Research progress of surface-modified graphene-based materials for tribological applications

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Abstract

Graphene’s many excellent properties have cemented it as an essential research topic in materials science and beyond. It is widely used in photoelectric materials, sensors, battery electrode materials, composites, and so on. Graphene has attracted particular attention in the field of tribology. However, graphene agglomerates easily, limiting its performance when used directly. Therefore, considerable research has focused on methods of modifying the surface of graphene to improve its tribological performance, by improving the dispersion stability, friction reduction, wear resistance, or a combination of these. This paper focuses on the research progress of surface modification of graphene-based materials for tribological applications. According to the reaction principles, surface modification methods can be divided into covalent surface modification, noncovalent surface modification, and surface modification by nanoparticles doping. Herein, the typical reaction processes of these modification methods and the anti-wear mechanism of modified graphene-based materials are introduced, and current research on the surface modification of graphene used in tribology is discussed.

1. Introduction

On 5 October 2010, two physicists, Andre Geim and Kostya Novoselov, from the University of Manchester, UK, won the Nobel Prize in Physics for their outstanding achievements in the research of graphene materials. In 2005, Geim and Novoselov prepared high-quality graphene monolayers for the first time. Graphene, the thinnest material to date, is a two-dimensional (2D) honeycomb lattice composed of single carbon atoms and is the basic building unit of all other graphitic materials. A single layer of graphene, owing to its 2D structure, is only a single atom thick (0.3354 nm) [1, 2]. Graphene can be wrapped into zero-dimensional fullerene, rolled into one-dimensional carbon nanotubes, or stacked into three-dimensional graphite [3]. It has a huge specific surface area and high transparency [4, 5], as well as excellent electrical [6–8], thermal [9, 10], mechanical [2, 11], electrochemical [12, 13], and optical properties [14]. Its excellent properties have led to its wide use in optoelectronics [15–18], sensors [19, 20], battery electrodes [21, 22], composites [23–25], composite coatings [26, 27], and energy storage and conversion devices [28–31].

In addition to the above applications, graphene has attracted significant attention in the field of lubrication due to its excellent physical and chemical properties [32–34]. With great potential in tribological applications, it is considered one of the most promising and attractive lubricating nanomaterials for tribological applications [35]. As a popular solid lubricant, it has excellent mechanical properties, low friction coefficient, and good wear resistance [36]. Graphene lubricants can be applied as a protective film on a substrate [37–40], as a reinforcing...
phase in various friction composites [41–43], or as an additive in various lubricants [44–47]. Graphene’s benefits as a lubricant stem from its 2D layered structure, which provides interlayer slip that significantly lowers its coefficient of friction compared to ordinary lubricants [48–50]. Essentially, the lubrication performance of solid graphene is regulated by the low shear strength between graphene sheets.

In sliding steel surface tests, a small amount of an ethanol–graphene solution can reduce the wear of sliding steel surfaces in air by nearly four orders of magnitude and the friction coefficient by six times [51]. Berman et al [52] summarized the friction coefficient of various solid lubricants. With a graphene coating with a thickness of only 1–2 nm, the dry and wet friction coefficients were only 0.15–0.20. Zhang et al [53] studied the tribological properties of graphene oxide (GO) as an additive in lubricating oil. The friction and wear performance of the Si3N4/GCr15 sliding pair were significantly improved by adding GO to the base oil; the average friction coefficient and wear scar width were reduced by 67.37% and 28.37% respectively. Hence, the excellent friction and wear resistance of graphene have made it a popular lubricant.

In-depth research has been performed on the friction-reducing and anti-wear performance of graphene. Various experimental approaches, calculation methods, and precision instruments have been employed to explore its lubrication and friction mechanism [54–57]. Numerous studies have shown that graphene reduces friction and wear by forming a physisorbed or chemisorbed film at the contact points between friction pairs. When contact stress is applied, the dispersed graphene is deposited on the contact area, easily shearing and effectively lubricating it (figure 1) [52, 58–61]. From experimental evidence, it is evident that graphene deposition is mediated by the plastic deformation of metal contact points. The high energy release that accompanies plastic deformation is beneficial to the physisorption or chemisorption of the graphene film on the substrate surface.

When graphene is fully dispersed in lubricating oil, its structure and morphology are stable, the shear mechanism is active, and a friction film is easily formed [62, 63]. Meanwhile, when graphene is used as a lubricating additive, it is deposited on the frictional surfaces, where it fills rough asperity gaps due to its small volume and removes scars and grooves on the frictional surfaces. This kind of repair or polishing can improve the tribological performance by reducing the surface roughness [64, 65].

Although graphene is widely used in tribology, many obstacles still exist to fully utilise its excellent tribological properties. On one hand, graphene is prone to irreversible aggregation and precipitation due to its insolubility, van der Waals forces, and π–π stacking between lamellae [66, 67], leading to the loss of wear resistance and anti-friction ability [68]. On the other hand, if graphene alone is used directly in tribology, its excellent anti-wear and friction-reducing performance may not be observed, limiting its application range. Currently, these problems have been solved most effectively by modifying the surface of graphene. This is done

![Figure 1. Schematic diagram of graphene in sliding contact.](image-url)
both to solve the problem of graphene agglomeration \cite{69,70} and to improve its anti-friction and anti-wear performance. The surface modification of graphene is widely studied, and there are many reports on related applications. Yet, the research progress of surface-modified graphene in tribological applications is rarely reported.

Thus, in this review, the research progress of modified graphene-based materials in tribological applications is summarized and analysed in terms of the reaction principle of surface modification. First, the excellent properties and wide applications of graphene, especially their tribological and lubrication mechanisms, are introduced. Then, according to the different modification principles, the surface modification methods applied in tribology are divided into covalent surface modification (chemical modification), non-covalent surface modification (physical modification), and modification by nanoparticles doping. Next, the reaction principle and anti-wear mechanism of different reaction types of these three surface modification methods are analysed and summarised in detail. Finally, the existing problems in the field of surface modification of graphene-based materials for tribological applications are analysed, with a prediction of future development trends. This review has significant potential for reducing industrial energy consumption and expanding the application range of graphene-based lubricants. The dispersion stability and tribological properties of various modified graphene-based materials prepared by different surface modification methods are shown in Table 1.

2. Covalent surface modification

In covalent surface modification of graphene-based materials, the active carbon–carbon double bonds (C=C) or oxygen-containing groups on the surface of graphene or GO are used as reaction sites. Surface modification occurs by covalent bond formation between the modifier and one of these groups \cite{91-94}. Many oxygen-containing groups exist on the surface and edges of GO, including hydroxyl groups, carboxyl groups, and epoxy groups. GO also contains some incomplete lattices. These oxygen-containing functional groups and defect sites have high reactivity \cite{95}, improving the possibility of covalent surface modification. Moreover, the high specific surface area of graphene is conducive to chemical modification \cite{96}.

There are two general routes for the covalent modification of graphene-based materials: the first is the formation of a covalent bond between a free radical or amphiphilic molecule and the carbon–carbon double bonds of graphene \cite{97,98}; the other is the formation of covalent bonds between organic functional groups and oxygen-containing groups on the surface of graphene or GO \cite{99}. However, modification via carbon–carbon double bonds is rare for tribological applications, and is not analysed in this paper. Modification via oxygen-containing functional groups can be divided into two reaction types depending on the modification site: hydroxyl covalent bonds, carboxyl covalent bonds, and epoxy covalent bonds. These typical reactions are used to introduce the research progress of covalent surface modification of graphene-based materials in the following sections.

2.1. Modification of hydroxyl covalent bond

Hydroxyl groups exist on the surface of GO. At present, there are two routes to modify the surface of GO via the hydroxyl groups to form covalent bonds. The first is an esterification reaction between the hydroxyl groups of GO and the carboxyl groups of the modifier \cite{100}. The other is a substitution reaction between the hydroxyl groups of GO and the halogen atoms of the modifier.

Mu et al \cite{71} used imidazole-1-ylphosphine dichloride (or 1H-1,2,4-triazol-1-ylphosphine dichloride) to covalently modify GO. The chlorine atoms in the modifier reacted with the hydroxyl group in GO, successfully grafting the modifier molecule onto the surface of GO to obtain modified GO (mGO) (Figure 2). The modification increased the solubility of GO in an ionic liquid from 1% to 3%, while homogeneity was maintained for six months. When 1.0% of the mGO was added to the ionic liquid, the average friction coefficient and wear loss of a metal surface were reduced by 9% and 73%, respectively. Modification enhanced the hydrogen bonding between the mGO and ionic liquid and improved the dispersion stability. Furthermore, the polarity of the mGO was strengthened, boosting the adhesion between the mGO and the metal surface. Consequently, a more stable lubricating film was formed, improving the friction reduction and wear resistance.

The principle of similar compatibility states that surface modification with groups similar to those present in the dispersion medium can improve the dispersion stability. This is a common approach to improving the dispersion stability of graphene-based materials. For example, to improve the dispersion stability of graphene-based materials in a silicone resin, organosiloxanes with a long chain structure were reacted with the hydroxyl groups of GO to obtain mGO with a larger interlayer spacing \cite{72}. After modification, the mGO was effectively dispersed in the silicone resin, and the resultant silicone coating had excellent wear resistance. The mGO sheets had good dispersion and compatibility in the polysiloxane matrix, and acted as an effective buffer between stainless steel and polysiloxane on the surface of the coating, resulting in good wear resistance.
Table 1. Research results of dispersion stability and tribological properties of modified graphene-based materials prepared by different methods.

| Method for modification | Substances for modification | Dispersion system | Dispersion stability | Lubricating material | COF decrease / Wear decrease | Mechanism of friction-reduction and anti-wear | References |
|-------------------------|-----------------------------|-------------------|---------------------|----------------------|-----------------------------|---------------------------------------------|------------|
| Covalent surface modification | Modification of hydroxyl covalent bond | 1H-1,2,4-triazol-1-yl phosphonic dichloride | Ionic liquid | More than six months | Ionic liquid | 9%/73% | Smooth and firm lubricating film. | [71] |
| | Polysiloxane oligomer | Polysiloxane matrix | Excellent dispersibility | Polysiloxane coating film | --/48% | Buffer effect between contact surfaces. | [72] |
| | Silane coupling | — | — | Aromatic polyimide (PI) matrix | 30.2%/71.2% | The spalling of worn surface was restrained. | [73] |
| | Oleic acid | Lubricant oil | Excellent dispersibility | Lubricant oil | 17%/14% | 1. compact and stable lubricating film. | [74] |
| | Azidodecane | Lubricant oil | More than one month | Lubricant oil | 16%/30% | 2. repair or polishing of friction surface. | [75] |
| | Alkylamine | Hydrocarbon solvents | Excellent dispersibility | Hexadecane | 26%/9% | 3. the graphene sheet was continuously provided on the contact surface. | [76] |
| | Dodecylamine | Commercial engine oil | More than one month | Commercial engine oil | 40%/- | | [77] |
| | Octadecylamine | 10W-40 oil | More than one month | 10W-40 oil | --/36% | | [78] |
| | Octadecylamine and dicyclohexylcarbodiimide | PAO6 base oil | 120 days(with dispersant) | PAO6 base oil | 44%/90% | | [79] |
| | Red phosphorus (P) | PAG base oil | More than two months | PAG base oil | 12%/98% | Composite chemical lubricating film. | [80] |
| Modification of epoxy covalent bond | Poly(2-aminothiazole)(PAT) | — | — | Composite coating | --/69.48% | A close cross-linking network was formed in the epoxy coating. | [81] |
| Non-covalent surface modification | π-π bond interaction | Sodium dodecyl benzene sulfonate(SDBS) | PAO base oil | Excellent dispersibility | PAO base oil | 74.78%/28.33% | Smooth and firm lubricating film. | [82] |
| | Poly(2-aminothiazole)(PAT) | — | — | Composite coating | --/69.48% | | [83] |
| | Water | | | | | | |
| Method for modification       | Substances for modification | Dispersion system | Dispersion stability | Lubricating material | COF decrease / Wear decrease | Mechanism of friction-reduction and anti-wear | References |
|-------------------------------|-----------------------------|-------------------|----------------------|----------------------|-----------------------------|---------------------------------|------------|
| Hydrogen bond interaction     | Poly(sodium 4-styrenesulfonate) (PSS) | More than several weeks | Multilayer ultrathin films | Good tribological properties | The stress, compression and shear between the film and substrate were reduced. Adhesion and buffering effects. | [84] |
|                               | Polydopamine (PDA)          | Water             | Excellent dispersibility | Composite coating   | Good tribological properties 38%/53% | Firm adsorption friction film. | [62] |
|                               | Poly(ethylene glycol 200) (PEG200) | PEG200            | Excellent dispersibility | PEG200               | | |
| Ionic bond interaction        | Cu nanoparticle            | —                 | —                    | Base oil             | Excellent tribological properties | Thin physical friction film. | [85] |
| Electrostatic action          | Cluster-cored star polymers (CSPs) | Organic solvents | Excellent dispersibility | Composite coatings | Excellent tribological properties | The modified graphene had good compatibility with polymer matrix. | [86] |
| ZrO2                          | Paraffin oil               | Excellent dispersibility | Paraffin oil | 20.7%/21.5% | The sliding friction changed into rolling friction | [87] |
| Surface modification by element doping | Nickel nanoparticles | —                 | —                    | Paraffin oil | 32%/42% | Physical deposition film | [88] |
|                               | Silver nanoparticle        | Engine oil        | More than two weeks   | Engine oil           | 30.4%/27.4% | Smooth and firm lubricating film | [35] |
|                               | Copper nanoparticle        | —                 | —                    | Paraffin oil         | 27.0%/52.7% | Nano copper reduced the stacking tendency of GO | [89] |
| Titanium(Ti) particles        | —                           | —                 | —                    | Aluminium Metal Matrix Composites | Excellent tribological properties | Composite chemical lubricating film. | [90] |
The similar compatibility principle can also be used to make graphene-based materials more compatible with a composite matrix, which improves the uniformity and stability of the composite. Li et al.\(^\text{[73]}\) used a silane coupling agent to modify graphene and prepared modified graphene/polyimide composites, which showed a lower friction coefficient and wear rate. The improved anti-friction and anti-wear performance was mainly attributed to the addition of modified graphene, which inhibited the spalling of large blocks on the worn surface and effectively increased the anti-deformation ability of the matrix. Therefore, only slight adhesive wear occurred.

2.2. Modification of carboxyl covalent bond

The carboxyl functional groups that exist at the edges of GO serve as another important modification site due to the high reactivity of the carboxyl group\(^\text{[101–104]}\). At present, two main methods are used to modify GO via covalent bonding to the carboxyl groups. The first is an esterification reaction between the carboxyl group of GO and the hydroxyl group of the modifier, which grafts the modifier to the GO surface\(^\text{[105]}\).

Zhang et al.\(^\text{[74]}\) studied the tribological properties of poly(\(\alpha\)-olefin) (PAO) lubricating oil prepared using oleic acid-modified graphene. Esterification of the carboxyl group in graphene with the hydroxyl group in oleic acid resulted in modified graphene with good lipophilicity. It was found that an addition of 0.02 wt\% modified graphene reduced the friction coefficient by 17\%, while the wear spot diameter decreased by 14\% with a 0.06 wt\% addition of modified graphene.

Although carboxyl groups have high reaction activity, the degree of reaction can be enhanced by activating the carboxyl groups by pre-treatment. Ismail and Bagheri\(^\text{[75]}\) first activated GO with SOCl\(_2\), then esterified 2,2-dipropyl-1,3-propanediol with the carboxyl group on the surface of GO to obtain mGO containing an alkynyl group. Azido dodecane was then connected through substitution reaction to obtain a new modified graphene material (figure 3). The results showed that the material had good lipophilicity, and the friction coefficient and wear loss were reduced by 16\% and 30\%, respectively.

The purpose of covalent modification is to react graphene-based materials with modifiers and graft desired groups. For these chemical reactions to take place, graphene-based materials must contain functional groups. Carboxyl groups are one kind of functional group that allow surface modification by chemical reaction. The chemical activity of carboxyl groups high, which facilitates the chemical reactions. Esterification is one of the chemical reactions that can occur at the carboxyl functional groups of graphene-based materials. Another method is to form amide bonds between the carboxyl groups of graphene and the amido groups of a modifier\(^\text{[106, 107]}\). For example, alkylamines with variable alkyl chain lengths are commonly used as the modifier to

![Figure 2. Process diagram of covalent bond modification of graphene oxide by imidazole-1-ylphosphine dichloride (Im) and 1H-1,2,4-triazole-1-ylphosphine dichloride (Tr). Reprinted from \([71]\), Copyright (2017), with permission from Elsevier.](image-url)
prepare alkyl-modified graphene [76, 77]. Alkylamines are excellent modifiers as they contain both amino and alkyl chains, making them compatible with hydrocarbon solvents. In this way, the modified graphene has excellent dispersion stability in hydrocarbon solvents such as lubricating oil. Furthermore, the lubricating oil has improved anti-friction and anti-wear properties.

To improve the modification efficiency, carboxyl groups can be grafted onto the surface of graphene in a directional manner without generating other interfering functional groups. Mungse and Khatri [78] first reduced GO with hydrazine hydrate, then acidified the reduced GO (rGO) with nitric acid, which selectively decorated the rGO surface with carboxyl groups. Subsequently, an amino group-containing long-chain alkyl modifier, octadecylamine, was reacted at high temperature with the carboxyl group of GO to form amide bonds (figure 4). The mGO had good dispersion stability in lubricating oil, exhibiting stability for over a month. Tribological tests showed that the surface-modified rGO was an effective additive for 10w-40 engine oil and significantly reduced the friction and wear of a steel ball.

Wu and colleagues [79] used octadecylamine and dicyclohexylcarbodiimide to modify graphene through the same chemical reaction. Combined with a dispersant, the dispersion of graphene in PAO6 base oil was stable for approximately four months. Compared with pure PAO6, the friction coefficient between sliding surfaces and the depth of wear marks on a steel plate were reduced by 44% and 90%, respectively. The researchers noted that the degree of reaction between the modifier and graphene was very low, and the modified graphene could not be stably dispersed in the lubricating oil due to fewer lipophilic groups grafted on the surface. Nevertheless, the addition of a dispersant increased the dispersed stably time to over four months. Low dispersibility and low

Figure 3. After the carboxyl group of graphene oxide was esterified with 2,2-dipropyl-1,3-propanediol, a new modified graphene resulted from substitution reaction with azido dodecane. Reprinted from [75], Copyright (2017), with permission from Elsevier.
Figure 4. Process flow chart of graphene modified by octadecylamine. (a) graphene oxide was prepared by Hummer’s method; (b) ammonia was used to reduce graphene oxide; (c) carboxylic acid was used to gently oxidise graphene; (d) after the carboxyl group was activated, graphene was modified with octadecylamine. Reprinted with permission from [78]. Copyright (2014) American Chemical Society.
degree of reaction are common problems in covalently modified graphene, making it difficult to identify suitable modification methods.

The above research mainly used modified graphene-based materials as a nano-additive to improve the friction-reducing and anti-wear performance of lubricating oil. The mechanism of lubrication involves the formation of a compact and stable lubrication film on the surfaces to prevent direct contact between friction pairs. This improves the overall lubrication performance of the oil. The dispersed graphene is easier to deposit on rough surfaces and can repair or polish rough frictional surfaces, reducing the friction coefficient and wear rate. Notably, it is important for graphene to be evenly and stably dispersed in the lubricating oil to continuously deposit graphene sheets on the contacting surfaces and therefore reduce friction and wear.

2.3. Modification of epoxy covalent bond

In addition to hydroxyl and carboxyl groups, epoxy groups (C–O–C) also exist on the surface of GO. Various researchers have studied covalent surface modification of GO via epoxy groups. The modification of graphene-based materials via epoxy groups requires a ring opening reaction to open the epoxy group and graft the modifier onto the surface of the graphene-based material.

Wu et al [80] used mechanical modification to synthesise covalently bonded phosphorus–graphene hybrids to use as a high-temperature lubricating oil additive. High-energy ball milling in a nitrogen atmosphere was used to open the epoxy groups on the graphene surface. Red phosphorus was then covalently bonded to form P–O–C bonds. The P–O–C bonds facilitated dispersion stability, and the phosphorus–graphene hybrids could be stably dispersed in a polyalkylene glycol (PAG) base oil for more than two months. As a 1.0 wt% additive the friction-reducing and anti-wear properties of the PAG base oil were improved, enhancing the wear resistance of high-temperature frictional surfaces. The improvement of tribological properties was attributed to the formation of friction films composed of FeO, Fe3O4, FeOOH, FePO4 and compounds with C–O–C and P–O bonds on the wear marks.

Zhu and colleagues [108] covalently modified GO via the epoxy groups and achieved good dispersion of mGO in water. Specifically, a novel water-dispersive graphene was synthesised by the nucleophilic ring opening reaction of the epoxy group on GO and primary amine group on 3-[1-(2-aminopropoxy)propane-2-aminopropoxy]-propane-1-sulfonate (PPS), followed by reduction with hydrazine hydrate. The PPS-modified GO nanosheets were used as a nano-reinforcing phase in a waterborne acrylic-modified alkyd resin (AMAR) coating. This improved the emulsion stability because the PPS-modified GO nanosheets adsorbed on the AMAR colloidal particles, acting as stabilisers (figure 5).

Although oxygen-containing functional groups such as epoxy groups provide great feasibility for covalent modification, it is important to note that the modification of oxygen-containing functional groups requires the use of strong acids or bases (to oxidise or reduce graphene), as well as modifying agents which may be toxic and odorous, which must be considered for practical applications.

Stable functional graphene-based materials can be prepared by covalent surface modification. Despite the benefits for dispersion stability and anti-friction and anti-wear properties, problems still exist. First, high-energy reagents or harsh reaction conditions used in covalent modification may produce vaguely defined nanoscale surface structures [109] and may destroy the conjugated π system of graphene, complicating the preparation of functional graphene-based materials. Second, the dispersion and tribological properties of modified graphene-based materials are not considerably improved due to the low degree of reaction and minimal grafting of modified materials on the surface [79]. The degree of modification of GO is limited, and a high degree of chemical reaction can only be realized by achieving complete layering [110]. Third, challenges arise in the differentiation of modification methods due to the low degree of reaction [110]. The modification degree of graphene-based materials is significantly lower than the defect degree, resulting in ambiguity of the test results [111]. Although analytical methods for product characterisation have improved in recent years, detailed analysis of the structure of covalently modified graphene-based materials is still difficult. Fourth, there have been no detailed analyses on the friction-reducing and anti-wear effect of covalently modified graphene, and the frictional processes have not been studied fully.

3. Non-covalent surface modification

Non-covalent surface modification is also widely used for the modification of graphene-based materials [112, 113]. Noncovalent modification refers to the modification of graphene-based materials through π–π bonding, hydrogen bonding, ionic bonding, and electrostatic interactions with a modifier substance to improve the dispersion stability or friction and wear resistance. Compared with covalent modification, non-covalent surface modification can ensure that the structure of graphene itself is not damaged, maintaining its unique properties.
3.1. \( \pi-\pi \) bond interaction

\( \pi-\pi \) bond interaction is the most attractive non-covalent modification route. Graphene has a \( \pi-\pi \) conjugated system, allowing it to form strong \( \pi-\pi \) bonds with substances with the same structure \([99, 114-116]\). Certain types of dispersant use this principle to achieve dispersion effects. Tong and colleagues \([81]\) modified graphene with sodium dodecylbenzene sulfonate (SDBS) and added it to PAO base oil, forming a uniform dispersion system. The benzene ring in the SDBS molecule attached via \( \pi-\pi \) bonding to the six-membered ring structure on the graphene surface. Steric hindrance of the long-chain alkyl molecules in SDBS caused repulsion between the particles, resulting in uniform dispersion of modified graphene in the lubricating oil. The lubricating oil containing modified graphene also showed excellent anti-friction and anti-wear performance; the friction coefficient was reduced by 74.78% and the wear spot size was reduced by 28.33%. This was due to the formation of a stable lubricating film on the friction surface owing to the stable dispersion of modified graphene.

The \( \pi-\pi \) interaction is used to graft modified groups on the surface of graphene to be uniformly dispersed in the epoxy system, and the crosslinking is tight. The use of poly(2-aminothiazole) (PAT) to modify exfoliated graphene sheets by \( \pi-\pi \) bonding resulted in excellent wear resistance of the modified graphene coating (figure 6) \([82]\). After 80 days of immersion, the coating with 0.5% modified graphene exhibited excellent barrier properties, reducing the wear rate by 69.48%. A denser cross-linking network formed during the epoxy curing process due to the \(-\text{NH}\) functional groups on the modified graphene. Thus, the graphene formed a stable transfer film on the worn surface, improving the hardness and wear resistance of the composite.

Most non-covalent bond modifications are used for attaching groups that are similar to the dispersion system onto the surface of the graphene-based material. Non-covalent bond modification differs from covalent bond modification as it uses weak interactions such as \( \pi-\pi \) bonds. However, there are great difficulties in distinguishing the mechanism by which graphene modification occurs by weak interactions, even though there are relatively abundant detection methods.
3.2. Hydrogen bond interaction
Strong hydrogen bonds can form between the oxygen-containing groups present on the surface of GO, such as hydroxyl and carboxyl groups, and other molecules. Thus, graphene can be modified by non-covalent hydrogen bonding. Liu et al. [83] adsorbed sodium 4-phenylene sulfonate (PSS) onto the surface of GO through hydrogen bonding and van der Waals forces. Finally, they reduced the GO using hydrazine hydrate to obtain sodium 4-phenylene sulfonate modified graphene sheet (PSS-GS). An aqueous solution of the PSS-GS maintained dispersion stability for several weeks. A film assembled with alternating layers of PSS-GS and polyethyleneimine (PEI) exhibited a low friction coefficient and long anti-wear life. This was due to the uniform and dense filling of PSS-GS in the film, which effectively reduced the stress, compression, and shear between the film and substrate.

The use of hydrogen bonding to modify graphene-based materials is also applicable in the field of wear-resistant coatings. A fluorographene composite coating was prepared by dispersing fluorographene, containing hydroxyl groups, in a mixed solution of water and ethanol, and then combining this solution with polydopamine (PDA) [84]. The fluorographene with hydroxyl groups exhibited good dispersibility. In addition, the composite coating had excellent tribological properties because it filled nano-gaps in the surface and lowered the contact roughness, effectively reducing adhesion and friction between the contact surfaces. Furthermore, the buffering effect of the PDA layer improved the tribological properties of the composite coating.

The molecules in the dispersion system were directly used to modify the graphene by non-covalent bonding to achieve a stable dispersion effect, and no other molecules are introduced. rGO was subjected to γ-ray radiolysis to form a hydrogen bond network between the residual oxygen functional groups of rGO and the oxygen atoms of poly(ethylene glycol) (PEG) [62]. The infrared spectrum of modified rGO is shown in figure 7. The modified rGO exhibited stable dispersibility. At a concentration of 0.03 mg ml⁻¹, the wear and friction coefficient of the friction surface were reduced by 55% and 38%, respectively. The uniformly dispersed modified rGO was adsorbed on the wear tracks of a steel surface, producing a low shear-strength film that acted as a solid lubricant, reducing the friction coefficient and improving the wear resistance.

3.3. Ionic bond interaction
Ionic bonding involves the electrostatic attraction between molecules with positive and negative charges. It can be used to modify graphene-based materials with other molecules, achieving non-covalent modification [117]. Zhang et al. [85] synthesised rGO/Cu nanocomposites by a chemical reduction method, whereby positively charged Cu ions were ionically bonded to the negatively charged GO nanosheets (figure 8). When the composite was added to lubricating oil, the wear resistance, load-carrying capacity, and lubrication performance were improved. The excellent tribological properties of the composites were attributed to a variety of factors, including their ability to move to the oil interface between the steel ball and matrix, where they smeared on the contact area, smoothed the surface roughness, and formed a thin physical friction film on the metal substrate.

A simple method to assist the exfoliation of dispersed graphene using ionic bonding between positively charged lithium ions and negatively charged hydroxyl groups was proposed by Wang et al. [118]. Graphene prepared by this method can be stably dispersed in water without ultrasonic treatment or surfactant. The lithium ions embedded into graphene by ionic bonding with the negatively charged hydroxyl groups, enlarge the interlayer spacing. Hydrogen bonding between the hydroxyl groups and water resulted in a hydrophilic effect, allowing for stable dispersion in water. This work inspired the preparation of hydrophilic and lipophilic graphene by ionic bond-based non-covalent surface modification; however, these methods have a weak force and weak adhesion, similarly to other types of non-covalent modification.
3.4. Electrostatic interaction

Electrostatic interaction is another non-covalent bonding method used to modify graphene-based materials. Wang et al. [86] used polyoxymethylene (POM)-cored star polymers (CSPs) as modifiers to prepare modified graphene by electrostatic interaction with rGO. The modified graphene nanosheets was stably dispersed in organic solvent, indicating that it could be compatible with polymer matrices and used as a reinforcing nanofiller to enhance the mechanical and tribological properties of composite coatings.

To take advantage of the electrostatic effect, the modifier is pre-treated to obtain an electric charge. For example, ZrO₂ nanoparticles were modified with 3-(aminopropyl)triethoxysilane (KH550) to obtain a positively charged ZrO₂-KH550 solution, which was then mixed with a negatively charged GO aqueous solution [87]. Electrostatic interaction caused the ZrO₂ nanoparticles to self-assemble onto the GO nanosheets, forming ZrO₂@GO nanocomposites. The nanocomposites exhibited good dispersion stability in liquid paraffin oil. The addition of 0.05 wt% ZrO₂@GO nanocomposites to paraffin oil reduced the friction coefficient and wear rate by 20.7% and 21.5%, respectively. The ZrO₂ nanoparticles and GO played a synergistic role in reducing friction and wear. The ZrO₂ nanoparticles bore part of the load on the friction surface and reduced the stress concentration;
in addition, they acted as ‘micro bearings’ to transform sliding friction into rolling friction. The GO layer formed a transfer film by sliding in the friction process, thus avoiding direct contact between the friction pair.

Compared with covalent modification, non-covalent modification is very attractive as the conjugated π system of graphene largely remains intact [119]. Non-covalent modification acts to adhere various chemical components to the surface of graphene-based materials through weak interaction without destroying or changing the atomic structure [120]. However, some problems still exist. First, the weak interaction between graphene-based materials and conjugates (such as surfactants) results in small and impermanent bonding forces between the substances [121]. The modification process can also introduce some unnecessary chemical components, affecting the application. Second, the detection methods need to be developed further to reduce the difficulty of distinguishing weak interactions. Third, the current research into non-covalent modification systems is incomplete, leaving many questions regarding the friction-reducing and anti-wear mechanism of modified graphene-based materials.

4. Surface modification of graphene-based hybrid materials

In addition to covalent and non-covalent modification, graphene-based hybrid materials can also be prepared by surface modification via doping. Doping with elements, compounds, or nanoparticles can improve the dispersion stability of graphene-based materials or improve the tribological properties [122]. Meng et al [88] prepared nickel nanoparticle-doped GO hybrid materials using supercritical carbon dioxide-assisted technology (ScCO₂). When used as a lubricating additive for paraffin oil with a content of 0.08%, the friction coefficient and wear zone diameter were reduced by 32% and 42%, respectively, compared to that with pure oil. These excellent results are due to the synergistic effect of the nickel nanoparticles and GO in the friction process. When deposited as a protective film, it reduces the friction effect during the wear process by preventing direct contact between the friction pairs.

The researchers also used ScCO₂ to prepare silver nanoparticle-doped graphene nanohybrids (Sc-Ag/GN) (figure 9). Lubricating oil with 0.06–0.10 wt% Sc-Ag/GN nanocomposites showed excellent lubrication performance [35]. The reduction in friction and wear were associated with the increase in interlayer spacing between the graphene nanosheets because of the silver nanoparticle decoration. This improved their dispersion stability in lubricating oil, preventing the graphene nanosheets from agglomerating during the friction process, so that it could exhibit its full lubricating activity.

Copper nanoparticles have also been used to modify GO, forming nano-Cu/GO composites, which exhibited excellent anti-wear properties [89]. Nano-copper and GO have a synergistic friction-reduction effect. GO nanosheets have a positive effect on filling voids and smoothing the interface, while copper nanoparticles reduce the accumulation tendency of GO. This reduces the blocking effect of GO at the front of the steel ball.
interface, allowing GO to form a thin protective film on the contact surface. In addition, copper nanoparticles can withstand and transmit stress, increasing the load uniformity.

Graphene hybrid materials decorated with metal nanoparticles can also be used as the reinforcing phase of metal matrix composites with a low friction coefficient and high wear resistance [90]. For the preparation of graphene hybrid materials by elemental doping, the reaction process is difficult to control quantitatively. Similarly, it is difficult to control the reaction sites. Moreover, it is difficult to distinguish this modification method from non-covalent modification. Finally, the friction mechanism needs to be studied further.

5. Friction-reduction and anti-wear mechanism of surface-modified graphene-based materials

This section summarises the mechanisms by which surface-modified graphene reduces friction and wear. There are three main mechanisms depending on the modification method.

The first mechanism involves improvements to the dispersion stability. When graphene is evenly distributed in the lubricating oil or matrix, it is more uniformly adsorbed or deposited on the friction surfaces, forming a more stable and uniform friction film. That is, the excellent tribological properties of graphene are maximised. The stable and uniform friction film prevents the direct contact of the friction pair and smooths rough surfaces. Most covalent modification methods and some non-covalent modification methods can achieve this effect. Moreover, some modification methods actually suppress wrinkling of the graphene surface during friction, which means that the friction film formed on the metal surface is smoother and has a larger contact area, thereby achieving a low friction coefficient. For example, the use of ionic liquids to modify graphene enhances its adhesion on the metal surface and reduces the impact of wrinkling [71, 123]. Cho et al [124] showed through atomic stick-slip imaging that mechanically exfoliated graphene suppresses surface wrinkling. Therefore, the graphene flakes maintain a large contact area with the substrate, resulting in low friction.

The second mechanism involves the synergistic role of the modifier and graphene in reducing friction and wear. For example, nanoparticles can convert sliding friction into rolling friction; combined with the friction film formed by graphene, this greatly improves the tribological properties of the material [87]. Some modifiers chemically react during the friction process and form a composite lubricating film with graphene. Xiao and Liu [125] revealed that, as the friction strength increases, the adsorbed or deposited graphene film between the contact surfaces breaks. A chemical reaction then takes place on the exposed surface, forming a new chemisorbed film that gradually replacing the physisorbed film. This film exists on the local contact surface, so the tribological properties are improved.

The third mechanism involves elemental doping and partial non-covalent modification methods to modify the surface of graphene to expand its application scope in composite materials. For example, when modified graphene is used as the reinforcement phase of composite friction materials, the composite reflect the excellent mechanical properties and wear resistance of graphene, improving the tribological properties.

6. Summary

Graphene’s excellent mechanical properties, low friction coefficient, and high wear resistance have placed increasing attention on graphene-based materials in tribology research. However, the unique structure of graphene reduces its solubility and dispersibility in solvents, rendering surface modification particularly important to take full advantage of the excellent properties of graphene in practical applications. While exploring the potential of graphene, scholars have also made progress in understanding the industrial applications of modified graphene. This paper reviews the various methods of modifying graphene-based nanomaterials to improve their dispersion stability or anti-wear and friction-reducing properties for tribological applications. Furthermore, the mechanisms by which these modification methods improve the anti-wear and friction-reducing performance of graphene is discussed.

The modification methods are divided according to the reaction principle, including covalent surface modification, non-covalent surface modification, and elemental and nanoparticle doping. Covalent modification methods depend on covalent bond formation between organic functional groups and GO oxygen-containing groups [99]. Non-covalent modification mainly depends on π–π bonding, hydrogen bonding, ionic bonding, and electrostatic interaction. Lastly, elemental and nanoparticle doping involves the addition of metal or compound nanoparticles to graphene-based materials to achieve the desired properties. These different modification methods expand the current tribological applications of graphene, such as its use as a lubricant additive, wear-resistant coating, wear-resistant composite, and so on. Among these categories of modification methods, it is believed that non-covalent bond surface modification is the worthiest of application. The
modification process is simple, safe, and environmentally friendly. Although non-covalently modified graphene has poor stability, it is suitable for use in a wide range of applications.

This article mainly reviews the application of surface-modified graphene-based materials in tribology. However, graphene also has many potential applications in other fields. In recent years, researchers have made considerable efforts towards materials with environmental protection functions, such as using functionalised Fe₃O₄ nanoparticles to adsorb caesium ions to reduce toxic pollution [126]. Modified graphene-based materials are also a potential adsorption material. For example, graphene–titanium dioxide hybrid materials prepared by the elemental doping modification method exhibit high-efficiency adsorption of methylene blue [127]. Similarly, covalently modified graphene-based materials using cetyltrimethylammonium bromide can selectively adsorb uranyl ions [128].

Modified graphene-based materials are also promising for electrical applications. For example, modification via covalent bonding can increase the conductivity of the graphene-based material, producing excellent electrode materials [129–131]. Element doping has been used to prepare graphene hybrid materials that can be used in energy storage and conversion devices [132, 133]. The modification of graphene-based materials can also be used to improve their suitability as catalysts for specific reactions. Covalent bonding, non-covalent bonding, and element doping have all been used for this purpose [134–136]. Covalently modified graphene-based materials have been used as nano-fillers in epoxy coatings to prepare corrosion-resistant coatings [137, 138]. The application of graphene-based materials in sensors has also attracted a lot of attention. Doped graphene-based hybrid materials have been used to make high-sensitivity flexible light detection sensors [139]. It can be seen that modified graphene-based materials have a wide range of application scenarios, reflecting huge industrial value.

Despite the progress in preparing suitable graphene-based materials for tribological applications, there are still many challenges and problems to be solved in future research. First, the three different most common modification routes each have downsides. The preparation of covalently modified graphene-based materials is complex, requiring harsh reaction conditions and dangerous reagents. In non-covalent modification, the unstable modifier is easily decomposed due to the high shear stress and high temperature of the friction surface [140]. In addition, the elemental and nanoparticle doping method requires strict reaction conditions, and the doping process is difficult to control quantitatively.

Second, the degree of modification is often low, with few methods to quantify the degree of modification [111]. This is particularly the case for covalent modification, as the content of modifier groups grafted on the surface of graphene-based materials is low, making it difficult to improve the dispersion stability or enhance the tribological properties.

Third, there are some problems in the identification of modification methods. For example, for non-covalent bond modification, the current detection methods have difficulty identifying different weak interactions. In addition, sometimes it is difficult to distinguish between modification by element doping and non-covalent bonding. Furthermore, the low modification degree makes covalent bonding modification difficult to distinguish.

Fourth, the mechanisms by which graphene modification reduces friction and wear needs to be further studied. In many studies, the mechanism is not studied in depth, relying on existing friction-reduction principles to explain the results and ignoring some possible situations.

Therefore, the current development of modified graphene in tribological applications needs further improvement. It is necessary to conduct in-depth research from the following aspects:

1. The surface modification of graphene-based materials should be scientifically optimised to develop more ideal modification methods. This includes improving the simplicity and safety, making methods more environmentally friendly, being able to control the number of groups and reaction sites, and creating more stable modified graphene. At present, some scholars have studied ways to control the reaction sites for covalent modification of graphene at the molecular scale [141]. In addition, safer and more convenient modification methods have been developed, that avoid the use of hazardous chemicals [142].

2. The degree of modification should be maximised as far as possible, and the number of modifier groups on the surface of graphene-based materials should be increased. The low degree of reaction makes it difficult to fully make use of the excellent properties of modified graphene. Therefore, it is important to consider many aspects to improve the degree of reaction, including increasing the reactivity of the surface and modifier groups, expanding the reaction area, and so on.

3. Modification methods should be clearly distinguished. The degree of modification of graphene and GO is usually much lower than the density of internal planar lattice defects, which obscures the detection results [111]. Hence, it is necessary to develop and apply new analytical tools for satisfactory structural characterisation to clearly distinguish different modification methods. In this way, we can further study the...
modification of graphene-based materials and provide insight into the optimisation of modification methods.

(4) The mechanism by which modification improves the friction-reduction and anti-wear performance should be further studied. The mechanism of friction reduction and wear resistance of modified graphene at the nanoscale can be explored through theoretical calculations and experimental research. Various physical, chemical, and structural changes may occur in the lubricating material during the friction process. Therefore, determining the mechanisms by which modification improves the frictional properties should provide insight into ways to further optimise the modification methods and further expand the application of modified graphene in tribological applications.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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