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Review

Graphene-Based Nanomaterials as Lubricant Additives: A Review

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Abstract: Reducing friction and wear by improving the tribological properties of liquid lubricants with additives is one of the most important research goals in tribology. Graphene is a typical two-dimensional (2D) nanomaterial, which has outstanding tribological performance when used as an additive in lubricants. In the past decade, various graphene-based nanomaterials have been fabricated by different methods and investigated as lubricant additives. This review aims at comprehensively overviewing the state-of-the-art graphene-based nanomaterials used as lubricant additives. Firstly, the synthesis methods and material structure are reviewed. Subsequently, the possible mechanism of graphene-based nanomaterials on friction-reduction and anti-wear was briefly discussed. Secondly, tribological properties of various graphene-based nanomaterials as lubricant additives were reviewed and discussed. Additionally, the applications of graphene-based nanomaterials in different lubricating scenarios are also discussed. Finally, challenges and future prospects of graphene-based lubricant additives are proposed.

Keywords: graphene-based nanomaterials; lubricant additive; dispersibility; anti-friction; anti-wear

Citation: Gao, Q.; Liu, S.; Hou, K.; Li, Z.; Wang, J. Graphene-Based Nanomaterials as Lubricant Additives: A Review. *Lubricants* **2022**, *10*, 273. https://doi.org/10.3390/lubricants10100273

Received: 22 September 2022
Accepted: 16 October 2022
Published: 21 October 2022

1. Introduction

The friction and wear of a machine during operation greatly affects the normal operation and service life of its mechanical components and can even have dangerous consequences [1]. Lubricating oil is an indispensable research object in tribology, and plays an important role in lubricating friction pairs, reducing friction, eliminating heat and wear particles, and preventing the corrosion of mechanical equipment. Remarkably, it plays a crucial role in reducing friction and wear when applied to mechanical parts, thereby prolonging the service life of machinery. At present, lubricating oils commonly used in various industries and research experiments are composed of base oils and various lubricant additives [2]. In order to meet the needs of different fields including ultra-low friction, wear, and extreme conditions, etc., new requirements have been placed on lubricating oils, such as high temperature and pressure resistance [3]. Lubricant additives could greatly improve the tribological performance of lubricating oils by endowing new properties and making up for disadvantages of the base oils. Many materials, including nanomaterials [4,5], ionic liquids (ILs) [6], and organic compounds [7], have been investigated and applied as lubricant additives. Among them, nanomaterials with atomic size and surface effects have attracted increasing attention since they can distinctly decrease the friction and wear by the self-repair and formation of the lubricating film [8,9] and could significantly reduce the harmful emissions compared to conventionally used organic additives such as zinc dialkyldithiophosphate (ZDDP) and molybdenum dithiocarbamate (MoDTC). As lubricant additives, nanomaterials can be physically or chemically absorbed on the contact surface of friction pairs during the rubbing process and then effectively improve the tribological properties of lubricants, which have been widely studied in the fields of tribology [10,11].

Graphene, with its unique layered honeycomb structure, is a perfect hexagonal lattice with a single atomic carbon plane constructed by sp^2-hybridized carbon atoms [12]. Graphene has excellent physicochemical and mechanical properties and can be used as additives to improve the tribological performance of the lubricants. Thus, graphene shows massive potential in reducing energy waste and improving the durability and reliability of mechanical components [13–16]. As derivatives of graphene, graphene oxide (GO) and reduced graphene oxide (rGO) inherit many physical and chemical properties similar to graphene [17], making them attractive basic materials to synthesize additives with improved dispersibility and lubrication properties. Generally, due to the abundant oxygen-containing functional groups on the surface or edge of GO nanosheets, it can be uniformly dispersed in water. However, it is challenging to maintain stable dispersion of GO nanosheets in oils, which limits its application as lubricant additives. In this regard, different kinds of graphene-based nanomaterials, such as functionalized graphene and graphene nanocomposites, can be synthesized through surface modification and combining other nanomaterials with GO nanosheets, which have been confirmed to represent feasible strategies to improve the dispersibility and tribological performance of graphene-based additives in oils [18,19].

To date, there are several reviews published on graphene from the perspectives of preparation, tribological application, and lubrication mechanisms. For instance, in 2014, Berman et al. [17] summarized tribological investigations of graphene, in particular as solid self-lubricating materials and as lubricant additives at the nano- and macro-scales. In 2015, Spear et al. [20] described the computational and experimental studies of graphene for interface lubrication. In 2020, Chouhan et al. [21] discussed chemical functionalization of GO and rGO, and their applications in lubricating oils as well as lubrication mechanisms. Sarno et al. [22] also described the research progress of GO/rGO nanosheets in tribology. In the same year, Liu and coworkers [23] summarized the fundamental mechanisms and lubricating behavior of graphene-family materials including graphene, GO, rGO, functionalized graphene, and composites of graphene. Recently, Zhao et al. [24] reviewed the synthesis methods, tribological properties, and lubrication mechanisms of graphene additives. However, a comprehensive view and discussion on the graphene-based nanomaterials for lubricant additive investigation and application should be further elaborated. In this review, we introduce the synthesis methods and structures of graphene-based nanomaterials and both summarize and discuss the research progress of lubricating additives in various lubricants by categorizing them into graphene-organic hybrids, graphene-nonmetallic nanocomposites, and graphene-metallic nanocomposites. The specific application of graphene-based nanomaterial additives in engineering is presented. Finally, the challenges and future prospects of graphene-based nanomaterial additives are proposed and discussed. This review may offer some guidance for optimizing graphene-based nanomaterial additives towards high-performance lubricants. The main components of this article are illustrated in Figure 1.

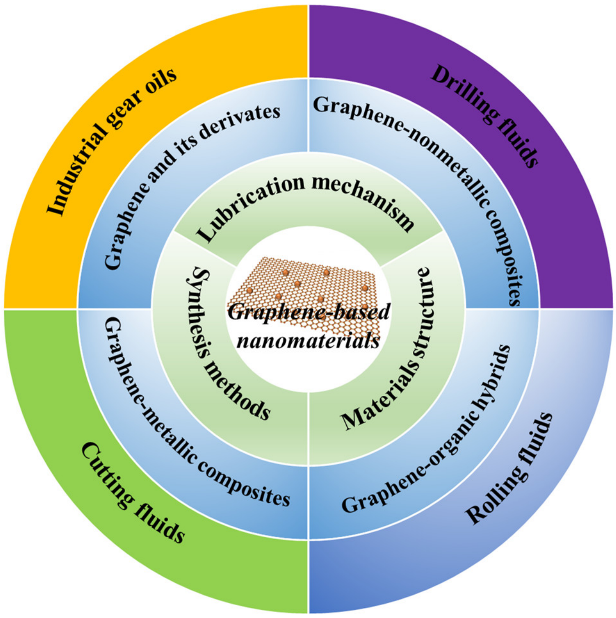

Figure 1. Schematic illustration of main components of this review.

2. Synthesis, Structure, and Lubrication Mechanism of Graphene-Based Nanomaterials

2.1. Synthesis Methods of Graphene-Based Nanomaterials

Developing new synthesis methods for graphene-based nanomaterials to improve their dispersibility in lubricants and to enhance their tribological performance is of great significance. There are several reviews which have summarized the preparation methods of graphene and its derivatives [20,23]. Therefore, in this review, we mainly discuss the synthesis methods of graphene-based composites/hybrids. Generally, the reported methods for preparing graphene-based composites/hybrids can be roughly divided into one-step strategies and multi-step strategies. The former mainly involves direct functionalization of graphene with organic molecules and in-situ growth of nanocrystallites on the surface of graphene. The multi-step strategy involves in-situ conversion of preloaded precursors on the graphene nanosheets, or ex-situ loading pre-prepared nanomaterials onto the surface of graphene. The combination of graphene nanosheets with other nanomaterials could result in good dispersibility in various lubricants, which is beneficial to their lubricating effects during the friction process [25]. In the following subsection, these synthesis methods will be discussed in detail.

2.1.1. One-Step Synthesis Strategy for Graphene-Based Nanomaterials

The one-step synthesis strategy is widely used in the preparation of graphene-based nanomaterials. Based on the support of graphene nanosheets and choosing suitable precursors, crystal nuclei of modifying materials can in-situ grow on the surface or edge of graphene nanosheets directly, and then the crystal nuclei can further grow into the desired materials with different dimensionalities, including nanoparticles (NPs), nanorods, nanoplates, and nanoflowers, etc. The advantages of this method are mainly that it can prepare graphene-based nanomaterials without tedious steps and any other protective surfactants or linker molecules, and that it can construct high crystallinity materials without post-treatment [26].

There are many one-step synthesis methods for preparing graphene-based nanomaterials, including hydrolysis or pyrolysis reaction [27], hydrothermal method [28], solvothermal method [29], in-situ reduction method [30], in-situ chemical deposition [31], co-precipitation [32], and so on. Among these methods, hydrothermal and solvothermal approaches are commonly used to prepare the graphene-based nanomaterials (since these methods are easy to accomplish and can construct high crystallinity materials). For example, in Min's report [33], CeO_2 NPs 3.5–4.5 nm in diameter were anchored on rGO nanosheets to form CeO_2/rGO nanocomposites via a hydrothermal method under mild conditions (140 °C and 24 h). The obtained nanocomposites can be well-dispersed into paraffin oil in temperature range of −7 °C to 160 °C, which exhibited better anti-wear performance than individual GO nanosheets and CeO_2 NPs. In another work, Zhou et al. [34] synthesized an rGO/ZrO_2 nanocomposite by a one-pot hydrothermal method. The size of the ZrO_2 NPs can be regulated by the proportion of precursors (i.e., zirconium oxychloride ($ZrOCl_2$) in GO dispersion).

Moreover, owing to the rich oxygen-containing functional groups on the surface of GO nanosheets, various organic molecules can interact with these groups by chemical or physical means to generate the desired nanomaterials. For instance, by nucleophilic substitution, *n*-octyl amine can react with epoxy group on the basal plane of to obtain basal plane-functionalized GO (b-GO) hybrid additive [35]. Recently, a graphene oxide/polyethylene glycol (GO/PEG) composite as water-based additive was prepared by a one-step sonication approach, in which GO and PEG are combined mainly by hydrogen bond [36].

Although the one-step synthesis strategy is simple and effective for synthesizing graphene-based composites/hybrids, studies have also shown that it is difficult to control the microstructure and the accurate component proportion of these nanomaterials by this strategy, which inevitably affects the physicochemical properties of the prepared nanomaterials. Therefore, developing other methods/strategies is important for synthesizing the desired graphene-based nanomaterials.

2.1.2. Multi-Step Synthesis Strategy for Graphene-Based Nanomaterials

A multi-step synthesis strategy for preparing graphene-based nanomaterials usually involves pre-preparation process and reaction process, which is an attractive synthesis strategy to fabricate graphene-based nanomaterials for lubricant additive applications. By the rational design of the multi-step process, graphene-based nanomaterials with the ideal composition and desired structure can be obtained.

The precursors of the designed materials can be pre-loaded on the surface of graphene nanosheets. Then, they would be transformed into the required materials by the followed reaction process to obtain graphene-based nanomaterials. For example, Song et al. [37] prepared the MoS_2/GO composites by a multi-step route. In their experiment, sodium molybdate was anchored and decomposed into MoO_3 on the surface of GO nanosheets, and then MoO_3 could be further reduced and sulfurized using l-cysteine as reducing agent and sulfur source to produce MoS_2/GO composites. In another work, rGO-Al_2O_3 nanocomposite was prepared by this synthesis strategy [38]. Firstly, rGO-AlOOH could be synthesized via a hydrothermal process using aluminium isopropoxide and GO as precursors. Then, the targeted rGO-Al_2O_3 nanocomposite was prepared by the heat-treatment of rGO-AlOOH.

Additionally, graphene-based composites/hybrids can be prepared by introducing organic molecular-modified nanomaterials onto the surface or edge of graphene nanosheets. In this process, nanomaterials with unique structures and morphologies are pre- synthesized and then they are grafted onto the graphene nanosheets via a physical or chemical reaction using proper organic linkers. For example, Zhang et al. [39] firstly decorated nano-boehmite (AlOOH) with 3-glycidoxypropyl-trimethoxysilane (GPTS) to obtain GPTS-AlOOH. Then the GPTS-AlOOH was anchored onto GO to obtain GO-GPTS-AlOOH nanohybrid by a coupled reaction. Moreover, considering the negatively charged nature of GO/rGO nanosheets due to the presence of oxygen-containing functional groups, GO/rGO-based composites could be fabricated by electrostatic self-assembly. For example, in Guo's study, nanosilica was firstly modified by 3-amino-propyltriethoxysilane (APTES) to obtain positively charged SiO_2 NPs named aminated silica. Then, aminated silica modified graphene oxide (SAG) was synthesized by an electrostatic self-assembly used as water-lubricant additive [40]. In another case,

$GO@SiO_2$ hybrid materials were also fabricated by the electrostatic self-assembly approach [41].

2.2. Structure of Graphene-Based Nanomaterials

The structure of graphene-based nanomaterials has a significant influence on their tribological properties as lubricant additives. Controlling the microstructure of GO/rGO nanosheets and graphene-based nanomaterials to improve their dispersibility and tribological properties in lubricants has been demonstrated [42,43]. Jin et al. [44] reported that ultra-flat rGO (UF#G) nanosheets as an additive in grease can afford improved tribological performance deriving from the good inter-layer-sliding effect of the ultra-flat nanostructure of UF#G. In contrast, the curly edge rGO (CE#G) and internal wrinkle rGO (IW#G) exhibited bad tribological performance, highlighting the importance of structural controlling of graphene-based nanomaterials.

Generally, the structure of graphene-based composites/hybrids can be roughly classified into supported structure, wrapped structure, and grafted structure.

For the supported structure, nanomaterials adhere onto the surface of graphene nanosheets to form a supported structure, which prevent nanomaterials and graphene reciprocally from agglomeration in lubricants [45,46]. As shown in Figure 2a, Zhao et al., prepared a Mn_3O_4/graphene composite with Mn_3O_4 NPs adhering onto the graphene surfaces and intercalating between the layers of graphene. This structure was beneficial to increasing the exfoliation degree of the graphene nanosheets and improving the dispersibility of Mn_3O_4/graphene in lubricating oils [47].

So far, nanomaterials with different morphologies, such as nanowires [45], nanorods [46], nanotubes [48], and nanofibers [49], can be supported on graphene nanosheets to obtain the desired nanocomposites. Zubir et al. [50] combined carbon nanotube (CNT) and carbon nanofiber (CNF) with graphene nanosheets via π–π interaction. As expected, improved physicochemical properties of rGO sheets were obtained for diverse applications. Furthermore, high performance nanofluid lubricants were prepared by adding GO and multi-walled CNTs (MWCNTs) into ILs [51]. By adhering CNT on the surface of GO nanosheets, a synergistic effect was obtained enhance the tribological properties of IL lubricants.

Apart from above-mentioned nanomaterials, MoS_2 nanosheets were prepared onto the surface of graphene nanosheet to obtain an incommensurate structure for improving the tribological performance of liquid lubricants. Hou et al. [52] prepared an rGO/MoS_2 heterostructures as additive in paraffin oil lubricants. As shown in Figure 2b–f, the MoS_2 nanosheets were anchored onto the surface of rGO. This unique heterostructure afforded excellent dispersibility and tribological properties in lubricating oils.

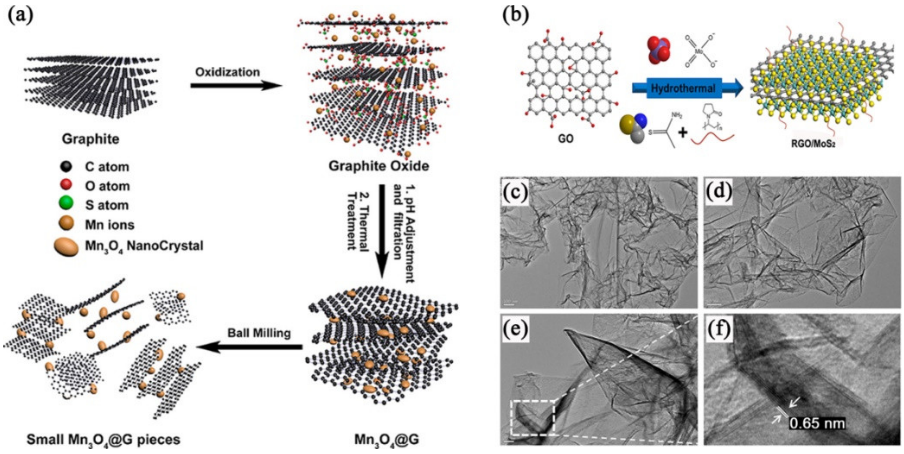

Figure 2. Synthetic process and structure of (**a**) Mn_3O_4@G (adapted from [45]), and (**b**) rGO/MoS_2 heterostructure. (**c**–**f**) Transmission electron microscopy (TEM) images of rGO/MoS_2 at different magnifications (adapted from [52]).

In addition to the supported structure, graphene nanosheets could wrap onto the surface of other nanomaterials to construct a wrapped structure. For instance, In Gu's work, functionalized carbon microspheres (f-CMS) were coated by GO nanosheets forming nanocomposites with a wrapped structure [53]. The prepared GO/f-CMS can be used as additive in engine oil. In 2018, Luo et al. [54] reported a SiC@graphene (SiC@G) composite with a wrapped structure. As shown in Figure 3, the as-prepared SiC@G composite consisted of three parts including SiC core, middle-covered graphene shell, and floating flat-blade graphene nanosheets, which exhibted good dispersibility and outstanding tribological performance in lubricating oil.

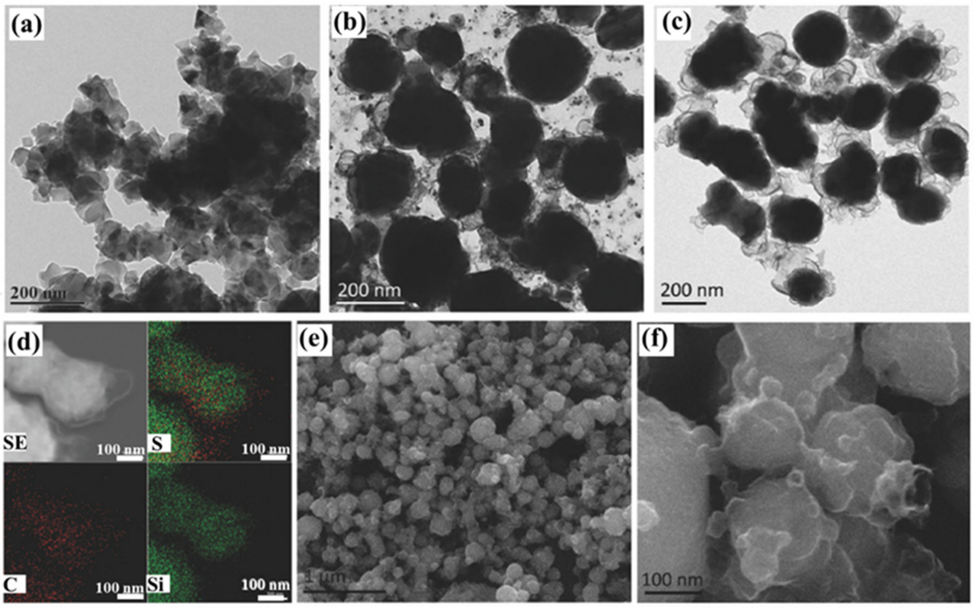

Figure 3. TEM images of (**a**) pristine SiC NPs, (**b**) SiC NPs irradiated by KrF pulsed laser, and (**c**) corresponding sample after washing. (**d**) Energy dispersive spectroscopy (EDS) elemental mapping of SiC@G. (**e**,**f**) Scanning electron microscopy (SEM) images of SiC@G after the acid etching and centrifugation (adapted from [54]).

For the grafted structure, graphene nanosheets can be modified by organic molecules to form a grafted structure, which could enhance the dispersibility of graphene in different lubricants. For example, Cai et al. [55] reported a novel fluid-like GO (FL-GO), in which γ-(2,3-epoxypropoxy) propytrimethoxysilane and polyether amine were grafted on the surface of GO nanosheets through covalent grafting and ring-opening reaction of epoxide group on GO. FL-GO as an additive in PEG oil can improve the tribological properties by forming a continuous and uneven lubricating film on the surface of friction pairs.

2.3. Lubrication Mechanism of Graphene-Based Nanomaterials

Graphene-based materials have attracted extensive attention as lubricant additives due to their layered structure, ease to shear, high strength, and outstanding chemical inertness properties. Chemical or physical modification of graphene and the construction of composite structures with other nanomaterials are considered as effective strategies to improve their tribological properties. In order to reveal their tribological behavior, the study of its underlying lubrication mechanism is of great importance. The lubrication mechanisms of graphene-based nanomaterials as lubricant additives can be mainly described by the following aspects: forming tribofilms, self-repairing effect, and rolling bearing effect [24,56].

As shown in Figure 4a, graphene-based nanomaterials can easily enter the friction interface and prevent the contact of friction surfaces due to their thin laminated structure, high specific surface area, high surface energy, and self-shear properties [57]. It can adsorb on the surfaces of rubbing materials to form a protective tribofilm during the friction process. In addition, NPs containing graphene-based composite can form a stable chemical tribofilm by tribochemistry reaction during friction. Moreover, during this process, graphene-based nanomaterials can be easily transferred to the uncovered area (Figure 4b) and increase the mechanical strength of tribofilm due to the load-bearing ability of nanomaterials [58,59]. Therefore, the rubbing surfaces covered by robust tribofilm can prevent the direct contact of the friction pairs and provide low shear strength and adhesion during the friction process.

In addition, the asperities and defects on the rubbing surfaces always lead to high coefficient of friction (COF) and wear rate. During the friction process, graphene-based nanomaterials can attach to the asperities and friction-induced defects to repair the worn surfaces and improve the tribological properties. Besides, the elevated pressure and temperature during rubbing process cause graphene nanosheets to break into small fragments, which facilitate mending the grooves and local pits and promoting the repairing effect. As seen in Figure 4c, for graphene-based nanomaterials, the self-repairing effect would be further strengthened via synergistic lubricating effects between graphene and other nanomaterials [60]. Nanomaterials, such as metal NPs, with good ductility and low melting point decorated on the surface of graphene play a role in self-repairing process. Also, nanomaterials can enter into grooves to repair worn surfaces and have the pinning function for graphene fragments on friction surfaces [61], which could enhance the tribological performance of graphene-based nanomaterials in lubricants.

Apart from forming tribofilm and self-repairing effects, graphene-based nanomaterials have excellent interlayer sliding performance due to the weak van der Waals' forces and π–π bond between interlayers of graphene [62,63]. Furthermore, nanomaterials with spherical shapes on graphene nanosheets can act as small ball bearing which roll between the contact zone and transform sliding friction to rolling friction partly (Figure 4d). Via this effect, it is beneficial to the relative movement of friction pairs and to further reduce friction and wear [64,65].

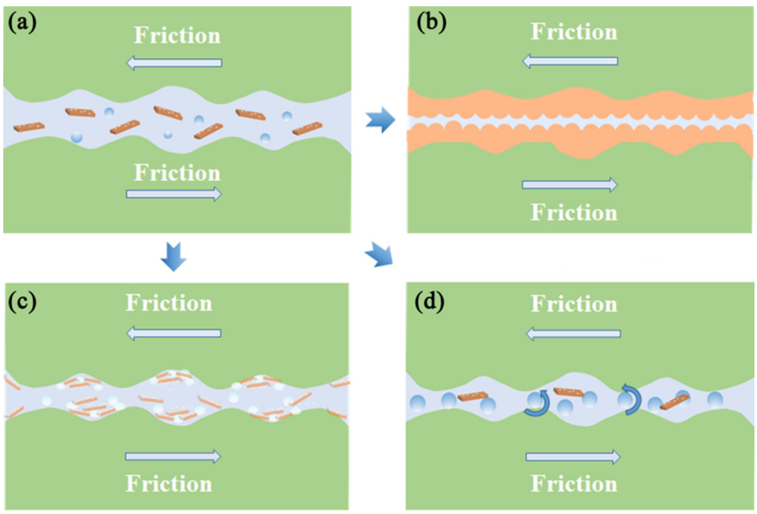

Figure 4. Schematic illustration of lubrication mechanisms of graphene-based nanomaterial additives: (**a**) Initial state; (**b**) Forming tribofilm; (**c**) Self-repairing; (**d**) Rolling bearing.

As mentioned above, various nanomaterials (including inorganic and organic nanomaterials) can readily combine with graphene nanosheets by different synthetic strategies. By rational structural design and controlling preparation conditions, a variety of structures of graphene-nanomaterials can be constructed, including supporting, wrapping, or grafting of nanomaterials on the surface or edge of graphene nanosheets.

Generally, the physicochemical properties of graphene-based additives, such as dispersibility and structural stability, etc., can be regulated by synthesis methods, structures, and the modifying materials. The presence of nanomaterials promotes the exfoliation degree and interlayer distance of graphene nanosheets, which could improve the interlayer slipping of graphene nanosheets and the dispersibility of graphene-based nanomaterials in lubricants. Consequently, thanks to the synergistic effects between graphene and the modifying materials, the graphene-based nanomaterials exhibit excellent tribological performances, such as anti-friction, anti-wear, and extreme pressure properties. Furthermore, it is necessary to understand the underlying lubrication mechanisms of nanomaterials in lubricants for complete evaluation and optimization of graphene-based nanomaterial additives. A number of mechanisms are proposed based on various characterization techniques. In this review, the lubrication mechanisms of nanomaterials are discussed mainly including forming tribofilm, self-repairing effect, and rolling bearing effects, etc. It is worth noting that different lubrication mechanisms during the friction process often co-exist. The combination of different mechanisms leads to the complexity of mechanism investigation to a certain extend.

3. Graphene-Based Nanomaterials as Lubricant Additives

3.1. Graphene and Its Derivatives as Lubricant Additives

3.1.1. Graphene Additives

Graphene with excellent mechanical properties can protect the frictional contact surface when used as lubricant additives. Besides, the good thermal conductance of graphene nanosheets could decrease the local temperature of the friction pairs, which could enhance the load-bearing capacity of the lubricating film. In addition, the weak interlayer interaction is also beneficial in improving its tribological properties [66,67]. Recently, graphene was applied to magnetorheological fluid (MRF) to improve its tribological and rheological properties [68]. Here, oil-soluble graphene was used as an additive in lubricant and MRF, which could greatly improve the tribological of lubricant and MRF.

3.1.2. GO Additives

GO can be dispersed in water without any surfactants or dispersants, so it is always applied in water-based lubricants [69–74]. Various factors such as the pH of GO solution, concentration, and oxidation degree of GO, and so on [75,76] affect the tribological properties of GO water-based lubricant additive. For instance, GO nanosheets with different oxidation degrees prepared by controlling the amount of oxidizing agent and reaction conditions exhibited various lubricating effects [76]. These phenomena are mainly attributed to the fact that the GO with a high oxidation degree contains more oxygen-containing functional groups and larger layer spacing, which affect the formation of adsorption and protection films and the tribological properties of the materials in turn.

Kumar et al. [77] used GO nanosheets as green additives in ethanol and SAE20W50 engine oil and investigated the tribological behavior using hypereutectic Al-25Si alloy disc and AISI 52100 bearing steel ball as the friction pairs. Due to the existence of GO on the contact region, the COF was reduced from 0.22 to 0.057 and wear volume was reduced by 60–70% for SAE20W50 engine oil containing 0.5 wt% GO. GO nanosheets can improve the lubrication effect of engine oil by the interlaminate shearing. In addition, GO is harmless, anticorrosive, making it promising for many different mechanical applications.

However, there is a severe agglomeration and restack phenomenon when GO is added to some non-polar solvents [78], which significantly affects its tribological performance and even causes serious wear to a certain extent. To solve this problem, decreasing oxygen-containing functional groups on GO nanosheets is an appealing strategy. Therefore, reduction of GO to rGO by different reduction methods has been investigated [79–83].

3.1.3. rGO Additives

Del Río et al. [84] prepared rGO by thermal treatment and used as additive in trimethylolpropane trioleate (TMPTO) and polyalphaolefin (PAO 40) base oil. rGO exhibited good dispersibility in TMPTO and PAO 40 base oil with various concentrations and could keep stable for a long time (244 h) at the concentration of 0.25 wt%. In contrast, although GO nanosheets could also disperse in TMPTO and PAO 40 base oil with ultrasonic assistance, it occurred subsidence after only 24 h, illustrating that the dispersibility of GO nanosheets in oil is worse than that of rGO. The tribological tests showed that the TMPTO and PAO 40 base oil with 0.25 wt% rGO achieved the best antiwear properties with 20% and 24% reductions in wear track widths for TMPTO and PAO 40 base oil, respectively.

In another work, Kamel et al. [85] reduced GO by hydrazine monohydrate and used the products as the additive in lubricating grease. Improve tribological properties of grease were observed. Zhao et al. [86] used GO as a precursor to prepare ultra-high exfoliation rGO (UH-rGO) by thermal reduction with the assistance of KOH and used as lubricant additives in PAO 6 oil and hydraulic oil. The UH-rGO has a distinct 2D layered microstructure with a large specific surface area, as well as little restack and agglomeration, and it can keep stable for a long time in lubricants. Meanwhile, due to the sliding-oriented transformation of UH-rGO, it can greatly enhance the tribological properties of lubricants in terms of anti-friction and anti-wear.

3.1.4. Doped Graphene Nanosheets

It has been demonstrated that doping heteroatoms, such as N, P, S, and B, into graphene nanosheets could further improve the tribological properties of graphene [25,87]. For example, Jaiswal et al. [88] prepared microwave-synthesized reduced graphene oxide (MRG), boron-doped MRG (B-MRG), nitrogen-doped MRG (N-MRG), and boron-nitrogen-co-doped MRG (B-N-MRG) by microwave-assisted technology and investigated their tribological behavior in paraffin base oil. The results showed that adding B-MRG, N-MRG and B-N-MRG into paraffin base oil could effectively decrease the COF and wear volume. Among them, B-N-MRG showed the best tribological performance and load-carrying properties due to the dual effect of nitrogen or boron. Chandrabhan et al. [89] synthesized N-rGO and studied its tribological behavior in the base oil. The N-rGO could be steadily dispersed in oil for six months and reduced the COF by 25% at a concentration of 3 mg/mL. The enhancement in tribological performance was due to the sliding friction and high mechanical strength of N-rGO.

3.1.5. Fluorinated Graphene

Fluorinated graphene (FG) is a 2D layered structure material with outstanding properties and can be used in many applications, including resistant coatings, photoelectric and thermoelectric equipment, as well as lubricant additive materials [90–92]. Many studies have shown that FG can reduce friction and wear as a lubricating material in various applications, but the preparation of the high-quality FG is very complex and high energy consumption. Besides, it is limited to being used in water-based lubricants due to its hydrophobicity [93]. In this regard, recently, through a simple hydrothermal method, Min et al. [94] obtained fluorinated graphene oxide (FGO) and fluorinated rGO (FrGO) (Figure 5a). As a novel and green water-based lubricant additive, numerous oxygen-containing functional groups on the surface of the resultant FGO greatly promoted its dispersibility in water. Moreover, water containing different concentrations of FGO showed reduced COF than pure water. Water with 0.7 wt% FGO showed the best tribological behavior with reduction of the COF by 41.4% and wear by 88.1%, which was better than the tribological behavior of FrGO with reduction of the COF (14.9%) and wear (54.2%) (Figure 5b,c). The better tribological behavior was attributed to the deposition of FGO on the worn surface and the formation of tribo-films (Figure 5d). This work provided a feasible green way to prepare the FGO with enhanced tribological performance in many applications.

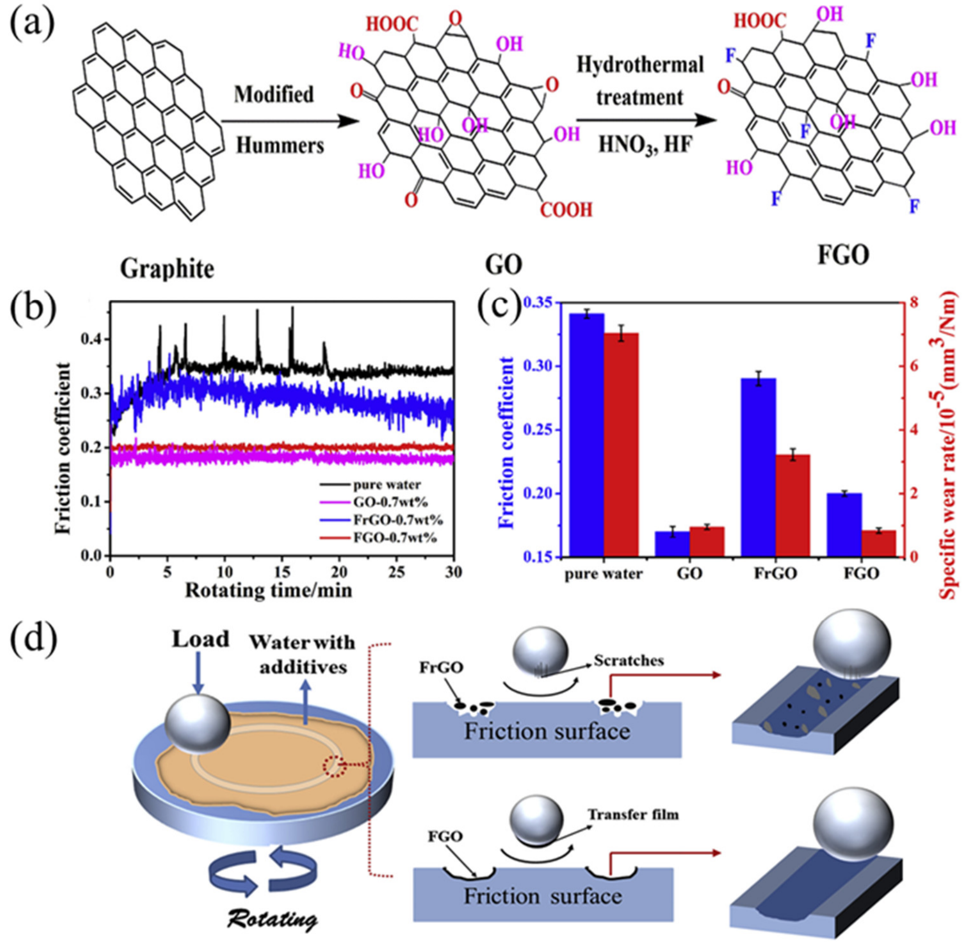

Figure 5. (**a**) Preparation of fluorinated graphene oxide. (**b**) COF and (**c**) wear rate for the water with GO-0.7 wt%, FrGO-0.7 wt%, and FGO-0.7 wt% at 5 N, 300 r/min, and duration of 30 min. (**d**) Friction mechanism model of water with FrGO and FGO additives (adapted from [94]).

To sum up, graphene nanosheets and its derivatives as additives are important performance-enhancers in tribology due to their unique 2D structure. These materials play a significant role in reducing friction and wear through forming lubricating film, as well as the shear and lamination of nanosheets on the contact surfaces to improve the lubricant performance of base oil lubricant. Some factors, such as pH, concentration, oxidation degree, microstructure of graphene nanosheets, and doping heteroatoms, also affect the tribological performance of graphene nanosheets. Meanwhile, it often suffers aggregation and restacking in non-polar liquids, deteriorating the tribological properties. Therefore, developing new methods to achieve stable graphene-based additives is highly necessary.

3.2. Graphene-Organic Hybrids as Lubricant Additives

The functionalization of graphene nanosheets with organic materials is often used to modulate the stability of graphene in base oils. On the one hand, covalent modifications can be achieved by the chemical reaction on the oxygen-containing functional groups, such as esterification, carbonyl reaction or acylation actions. On the other hand, by van der Waals interaction and π–π stacking, non-covalent modifications of graphene nanomaterials could be achieved [95]. In the following part, we mainly discuss the modification of graphene nanosheets by organic molecules with different functional groups, as well as the modification of graphene nanosheets by surfactants and ionic liquids.

3.2.1. Graphene-Organic Compound Hybrids

Alkylated Compound Modified Graphene

The alkylation of graphene nanosheets has been considered as one of the most effective methods to synthesize graphene-based hybrids. A number of studies have demonstrated that alkylated functionalization could enhance the dispersibility of GO in organic solvents [96].

Long alkyl chains organic compounds, such as octadecylamine (ODA), could be grafted on the edge and defect sites of GO nanosheets through covalent linkage to obtain the functionalized rGO [97]. The ODA-rGO sheets showed stable dispersibility and excellent tribological performance in the base oil. Their excellent tribological performance was mainly due to the low resistance to shear enabled by the weak van der Waals interaction of ODA-rGO sheets and the continuous existence of nanomaterials on the contact surface due to the good dispersibility. In another case, alkylated GO/rGO was synthesized by covalent interaction between GO nanosheets and octadecyltrichlorosilane (OTCS) and octadecyltriethoxysilane (OTES). The octadecyl chains could be readily grafted on the surface of GO nanosheets [98]. The obtained alkylated GO/rGO could be well-dispersed in the polyol lube oil due to the van der Waals interaction between the octadecyl chain of alkylated GO/rGO and octadecenyl chains of polyol ester.

Through the asymmetric chemical modification of GO, the properties of the material will be further regulated. Wu et al. [99] synthesized the modified GO (MGO) by asymmetric chemically modified with myristyltrimethylammonium bromide (TTAB) and investigated the tribological behavior of MGO additive in oil-in-water emulsion (Figure 6a,b). The MGO grafted long chain quaternary ammonium could disperse well in base emulsion lubricants. The MGO-emulsion can improve the tribological performance by reducing COF and wear, which is attributed to the formation of adsorption film, transfer film, and tribo-film on the contact surface.

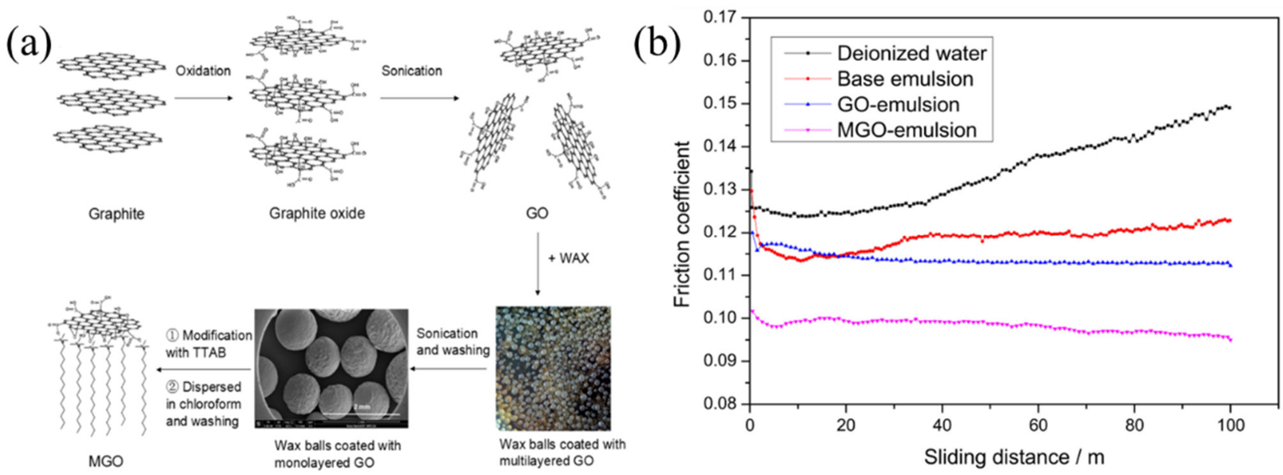

Figure 6. (**a**) Preparation process of GO and MGO. (**b**) The COF of contact surfaces lubricated with the prepared fluids (adapted from [99]).

Organic silane can be used to modify GO by chemical reaction and improve the physical and chemical properties of GO as additives [100]. In Liu's study [101], hexadecyltrimethoxysilane (HDTMS) and octyltrimethoxysilane (OTMS) were employed to modify GO. The tribological performance of liquid paraffin containing the modified GO was evaluated. The HDTMS-GO and OTMS-GO could reduce the COF of liquid paraffin lubricant by 34.0% and 15.5%, respectively. Moreover, HDTMS-GO exhibited better organic compatibilities due to the long alkyl chain in HDTMS and it could disperse more homogeneously in paraffin. In addition, GO-based Pickering emulsion was prepared and used as lubricant additives to enhance the tribological properties [102]. Due to the strong absorption and steric repulsion of alkyl chains, basal functionalized GO (bGOs) could be orderly arranged at the steel surfaces to form a hydrophobic lubricating film and showed good protective effects.

Amine compound modified graphene

It has been reported that alkylamine modification can change the surface properties of GO nanosheets, in which alkylamines with long hydrophobic alkyl chain and hydrophilic amine groups [103]. Grafting alkylamines with different branch-chain lengths on GO will affect their physicochemical properties [104]. In addition, studies have demonstrated that amine compounds and the combination of amines and GO exhibit outstanding performance in solid-liquid lubrication [105].

In 2019, Paul et al. [106] functionalized GO with dodecylamine to synthesize composites (DAG) and investigated the tribological behaviors in commercial engine oil. The study showed that the outstanding dispersibility of DAG in engine oil was beneficial to reduce COF (~40%) and wear volume. During the sliding process, it would occur tribo-chemical reaction due to the friction-generated heat, which is conducive to the formation of protective tribo-film on the contact surfaces.

Apart from achieving anti-friction and anti-wear, amine functionalized graphene could also accomplish macroscale superlubricity in dihydric alcohol aqueous solutions on the Si_3N_4 ball and sapphire disc friction pairs [107]. Due to the strong adhesive force of amino groups on the surface of aminated GO nanosheets and SiO_2, it could form a robust adsorption film and SiO_2-containing boundary layer on the worn surface via tribochemical reactions, which result in lower wear rate and COF. The study illustrated that the amino groups on the surface of GO greatly affected the performance of GO and provided important guidance for the research of GO in tribology.

Other organic compound modified graphene

The lubricating effects of nanomaterials are always influenced by the presence of minor heterogeneous elements, such as S, N, and P. For example, the presence of sulfur elements can render the lubricant good tribological performance, especially the pressure-bearing performance [108]. For examples, Zhang et al. [109] synthesized GO-D and GO-T nanosheets by grafting 1-dodecanethiol and tert-dodecylmercaptan onto the carboxyl group of GO, respectively. The prepared GO-D and GO-T could be dispersed stably in the rapeseed oil (RSO) (Figure 7a). Due to the formation of tribo-film containing sulfur element, lubricants with GO-D and GO-T nanosheets exhibited low shear strength between friction pairs. Hence, their tribological properties were better than that of GO counterpart (Figure 7b). In another work, Gan et al. [110] successfully synthesized ultra-dispersive monolayer GO nanosheets by grafting 1-ethyl-3-methyl imidazolium dicyanamide (EmimN(CN)$_2$) on the surface of GO and used them as the additive in water (Figure 7c). The results showed that the GO-EmimN(CN)$_2$ showed a high exfoliation degree and good re-dispersibility in water. GO-EmimN(CN)$_2$ could greatly improve the tribological properties of water and superior to multilayer GO in water (Figure 7d). This study paved a way for studying the performance of amine-functionalized GO for many applications in tribology.

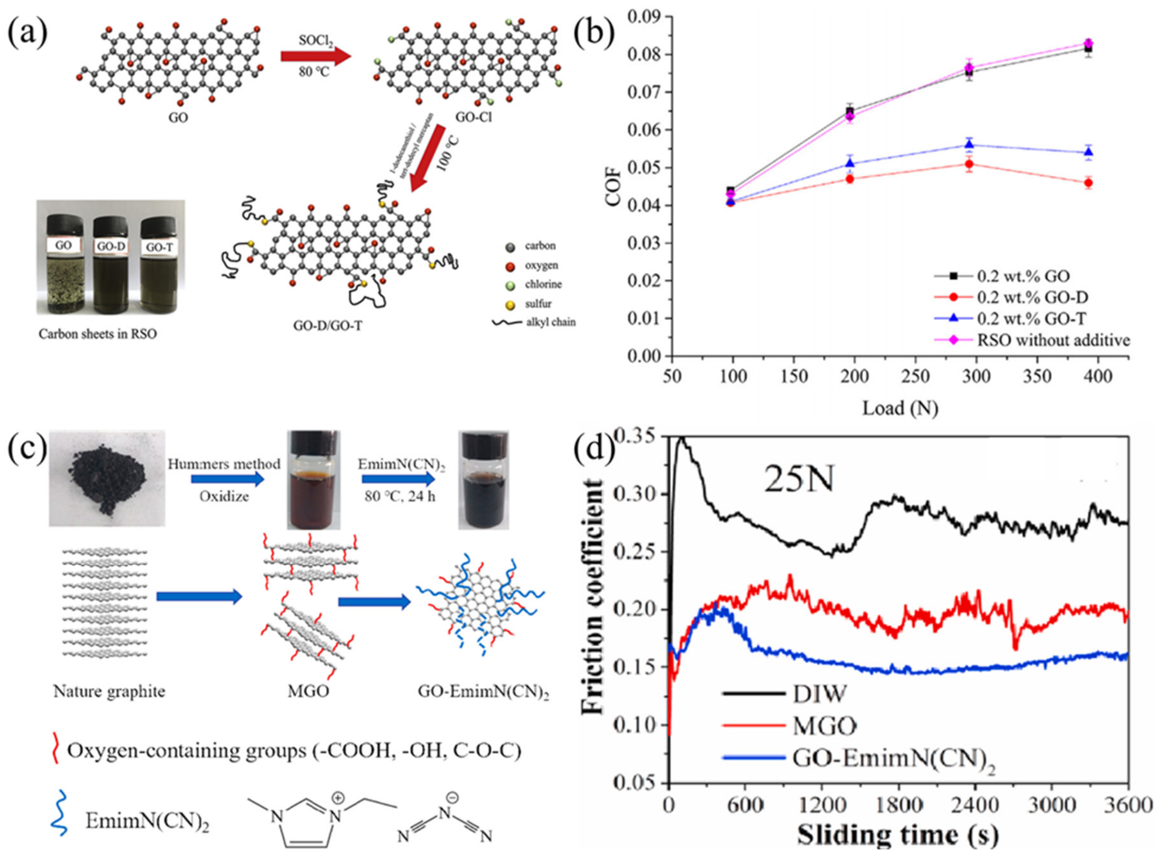

Figure 7. (**a**) Schematic illustration of synthesizing GO-D and GO-T. (**b**) Relationship between normal load and COF of GO, GO-D, and GO-T dispersions (adapted from [109]). (**c**) Preparation process of GO-EmimN(CN)$_2$. (**d**) Friction curves of steel plates lubricated with pure water, 1.6 mg/mL MGO and GO-EmimN(CN)$_2$ dispersions at 25 N (adapted from [110]).

Sulfur-doped graphene oxide (SA-GO) composites were synthesized by sulfuration and alkylation and used as lubricant additives in 928 oil and PAO 4 oil [111]. Due to the high sulfur content and –C–S–C– bonds in SA-GO composites, the SA-GO nanosheets displayed good dispersibility in lubricant oil and can reduce the wear scar diameter with 928 lubrication oil (43.2%) and PAO 4 oil (17.2%). In addition, Sun et al. [112] reported that the existence of nitrogen elements could promote the anti-corrosion properties of water on metal surface. The water lubricant containing a low concentration of nitrogen-containing composites displayed good lubricant behavior.

3.2.2. Graphene-Polymer Hybrids

Carbon Chain Polymer Modified Graphene

Recently, graphene-polymer hybrids have been synthesized and used as lubricant additives due to their flexibility and good thermal and mechanical properties. In addition, modification of graphene nanosheets could be also achieved by introducing the long carbon chain or heterochain polymer via covalent interaction, which further improves the dispersibility and stability, as well as tribological properties of graphene nanosheets in lubricants. Lots of carbon chain polymer materials, such as polyvinylidene difluoride (PVDF), polytetrafluoroethylene (PTFE), and poly(ether-ether-ketone) (PEEK), etc. can be used as additive. For example, Li et al. [113] prepared an RGO/PVDF nanocomposite and investigated their tribological behavior in paraffin oil lubricant. The tribological tests showed that the RGO/PVDF composite with a concentration of 0.5 wt% reduced the COF and wear of paraffin oil by 44.4% and 98.7%, respectively. The outstanding tribological properties were attributed to the formation of lubricant films and self-healing effect of globular nanocomposite on the contact of friction pairs.

PTFE is one of the promising solid lubricants in many fields but it exhibits poor dispersibility and wettability in water due to its hydrophobic properties and low surface energy. To overcome this shortcoming, Yang et al. [114] synthesized a GO@PTFE composite material by the electrostatic self-assembly method and used it as the water-based lubricant additive. The GO@PTFE composite exhibited good dispersion stability and wettability in water. The tribological tests showed that the GO@PTFE composite could reduce the COF of water by 77%, which is lower than that of GO and PTFE alone. This performance was mainly due to the synergistic effect between GO and PTFE and the formation of tribo-films on the contact surface.

Heterochain Polymer Modified Graphene

In addition to carbon chain polymer, graphene can also be modified by the heterochain polymers to synthesize graphene-polymer hybrids, in which macromolecular chains contain hetero atoms, such as O, S, and N. For example, Kumar et al., prepared GO/poly(Cn-acrylate) nanocomposites by grafting the poly(Cn-acrylate) chains on the surface of GO assisted with initiators [115]. The grafted amount of polyacrylates on the surface of GO could regulate the dispersibility of nanocomposites in oil. The tribological tests showed that the GO/poly(Cn-acrylate) nanocomposites reduced the COF and wear by 42% and 34%, respectively. Then, they grafted polyacrylamide (PAM) on the surface of GO to prepare FGO-PAM composites by microwave-assisted surface initiated-redox polymerization (SI-RP) methods [116]. As an additive in aqueous medium, FGO-PAM promoted the lubrication effect by reducing COF (46–55%) and wear volume (13–37%), which results from the formation of lubricating nanolayers of the nanocomposite on the contact surface of friction pairs.

Polyethyleneimine (PEI) as a water-soluble polymer can be used to improve the dispersion stability of graphene in water. In Liu's study, GO is chemically modified with PEI by the reaction between the epoxy groups of GO and amine groups in the PEI [117]. The as-prepared PEI-rGO could be stably dispersed in water and water containing 0.05 wt% of PEI-rGO exhibited the best tribological behavior by reducing the COF (56.4%) and wear volume (45.0%) on the steel/steel pairs. In another case, Yang et al. [118] prepared a liquid-like graphene by grafting the amino-terminated block copolymer on the surface of GO to form a core-shell structure and investigated their tribological performance as an additive in water. This material can be dispersed into water and many different organic solvents for a long time. As an additive to water lubricant with a concentration of 50 mg/mL, it could reduce the COF and wear by 53.9% and 91%, respectively. In addition, Wei et al. [119] prepared GO/brush-like chitosan copolymers (chitosan-graft-poly(N-isopropylacrylamide), denoted as Chitosan-g-PNIPAM) nanohybrids using an in-situ non-covalent assembly strategy. The as-prepared GO/Chitosan-g-PNIPAM nanohybrids could be dispersed well in water lubricants and exhibited excellent tribological performance at high contact load, which provided a novel method to develop green graphene-polymer composites as lubricant additive in various tribology application.

3.2.3. Surfactant Modified Graphene

Surfactants are frequently used to improve the dispersion and stability of additives in lubricants. Surfactants are divided into ionic surfactants, nonionic surfactants and amphoteric surfactants. Due to the strong physical interaction forces including van der Waals forces and hydrogen bonds, the surfactants could physically adsorb on the surface of graphene to prevent aggregation of graphene nanosheets in liquid lubricants [120].

Hexadecyl trimethyl ammonium bromide (CTAB) is often used to promote the dispersibility of NPs in organic solvents. Under mild conditions, CTAB-functionalized graphene nanosheets were prepared [121]. The modified graphene showed enhanced dispersibility both in water and organic solution.

Peng et al. [122] used anionic surfactant, sodium dodecyl sulfate (SDS), to modify GO and rGO as additive in water. After functionalization, the tribological performance of GO was better than rGO, which was mainly attributed the stable dispersion of functionalized GO in water and thin laminated graphitic structure. Besides, β-Lactoglobulin (BLG), a stable amphiphilic biopolymer without toxicity, can be used to modify GO to improve the stability of GO in various lubricants [123]. The prepared BLG-functionalized GO (BLG-RGO) was prepared by noncovalent modification. The BLG-RGO showed excellent dispersibility in water for a long time (>8 months) and it can greatly reduce the COF and wear volume by 37% and 45%, respectively.

3.2.4. Ionic Liquid Modified Graphene

ILs are novel and green solvents and can be used in many fields, including nanomaterial synthesis, purification, electrochemistry, and catalysis. ILs have unique physical and chemical properties, such as lower volatility, higher thermal stability, good electrical conductivity, intrinsic polarity, and good affinity to engineering surfaces [6]. Recently, ILs show bright application prospects in tribology both as high-performance lubricant additives and lubricant materials [124]. ILs could protect the sliding surfaces by forming boundary lubricating films that contain adsorption layers and tribo-chemical reaction protective films. Recently, with a further understanding of the properties and structural regulation of ILs, the modification of GO by ILs has attracted increasing attention to enhance the dispersibility and stability of functionalized GO in the base oil. Fan et al. [125] used alkyl imidazolium ILs to modify GO by ring-opening reaction of epoxy groups and successfully prepared MGO that was applied as additive in multialkylated cyclopentanes. The modification of GO with ILs could enhance the physicochemical properties of GO, such as thermal and chemical stability, compatibility, and dispersibility in lubricants. Multialkylated cyclopentanes containing MGO additives on steel/steel pairs showed distinct reduction of the COF (27%) and wear (74%), indicating an important role of ILs-modified graphene materials as lubricant additives.

Due to the variable structure, flexible design, and adjustable characteristics of ILs, ILs can be rationally used to modify GO. For example, hydroxyl-terminated ILs decorated GO was prepared by a simple liquid phase method [126]. The modified GO (ILCAs-GO) could be well dispersed in water and showed good lubricity due to the deposition of ILCAs-GO on the surface of friction pairs by electrostatic adsorption during the friction process. The continuous deposition of ILCAs-GO on friction surfaces improved the wettability of water on contact surface and realized the self-healing and self-wetting ability, which could effectively protect the surface of the friction pairs.

Lots of studies have demonstrated that graphene nanosheets modified by organic materials can provide strong chemically bonded tribo-films on the contact surface of friction pairs and the nanocomposites can reduce the friction and wear [127]. In order to strengthen the synergistic effect of nanocomposites, Gan et al. [128] prepared a novel IL-GO/Cu nanocomposite by modifying GO/Cu with 1-aminoethyl-3-methyl imidazolium nitrate ILs through covalently functionalization and electrostatic interaction (Figure 8a). They found that the IL-GO/Cu nanomaterial with sandwich-like structure could be well dispersed in PEG 200, which could improve the tribological properties of PEG 200 by reducing COF and wear with 40.1% and 47%, respectively (Figure 8b). This is mainly attributed to the synergistic lubrication effects which resulted from the formation of the boundary tribo-films including adsorbed/transfer/tribo-chemical film, as well as the "third body" with Fe/Cu nanocrystals-embedded graphene-like structure during the friction process. Song et al. [129] synthesized a SiO_2@GO@MEIMBScB (MEIMBScB: 1-methylimidazolium bis(salicylato)borate) nanocomposite which is composed of SiO_2@GO modified by MEIMBScB ILs. The as-prepared nanocomposites were used as the additive in PEG 400 and could greatly reduce the COF and wear with 57.27% and 16.98%

at the optimal concentration (Figure 8c,d). Since ILs could enhance the reaction between nanoparticles and worn surfaces, the tribofilm formed by SiO_2@GO@MEIMBScB nanocomposite could be strongly bonded on the contact surface of steel and thus provided a good tribological performance (Figure 8e). These studies would provide guidance in developing novel lubricant additives for different applications.

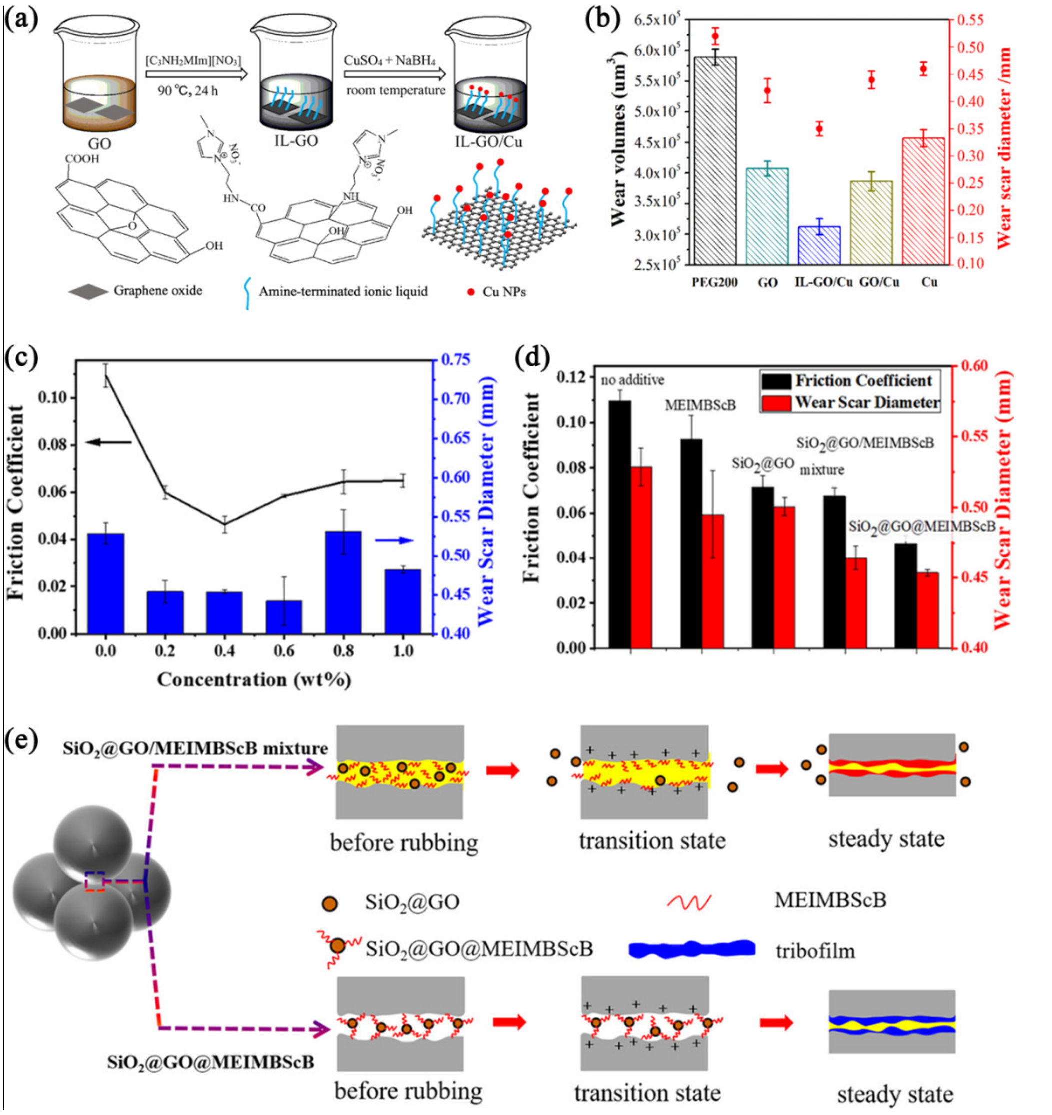

Figure 8. (**a**) Schematic illustration of preparation process of Synergistic lubricating effects of IL-GO/Cu composite. (**b**) Wear volumes and the wear scar diameter on lower ball lubricated by pure oil and hybrid lubricants at 392 N (adapted from [128]). (**c**) COF and wear scar diameter of PEG 400 containing different concentrations of SiO_2@GO@MEIMBScB. (**d**) Average friction coefficient and wear scar diameter of PEG400 containing 0.4 wt% additives. (**e**) Tribological mechanisms of the SiO_2@GO/MEIMBScB mixture and SiO_2@GO@MEIMBScB (adapted from [129]).

Compared with individual graphene, graphene modified by organic materials accomplish the controllable regulation of structure and surface/interface properties of graphene nanosheets. By rational design and appropriate preparation method, graphene-organic compound hybrids with improved dispersibility in various liquid lubricants can be achieved, which plays an important role in enhancing the tribological performance of the corresponding systems. In addition, the graphene-organic hybrid nanomaterials can form robust tribo-films on the contact surface of friction pairs in the rubbing process and expand the application scenarios of graphene lubricants. Apart from combining with organic compounds, inorganic nanomaterials supported or anchored on graphene nanosheets are another appealing strategy for improving physicochemical properties of graphene-based nanomaterials. In the following subsections, we discuss graphene-inorganic nanocomposites for lubricant additive applications, including graphene-nonmetallic nanocomposite and graphene-metallic nanocomposites.

3.3. Graphene-Nonmetallic Nanocomposite Additives

Oxygen-containing functional groups on the surfaces or edges of GO can provide reaction sites for combining nonmetallic nanomaterial by van der Waals force, electrostatic force, etc., which would bring new properties to graphene-based nanomaterials, such as improved dispersibility, good stability, and enhanced tribological property, etc. In the following, graphene-carbon nanocomposite, graphene-nonmetal oxide, and other nonmetallic compounds combined with graphene as lubricant additives are summarized and discussed.

3.3.1. Graphene-Carbon Nanocomposites

Carbon materials with excellent mechanical performance, high thermal conductivity, and chemical stability [130] perform an important role in lubrication. It is expected that combining graphene with the carbon materials can generate high-performance nanocomposites to improve the lubricating performance.

As common 0D carbon nanomaterials, CQD [131], ND [132], and fullerenes [133] have excellent tribological properties. Wu et al. [134] developed a mixed water lubricant containing GO and ND additives. The lowest COF of 0.03 was obtained using water lubricant containing 0.1 wt% GO and 0.5 wt% ND. This good tribological behavior was ascribed to the synergistic effect of GO sliding and ND rolling effect. Another carbon-hybrid material composed of CQD and GO was prepared by tuning the carbonization degree of citric acid monohydrate (CA) [135]. The obtained material showed excellent solubility in the PEG synthetic lube base oil and excellent tribological properties with COF reducing by 60.8–71.4%. Here, the good lubrication performance is due to the production of defects and orderly carbon structure in the lubricating films.

Besides 0D carbon materials, 1D CNTs have gradually become appealing candidates as lubricant additives due to their excellent physical and chemical properties [136,137]. For instance, Min et al. [65] synthesized GO/MWCNTs–COOH hybrids by a vacuum filtration method and used them as an additive in water-based lubricant. The GO nanosheets and MWCNTs–COOH were combined by π–π interaction. The prepared hybrids showed excellent dispersibility and lubrication properties in water, and the lowest COF and wear volume were obtained at the concentration of 0.7 wt%. This is due to the fact that during the friction process, GO nanosheets was transferred on the contact surface to form a tribo-film and protected the friction pairs. Meanwhile, MWCNTs–COOH played a micro-bearing effect and it can transform the sliding friction into rolling friction on the worn region. Therefore, the synergistic effect between GO and MWCNTs–COOH improved the tribological properties of water lubricants.

3.3.2. Graphene-Nonmetallic Compound Nanocomposites

Silica nanoparticles can be used as a traditional lubricant additive to enhance the tribological performance of lubricants. In order to improve the tribological performance of silica nanoparticles, researchers have paid attention to the functionalization of silicon nanoparticles by combining graphene materials. Lv et al. [138] and Huang et al. [139] prepared GO/SiO_2 hybrids and GO/SiO_2 nanoslurries by mixing the GO and SiO_2 with different proportions in water. They demonstrated that GO nanosheets and SiO_2 nanoparticles have a synergistic effect by forming the tribo-films and transforming the sliding friction into rolling friction to further improve the tribological properties of the material. In another case, a silica/GO nanocomposite was synthesized by a hydrothermal method.

When used as the additive in ethylene glycol lubricants [140], the silica/GO nanocomposites reduced the COF (38%) and wear volume (31%) of ethylene glycol on the steel/steel.

Graphitic carbon nitride (g-C_3N_4) can be used in tribological applications due to its mechanical sliding properties of a layered structure during the friction process [141]. In 2018, He et al. [142] prepared g-C_3N_4/GO mixed suspension lubricants and investigated the tribological behaviors of GO, g-C_3N_4 and the g-C_3N_4/GO. The prepared g-C_3N_4/GO reduced the COF and wear of water-based lubricants by 37% and 19.6%, respectively. Even under high loads or speeds, it also exhibited superior tribological behavior due to its unique composite structure, which illustrated that the g-C_3N_4/GO could be applied to complex environments.

Hexagonal boron nitride (h-BN) with an ultra-flat surface can be used as high-performance additive in various lubricants due to its weak van der Waals bond between the layers [143,144]. Samanta et al. [145] obtained a h-BNAS@GO (h-BNAS: (3-aminopropyl) trimethoxysilane-grafted h-BN) composite by covalently grafting the h-BN nanosheets on the surface or edge of GO nanosheets (Figure 9a). When used as additive in heavy paraffin oil, these h-BNAS@GO composites could improve the cushioning lubricating barrier into the interfaces, reduce the interlayer interaction, and accelerate the shear of lamellae on the contact surfaces. Hence, under different loads and sliding velocities, the h-BNAS@GO composites always exhibited excellent tribological properties in lubricant oil, which were better than that of the component material of the h-BNAS@GO composites. Particularly, the h-BNAS@GO composites reduced the COF by 50.7% and 41.18% under the load conditions of 10 N and 40 N, respectively (Figure 9b,c).

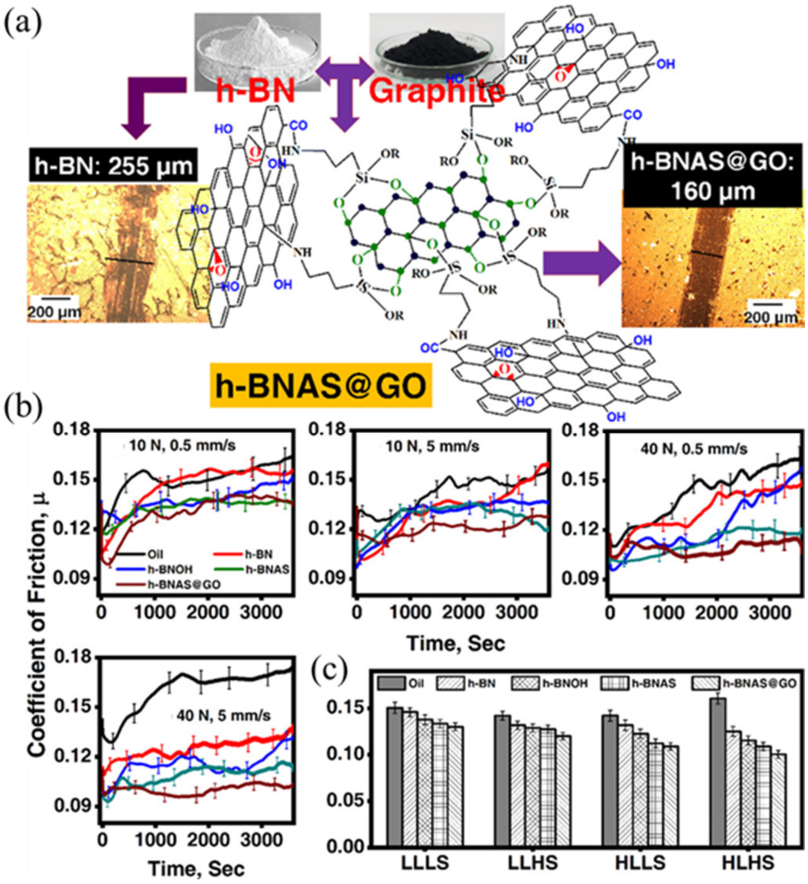

Figure 9. (**a**) Schematic diagram of the structure of the h-BNAS@GO composite material. (**b**) Variation in COF with sliding time from the ball loading macrotribometric studies for the prepared samples under different conditions. (**c**) Comparison of COF values (adapted from [145]).

3.4. Graphene-Metallic Nanocomposites as Lubricant Additives

Metal or metallic compound NPs with different structure and size have great influences on the tribological properties of lubricants. However, metallic nanomaterials are prone to agglomeration in lubricants due to their small size and larger specific surface area, which inevitably affect the tribological properties. To solve this issue, researchers have prepared a number of graphene-metallic nanocomposites to inhibit the agglomeration of nanoparticles and prevent graphene restacking simultaneously, and further improve tribological properties of nanomaterials additives [146]. Generally, metallic nanomaterials used as additives mainly include metals, metal oxides, metal sulfides, and metal salts, etc.

3.4.1. Graphene-Metal NP Nanocomposites

Metal NPs can be adhered to the surface or edge of graphene nanosheets to form graphene-metal NP nanocomposites. These nanocomposites used as lubricant additives can improve the tribological properties [147]. Through a facile one step in-situ reduction method, Jia et al. [148] prepared Cu/rGO composites and studied their tribological performance in PAO lubricants. It is demonstrated that the COF could be reduced from 0.10 to 0.055 and wear scar diameter could be reduced from 0.75 mm to 0.35 mm with a Cu/rGO concentration of 0.5 wt%. Similarly, other metal NPs/GO nanocomposites, such as Ag/rGO [30,64], Al/graphene [149], and so on, have been studied as lubricant additives to improve the tribological performance of lubricants.

Nanocomposites can be efficiently prepared by the supercritical fluid technique [150]. Meng et al. [31,151] synthesized Sc-Cu/GO and Sc−Ni/GO nanocomposites by an in-situ chemical deposition method under the condition of supercritical CO_2 ($ScCO_2$) and used them as the additive of liquid paraffin oil. The experimental results showed that the small size Cu or Ni NPs were uniformly anchored on the surface of GO nanosheets forming Sc-Cu/GO and Sc−Ni/GO nanocomposites, which was conducive to forming the lubricating films and protected the contact regions. Then, Sc−Au/GO nanocomposites were prepared using the same synthesis method (Figure 10) [152]. The Au NPs were distributed on the surface of GO sheets and the as-prepared Sc-Au/GO nanocomposites were well dispersed in the PAO 6 oil. The COF and wear volume of PAO 6 with 0.10 wt% Sc-Au/GO nanocomposites distinctly reduced by 33.6% and 76.8% (Figure 10a–c). During the friction process, the synergistic effect was beneficial to the interlamination sliding. In addition, when the GO nanosheets were deformed and ruptured, the Au NPs would repair the ruptured film and protect the surface of friction pairs continuously.

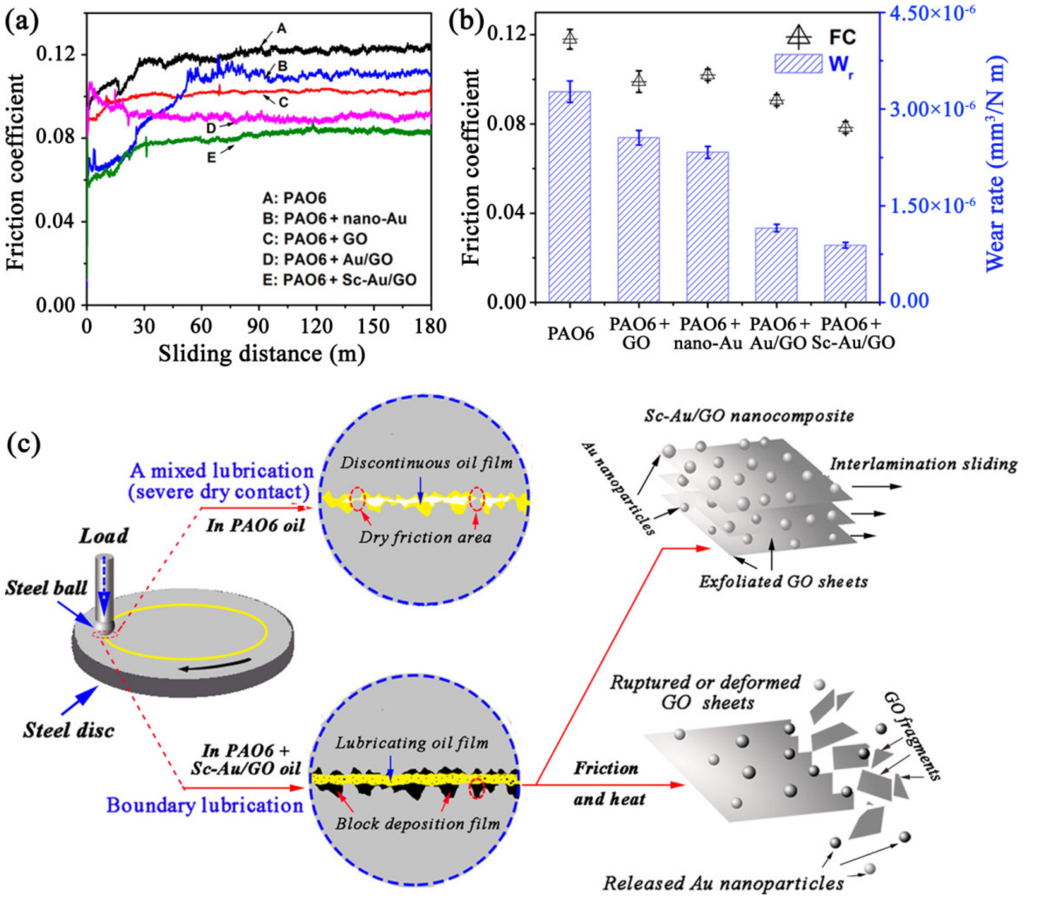

Figure 10. (**a**) COF curves of PAO 6 oil and PAO 6 oil containing different nanoparticle with 0.1 wt% (GO, nano-Au, Au/GO, and Sc-Au/GO). (**b**) Average COFs (FCs) and wear rates (W_{rs}) of the corresponding discs lubricated with these oils. (**c**) Schematic of the lubricating models of PAO 6 oil and the Sc-Au/GO dispersed oil (adapted from [152]).

3.4.2. Graphene-Metal Oxide Nanocomposites

Metal oxide NPs are usually used as additives to improve the lubricating behavior, including extreme pressure and anti-wear properties, due to their high wear resistance and hardness. These metal oxide NPs mainly include Fe_2O_3, CuO, TiO_2, Mo_3O_4, ZnO, and so on. GO nanosheets or its derivatives are often used as the precursor to prepare the graphene-metal oxide nanocomposites.

In 2012, Song et al. [153] synthesized a α-Fe_2O_3/GO composites by a facile hydrolysis route and used them as the additive in liquid paraffin lubricant. α-Fe_2O_3 nanorods with size of 3–5 nm in diameter and 15–30 nm in length were adhered to GO nanosheets. These α-Fe_2O_3/GO composites showed satisfied antifriction properties in the base oil.

Several studies have verified the friction-reducing capacities of ZrO_2/GO composite [154]. Huang et al. [155] proved that the ZrO_2/GO hybrid can be widely used in water and paraffin oil lubricants. ZrO_2 nanoparticles with small size were homogeneously dispersed on the surface of rGO nanosheets. The rGO/ZrO_2 composites exhibited excellent dispersibility and tribological properties in the water and paraffin oil lubricants. Similarly, ZrO_2@GO nanocomposites were synthesized by an electrostatic self-assembly method [156]. The results showed that ZrO_2@GO nanocomposites used as additives exhibited good dispersibility in paraffin oil, and displayed outstanding tribological behaviors by reducing COF (20.7%) and wear (21.5%). Ma et al. [157] synthesized hierarchical-structured FG/ceria (FG/CeO_2) nanocomposite through a simple sonication-assisted solvothermal method. The FG/CeO_2 nanocomposite could improve the dispersibility and tribological properties of FG in oil lubricants.

Other graphene-metal oxide nanocomposites, such as CuO/rGO nanocomposites and GO-Al_2O_3 hybrid NPs can also improve the lubrication property of lubrication [158–161].

3.4.3. Graphene-Metal Sulfide Nanocomposites

Metal sulfides have been considered as significant solid lubricants and lubricant additives for a long time [162]. MoS_2 is frequently applied as a lubricant additive due to its excellent mechanical property, chemical stability, and layered structure [163,164]. rGO/MoS_2 heterostructure nanocomposites were synthesized by the one-pot hydrothermal method [165]. MoS_2 was growing vertically on the skeleton of rGO nanosheets. The as-prepared rGO/MoS_2 nanocomposites could be stably and uniformly dispersed in gear oils due to its steric hindrance effect. These nanocomposites used as additive exhibited excellent tribological performance by reducing the COF (~16.7%) and wear (80%), which was due to the formation of protective lubricating film and the lower shear strength of the inherent lattice mismatch between rGO and MoS_2.

Zhang et al. [166] prepared FeS_2/rGO heterojunction nanocomposites by a hydrothermal method and investigated the tribological properties as additive in liquid paraffin base oil on a ball-plate tribotester. The results showed that the FeS_2/rGO heterojunction nanocomposites enhanced the tribological properties of paraffin oil. The tribological behaviors were affected by the concentration of nanocomposite additives. The enhanced lubricating effect was mainly due to the unique layered structure of FeS_2 and rGO, the filling of FeS_2/rGO composites in the micro-gaps of the worn surfaces and forming continuous tribo-films on the contact surface. Similarly, WS_2/graphene nanocomposites (WS_2/GP) were synthesized by anchoring the WS_2 NPs onto the graphene surface [167]. The WS_2/GP nanocomposites additive in PAO 4 oil exhibited good dispersibility and tribological performance, and the excellent anti-friction and anti-wear properties can be attributed to the formation of a tribo-film on the contact surface of friction pairs.

3.4.4. Graphene Combined with Other Metal Containing Compounds

Beyond graphene, other 2D nanomaterials with layered structures and large specific surface area can be used as lubricant additives, such as MXene [168–170], layered double hydroxide (LDH) [171,172] and their composites [173]. LDH with unique 2D structural and unique physicochemical properties also has attracted attention as lubricant additives [168]. LDH has rich positive charges on its surface, which is conducive to being absorbed on the surface of GO nanosheets with negative charges [174]. The LDH/GO nanosheets were uniformly dispersed in PAO 4 oil due to the lamellar structure of LDH. The LDH/GO nanosheets could greatly improve the tribological properties of PAO 4 oil in terms of anti-wear, friction-reducing performance, and bearing load capacity.

Researchers also showed that LaF_3 has good tribological properties as the lubricant additive [175]. Hou et al. [176] and Yang et al. [177] synthesized LaF_3-GO nanohybrids and these materials were used as additive in water and liquid paraffin, respectively. The as-prepared LaF_3-GO nanohybrids could significantly enhance the tribological properties of water and liquid paraffin since the materials could be deposited and fill the gaps on the steel contact surface to form a protective lubricating film. In addition, in order to investigate the tribological performance of zinc borate particles on GO nanosheets, Cheng et al. [178] prepared the zinc borate/graphene oxide (ZB/GO) nanocomposites by liquid phase assisted with ultrasonic methods and further modified by oleic diethanolamide (OD) to obtain OD-ZB/GO materials (Figure 11a). The OD-ZB/GO materials had superior dispersibility in the 500 SN base oil (Figure 11b). The tribological test indicated that oil containing OD-ZB/GO with different concentrations had various tribological behaviors and at the concentration of 2.0 wt%, it could greatly reduce the COF and wear scar diameter by 48.2% and 40.0%, respectively (Figure 11c,d).

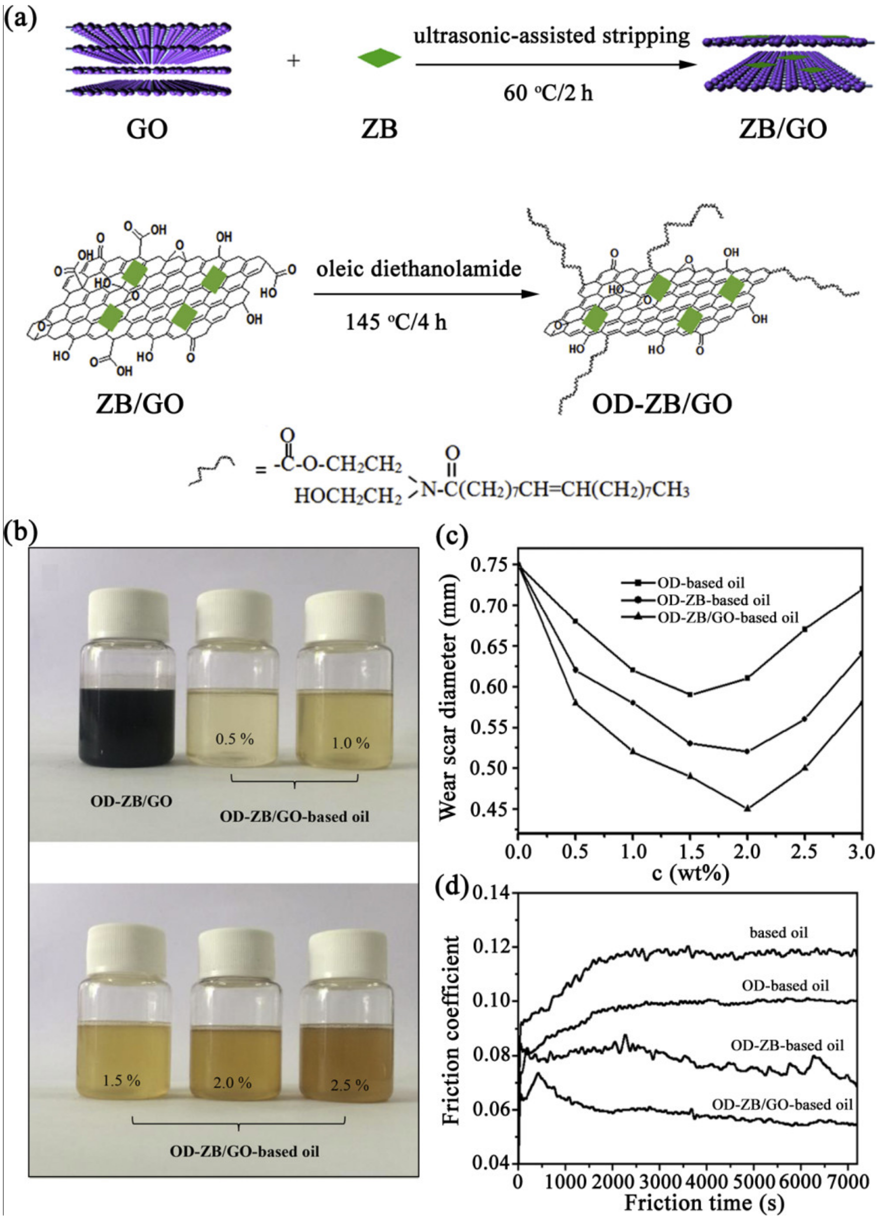

Figure 11. (**a**) The preparation and modification of ZB/GO. (**b**) Dispersion photos of OD-ZB/GO in the 500SN base oil with different contents. (**c**) The wear scar diameter (WSD) of the OD-based oil, the OD-ZB-based oil, and the OD-ZB/GO-based oil. (**d**) The friction coefficient curves of the 500SN base oil, the OD-based oil (2.0 wt%), the OD-ZB-based oil (2.0 wt%) and the OD-ZB/GO-based oil (2.0 wt%) (adapted from [178]).

Based on the above analysis, additives composed of graphene and other nanomaterials display excellent tribological performance. Among these additives, graphene-metallic nanomaterials can be dispersed in various liquid lubricants to promote the tribological properties in terms of friction reduction and anti-wear performance, which is mainly due to the fact that the metallic nanoparticles can attach to the shear surface of the fresh friction contact region and form a protective film to reduce direct contact between friction pairs. Meanwhile, small NPs distributed on the surface of graphene provide the micro-bearing effect and can transform the sliding friction into rolling friction during the rubbing process. Due to the complementarity between nonmetallic compound nanomaterials and graphene, graphene-nonmetallic compound nanomaterials can present distinguished tribological properties.

As mentioned above, inorganic nanomaterials can be used as modifiers to functionalize graphene nanosheets, which can improve the tribological performance of graphene to a large extent. In order to further improve the dispersion stability and lubricating effects of graphene-based nanomaterials in different lubricants, more and more researchers have devoted to preparing the graphene-based nanomaterials via functionalizing graphene with two or more nanomaterials as the modifiers [179–181]. Improved tribological performance of graphene-based nanomaterials renders it broad application prospects. In the next section, we present the application of graphene-based nanomaterials focusing on the engineering field.

4. Application of Graphene-Based Nanomaterials as Lubricant Additives

There are various graphene-based nanomaterials which can be used as additives in specific lubricants in the engineering and industrial manufacture fields, such as for drilling fluids, rolling and cutting fluids, and industrial gear oils.

4.1. Drilling Fluids

With the development of drilling technology, drilling fluids, including oil-based and water-based fluids, have been widely applied in various industrial productions, which could promote the exploration and development of unconventional oil and gas resources. There are still some challenges for the lubricating performance of drilling fluid under high-temperature over 200 °C. To meet this demand, an organic-sulfonate functionalized graphene was prepared by modifying graphene with sodium dodecylbenzene sulfonate (SDBS) [182]. The obtained SDBS/graphene used as the additive in water-based drilling fluids can improve the resistance to high-temperature of drilling fluids. The results showed that SDBS/graphene in the base slurry had an excellent tribological performance by reducing COF and wear at room temperature and even at a high temperature of 240 °C.

4.2. Rolling Fluids

Cold rolling technology is a significant fabrication technique used to obtain rolled steel with the designed dimensions and mechanical properties. A suitable rolling fluid plays an important role in the metal forming process. Studies have demonstrated that water fluids containing graphene-based nanomaterials can be applied as environmentally friendly lubricants for rolling process [183]. For example, Du et al. [184] prepared GO-TiO_2 nanocomposites using solvothermal methods. They studied the lubricant performance of GO-TiO_2 nanofluids (0.5 wt% in water) using a four-ball tribometer and two-high rolling mill. The GO-TiO_2 nanofluids showed good anti-friction and anti-wear performance, which was ascribed to the good dispersion of nanocomposites in water (Figure 12a,b). GO-TiO_2 nanocomposites could easily absorb on the valleys and peaks of the strip surface and promote the formation of lubrication film on the contact surface, thereby preventing the direct contact between the roller and the surface of the steel sheet (Figure 12c). Besides, Xie et al. [185] investigated the tribological behaviors of the SiO_2/graphene in water-based lubricants. The SiO_2/graphene exhibited good dispersibility, lubricating and rolling lubrication effects, and load-bearing capacity in water-based lubricants, which was attributed to the formation of transfer films during the friction process. Moreover, the SiO_2/graphene combinations applied to magnesium alloy rolling could effectively decrease the rolling force and enhance the rolling quality of magnesium alloy.

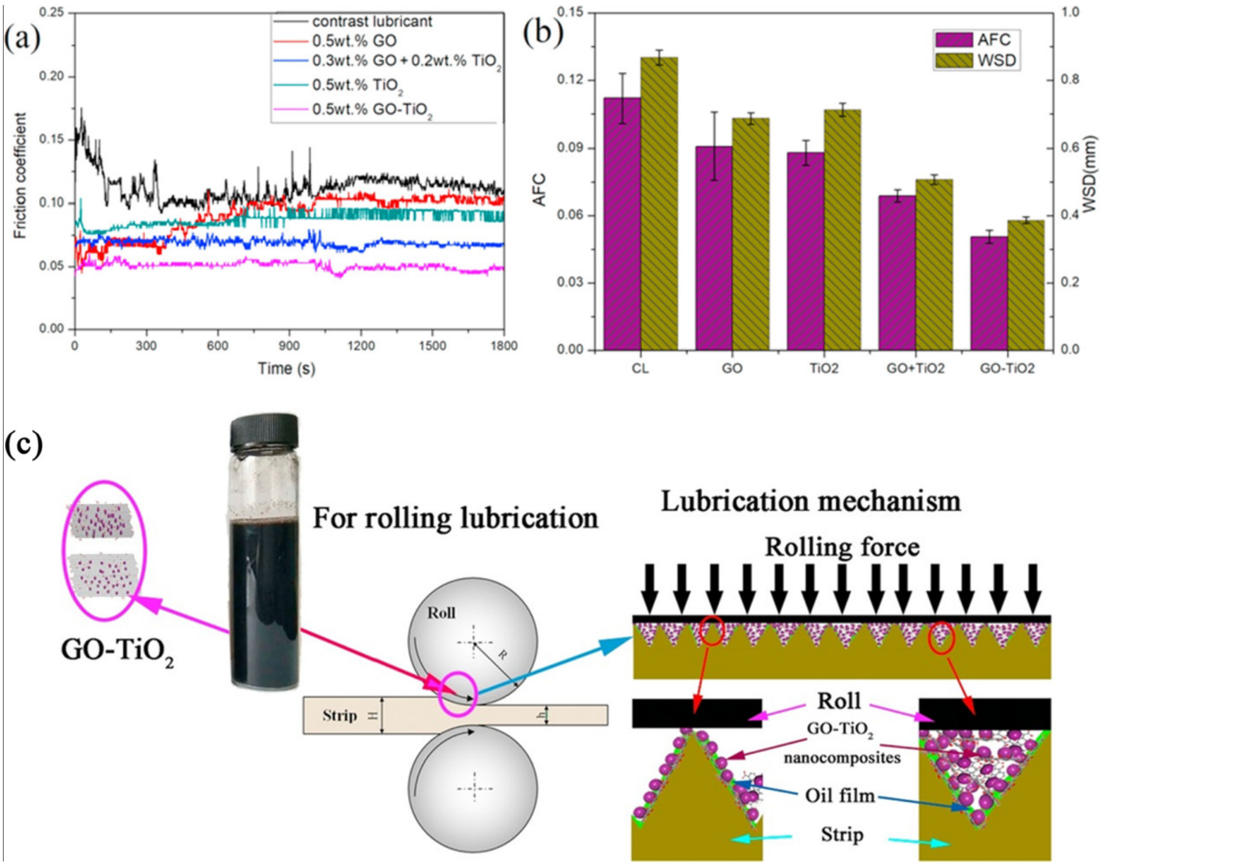

Figure 12. (**a**) COFs, (**b**) AFC and WSD of the wear scars lubricated by control group and GO, TiO_2, GO+TiO_2, and GO-TiO_2 nanofluids. (**c**) Schematic of GO-TiO_2 nanofluid rolling lubrication mechanism (adapted from [184]).

4.3. Cutting Fluids

Cutting fluids can cool equipment and remove the abrasive dust away from the machining zone when applied to the cutting technique. Previous studies indicated that graphene nanoplatelets used as an additive in cutting fluids could reduce the cutting energy due to the decreasing of the COF [186]. Minimum quantity lubrication (MQL) technologies using oil lubricants as cutting fluids have been broadly used for metal cutting [187]. Lv et al. [137] developed an MQL technology by using water-based lubricants containing GO/SiO_2 hybrid nanoparticles as cutting fluids. The tribological experiment results indicated that the GO/SiO_2 water-based cutting fluids could significantly improve machining performance by decreasing the COF and worn scar diameter since the GO/SiO_2 hybrid nanoparticles could easily enter in friction surface and form composite tribo-films to prevent the direct contact and smoothen asperities on the friction pairs. Sharma et al. [149] evaluated the machining performance of cutting fluid containing alumina-graphene (Al-GnP) hybrid nanoparticles on AISI 304 steel by the MQL technique (Figure 13). The results showed that the smaller contact angle (wettability) for the Al-GnP hybrid nanofluid was beneficial to enhancing the spreadability of lubricants and then the Al-GnP hybrid exhibited excellent tribological performance in lubricants. The outstanding tribological performance was due to the synergic lubricating effect between GnP and Al nanoparticles, which was better than the only ball-bearing effect of Al nanoparticles.

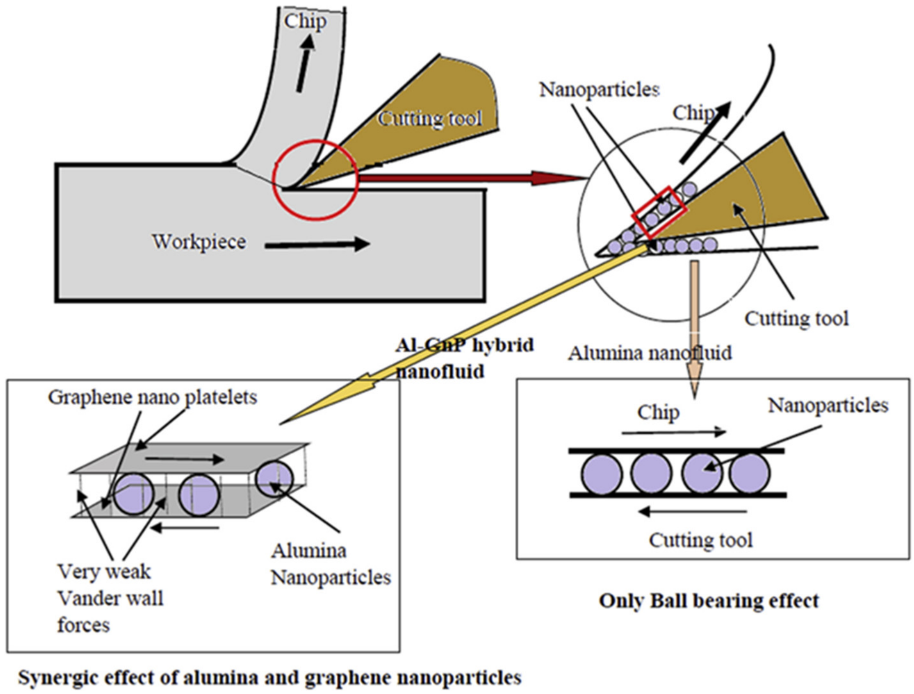

Figure 13. Synergic effect of alumina and Al-GnP nanoparticles trapped between the sliding surfaces (adapted from [149]).

4.4. Industrial Gear Oils

Due to its good transmission capacity and bearing capacity, gear transmission can be used in wind power, marine machinery, the chemical industry, etc. Lubricants for gear transmission should have anti-friction and anti-wear properties, noise reduction, and shock absorption properties. Graphene-based nanomaterials can improve the lubricating effects of gear oil lubricants [188]. Fan et al. [189] synthesized heterostructured rGO/MoS_2 nanocomposites by one-pot hydrothermal methods and used the composites as additives in industrial gear oils. The as-prepared composites exhibited good dispersibility and tribological performance in industrial gear oils. The excellent tribological performance was due to the formation of lubricating films and the low shearing force of layers, which had great application prospects in industrial fields.

5. Conclusions and Outlooks

In this review, we summarized the recent progress which has been made in graphene-based nanomaterials for lubricant additive applications, mainly focusing on synthesis strategies, structure, lubrication mechanism, tribological performance evaluation, and applications of graphene-based nanomaterial additives. Remarkably, by combining graphene with other materials, their dispersibility, stability and tribological property can be readily regulated and improved. Specifically, graphene-based nanomaterials can be dispersed in many different lubricants to meet various environmental conditions and can further expand the application of graphene-based nanomaterials in tribology.

Although great breakthroughs and developments of graphene-based nanomaterials as lubricant additives have been achieved, there are still some difficulties and challenges to be overcome:

(1) Some traditionally used organic and inorganic components (such as SDS [122], MoS_2 [163], etc.) in the graphene-based nanomaterials contain sulfur elements, which easily cause a release of pollutants. Therefore, preparing “green” graphene-based nanomaterials without reducing friction and wear properties as effective lubricant additives is highly desired.

(2) Different preparation methods or modifiers have a great influence on the antifriction and anti-wear properties of the prepared nanomaterials, making it greatly difficult to provide guidance for the follow-up research. More scientific details, including the degree of modification (the amount of modifier on graphene), the structure-property relationship, and the synergetic effect between different components, etc., need to be further explored.
(3) The dispersion stability of graphene-based nanomaterials in various liquid lubricants has not been fully solved. Specifically, organic modifiers are prone to degrade due to the friction-induced heat during the rubbing process, which leads to re-aggregation of graphene nanosheets in the lubricants. Thus, investigation on materials degradation and long-term stability of graphene-based nanomaterials is still necessary.
(4) As for the lubricating mechanism, systematical elaboration on the lubrication mechanism of different types of graphene-based nanomaterials as lubricant additives is few. It is unclear about the influence of each component on the tribological properties, such as the interaction of additive materials and lubricants, the synergistic lubrication effect of components in nanomaterials, and so on. Combination with advanced characterization techniques and theoretical calculation is needed to further elaborate relevant mechanisms.
(5) Most of the reported graphene-based nanomaterial additives were studied at room temperature and on a laboratory scale. Developing new additives with good tribological property under extreme conditions or in multi-environment is needed in the future. Furthermore, low-cost, large-scale preparation routes, and tribological performance evaluation in real application are crucial for the practical application of these additives.

It is expected that significant advancements of graphene-based nanomaterials with desired properties can be achieved by addressing abovementioned challenges in the following several years.

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

Funding: This research was funded by the National Natural Science Foundation of China (grant number 52175203) and Yantai Zhongke Research Institute of Advanced Materials and Green Chemical Engineering (AMGCE017).

Data Availability Statement: Not applicable.

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

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