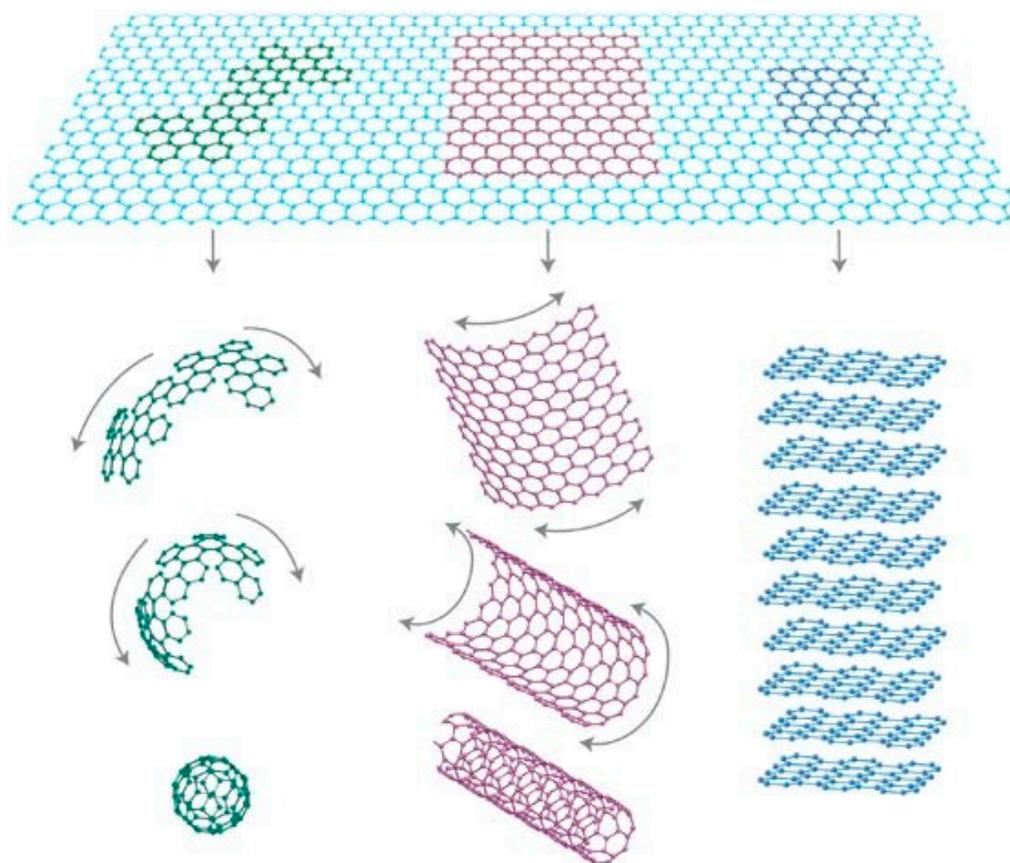


Figure 1. Graphene and its derivatives: 0D fullerene, 1D carbon nanotubes, and 3D graphite. Reprinted with permission from [37]. Copyright@ Springer–Nature.

2. Physicochemical Properties and Fabrications of Graphene

2.1. Physicochemical Property

The special chemical structure of graphene determines its unique chemical properties. The basic building block of graphene is the extremely stable six-membered benzene ring, which makes the structure of graphene particularly stable, and the general chemical methods cannot destroy its structure [38]. Furthermore, graphene also contains boundary groups and plane defects, which determine that graphene can provide adsorption sites for chemical reactions. Additionally, owing to its own large π conjugated system, graphene has a relatively negatively charged system and can react with many oxidants. These unique physicochemical properties enable graphene to undergo chemical reactions through boundary functional groups while well-maintaining the stability of its main framework [37]. Therefore, nowadays, researchers mostly apply graphene oxide (GO) and functionalize the oxygen-containing functional groups, such as carboxyl groups and hydroxyl groups, on the surface of GO to prepare novel GO-based materials [39] with higher adsorption capacities to heavy metals. The chemical structure of GO is disclosed in Figure 2.

The structure characterizations of graphene and GO, including Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Brunauer–Emmett–Teller (BET), scanning electron microscope (SEM), and transmission electron microscopy (TEM), are depicted in Figure 3 [41].

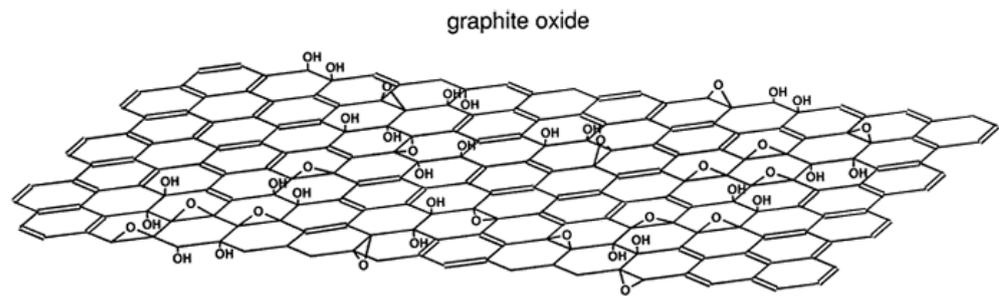


Figure 2. Chemical structure of GO. Reprinted with permission from [40]. Copyright@ Elsevier.

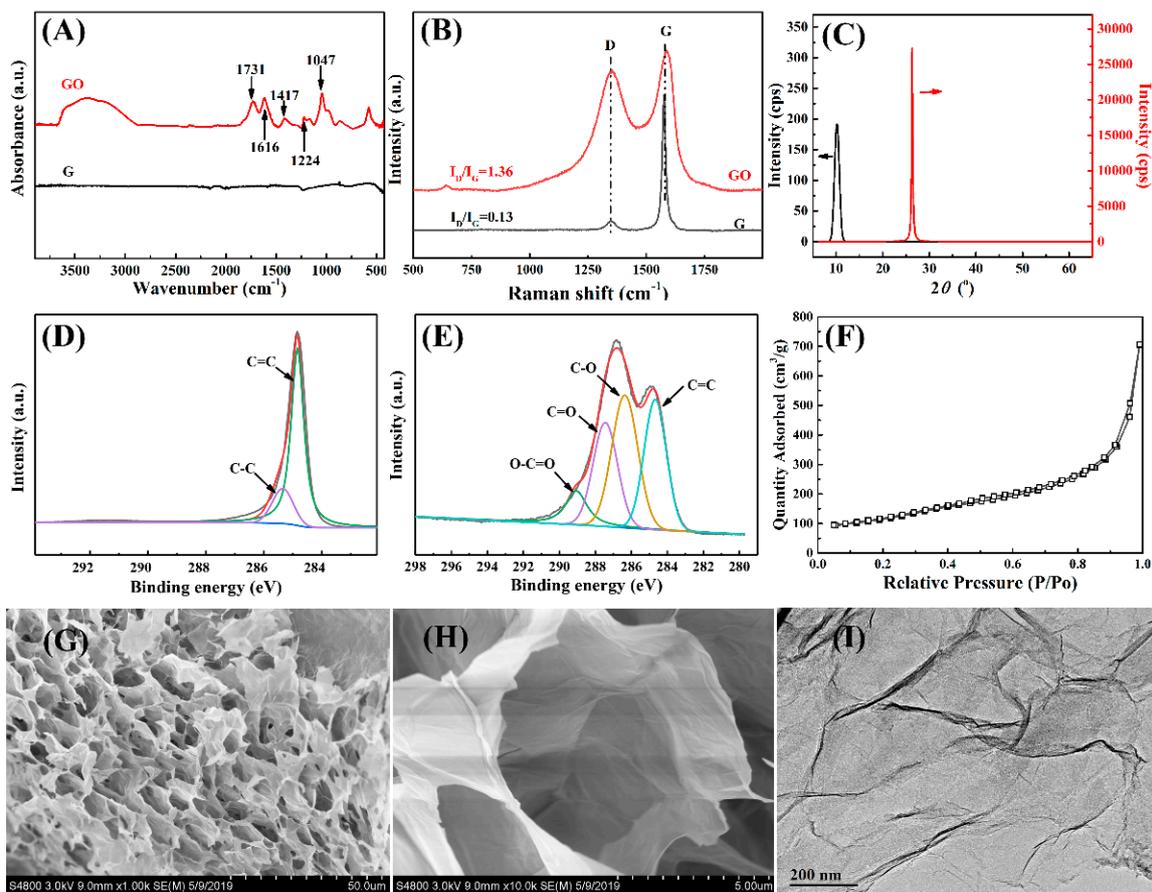


Figure 3. Characterizations of graphene (G) and GO: (A) FTIR spectra; (B) Raman spectra; (C) XRD patterns (the black line is GO, the red line is graphene); high-resolution C 1s XPS spectra of (D) graphene and (E) GO; (F) nitrogen adsorption–desorption curve of GO obtained from BET test; (G) and (H) SEM images of GO; and (I) TEM image of GO. Reprinted with permission from [41]. Copyright @Springer–Nature.

As depicted in Figure 3A, there is no obvious absorption peak in the FTIR spectrum of graphene. By contrast, the absorption peaks at 1735, 1617, 1220, and 1047 cm^{-1} are visibly observed in the FTIR spectrum of GO, originating from the stretching vibration of C=O in the carboxyl group, C=C, C–O, and C–O–C, respectively [42]. In the Raman spectrum of graphene, Figure 3B, the intensity of the G–band (sp^2 C=C bond stretching vibration) is significantly higher than that of the D–band (structural defects), whereas in the Raman spectrum of GO, the D–band is clearly increased and G–band is declined, illustrating the oxidation of graphene [43]. In the XRD pattern of graphene, Figure 3C, there is a characteristic diffraction peak at $2\theta = 26.38^\circ$, while that of GO is at $2\theta = 10.13^\circ$. This arises from the (increase of interlayer distance by the introduction of oxygen-containing

functional groups into graphene sheets because of oxidation [44]. Figure 3D,E shows the high-resolution C1s XPS spectra of graphene and GO, respectively. It is found that only two peaks at 284.8 and 285.3 eV, attributed to C=C and C–C, respectively, are deconvoluted in the high-resolution C 1s XPS spectrum of graphene, while four peaks at 284.6, 286.4, 287.5, and 289.1 eV, corresponding to C=C, C–O, C=O, and O–C=O, respectively, are noticed in that of GO [45]. Figure 3F provides the nitrogen adsorption–desorption curve of GO obtained from the BET test. This curve exhibits a typical IV adsorption–desorption profile, implying mesoporous characteristics of GO. Figure 3G,H is the SEM images of GO at different magnifications. Many diverse micropores are seen in the SEM image of GO because of the freeze–drying process, which may be beneficial for the adsorption of heavy metals. The TEM image of GO is drawn in Figure 3I. It is noted that there are many folds on the graphene sheets of GO, which are from the covalent bond or physical interaction between the oxygen–containing functional groups formed during the oxidation process [41].

2.2. Fabrications of Graphene

Generally, preparation methods for graphene include the mechanical exfoliation method, chemical redox method, chemical vapor deposition method, epitaxial growth method, electrochemical method, and organic synthesis method, etc. [46].

2.2.1. Mechanical Exfoliation Method

The mechanical exfoliation method serves as an effective method manufacture graphene [47]. The basic principle of mechanical exfoliation is to exfoliate graphene from graphite sheets through physical force and other external forces [48]. It contains many exfoliation methods, such as micromechanical exfoliation, ball milling, fluid dynamics, and ultrasonic exfoliation [49]. The most classic mechanical exfoliation method is the directional isocationic pyrolysis of graphite material by Novoselov et al. [27], then the products were transferred with photoresist to the substrate also with photoresist, and the substrate was repeatedly peeled off with tape. After that, the substrate was immersed in an acetone solution, and then the graphene was taken out by using a single crystal silicon wafer, and the acetone was ultrasonicated to obtain the first graphene. Ball milling is also a more commonly used mechanical exfoliation method. Deng et al. [50] used wet ball milling to disperse graphite into N–methylpyrrolidone (NMP) solution system with NMP as the dispersion medium and successfully separated graphene through the interaction with the surface of graphene. The experimental results showed that the graphene sheets were decreased rapidly with the increase of ball milling time. Figure 4 depicts the illustration for graphene exfoliation during the ball milling process.

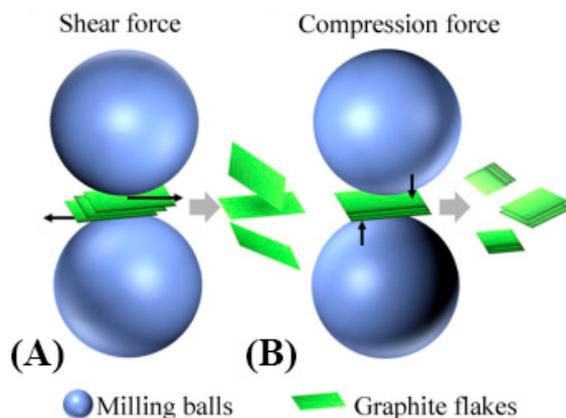


Figure 4. Schematic illustration for graphene exfoliation by ball milling. (A) Shear force–induced exfoliation; (B) Compression force–induced fracture. Reprinted with permission from [50]. Copyright@ John & Wiley Inc.

In this process, two forces, which were named shear force and compression force, were generated. The graphite could be separated by shear force from their outer surfaces and made smaller by the compression force. Finally, the graphene exfoliation was achieved under the action of these two forces. The mechanical exfoliation method is simple and effective, and the prepared graphene is of high quality, which could be widely used in the study of graphene. However, this method consumes a lot of time and energy, is difficult to be controlled accurately, and is not suitable for large-scale production of graphene.

2.2.2. Chemical Redox Method

Currently, the chemical redox method is the most widely used preparation method of graphene [51]. The mechanism of the chemical redox method is to insert small molecules of strong acid into the middle of the graphite layer by treating the graphite powder with strong acid and then adding a strong oxidant into the reaction system for oxidation [52]. This thereby destroys the complete crystal structure of the graphite and introduces oxygen-containing functional groups on the surface of graphene to gain the GO with good dispersibility, and finally reduces GO by different reduction methods according to requirements for obtaining the graphene with desired size and thickness [53].

Oxidation is a key step in the preparation of graphene by the chemical redox method. The preparation methods of GO mainly include the Brodie, Staudenmaier, and Hummer’s methods [54,55]. Researchers are constantly researching and improving the preparation method of GO, especially Hummer’s method. For example, Marcano et al. [56] reported the improved Hummer’s method for the preparation of graphene. They increased the dosage of concentrated sulfuric acid and potassium permanganate without adding sodium nitrate and oxidized graphite in a mixture of sulfuric and phosphoric acid. The detailed procedure is listed in Figure 5. The advantage of this improved Hummer’s method was that it would not release toxic gases, such as NO_2 , N_2O_4 , and had relatively higher yields, but the addition of phosphoric acid would increase the production cost and cause a series of environmental problems.

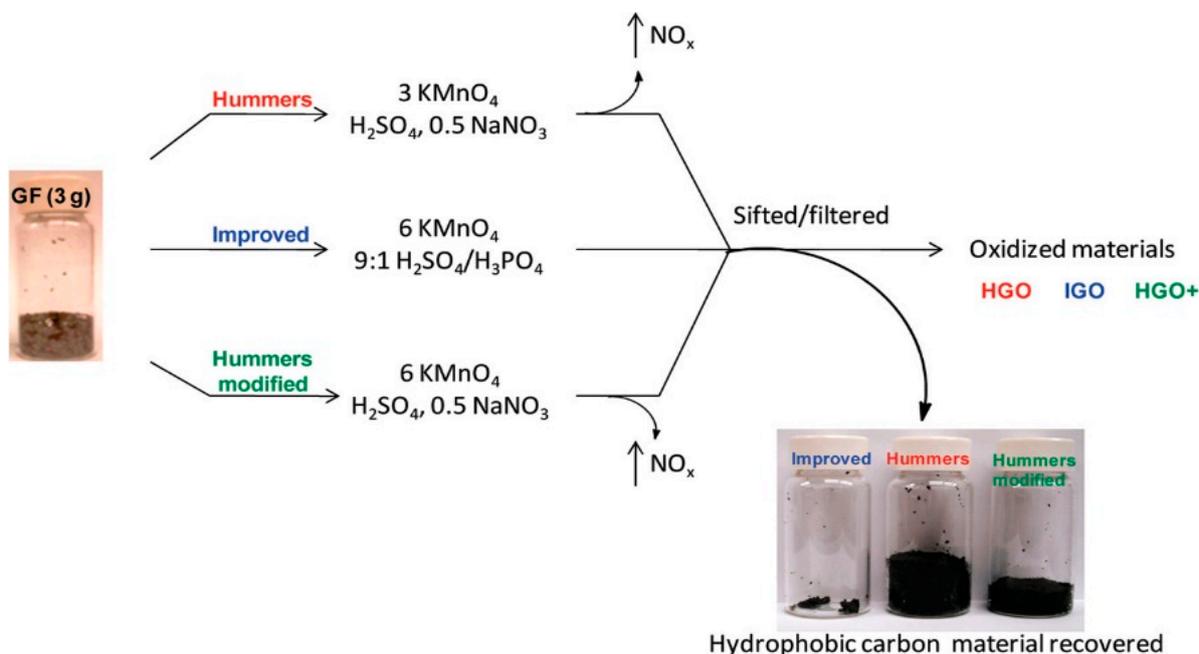


Figure 5. Preparation procedure of improved Hummer’s method of graphene. Reprinted with permission from [56]. Copyright@ ACS publications.

2.2.3. Chemical Vapor Deposition Method

Chemical vapor deposition (CVD) is a controllable method for preparing graphene [57]. The principle is that the reaction occurs under high temperature and gaseous conditions by using thin metal films and single metal crystals or polycrystals as a plane substrate, then carbon atoms are deposited on the surface of substrate through high-temperature annealing, and finally, the plane substrate is removed by corrosion and other methods to obtain graphene [58]. Nam et al. [59] utilized the different platinum (Pt) substrates, including sputter-deposited films, e-beam deposited films, and polycrystalline Pt foil, to serve as the substrate for the low-pressure CVD growth of graphene. The results illustrated that the Pt thin films deposited by high-temperature sputtering were the best Pt substrate for the growth of homogeneous, single-layer graphene with a thickness down to 25 nm. Dato et al. [60] proposed a novel method to synthesize graphene sheets in the gas phase in a substrate-free pressure microwave plasma reactor. Graphene sheets were synthesized by passing liquid ethanol droplets into an argon plasma. The results demonstrated that the graphene could be fabricated without three-dimensional materials or substrates, suggesting a possible route to large-scale synthesis of graphene. CVD is suitable for the large-scale preparation of graphene and is the most widely used method in the industry [61]. This method has the characteristics of easy operation and high controllability and is currently the main preparation method in the field of graphene growth.

2.2.4. Epitaxial Growth Method

Epitaxial growth is a method for growing new crystal layers based on crystal layers as the substrate [62]. The volatility and coagulation of the substrate play a decisive role in the growth of graphene on the substrate. When the matrix leaks and becomes more volatile than condensable, the graphene could be generated from carbon atoms on the matrix [63]. Berger et al. [64] found that the silicon atoms on the surface of silicon carbide were vaporized when heated under high vacuum or normal pressure over 1000 °C, and the remaining carbon atoms would re-aggregate during the cooling process and form the graphene on the surface of the inner layer of silicon carbide. This is the main mechanism for the epitaxial growth method. According to the types of selected substrates, the epitaxial growth method can be divided into the silicon carbide epitaxial growth method and the metal surface epitaxial growth method, respectively. Both methods have their advantages and disadvantages. The silicon carbide epitaxial growth method can produce high-quality single-layer or few-layer graphene, but the energy consumption required is too high, which is not suitable for large-scale production, and the subsequent process of transferring graphene is complicated. On the contrary, the metal surface epitaxial growth method can achieve the purpose of large-scale preparation of graphene by adjusting the parameters. However, the quality of graphene still needs to be improved.

2.2.5. Electrochemical Method

The electrochemical method is a new method for preparing graphene developed in recent years [65]. As demonstrated in Figure 6A, the graphite could act as the working electrode to produce various graphene and graphene-based materials in the presence of electrolytes [66]. Its principle is to drive the charged anisotropic ions through electrolysis to expand the graphite electrode inserted into the mixture, thereby exfoliating graphene. As illustrated in the electrochemical exfoliation of Figure 6B, when the power supply is applied to the graphite electrode, the positively charged ions (e.g., Li^+) or negatively charged ions (e.g., SO_4^{2-}) would be attracted to the graphite electrode in the cathodic or anodic exfoliation, respectively [67]. The ions, electrolyte molecules, or co-intercalating species in electrolytes would be firstly intercalated into the graphene layers of graphite to yield the graphene and graphene-based materials. The main advantages of this method are that the voltage and current can be precisely adjusted, the preparation process is reproducible, the reaction is easy to be controlled, and the cost is low. Nevertheless, the morphology and structures of graphene fabricated by this method are prone to the formation of defects.

Therefore, for this method, there are still many technical barriers to be broken through. Tang et al. [68] prepared a few-layers of water-dispersible graphene with ultrafiltration of up to 99%, a thickness of less than six atomic layers, and a lateral size of 1~50 μm by rationally designing the electrolyte (NaOH + *p*-phthalic acid) and selecting highly oriented pyrolytic graphite (HOPG) as anode material. Meanwhile, the as-prepared graphene exhibited a high dispersibility (2.5 mg mL⁻¹) and excellent stability (over six months).

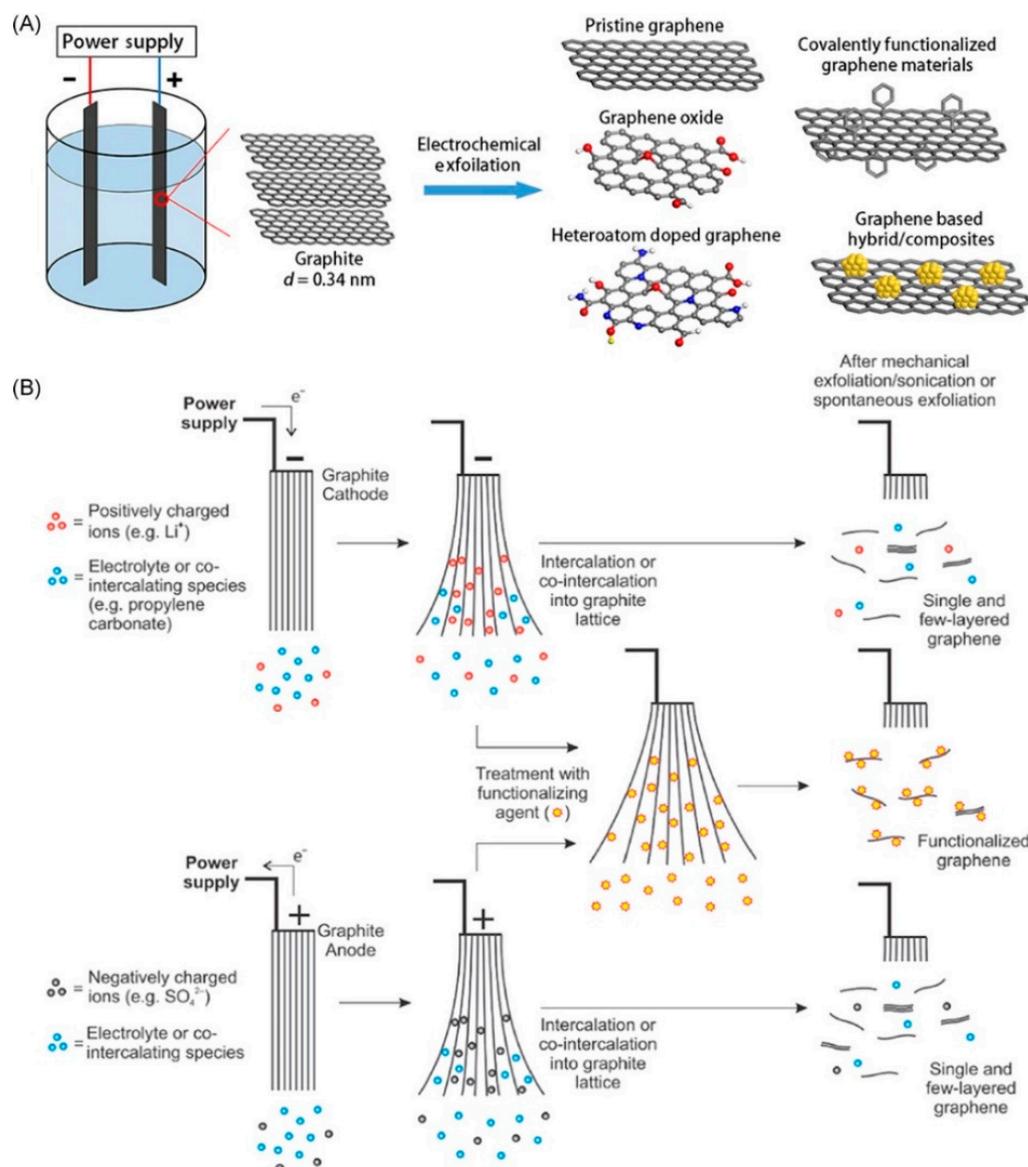


Figure 6. (A) Illustration for electrochemical exfoliation of graphite to produce various graphene materials; (B) schematic of cathodic and anodic exfoliation mechanisms. Reprinted with permission from [66,67]. Copyright@ Elsevier and John & Wiley Inc., respectively.

2.2.6. Organic Synthesis Method

The organic synthesis method is a powerful alternative in fabricating graphene-type structures [69], which uses the traditional organic synthesis method by starting from small organic molecules through a gradual reaction to synthesize graphene. Organic synthesis is a very controllable synthesis method. In this method, graphene with different sizes and thicknesses can be produced by designing synthesis routes. Dössel et al. [70] synthesized graphene nanoribbons with perfect structure by designing a synthetic route in the organic synthesis method. Unfortunately, there are still problems, such as many reaction steps, a

long reaction time, and more materials required when graphene is synthesized on a large scale by this method.

3. Graphene-Based Materials for Heavy Metal Removal

3.1. Influencing Factors on Heavy Metal Removal

Some influencing factors on heavy metal removal, including solution pH, adsorbent dose, heavy metal concentration, treatment time, and temperature, are listed below.

3.1.1. Solution pH

Solution pH is an important parameter to affect the adsorption of heavy metals since the heavy metals exhibit pH-dependent chemistry. Taking Cr(VI) as an example, there are several species of Cr(VI) in an aqueous solution with different pH values. In general, as a strong acid, in the aqueous solution, H_2CrO_4 could be ionized to the form of HCrO_4^- and CrO_4^{2-} . In the $\text{pH} < 2$ solutions, H_2CrO_4 and HCrO_4^- are present; in the pH range of 2~4, HCrO_4^- is dominating form; when the solution's pH is higher than 4, CrO_4^{2-} appears, and its content rises with the increase of the solution's pH; when the pH is higher than 9, only CrO_4^{2-} exists in the solution. Thus, Cr(VI) removal performance by the adsorbents is highly dependent on the existing form of Cr(VI), especially for the adsorbent with surface functional groups. For instance, the amino group functionalized adsorbents favour chelating with HCrO_4^- rather than H_2CrO_4 and CrO_4^{2-} . As a result, the amino group functionalized adsorbents could not provide good Cr(VI) removal performance in a strong acidic and alkaline solution [71].

3.1.2. Adsorbent Dose

In the adsorption process, the adsorbent dose could affect the active sites of adsorbents to the adsorption of heavy metals; thus, the heavy metal removal performance normally increases with coinciding increases in the adsorbent doses [72].

3.1.3. Heavy Metal Concentrations

The heavy metal concentrations have an obvious influence on heavy metal removal. This is because as the heavy metal concentrations increase, the active sites on adsorbents may gradually become saturated by the heavy metals, wherein the adsorbents cannot hold on to the excess heavy metals, leading to the decreased heavy metal removal performance or adsorption equilibrium [73].

3.1.4. Treatment Time and Kinetics

Treatment time is a key factor for heavy metal removal by adsorbents since it is associated with the adsorption kinetics, which is very significant in designing the adsorption reactors in the industry [74]. The kinetics could determine the heavy metal uptake rate for controlling the residence time of adsorbate uptake at the solid-liquid interface. Generally, there are two models to describe the adsorption kinetics: pseudo-first order and pseudo-second order, as listed in Equations (1) and (2), respectively [75].

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 \times t \quad (1)$$

$$\left(\frac{t}{Q_t}\right) = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (2)$$

where k_1 is the adsorption rate constant of the pseudo-first-order model (min^{-1}), k_2 is the adsorption rate constant of the pseudo-second-order model ($\text{g mg}^{-1} \text{min}^{-1}$), Q_e stands for the adsorption capacity at equilibrium time (mg g^{-1}), and Q_t is the amount of metal adsorbed at time t (mg g^{-1}).

3.1.5. Temperature and Thermodynamics

The temperature could affect the adsorption process of heavy metals. As the adsorption process is exothermic, the subsequent increasing temperature is not beneficial for adsorption. Conversely, the rising temperature is favorable to the adsorption in the endothermic adsorption process. The temperature effect on the adsorption is related to the adsorption isotherm [76]. The adsorption isotherm delineates the adsorption equilibrium of adsorbate at the surface of an adsorbent. There are two commonly used models, including Langmuir and Freundlich isotherm models, to explain the solid–liquid adsorption process for thermodynamics. They can be expressed as Equations (3) and (4), respectively [77].

$$q_e = \frac{abC_e}{1 + bC_e} \quad (3)$$

$$q_e = k_f C_e^\eta \quad (4)$$

where C_e is the equilibrium concentration (mg L^{-1}) of heavy metal, q_e is the adsorbed heavy metal amount at equilibrium (mg g^{-1}), a (mg g^{-1}) and b (L mg^{-1}) are Langmuir isotherm parameters, k_f is the Freundlich equilibrium constant, indicating the extent of adsorption, and η is the power term of the Freundlich isotherm and the heterogeneity factor, illustrating the intensity of adsorption. The Langmuir model means the adsorption occurs at the monomolecular layer, whereas the Freundlich model focuses on the adsorption on an energetically heterogeneous surface.

3.2. Heavy Metal Removal Performance by Graphene-Based Materials

Graphene and GO have attracted much more attention in the field of heavy metal removal because of their large specific surface area. GO especially has various active oxygen-containing functional groups on its surface, which can provide many effective active sites for the adsorption of heavy metals. For instance, Rout et al. [78] used hydrazine monohydrate to reduce GO for producing the reduced GO (RGO) with a mean pore diameter of 3.08 nm and sharp peaks in the pore size distribution between 3.08 and 23.88 nm. They found that the maximum adsorption capacity of phenol by RGO achieved 602.41 mg g^{-1} with the RGO amount of 0.4 g L^{-1} , solution pH of 8.0, and adsorption time of 75 min at 30°C . Wang et al. [79] compared the adsorption and co-adsorption of naphthalene, 1-naphthol, and Cd(II) on GO, chemically reduced graphene (CRG), and annealing reduced graphene (ARG) to determine the unique adsorption properties of graphene nanosheets. The results revealed that the order of adsorption capacity to organic pollutants was $\text{CRG} > \text{ARG} > \text{GO}$, and the adsorption of 1-naphthol by these three adsorbents was stronger than that of naphthalene. GO, with more functional groups on CRG and ARG, exhibited a strong affinity to Cd(II). The adsorption of Cd(II) onto GO and CRG facilitated the co-adsorption of naphthalene and 1-naphthol via a surface bridging mechanism. Notably, even though ARG did not display obvious Cd(II) adsorption, the suppressed co-adsorption of naphthalene on ARG might be from the sieving effect of hydrated Cd(II) binding to the micropore edges on ARG. This study not only reflected the good adsorption properties of graphene materials but also supported the conclusion that graphene materials could simultaneously adsorb heavy metals and organic pollutants in wastewater. Xue et al. [80] explored GO nanosheets for the adsorption of Cd(II) in acidic aqueous solutions. The results illustrated that the removal efficiency of Cd(II) was increased from 6.29 to 96.72% by increasing the adsorbent dosage from 0.02 to 2.00 g L^{-1} . The adsorption capacity of Cd(II) was greatly enhanced when the solution pH was increased from 2.02 to 4.01. Moreover, the reaction reached adsorption equilibrium within 120 min, and the maximum Cd(II) adsorption capacity was about 44.64 mg g^{-1} at the adsorbent dosage of 0.50 g L^{-1} . The experimental results of this work well demonstrated that graphene materials had good adsorption properties to Cd(II) in suitable conditions.

4. Modified Graphene Materials for Heavy Metal Removal in the Tobacco Industry

4.1. Modification of Graphene Materials

Even though graphene and GO could be widely applied in heavy metal removal, as aforementioned above, the abundant oxygen-containing functional groups on the surface of GO make it well-dispersed in the water. As a result, they are difficult to be separated from wastewater after treatment. Therefore, it is required to modify the graphene and GO materials to solve this problem. Commonly, there are two types of modification methods for graphene and GO materials: covalent bond modification and non-covalent bond modification [81].

The covalent bond modification mainly utilizes the active groups on its surface to chemically react with other molecules to achieve the modification of graphene. According to the different reaction molecules, covalent bond modification can be divided into small organic molecule modification and polymer modification. The small organic molecule modification occurs through the reaction of a small organic molecule with functional groups on the surface of GO. It mainly contains the ring-opening reaction of the hydroxyl and epoxy groups, the diazotization reaction of a conjugated plane, the isocyanate and cycloaddition reactions, etc. Stankovich et al. [82] treated GO with organic isocyanates. The degree of GO modification could be attained by controlling the reactivity of isocyanates or the reaction time. The polymer modification introduces the long polymer chains to change the structural properties of GO.

The non-covalent bond modification is generally accomplished by physical adsorption or polymer wrapping on the surface of GO. This method could maintain the structural properties of GO without destroying its intrinsic structure and improving its solubility. The non-covalent bond modification of GO mostly includes a π - π bond and hydrogen bonding functionalization. Both graphene and GO have highly conjugated systems, which makes it easy to interact with molecules with a π conjugated structure through π - π interaction to achieve modification. Yang et al. [83] manufactured a novel GO-doxorubicin hydrochloride nanohybrid (GO-DXR) by the hydrogen bonding and strong π - π stacking interaction between DXR and GO. Therefore, the loading and release behaviours of DXR on GO disclosed a strong pH-dependent property.

The preparation of magnetic GO nanocomposites is also a good way to solve the separation problem after treatment. By introducing the magnetic nanoparticles onto GO, the adsorbents could be efficiently separated from the solution by a permeant magnet after adsorption of heavy metals. This allows the magnetic GO nanocomposites to be applied in the field of wastewater treatment potentially. The commonly used methods for the fabrication of magnetic GO nanocomposites include the self-assembly method, sol-gel method, chemical co-precipitation method, chemical grafting method, hydrothermal method, high-temperature annealing process, etc.

For example, Adel et al. [84] manufactured the magnetic separable MgFe_2O_4 /crumbled reduced GO nanoparticles by self-assembly method via electrostatic interactions. Gabris et al. [85] synthesized the silica-cyanopropyl functionalized magnetic GO (MGO/ SiO_2 -CN) hybrid nanomaterial derived by the sol-gel method. Cai et al. [86] prepared magnetic carbon microfibers supporting iron/nickel bisalloy (FeNi@CMFs) in a single step by using the electrospinning method combined with the high-temperature annealing method at an optimal condition of 5 wt% mass fractions of metal salts (ferric nitrate and nickel nitrate) annealed at 800 °C for 60 min in 5% (v/v) hydrogen/argon atmosphere.

Wang et al. [41] treated GO with polyacrylic acid (PAA) in order to bring the carboxylic groups to the surface of GO. After that, the GO functionalized with carboxylic groups reacted with the magnetite (Fe_3O_4) nanoparticles modified by amine groups through chemical grafting to produce the magnetic GO nanocomposites, as shown in Figure 7.

The modification of graphene and GO could solve the dispersion problem of GO in water and assist the GO to be separated from water more easily, which could make GO be better exploited in heavy metal removal and wastewater treatment.

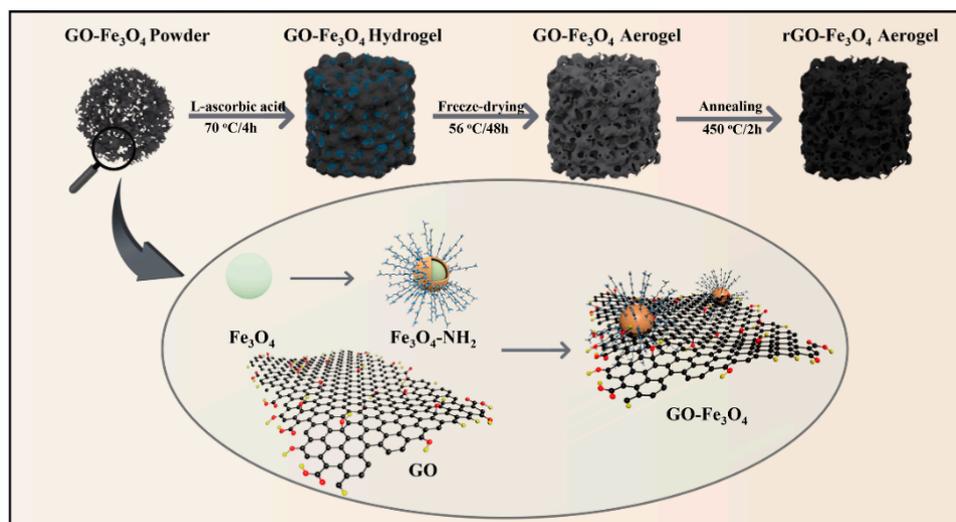


Figure 7. Covalently bonded Fe_3O_4 nanoparticles onto graphene. Reprinted with permission from [41]. Copyright@ Springer–Nature.

4.2. Modified Graphene Materials for Heavy Metal Removal

In recent years, modified graphene materials have received extensive attention in the field of heavy metal removal. The treatment of heavy metals in wastewater by modified graphene materials mainly contributes to physical adsorption and redox reaction. Physical adsorption directly adsorbs heavy metals by using their physical properties of a large specific surface area. Redox reaction is to reduce the valence state of heavy metals through redox reaction after adsorption, which is mostly applied to treat heavy metals with high chemical valence and high toxicity in wastewater.

Fan et al. [87] used magnetic chitosan (MC) to modify GO for manufacturing a magnetic chitosan/graphene oxide (MCGO) material by a facile and fast process to remove Pb(II) from an aqueous solution. The results illustrated that the MC was assembled on the surface of GO layer in a high-density form and could obviously increase the specific surface area of GO. Furthermore, the adsorption of Pb(II) by MCGO was observed to be strongly solution pH-dependent and mainly ascribed to the abundant functional groups on the surface of MCGO. The maximum adsorption capacity of Pb(II) was estimated to be 76.94 mg g^{-1} , as gained from the Langmuir model. This newly developed MCGO was a good adsorbent material for Pb(II) removal. Kumar et al. [88] produced a novel chitosan functionalized GO material for the efficient adsorption of As(V)/As(III). The results revealed that the maximum adsorption capacity of As(V) and As(III) by chitosan functionalized GO material was 64.27 mg g^{-1} and 71.9 mg g^{-1} , respectively. Abaszadeh et al. [89] adopted Fe_3O_4 nanoparticles and 5-amino-1,10-phenanthroline (APhen) to functionalize GO in the presence of N,N' -dicyclohexylcarbodiimide (DCC) to produce magnetic nanocomposites of MGO@APhen, which exhibited a high Pb(II) removal efficiency up to 97.2% and excellent reusability during six cycles after being recycled by a supermagnet.

Chi et al. [90] prepared a novel magnetic surface-ion-imprinted polymer (IIP) by using As(III) as a template and GO/ Fe_3O_4 as support, Figure 8A, which displayed a high selectivity of As(III) in the presence of other competing components, such as As(III)/Mg(II), As(III)/Ca(II), As(III)/ HCO_3^- , As(III)/ PO_4^{3-} , As(III)/ SO_4^{2-} , and As(III)/HA, have excellent reusability with an adsorption efficiency of 75% after five cycles of regeneration and reuse (Figure 8B). Xing et al. [91] modified magnetic GO/ Fe_3O_4 (MGO) with ethylenediaminetetraacetic acid (EDTA) groups by the silanization reaction between N -(trimethoxysilylpropyl) ethylenediaminetriacetic acid and $-\text{OH}$ on the surface of MGO (MGO-EDTA), as shown in Figure 9, which performed a high Pb(II) adsorption capacity of up to 211.3 mg g^{-1} coming from the chelating ability of EDTA.

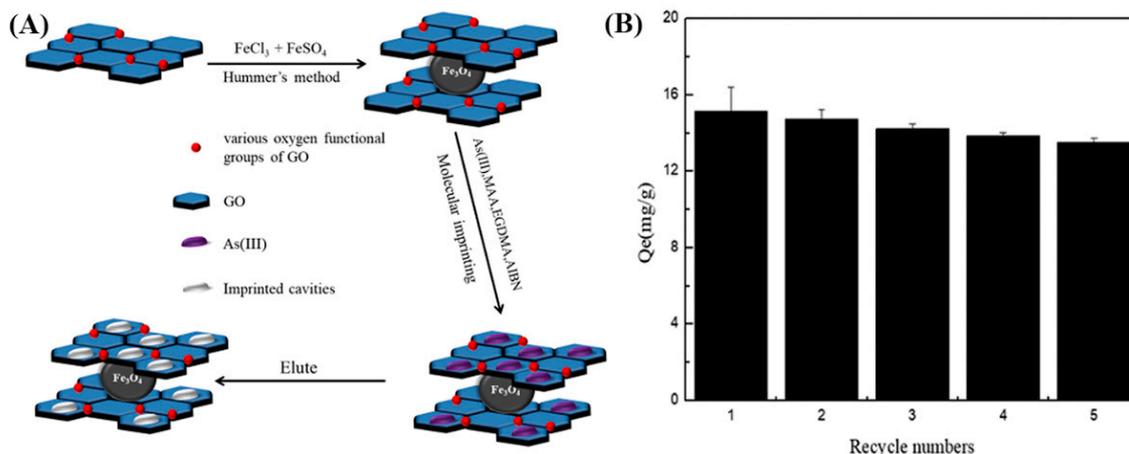


Figure 8. (A) Schematic for the synthesis of MGO–As(III)–IIP; (B) effect of regeneration cycles on the adsorption capacity. Reprinted with permission from [90]. Copyright@ Elsevier.

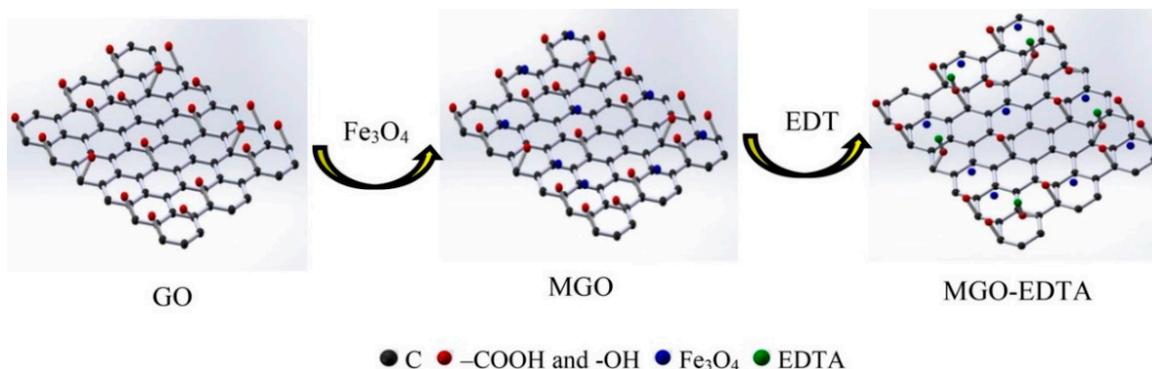


Figure 9. Illustration for the preparation of MGO–EDTA. Reprinted with permission from [91]. Copyright@ John Wiley & Sons.

In summary, the modified GO materials express excellent heavy metal adsorption properties relative to GO. Researchers have devoted themselves to the various modified GO materials for heavy metal wastewater treatment. However, the selectivity of heavy metals in the treatment by modified GO materials is rarely discussed. Thus, an extensive investigation on enhancing the selectivity of heavy metals for modified GO materials is still required.

4.3. Modified Graphene Materials for Heavy Metal Removal in the Tobacco Industry

There are more than 8000 kinds of chemical substances that can be detected in the smoke produced by cigarettes during the combustion process [92]. In 1990, Hoffman from the United States proposed 43 kinds of substances, such as As, Cd, Cr, Pb, Ni, Hg, and others, that were most harmful to the human body and were called the Hoffmann list. Among them, these heavy metals could be accumulated in the organs of the human body, causing serious harm to human health [93]. The heavy metals in cigarette smoke mainly come from two aspects. On the one hand, soil and air pollution, improper use of pesticides and fertilizers, irrigation water pollution, and other factors during the planting process of tobacco plants exceed the standard of heavy metals in tobacco leaves. On the other hand, the heavy metals may be from the auxiliary materials used in cigarettes, such as cigarette paper, filter rods, additives, etc. When the cigarette is burned, the heavy metals are released and mixed into the smoke, further entering the human body. Although New Tobacco Products such as Electronic Nicotine Delivery Systems (ENDS), i.e., e-cigarettes, are now emerging, those products still have risks due to the limitations of product technology, form,

and appearance. The smoke also contains a large number of heavy metal particles, which will also result in harm to the human body [94]. Lerner et al. [95] found that copper was 6.1 times higher than previously reported for conventional cigarette smoke in e-cigarettes per puff. They believed that the detection and removal of heavy metals from e-cigarettes and their components should raise concerns about the safety of their usage and the disposal of e-cigarette waste.

Graphene and its composite materials as adsorbents or additives have important application prospects in the fields of smoke composition detection, removal of heavy metals in cigarette materials, and New Tobacco Products. For example, Palisoc et al. [96] used graphene to fabricate an effective gold nanoparticle/graphene/Nafion-modified glassy carbon electrode, which had more merits for the detection of Pb(II), Cd(II) and Cu(II) in cigarettes. Guo et al. [97] established an electrochemical sensor consisting of rGO/MoS₂/chitosan (CS) nanocomposite-modified glassy carbon electrode, which exhibited wide detection sensitivity for Pb(II) in tobacco leaves in the range of 0.005–0.05–2.0 μ M, with excellent performance in reproducibility, stability and anti-interference ability. The limit of detection (LOD) was 0.0016 μ M. It provided a new approach to the determination of Pb(II) in tobacco leaves with low content.

Taking the removal of heavy metals from smoke as an example, Yu et al. [98] coated the lyophilized oxidized multiwalled carbon nanotubes/GO composite on the surface of cellulose acetate in the cigarette filter. When the weight ratio of the oxidized multiwalled carbon nanotubes: GO: filter was 1:1:62, the modified filter demonstrated an excellent adsorption performance with the removal efficiency of 83 and 78% to Cd(II) and Cr(VI), respectively, Figure 10.

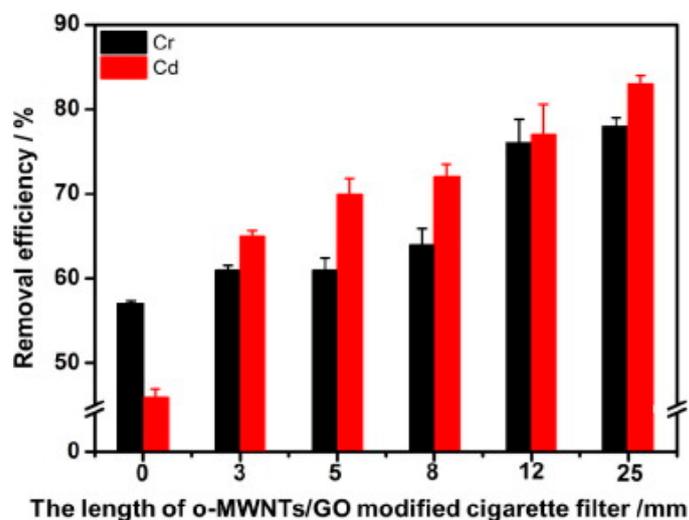


Figure 10. The effect of the length of o-MWNTs/GO modified cigarette filter on Cd(II) and Cr(VI) removal from mainstream smoke (with a dosage of 4 mg). Reprinted with permission from [98]. Copyright@ Elsevier.

At present, the research on graphene and its composite materials in the field of the tobacco industry for the detection and removal of heavy metals has been relatively extensive. It is believed that graphene and its composite materials will also have huge application space and development prospects in the tobacco industry in the future.

In order to better understand the removal efficiency of GO and GO-based materials to heavy metals, the synthesis methods and removal efficiency, as well as adsorption conditions, are laid out in Table 1.

Table 1. Heavy metal adsorption capacity/removal efficiency, as reported in the literature.

Materials	Synthesis Method	Heavy Metal	Treatment Conditions	Maximum Adsorption Capacity (mg g ⁻¹)	Ref.
GO	Modified Hummer's method	Cd(II)	Room temperature, pH = 5, 10 mg L ⁻¹ Cd(II), 24 h equilibration time	35.7	[79]
GO	Hummer's method	Cd(II)	T = 303.15 K, pH = 4.00, 0.50 g L ⁻¹ adsorbents, 0.02~5 g L ⁻¹ Cd(II), 12 h equilibration time	44.64	[80]
Magnetic chitosan/GO	Modified Hummer's method	Pb(II)	T = 30 ± 0.2 °C, pH = 5, 0.8 g L ⁻¹ adsorbents, 0.02~14 mg L ⁻¹ Cd(II), 12 h equilibration time	76.94	[87]
Chitosan-functionalized GO	Improved Hummer's method	As(V)/As(III)	T = 30 °C, pH = 5.5, 8 g L ⁻¹ adsorbents, 30~500 ppm As(V)/As(III)	71.9/64.2, respectively	[88]
MGO@APhen		Pb(II)	Room temperature, pH = 6.5, 0.5 g L ⁻¹ adsorbents, 10 ppm Pb(II)	The removal efficiency of 97.2%	[89]
MGO ion-imprinted polymer	Modified Hummer's method	As(III)	T = 25 °C, pH = 5, 5 g L ⁻¹ adsorbents, 0.5~20 mg L ⁻¹ As(III), 24 h equilibration time	49.42	[90]
MGO-EDTA	Hummer's and Offeman's methods	Pb(II)	T = 20 °C, pH = 1~10, 0.5 g L ⁻¹ adsorbents, 10~150 mg L ⁻¹ As(III), 3 h equilibration time	211.3	[91]

5. Conclusions, Challenges, and Perspectives

With the rapid development of society and industry, heavy metal wastewater pollution has become more and more serious, resulting in a tighter supply and demand for water resources. Consequently, it is urgent to solve the heavy metal wastewater pollution problem. The graphene-based materials with unique physicochemical properties have received intensive attention in the field of heavy metal wastewater treatment, especially, in the tobacco industry. Recently, the application of graphene-based materials for heavy metal treatment has made a great progress, but there is still a long way to go to face the heavy metal wastewater treatment problem. In view of the current research status of graphene-based materials in the field of heavy metal wastewater treatment, the main work in future research is to design and synthesize novel functionalized graphene-based composite materials with high heavy metal adsorption capacities. It will be basically developed in three directions. First, the more modified graphene-based materials with different functions should be manufactured to attain relatively stronger adsorption properties. Secondly, the research on the effect of competing for heavy metal ions in wastewater on the adsorption of graphene-based materials should be deepened. At present, researchers have mostly studied the effect of functionalized graphene materials on a certain heavy metal. However, there are often multiple heavy metal ions in real wastewater. In this situation, the functionalized graphene materials for treating a single heavy metal are difficult to be applied in a real wastewater system. It is more practical to develop functionalized graphene-based materials to remove the multi-component heavy metal ions. Thirdly, the cost for the current modification method of graphene-based materials is relatively high, which severely limits the applications of graphene-based materials in practical application. To seek a new method for the preparation of graphene-based materials at a low cost is the future pursuit for heavy metal treatment in the tobacco industry on a large scale.

Author Contributions: Writing—original draft preparation, X.X., J.Z. and Y.W.; conceptualization, writing—review and editing, H.G. and S.W.; supervision, H.G.; project administration, H.G.; funding acquisition, H.G. and Q.W. All authors have read and agreed to the published version of the manuscript.

Funding: The authors are grateful for the support and funding from the Fundamental Research Funds for the Central Universities (2022-4-YB-03). This work is supported by Shanghai Science and Technology Commission (19DZ2271500).

Data Availability Statement: Not applicable.

Acknowledgments: We thank the support from the Shanghai Key Lab. of Chemical Assessment and Sustainability.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

Cr	Chromium
Cd	cadmium
As	arsenic
Hg	mercury
Pb	lead
Pt	platinum
GO	graphene oxide
CVD	chemical vapor deposition
HOPG	highly oriented pyrolytic graphite
RGO	reduced GO
CRG	chemically reduced graphene
ARG	annealing reduced graphene
GO-DXR	GO-doxorubicin hydrochloride nanohybrid
MCGO	magnetic chitosan/graphene oxide
APhen	5-amino-1,10-phenanthroline
DCC	N,N'-dicyclohexylcarbodiimide
MGO	magnetic graphene oxide
EDTA	ethylenediaminetetraacetic acid
ENDS	Electronic Nicotine Delivery Systems
LOD	limit of detection

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