

Nanolubricant additives: A review

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Abstract: Using nanoadditives in lubricants is one of the most effective ways to control friction and wear, which is of great significance for energy conservation, emission reduction, and environmental protection. With the scientific and technological development, great advances have been made in nanolubricant additives in the scientific research and industrial applications. This review summarizes the categories of nanolubricant additives and illustrates the tribological properties of these additives. Based on the component elements of nanomaterials, nanolubricant additives can be divided into three types: nanometal-based, nanocarbon-based, and nanocomposite-based additives. The dispersion stabilities of additives in lubricants are also discussed in the review systematically. Various affecting factors and effective dispersion methods have been investigated in detail. Moreover, the review summarizes the lubrication mechanisms of nanolubricant additives including tribofilm formation, micro-bearing effect, self-repair performance, and synergistic effect. In addition, the challenges and prospects of nanolubricant additives are proposed, which guides the design and synthesis of novel additives with significant lubrication and antiwear properties in the future.

Keywords: nanolubricant additive; dispersion stability; tribological properties; lubrication mechanism

1 Introduction

Energy loss is an unneglected problem especially in the energy-shortage world, for instance, in a typical passenger car, 79% of fuel accounts for the energy loss, as shown in Fig. 1 [1]. Friction and wear are the main causes of energy loss and mechanical failure [2,3]. Approximately 1/3 of the world's primary energy originates from friction consumption, and nearly 1/2 of the power of transportation equipment is consumed in friction [4]. Especially, about 4/5 of mechanical failure mainly results from worn-out parts. In addition, friction also causes serious problems with surface corrosion and environmental pollution. Therefore, reducing friction and wear plays an important role in prolonging mechanical equipment service life and in saving energy and emission

reduction. Lubrication is one of the most effective ways to control friction and wear, which is of great significance for energy conservation, emission reduction, and environmental protection [5].

Various methods have been adopted to minimize

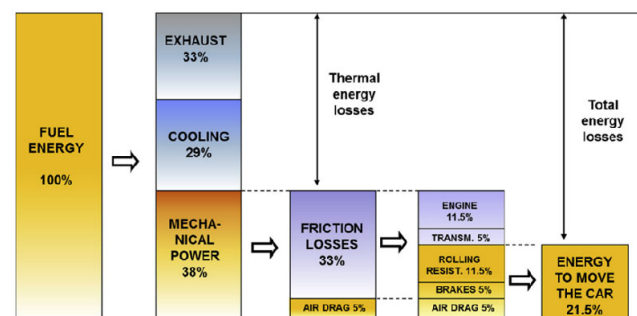


Fig. 1 Breakdown of passenger car energy consumption. Reproduced with permission from Ref. [1], © Elsevier, 2019.

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friction and wear to satisfy the requirements of energy-saving. For instance, the optimization of the groove texture profile can further enhance the load-carrying capacity of oil film under the conditions of hydrodynamic lubrication [6]. Besides, lubricants which mainly include solid lubricants and liquid lubricants are widely used for lubrication. There are many advanced solid lubricants such as molybdenum disulfide (MoS_2) film [7], diamond-like coating [8], entangled carbon nanotube (CNT) film [9], and polymer material [10, 11]. However, their tribological properties are directly influenced by the friction environment, and they are prone to being a wear-out failure after serving for a long time. Liquid lubricants can form a hydrodynamic or elastohydrodynamic lubrication film on friction interfaces during sliding friction, therefore widely used in the mechanical industry. Apart from lubricating oils, ionic liquids can sometimes be used as liquid lubricants [12]. When mechanical equipment is under start-up and shutdown stages and/or under extreme friction conditions, liquid lubricants cannot form a stable lubricating film between the friction pairs. Under such circumstances, boundary lubrication and mixed lubrication states occur, and result in severe friction and wear. Using lubricant additives is one of the most effective ways to reduce friction and wear under boundary lubrication. Traditional lubricant additives such as organic phosphates, organic sulfides, and organic metallic compounds, have good dispersing stabilities and tribological properties, but they all have different degrees of problems, such as toxicity, releasing sulfated ash, phosphorous and sulfur (SAPS, which would cause air pollution such as acid rain and haze weather [13]) and chemical corrosion. Although other additives such as ionic liquids have outstanding tribological performance and are environmental-friendly, they are high in cost, which restricts the application in industry [14, 15].

Nanomaterials because of atomic sizes and surface effects, display unique physical and chemical properties and have been widely investigated in the field of tribology. Nanomaterials using as lubricant additives can greatly improve the tribological properties of lubricating oil and have outstanding effects on reducing energy consumption and environmental protection [16]. Therefore, this review focuses on

the development of nanolubricant additives, mainly including nanometal-based additives, nanocarbon-based additives, and nanocomposite-based additives. Their tribological properties are firstly systematically discussed. The dispersion stabilities of the nano additives are then described in detail. Furthermore, the review summarizes the lubrication mechanisms of nanolubricant additives including tribofilm formation, micro-bearing effect, self-repair performance, and synergistic effect. Finally, the challenges and prospects of nanolubricant additives are proposed.

2 Nanolubricant additives

With the development of nanotechnology, nanomaterials have become one of the most attractive fields in physics, chemistry, and materials science. Nanomaterials as lubricant additives because of their small sizes are easy to enter friction contact areas and can form a protection tribofilm, thereby preventing the surface of friction pairs from being worn. In addition, nanomaterials have high surface activity, which can improve the film-forming stability of protection tribofilm by physical and/or chemical adsorption effects. There are three basic types of nanolubricant additives: nanometal-based additives, nanocarbon-based additives, and nanocomposite-based additives, as shown in Table 1.

2.1 Nanometal-based lubricant additives

The nanometal-based lubricant additives mainly include pure metals, metal oxides, metal sulfides, metal hydroxides, and metal salts. In the 1980s–1990s, Hisakado et al. [17] found that Cu nanoparticles as lubricant additives displayed excellent tribological properties in base oils for the first time. Then, Cu nanoparticles with good dispersed performance in lubricant were prepared by surface chemical modification [18, 19], as shown in Figs. 2(a) and 2(b). They also revealed the outstanding antifriction properties of modified Cu nanoparticles at a concentration of 0.3 wt% under different friction conditions, as shown in Figs. 2(c) and 2(d). Other nanometal materials with low melting points and weak shear forces such as Ag and In–Sn alloy nanoparticles have also been studied as nanolubricant additives [20, 21].

Table 1 Types of nanolubricant additives.

Types of nanolubricant additives		Examples
Nanometal-based lubricant additives	Pure metal	Cu [22, 23], Ag [21, 24], Fe [25, 26], Pd [27, 28], Ni [29]
	Metal oxide	CuO [30–32], ZnO [33, 34], Al ₂ O ₃ [35], TiO ₂ [36–38], ZrO ₂ [39]
	Metal sulfide	WS ₂ [40–42], MoS ₂ [43–46], CuS [47], ZnS [48]
	Metal hydroxide	La(OH) ₃ [49], LDHs [50–51]
	Metal salt	CaCO ₃ [52], LaF ₃ [53–55], ZrP [56], Calcium Borate [57,58], Zinc Phosphate [59]
Nanocarbon-based lubricant additives	Pure carbon	Nano Diamond [60,61], Fullerenes [62], Carbon Nanotubes [63, 64], Graphene [65–67]
	Polymer	PTFE [68,69], PSS [70], PVP [71]
Nanocomposite-based lubricant additives		Cu@SiO ₂ [72], Al ₂ O ₃ @TiO ₂ [73], Cu@MoS ₂ [74], G@MoS ₂ [75], α -Fe ₂ O ₃ @GO [76], FeS ₂ @G [77], Ag@G [78, 79], Cu@GO [80], Mn ₃ O ₄ @G [81], La ₂ O ₃ @PI [82], Alumina@MWCNT [83]

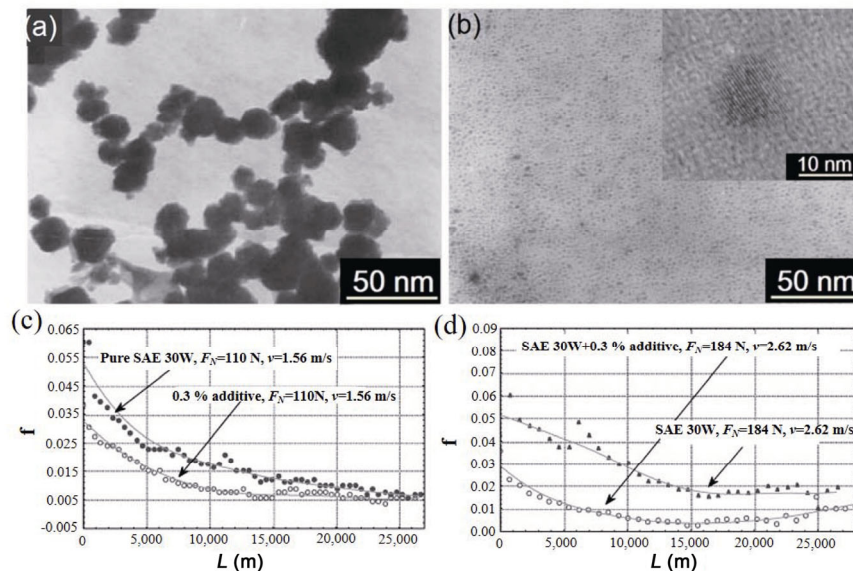


Fig. 2 Transmission electron microscope (TEM) images of (a) pure Cu nanoparticles and (b) Cu nanoparticles modified by chemical method. Reproduced with permission from Ref. [18], © Elsevier, 1999. (c, d) The tribological properties of the nanoparticle as lubricant additives. Reproduced with permission from Ref. [19], © Elsevier, 2002.

Current researches have also confirmed the improved tribological properties with the addition of metallic nanoparticles such as Fe, Pd, Ni, etc. [25–29]. Through comparative studies, it is found that metal oxides such as ZnO [33, 34], TiO₂ [36–38], and ZrO₂ [39] have good lubrication properties, and the properties of nanometal oxides are closely related to particle size, hardness, and concentration. Wu et al. [84] indicated that CuO nanosheets apparently enhanced the antiwear performance of self-lubricating carbon fibers reinforced polytetrafluoroethylene (PTFE) as additives. Moreover, the research also found that CuO nanosheets exhibited superior antiwear

properties to commercial CuO nanogranules. In addition, metal sulfides as lubricant additives have attracted much attention in the lubrication field. For example, MoS₂ and tungsten disulfide (WS₂) can chemically interact with friction pairs and produce a stable adsorption film on rubbing surfaces, so that the tribological properties of lubricants can be effectively promoted under some extreme friction conditions [85]. Recently, Yi and Zhang [86] found that the tribological properties of MoS₂ with lamellar morphology were much better than that of petal structure, indicating that MoS₂ with lamellar structure had high chemical activity

and was easier to display interlayer sliding effect. Moreover, Hu et al. [87] confirmed that spherical MoS₂ nanoparticles had a superior antioxidant effect to MoS₂ nanoparticles with layered structure, which further enhanced the lubrication stability. Chen et al. [88] revealed that ultrathin MoS₂ nanosheets had much better extreme pressure characteristics than other metal sulfides because the ultrathin nanosheets were easier to enter the friction contact areas.

Moreover, metal hydroxides have also been proved to show outstanding lubrication performance, and among them, layered double hydroxides (LDHs) are the most representative. Owing to the laminated structure, small particle size, and high chemical activity, LDHs powders exhibit excellent friction and wear reduction properties especially under boundary lubrication conditions [50,51]. Apart from LDHs, La(OH)₃ nanoparticles, another kind of metal hydroxide, have also been proved to be effective lubricant additives. Zhao et al. [49] synthesized La(OH)₃ nanoparticles with granular shapes by sol-gel method and confirmed the enhanced friction-reduction and wear-resistance properties of base oil with the addition of La(OH)₃ nanoparticles. Metal salts also have the potential for lubricant additives. CaCO₃ nanoparticles were investigated as lubricant additives in the early 2000s. And the researches demonstrate that CaCO₃ nanoparticles can facilitate obvious lubricating effect via the formation of tribofilm [52]. In addition, He et al. [56] confirmed the excellent antifriction performance of α -Zirconium phosphate (ZrP) nanoplatelets as lubricant additives. The results revealed that the friction coefficient was reduced by 65% and 91% in comparison with mineral oil and water respectively. The research attributed the outstanding friction-reduction properties to viscosity modification and intermolecular interaction. Comparative studies on the tribological properties have also been conducted on calcium borate [57,58], zinc phosphate [59] and LaF₃ [53–55].

2.2 Nanocarbon-based lubricant additives

Compared with metal sulfide additives, carbon nanomaterials with good chemical stability and excellent mechanical properties offer excellent tribological

properties together with environment-friendly performances for a sustainable future. Nanocarbon-based lubricant additives contain pure carbon and polymer, based on the chemical elements. Furthermore, according to various dimensions, pure carbon lubricant additives mainly include carbon quantum dot (CQD) (0D), nanodiamond (0D), fullerene C60 (0D), carbon nanotubes (1D), graphene (2D) and graphite (3D) [89]. Tu et al. [90] revealed that CQD enhanced the tribological properties of polyethylene glycol. Kim et al. [91] found that diamond nanoparticles can effectively promote the lubrication properties of base oil. Joly-Pottuz et al. [92] studied the tribological properties of nanodiamond compared with fullerene as lubricant additives. Diamond nanoparticles are prone to scratching rubbing surfaces during the sliding process. For comparison, fullerene because of shear deformation or even peeling into lamellar has better wear resistance. Liu et al. [93] concluded that the surface-modified carbon nanotubes can disperse well in the base oil, and it can form a “molecular brush” arrangement on rubbing surfaces and display a micro bearing-rolling lubrication effect. Zhang et al. [94] found that CNT walls were easily opened under high load and peeled off into graphene-like lamellar layers, so that good tribological property could be achieved through an interlayer-sliding effect. Graphene was first used in the research of nanolubricant additives for the first time in 2011 by Berman et al. [95]. After that, the investigation and application of graphene lubricant additives have been rapidly developed in recent years. Apart from pure carbon, polymer nanoparticles are also investigated as lubricant additives [96]. Kumar et al. [69] synthesized lithium greases with PTFE nanoparticles as additives and revealed the enhanced friction reduction and wear resistance properties with the addition of PTFE nanoparticles. Moreover, the study implied that size and shape were two factors that affect the lubricating performance. The tribological properties of poly (sodium 4-styrenesulphonate) (PSS) and polyvinylpyrrolidone (PVP) were investigated by Wang et al. [70] and Tu et al. [71]. The research confirms that the polymer nanoparticles can improve the antifriction and wear resistance of base lubricants effectively.

Graphene, a typical 2D nanomaterial, displays green lubricating and self-lubricating properties. Especially, superlubricity and ultrahigh wear resistance can be achieved by graphene [97–100]. The state of graphene layers during the friction process is illustrated in Fig. 3(a). Compared with single-layer graphene, multilayer graphene exhibits a much lower friction coefficient and much higher stability, as shown in Fig. 3(b). Moreover, graphene shows more potential for application in lubrication than other lubricant additives. Mechanical exfoliation is regarded as an effective method to prepare graphene with fewer layers. Berman et al. [95] revealed that small amounts of few-layer graphene can significantly improve the tribological performance. The results indicated that the friction coefficient and wear of graphene-containing ethanol solution reduced by a factor of 6 and almost 4 orders of magnitude respectively. However, the quality of the mechanical-exfoliation product is not guaranteed because the related operation is difficult to control. In addition, the cost of mechanical exfoliation is high and the efficiency is very low. Thus, other methods to prepare graphene have been developed. Eswaraiah et al. [101] exfoliated ultrathin graphene from graphite oxide with the assistance of focused solar radiation and investigated the tribological properties of graphene as additives. The results exhibited that the friction-reduction, antiwear, and extreme pressure properties were improved by 80%, 33%, 40% respectively. Mungse et al. [102] synthesized graphene from graphene oxide via a chemical reducing agent and indicated that graphene significantly enhanced the tribological properties. Schlüter et al. [103] examined the tribological performance of thermally reduced graphite oxide and confirmed its excellent properties on friction reduction and wear resistance. The reduction of graphite oxide has advantages on operation and cost, but the reduction procedure will lead to structural defects on graphene [104]. During thermal reduction, the release of gases will form holes and wrinkles on the graphene structure, which affects the lubricating performance. With the assistance of some chemical agents, such as H_2SO_4 and KOH , Zhao et al. [105] have found that the structural defects of graphene during thermal reduction can be inhibited, which shows great

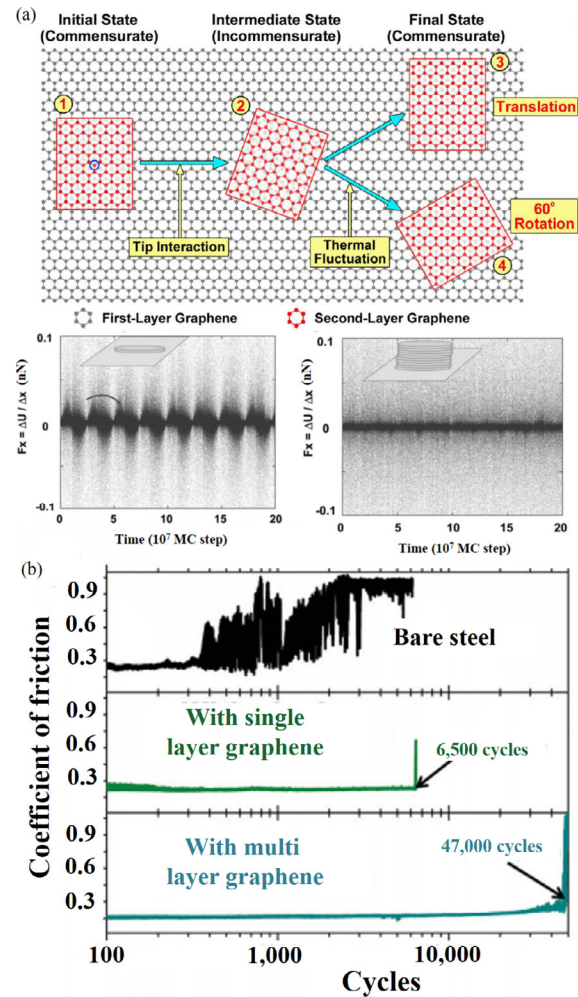


Fig. 3 (a) Superlubricity of graphene when graphene nanosheets slide on graphene surface by commensurate-incommensurate state. Reproduced with permission from Ref. [97], © Royal Society of Chemistry, 2012; Ref. [100], © American Chemical Society, 2013. (b) The friction coefficient of graphene with ultra-high wear resistance. Reproduced with permission from Ref. [98], © Wiley, 2014.

meanings to obtain graphene with excellent antifriction and antiwear properties.

2.3 Nanocomposite-based lubricant additives

Compared with metal-based and carbon-based lubricant additives, nanocomposite-based additives have outstanding lubricating properties because the additives can form a composite tribofilm on friction interfaces and have a synergistic lubricating effect. Zhang et al. [72] prepared Cu@SiO_2 nanocomposites and the results exhibited a considerable improvement of tribological properties. Luo et al.

[73] investigated the lubricating effect of $\text{Al}_2\text{O}_3@\text{TiO}_2$ nanocomposites as lubricant additives and confirmed the superior tribological properties of nanocomposites compared with pure Al_2O_3 or TiO_2 nanoparticles. Moreover, a nanotube is a typical matrix of 1D nanocomposites. Li et al. [106] synthesized PVA@CNTs nanocomposites and found that both load-carrying capacity and anti-wear properties were improved with the addition of nanocomposites. Yu et al. [107] prepared room temperature ionic liquid (RTIL)@multi-walled carbon nanotubes (MWCNTs) composite and revealed good friction-reduction and antiwear properties. Comparative tribological tests are also conducted on 2D nanocomposites. 2D nanocomposites are composites with a layered structure, such as MoS_2 -based and graphene-based nanocomposites, and they are regarded as a promising material for lubricant additives in the future. Jia et al. [74] prepared $\text{Cu}@\text{MoS}_2$ nanocomposites and investigated their tribological properties as lubricant additives. The experiments revealed that the optimal concentration of nanocomposites is 0.5 wt%, and the average friction coefficient and wear scar width were reduced by 37.8% and 28.5% compared with other additives in pure sunflower oils, respectively. Furthermore, significant antifriction and antiwear effects are also achieved by dispersing graphene-based nanocomposites into base lubricants. Song et al. [75] synthesized MoS_2 @graphene (MoS_2 @G) composites and investigated their tribological performance. The

results revealed that MoS_2 @G nanocomposites can improve antifriction and antiwear properties. Song et al. [76] examined the lubricating performance of $\alpha\text{-Fe}_2\text{O}_3$ @GO composites and the results confirmed the tribological properties of this nanocomposite are better than both Fe_2O_3 nanoparticles and graphene nanosheets. The friction coefficient and wear scar diameter of friction pairs can be reduced by 67% and 70%, respectively. Other graphene-based nanocomposites, such as FeS_2 @G, $\text{Ag}@\text{G}$ and $\text{Cu}@\text{GO}$, exhibit good antifriction and antiwear performance as well [77–80]. Generally, nanocomposites are mainly prepared by hydrothermal method. It is easy to control the shape and distribution density of nanoparticles on nanocomposites. Especially, Zhao et al. [81] prepared Mn_3O_4 @G nanocomposites via *in situ* green methods and investigated their tribological properties as shown in Fig. 4. The results showed that the friction coefficient and wear depth were respectively reduced by 75% and 97% in comparison with base oil at a very low concentration (0.075 wt%).

Nanolubricant additives have prominent antifriction and wear-reduction properties, and they are regarded as the alternatives of traditional lubricant additives. Although metal sulfide nanomaterials such as MoS_2 and WS_2 display significant antifriction and antiwear properties among all these categories, the high content of sulfur results in severe corrosion of friction pairs and would be discarded due to environmental concern. Carbon-based nanomaterials

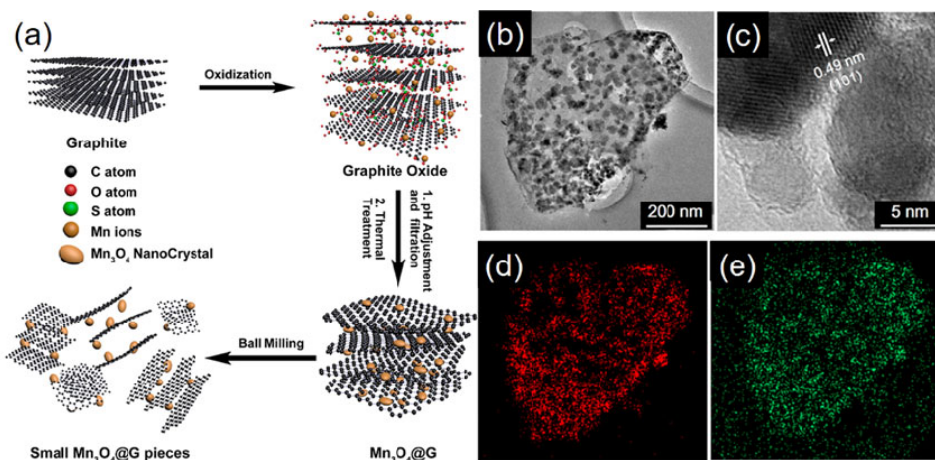


Fig. 4 (a) Synthesis schematic of Mn_3O_4 @G nanocomposites by an *in situ* green method, (b, c) TEM images of the nanocomposites, element mapping of (d) Mn and (e) O. Reproduced with permission from Ref. [81], © American Chemical Society, 2019.

offer both good tribological properties and environment-friendly performance for a sustainable future. Especially, graphene and graphene-based nanocomposites exhibit outstanding friction-reduction and wear-resistance properties and are also regarded as potential candidates for green and effective lubricant additives.

3 Dispersion stability of nanolubricant additives

Nanoparticles have high values of specific surface area, which leads to the increase of intermolecular forces, thereby exacerbating the aggregation of nanoparticles. Many research efforts have been directed towards producing stable nanolubricant additives, but even after several decades of research, the full potential of employing nanoparticles as lubricant additives has been severely limited because of the poor interfacial interaction between the additives and lubricants. Hence, it is necessary and instructive to analyze the factors affecting the dispersion stability and to explore the methods for enhancing the dispersion stability of nanoadditives.

3.1 Affecting factors

The natural characteristics of nanoparticles such as size, shape, and concentration in lubricants have great impacts on the dispersion stability. As known, nanoparticles with large specific surface areas and high surface activities are prone to forming intimate contact with each other, resulting in the aggregation of nanoparticles and weakening the dispersion stability. According to the Stokes law [108], $v = \frac{2r^2g(\rho_1 - \rho_2)}{9\eta}$ (v represents the sedimentation velocity, r represents radius of nanoparticles, g means gravitational acceleration, ρ_1 means density of nanoparticles, ρ_2 represents the density of the base fluid, and η means viscosity of base fluid), is established to illustrate the affecting factors of sedimentation velocity. According to the Stokes law, the sedimentation velocity of nanoparticles is proportional to the square of the radius. Thus, the decrease of radius results in slow sedimentation velocity and enhanced dispersion stability. Choi et

al. [109] confirmed that smaller Ag nanoparticles (7 nm) showed better dispersion stability than larger ones (50 nm). However, with the decrease in particle size, the surface energy of nanoparticles increases, and the aggregation intensifies. Therefore, using small nanoparticles and preventing aggregation should be taken into consideration simultaneously. In addition, the effect of shape on dispersion stability is related to the aspect ratio (length/diameter) of nanoparticles. Nanoparticles with high aspect ratio are more likely to agglomerate, which means spherical-shaped nanoparticles exhibit better dispersion stability than those with rod and tube-shaped ones [110]. Xing et al. [111] confirmed that fullerene C60 nanoparticles exhibited better dispersion stability than CNTs, which was attributed to the low aspect ratio of C60. Furthermore, the concentration of nanoparticles is another influential factor. High concentration makes nanoparticles closer to each other and increases the Van Der Waals attraction forces, so nanoparticles are easy to agglomerate at high concentrations. Kotia et al. [112] conducted experiments on dispersion stability of Al₂O₃ nanoparticles in gear oil at various concentrations (0.5 vol%, 1 vol%, 1.5 vol%, 2 vol%) and discovered that the suspension with the lowest concentration (0.5 vol%) was the most stable over time. The characteristic of base lubricants, such as pH value also plays an essential role in the dispersion stability of the suspension. Recent researches have confirmed that an optimal pH value can prevent the aggregation of nanoparticles, thereby enhancing the dispersion stability. For instance, Zhu et al. [113] revealed that when the pH value was 9–9.5, CaCO₃ nanoparticles exhibited the best stability in distilled water. As known, when the pH value is near isoelectric point (IEP) of nanoparticles, the agglomeration is intensified, thereby leading to poor dispersion stability. The research carried out by Chang et al. [36] confirmed that the optimal pH value of TiO₂ nanofluid (pH 7) was departed from IEP (pH 4).

3.2 Methods to improve dispersion stability

As known, the incorporation of solid nanoparticles into a liquid lubricant always results in difficulties uniformly disperse. There is a sizable volume of

literature reported on the dispersion techniques such as physical methods, chemical methods, and self-dispersed methods. These dispersion methods are introduced here, and typical results on the dispersion in lubricants by these methods are demonstrated in Table 2.

3.2.1 Physical methods

There are many physical suspension processes such as mechanical stirring, ultrasonication, ball milling, and high-pressure homogenization. Molsheh et al. [114] found that the dispersion stability of three different nanoparticles (MoS₂, WS₂, hexagonal boron nitride (h-BN)) in CIMFLO 20 with ultrasonic treatment was better than that with mechanical shaking and stirring. The ultrasonic time is an essential factor that should be taken into consideration when preparing a stable suspension with the assistance of ultrasonication. Nanolubricant additives exhibit the best dispersion

stability only after ultrasonication for an optimum time. Kumar et al. [68] compared the stability of PTFE particles in base lubricant with various ultrasonic time (30, 40, 60, and 90 min). The results revealed that the optimal ultrasonic time was 60 min, and the suspension remained stable for 15 days shown in Fig. 5(a). Similar research is conducted by Sharif et al. [115]. They found that ultrasonication has a significant effect on reducing particle size, thereby enhancing the dispersion stability of Al₂O₃ aqueous fluids, as shown in Fig. 5(b). In addition, ball milling and high-pressure homogenization are also used in the preparation of lubricants. Ball milling is more efficient in breaking up the aggregated particles than ultrasonication. Ettefaghi et al. [116] found that copper oxide nanoparticles in SAE 20W50 with planetary ball mill method had less precipitation after 720 h than that with ultrasonic treatment.

Table 2 The dispersion stability of various nanolubricants.

Dispersion	Additives	Lubricants	Dispersion Processes	Stabilities	References
Physical methods	PTFE/ MoS ₂ Nanolayer coated carbon spheres (CS-MoS ₂)/ MoS ₂ , WS ₂	150 N/ 5W30/ PAG	ultrasonication	For 15 days/ 14 days/ 14 days	[68, 117, 118]
	CuO	20W50/ Engine oil	Ball milling	For 30 days/ 5 days	[116, 119]
	hBN/ CNTs/ CuO, TiO ₂	15W40/ transformer oil/ water	High shear homogenization	For 14 days/ 1 day/ 8 days, 21 days	[120–122]
Chemical methods	SWCNHs/ CuO/ graphene	Water/ gear oil/ PAO4	Using surfactants (SDS/OA/Span80)	For 39 days/ 30 days/ 28 days	[121, 123, 124]
	ZrO ₂ / Al ₂ O ₃ / graphite	machine oil/ Naphthenic oil	Using silane coupling agent (KH560/ KH570)	For 30 days/ 20 days/ 60 days	[35, 39, 125]
	SiO ₂ / Ag/ Cu@CNTs/ WS ₂ / MoS ₂	Liquid paraffin/ PAO/ rapeseed oil/ PAO6/ PAO10	Using surface modification agents (OA/TBBT, C12/ PDA/ oley amine/ NOM)	For 30 days/ 90 days/ 10 days/ 180 days/ 7 days	[126–130]
Self-dispersed methods	Crumpled Graphene ball/ heRGO/ SRGO	PAO4/ PAO6/ Hydraulic oil	Ultrasonication/ stirring	For about 1 day/ 4 days/ 10 days	[131–133]
	ZnO@G/ WS ₂ @G/ CeO ₂ @G/ Ag@rGO	Ester oil/ PAO4/ liquid paraffin/ liquid paraffin	Ultrasonication	For more than 5 days/ 7 days/ 1 day/ 60 days	[79, 134–136]

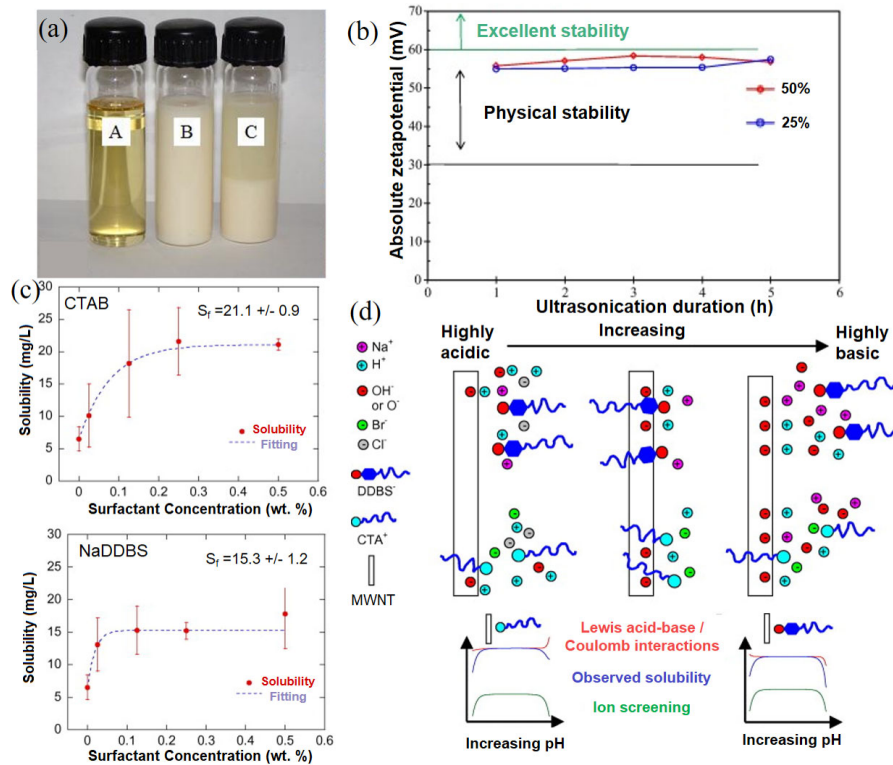


Fig. 5 (a) PTFE nanolubricants after 7 days of preparation (A-base oil, B-PTFE nanolubricant with 1-hour ultrasonication, C-PTFE nanolubricant with 30-min ultrasonication). Reproduced with permission from Ref. [68], © Elsevier, 2013. (b) Effect of ultrasonication on the dispersion stability of Al_2O_3 . Reproduced with permission from Ref. [115], © Elsevier, 2015. (c) Nanotube dispersibility with varying surfactant concentrations for CTAB, NaDDBS, and (d) schematic representation of the effect of surfactants. Reproduced with permission from Ref. [137], © Elsevier, 2011.

Moreover, high-pressure homogenization is effective in enhancing dispersion stability and it is simple to operate. Wan et al. [120] dispersed h-BN nanoparticles into SAE 15W40 with the assistance of high shear homogenizer. This work indicated that the suspension remained stable for more than 14 days. Other researches carried out by Fontes et al. [121] and Fedele et al. [122] have also confirmed that high shear homogenization was a useful method to prepare a stable and uniform dispersion of nanoparticles. In general, several physical methods above are always synthetically used to ensure the stability and uniformity of the nanoparticles in base lubricants.

Moreover, the use of surfactants is important to enhance the dispersion stability of nanoparticles during physical processes. Surfactant molecules adsorb onto the surface of nanoparticles and form a micelle-like structure to provide a physical “cushion” between colliding particles, thereby reducing the interaction of nanoparticles. There are four typical

classes of surfactants: anionic (with negatively charged head groups), cationic (with positively charged head groups), non-ionic (without charged groups in its head or neutral), and amphoteric (with zwitterionic head groups) [138]. The effect of surfactants: sodium 4-dodecylbenzenesulfonate (NaDDBS), hexadecyl(trimethyl)azanium bromide (CTAB), oleic acid, sodium dodecyl sulfate (SDS), and span80 on the improvement of dispersion stability was investigated in the following experiments. Clark et al. [137] investigated the effect of NaDDBS and CTAB as surfactants, as shown in Fig. 5(c). Surfactant molecules adsorbed on the surface of carbon nanotubes, which reinforced the interaction between nanoparticles and water, thereby inhibiting the aggregation of nanoparticles and significantly improving the dispersion stability. Ali et al. [139] dispersed Al_2O_3 and TiO_2 nanoparticles into engine oil 5W30, in which oleic acid was used as surfactants. According to the results of dynamic light scattering,

the peak diameters of these two nanoparticles had a little increase, which meant only a slight agglomeration occurred in the dispersion. Ali et al. [140] also confirmed the dispersion of $\text{Al}_2\text{O}_3/\text{TiO}_2$ nanocomposites remained stable for 14 days with the addition of oleic acid as surfactants. Another study carried out by Kole and Dey [123] indicated that CuO nanoparticles remained stable for 30 days in gear oil with the assistance of oleic acid as surfactants. SDS was used as surfactants to prepare the water-based suspension of single-wall carbon nanohorns (SWCNHs) in the research carried out by Laura et al. [121]. Zheng et al. [124] added span80 when preparing the dispersion of graphene, and the results revealed that there was no sedimentation in dispersion within 28 days after preparation. Huang et al. [141] dispersed graphene into liquid paraffin with the assistance of span 80. The results revealed that the addition of span 80 improved the stability of suspensions in comparison with the suspensions without surfactants.

3.2.2 Chemical methods

Chemical methods mean using chemical agents to chemically modify the surfaces of nanoparticles for improving dispersion stability. Surface modification agents, including organic modification agents and silane coupling agents, mainly deal with the stabilization problem of inorganic nanoparticles in the base oil. The organic compounds used as modification agents usually comprise polar groups and long alkyl chains that can chemically adsorb onto the inorganic nanoparticles, which enables inorganic nanoparticles to be uniformly dispersed in an organic solvent. In addition, silane coupling agents, which have 1–3 alkoxy groups and 3–1 organic functional groups, are used to modify nanoparticle surfaces. With the assistance of surface modifiers, aggregation of nanoparticles is inhibited and nanolubricants can remain stable for a long time. Metallic particles with chemical modification exhibit enhanced dispersion stability in comparison with untreated particles. Xiong et al. [142] used tetradecyl hydroxamic acid as a modifier and synthesized oil-soluble Cu nanoparticles. The results showed that no signs of aggregation were found in lubricants. Sánchez-

López et al. [27] prepared tetrahydrofuran-modified Pd nanoparticles and toluene-modified Au nanoparticles. The research confirmed that both of them presented good dispersion stability. Peng et al. [128] used oleic acid to modify SiO_2 nanoparticles and revealed that the suspension remained stable for more than 30 days. Ma et al. [39] modified ZrO_2 nanoparticles with γ -(2,3-epoxypropoxy) propyltrimethoxysilane (KH560) and found that the average diameter of nanoparticles in the suspension obviously decreased and there was no aggregation. Wu et al. [130] modified MoS_2 nanosheets with n-Octadecyl mercaptan (NOM) and found that the suspension remained stable for 7 days as shown in Fig. 6(a). Other carbon materials such as carbon nanotubes and graphene nanosheets can also be dispersed uniformly and stably with surface modification. For instance, Chen et al. [143] modified carbon nanotubes by esterification reaction with fatty acid and achieved good dispersion stability of carbon nanotubes in liquid paraffin. Wang et al. [129] synthesized Cu@CNT composites with polydopamine (PDA) as a modifier and revealed the excellent dispersion stability of the nanocomposite (stable for 7 days) in comparison with carbon nanotubes (stable for 2 days), as shown in Fig. 6(b). In addition, the surface modification of graphene has been widely investigated. Hydrothermal-prepared graphene oxide as the precursor of graphene contains a large quantity of oxygen groups such as hydroxyl and carboxyl groups. These oxygen groups can be replaced by other functional groups during the surface modification process. What is more, these functional groups are chemically adsorbed on graphene after reduction, therefore, the dispersion stability can also be improved. Oleic acid, octadecyl amine, primary amine, amino acid, and amino siloxane can be used as the modifier of graphene [144–146]. Zhang et al. [146] synthesized graphene nanosheets with outstanding dispersion stability via modification of oleic acid at 80 °C for 3 h. Han et al. [147] synthesized alkyl-functionalized graphene oxide and the results confirmed that the dispersibility of modified graphene oxide in poly alpha-olefin (PAO)4 was reinforced in comparison with that of unmodified graphene oxide, as shown in Fig. 7.

Although nanoparticles with surface modification have significant improvement on dispersion stability, the introduction of atoms and functional groups may destroy the structure of nanoparticles and conceal the nature characteristics of nanoparticles. Therefore, it is of great importance to enhance the dispersion stability of nanoparticles and maintain the nature characteristics simultaneously.

3.2.3 Self-dispersed methods

Physical suspension methods are green, simple, and

economical, and widely used in the previous research, but nanoparticles with physical treatment are prone to secondary agglomerating and being unstable in lubricants. Although chemical methods can significantly enhance the dispersion stability, the addition of chemical agents reduces the natural characteristics of nano additives and affects the tribological properties of nanolubricants at the same time. Therefore, it is necessary to develop self-dispersed methods to prepare a stable and uniform suspension. Current studies have found that the dispersion

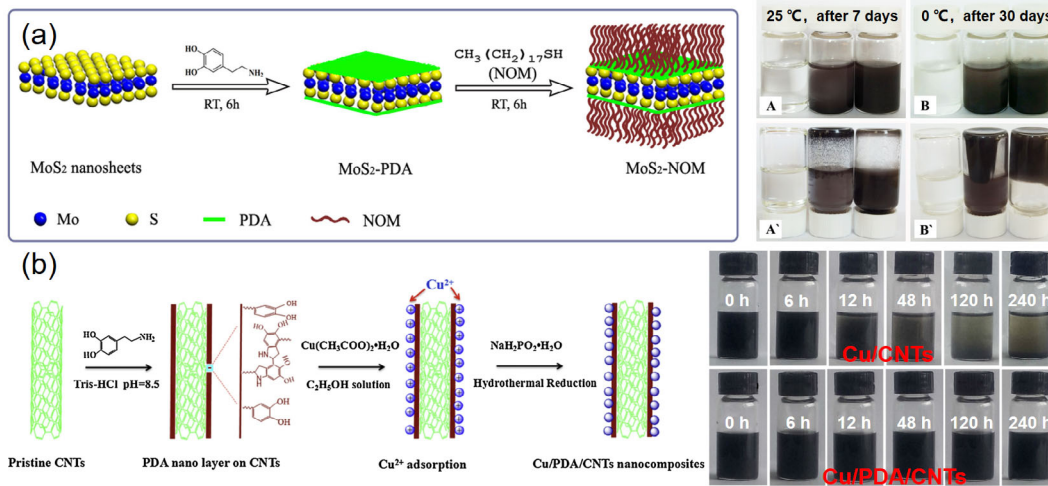


Fig. 6 (a) Preparation and dispersion stability of NOM modified MoS₂ nanosheet. Reproduced with permission from Ref. [130], © American Chemical Society, 2018. (b) Preparation and dispersion stability of copper/carbon nanotube composite. Reproduced with permission from Ref. [129], © Elsevier, 2018.

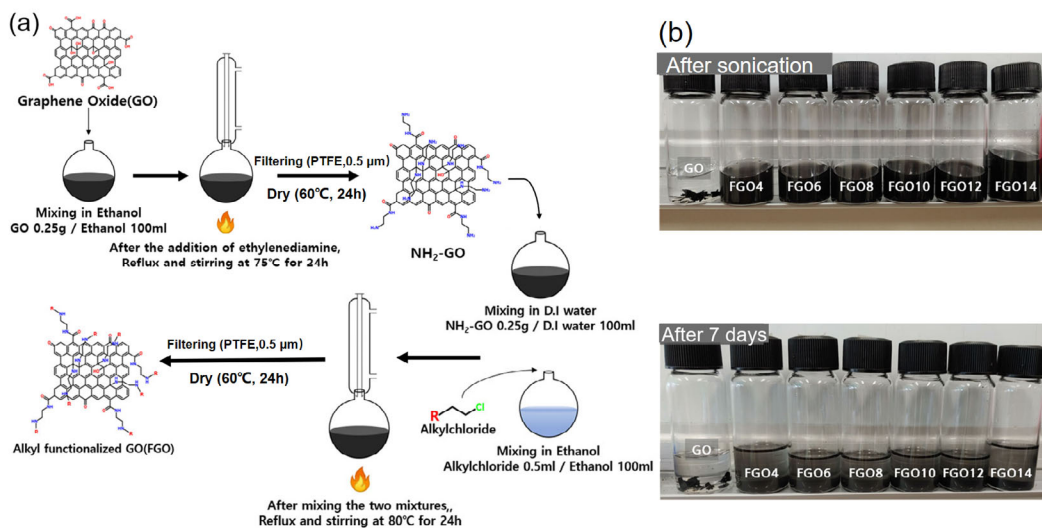


Fig. 7 (a) Preparation and (b) dispersion stability of alkyl-functionalized graphene oxide. Reproduced with permission from Ref. [147], © John Wiley and Sons, 2020.

stability of nanoparticles can be enhanced via the structure regulation of nanoparticles. Dou et al. [131] prepared crumpled graphene balls by capillary compression is rapidly evaporating aerosol droplets of GO sheets. Furthermore, they compared the dispersion stability of four carbon additives (graphite, reduced graphene oxide, carbon black, and crumpled graphene balls) in PAO4. The results showed that after 20 h, obvious sedimentation was observed in the other three suspensions except for crumpled graphene balls suspension, which confirmed that crumpled graphene balls had good self-dispersion properties. It is because the additives with crumpled and spherical shape can reduce the attraction between particles and prevent them from restacking, thereby inhibiting aggregation and enhancing dispersion stability. In addition, highly exfoliated graphene exhibits better dispersion stability than multilayer graphene, because of the high value of the specific surface area of highly exfoliated graphene which increases the interaction between graphene and lubricant molecules, enhances the steric hindrance, and prevents the restacking of graphene. Li et al. [132] exfoliated graphene with the assistance of KOH and investigated the dispersion stability. According to the research, the specific surface area (SSA) could be controlled via adjusting the weight ratio of KOH and GO. They also found that highly

exfoliated reduced graphene oxide (heRGO) suspension remained stable for more than 4 days while obvious separation appeared in the suspension of graphene prepared without the assistance of KOH (tRGO) only after 2 days, which indicated that heRGO processed a more excellent self-dispersion characteristic in comparison with tRGO. The higher SSA value of heRGO ($829.5 \text{ m}^2/\text{g}$) than that of tRGO ($384.5 \text{ m}^2/\text{g}$) explained the superior dispersion stability. Zhao et al. [133] further prepared superhigh-exfoliated reduced graphene oxide (SRGO) and conducted tribological experiments on it, as shown in Fig. 8. The SSA of SRGO reached $1,665 \text{ m}^2/\text{g}$ which was over twice than that of above graphene. The results revealed that after 10 days, SRGO suspension was still stable while apparent sediment appeared in the dispersion of other graphene nanosheets. According to the above three types of research, structure plays an essential role in dispersion stability. The evolution of the chemical structure of nanoparticles can also have a significant improvement in the dispersion stability. Wang et al. [79] revealed that Ag@graphene with laser irradiation (L-Ag@rGO) exhibited more excellent self-dispersed properties than Ag@GO. The results also showed that the suspension of L-Ag@rGO remained stable for 60 days, while Ag@GO dispersion remained stable only for 30 days, as shown in Fig. 9. The research confirmed that the removal of oxygen

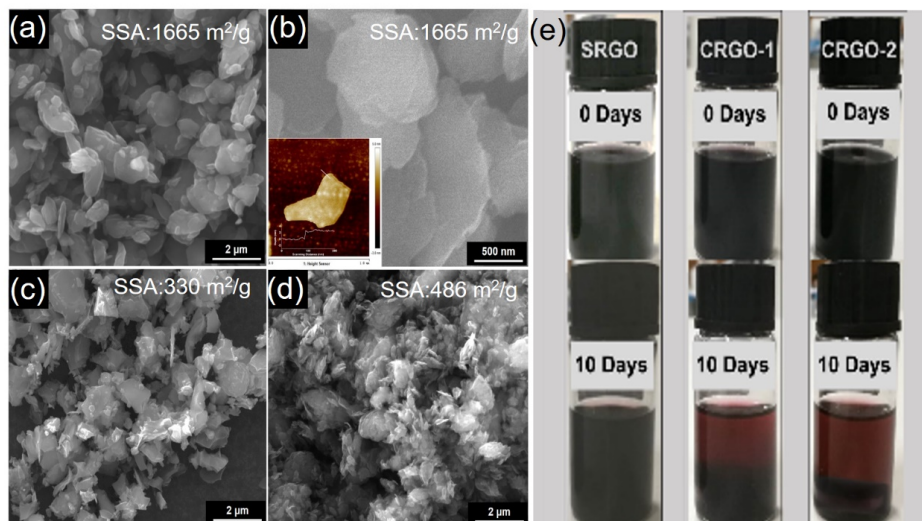


Fig. 8 SEM morphology images of (a, b) SRGO, (c) CRGO-1, and (d) CRGO-2. The inset of (b) is an AFM image of the SRGO nanosheets and the height profile is collected along the right line shown in the image. (e) Dispersion stability of nanolubricants with different graphene. Reproduced with permission from Ref. [133], © Elsevier, 2020.

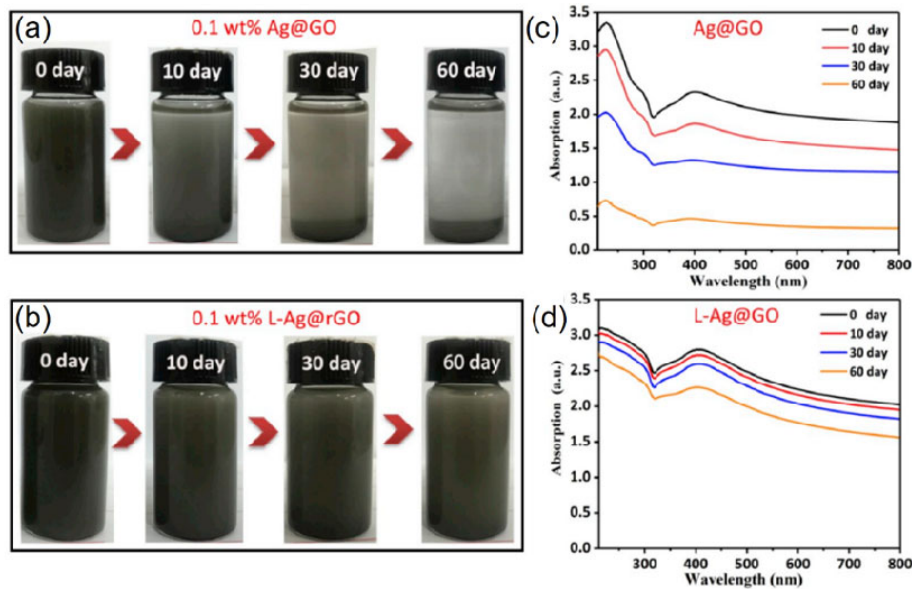


Fig. 9 Dispersion stability of (a) Ag@GO suspension and (b) L-Ag@rGO suspension; UV-vis absorption spectra of (c) Ag@GO and (d) L-Ag@rGO particles in a base oil for different static times. Reproduced with permission from Ref. [79], © Elsevier, 2020.

in graphene changed chemical structure of nanoparticles which improved the dispersion stability. In addition, the nanoparticles decorated on the surface of nanocomposites can significantly improve dispersion stability as well. Song et al. [76] prepared $\text{Fe}_2\text{O}_3@\text{G}$ nanolubricant additives and it is found that the agglomeration of the graphene nanosheets was prevented. And Zhao et al. [81] demonstrated that Mn_3O_4 nanoparticles loaded on the graphene surfaces obviously improved the dispersion stability because the nanoparticles can reduce the intimate contact areas between the nanoadditives and inhibit graphene agglomeration. Therefore, by the structure regulation of nanoparticles, the dispersion characteristics of nanoadditives in lubricating oil can be improved efficiently. It is of great significance to optimize the dispersion stability of nanolubricant additives by self-dispersed methods and to further study their lubrication performances and mechanisms.

4 Lubrication mechanisms of nanolubricant additives

The lubrication mechanisms of nanoparticles can be briefly concluded into five aspects: formation of tribofilm, rolling bearing effect, the transformation of microstructure, synergistic effect, and surface

repairing effect. Table 3 shows the lubrication mechanisms of various nanolubricant additives.

4.1 Formation of tribofilm

Because of the high values of specific surface area and surface energy, nanoparticles are easy to form a protective film on the contact surfaces by adsorption or chemical reactions, as shown in Fig. 10. The formation of tribofilm can avoid direct metal-to-metal contacts and play an important role in lubrication. The polarity of molecules significantly influences the film formation. For instance, an enrichment effect in the Hertz contact region was observed when dispersing polar additive molecules into a nonpolar base oil, which can be explained by the interaction between polar additive molecules and the steel surface. However, there was no enrichment effect for nonpolar molecules dispersed into the nonpolar base oil and polar molecules dispersed into polar base oil [148]. Nanolubricant additives with low chemical activity such as copper, silver, and graphene always form a physical adsorption tribofilm. Desanker et al. [149] confirmed the physical adsorption film which was formed by deposited silver nanoparticles via a scanning electron microscope (SEM) and energy dispersive spectrometer (EDS) analyses. Apart from physical adsorption film, nanoparticles containing

Table 3 Lubrication mechanisms of nanolubricant additives.

Type	Additives	Lubrication mechanisms
Nanometal-based additive	Cu [23, 25, 150]	Formation of tribofilm; rolling bearing effect; surface repairing effect
	Ag [21, 24]	Formation of tribofilm, synergistic effect
	Ni [29, 151]	Formation of tribofilm; surface repairing effect
	Pd [27, 28]	Formation of tribofilm
	CuO [152, 153]	Tribofilm formation; rolling bearing effect; surface repairing effect
	Al ₂ O ₃ [35]	Formation of tribofilm; rolling bearing effect
	ZnO [33, 154]	Tribofilm formation; surface repairing effect
	TiO ₂ [155–157]	Formation of tribofilm; rolling bearing effect; surface repairing effect
	MoS ₂ [158, 159]	Tribofilm formation; surface repairing effect
	WS ₂ [160, 161]	Formation of tribofilm; rolling bearing effect
	LaF ₃ [53, 54]	Tribofilm formation
CaCO ₃ [52]	Formation of tribofilm	
CeBO ₃ [162]	Formation of tribofilm	
Nanocarbon-based additive	Graphene [163, 164]	Tribofilm formation; transformation of microstructure
	CNT [94]	Tribofilm formation; rolling bearing effect; transformation of microstructure
	Diamond [91]	Rolling bearing effect
	PTFE [68]	Formation of tribofilm
Nanocomposite-based additive	Cu@SiO ₂ [72]	Tribofilm formation, surface repairing effect
	Al ₂ O ₃ @SiO ₂ [165]	Synergistic effect
	Cu@GO [80]	Synergistic effect
	Au@GO [166]	Synergistic effect
	Mn ₃ O ₄ @G [81]	Synergistic effect
	GNS@MoS ₂ [75]	Synergistic effect
	SOCNTs@MoS ₂ [167]	Formation of tribofilm; synergistic effect
Co(ReO ₄) ₂ @MoS ₂ [168]	Tribofilm formation	

polar atoms are capable to form a more stable chemical tribofilm which is achieved by tribochemistry reaction during the friction process. Ratoi et al. [169] analyzed the components of the tribofilm formed by WS₂. They revealed that the tribofilm could be mainly divided into four layers: the top layer consisted of exfoliated WS₂ nanoparticles; the second layer contained WS₂, WO₃, iron oxide, and sulfide, Fe and W; the third layer included WO₃, Fe and W; and the bottom layer consisted of Fe and W. Chen et al. [162] investigated the tribological properties of CeBO₃ nanoparticles and studied the lubrication mechanism. The research showed that the formation of tribofilm consisted of B₂O₃, CeO₂, and FeO₃ as the main mechanism, which explained

the outstanding antifriction and antiwear performance. The lubrication mechanism of CaCO₃ was also studied by Zhang et al. [52]. They indicated the formation of tribofilm containing CaCO₃, CaO, Fe₂O₃, and some organic compounds. Kumar et al. [69] found that the excellent tribological properties of PTFE were attributed to the formation of tribofilm of FeF₂ on rubbing surfaces.

4.2 Rolling bearing effect

Nanoparticles with spherical shapes can roll between the asperities of friction surfaces, which transforms sliding friction to rolling friction at a micro-area interface, as shown in Fig. 11. Sia et al. [170] found

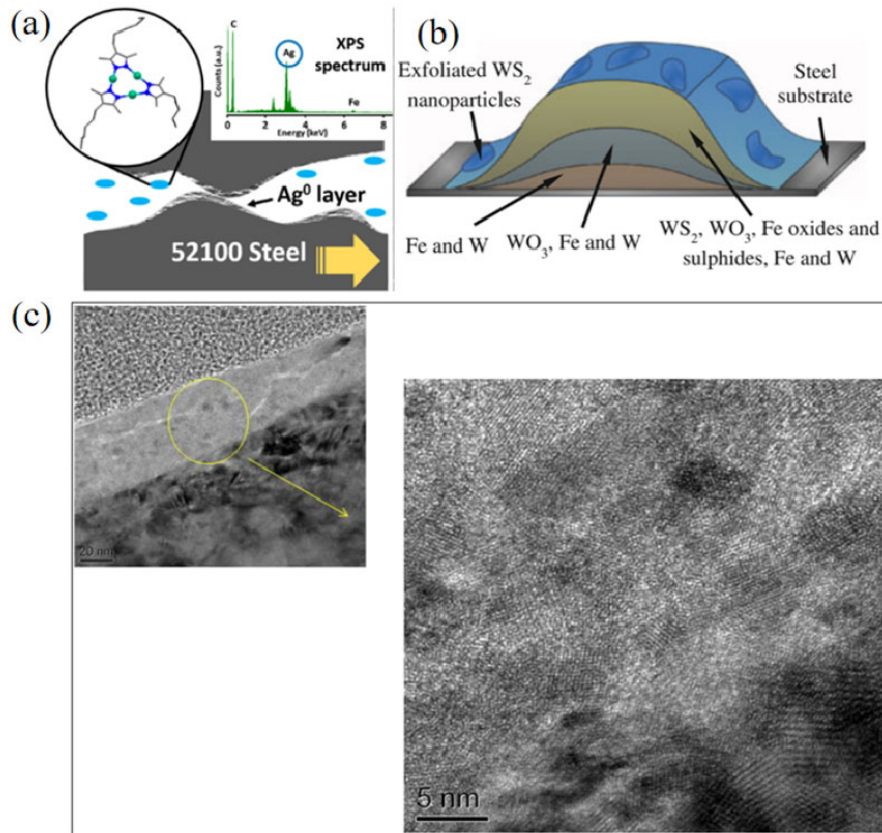


Fig. 10 (a) Model of physical adsorption film. Reproduced with permission from Ref. [149], © American Chemical Society, 2016. (b) Model of WS_2 chemical tribofilm. Reproduced with permission from Ref. [169], © Springer Nature, 2013. (c) SEM micrograph of MoS_2 tribofilm. Reproduced with permission from Ref. [171], © John Wiley and Sons, 2016.

that SiO_2 nanoparticles acted as rolling bearing during friction and exhibited friction-reduction and wear-resistance properties. Rapoport et al. [160] revealed that fullerene-like WS_2 nanoparticles obviously enhanced the tribological properties, which could be explained by the slow release of WS_2 nanoparticles from the matrix and their rolling effects on rubbing surfaces. Kim et al. [91] indicated that the friction-reduction properties of nanodiamond were possibly owing to its rolling effect. In addition, polymer nanoparticles can form a tribofilm on the contact surfaces and have the same function as ball bearing at low load during friction. However, when the applied load is high, the rolling bearing effect is prone to failure [93]. Sui et al. [172] investigated the tribological properties of hairy silica nanoparticles and it was found that the outstanding friction-reduction and wear-resistance performances were partly attributed to the rolling bearing effect. The research also implied that the rolling bearing effect

was enhanced with the increase of size. Bao et al. [173] found that film thickness is an important factor affecting the lubrication mechanisms and they indicated that the rolling bearing effect was the dominant lubrication mechanism when the film thickness was an approach to the particle size. However, when the film is thin, nanoparticles tend

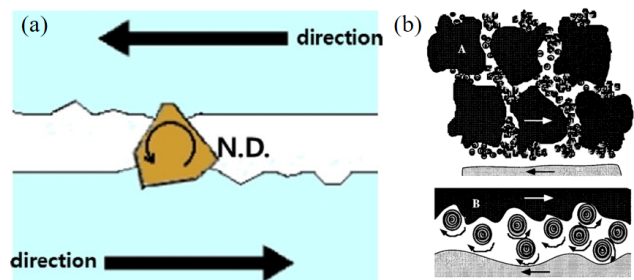


Fig. 11 (a) Rolling bearing effect of nanodiamond. Reproduced with permission from Ref. [91], © Elsevier, 2013. (b) Rolling bearing effect of fullerene-like WS_2 nanoparticles. Reproduced with permission from Ref. [160], © American Chemical Society, 2001.

to form a transfer film.

4.3 Transformation of microstructure

The microstructure is an important nature characteristic of nanoparticles such as carbon nanotubes, graphene, and nanodiamond. High pressure and heat during the friction process may destroy the original microstructure and produce a new microstructure. And the evolution of microstructure results in the variation of tribological performance. The microstructure of nanocarbon materials tends to be ordered during the friction process, thereby enhancing the antifriction and antiwear properties [174,175]. Joly-Pottuz et al. [92] revealed the transformation of fullerene to graphene during the tribological experiments and indicated that with the change of microstructure, a good lubrication effect was obtained. Zhang et al. [94] found long carbon nanotubes tended to be shortened when the applied load was low. The short nanotubes are easy to enter the contact surfaces to form a protective film, meanwhile, the intertwining of nanotubes is inhibited and the rolling effect is enhanced with the reduction of length. However, at high applied load, graphene-like components with lamellar structure are formed from original nanotubes, and excellent tribological properties are achieved, as

shown in Fig. 12(a). According to the research carried out by Zhao et al. [164], highly exfoliated graphene tended to overlap and order under pressure and shearing forces, and then formed a stable and lamellar adsorption film parallel to the sliding direction on the contact surfaces, thereby significantly improving the tribological properties, as shown in Fig. 12(b). However, the frictional trend of originally oriented graphene is quite opposite. The graphene layers which were integrated and oriented originally were damaged during friction and further scratched the friction interfaces. After long-time friction, the microstructure of the graphene nanosheets becomes disordered, which leads to lubrication failure [95, 176]. Therefore, the transformation of microstructure plays an important role in tribological properties, especially for nanocarbon-based additives.

4.4 Synergistic effect

Nanolubricant additives are not isolated in lubricating oil or grease, and they often cooperate with other additives, lubricating oils, and modified friction surfaces to achieve a synergistic effect. Ghaednia et al. [24] indicated that the excellent tribological properties of silver nanoparticles were attributed to the synergistic effect between silver nanoparticles and base lubricants. Jiao et al. [165] revealed that

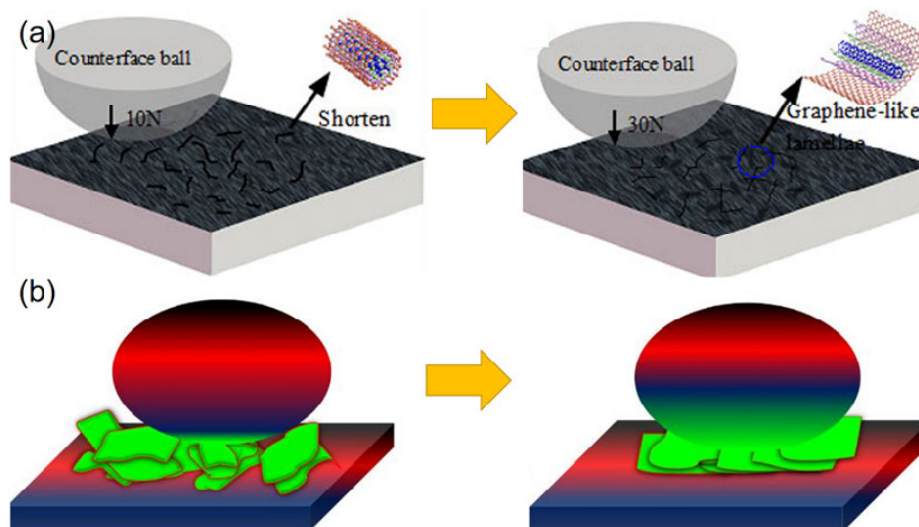


Fig. 12 (a) Transformation of CNTs to graphene under friction. Reproduced with permission from Ref. [94], © Elsevier, 2014. (b) The transformation of high-exfoliated graphene to graphite under friction. Reproduced with permission from Ref. [164], © Elsevier, 2018.

$\text{Al}_2\text{O}_3@\text{SiO}_2$ nanocomposites had superior tribological properties to either Al_2O_3 or SiO_2 , which was because of the synergistic effect of these nanocomposites. Apart from nanocomposite-based lubricant additives, a synergistic effect can also be observed between nanolubricant additives and modified surfaces by certain surface treatments such as nitriding, coating and texturing [177–179]. Nanocomposite can enhance both dispersion stability and tribological properties. Further analyses have confirmed that the graphene nanosheets and nanoparticles have a synergistic effect by forming a composite-based tribofilm on the friction interfaces as shown in Fig. 13. The particles anchored on the graphene layers sometimes have the rolling bearing effect to further improve antifriction and antiwear performance as well. The synergistic effect of $\text{Cu}@r\text{GO}$ nanoparticles was confirmed in the research carried out by Zhang et al. [180]. Meng et al. [166] revealed the excellent tribological properties of $\text{Au}@r\text{GO}$ nanocomposites and the lubrication

mechanisms. They indicated that the $\text{Au}@r\text{GO}$ nanocomposites deposited on the contact surfaces and formed a physical protective film. Meanwhile, the nanocomposites also absorbed oil molecules to provide a good boundary lubricating state. Moreover, the released Au nanoparticles and ruptured or deformed GO fragments exhibited a synergistic lubricating effect simultaneously. Zhao et al. [81] studied $\text{Mn}_3\text{O}_4@\text{graphene}$ nanocomposites with a sandwich-like nanostructure and revealed that graphene nanosheets were easy to slide between layers under friction, and Mn_3O_4 nanoparticles rolled at meantime to further reduce friction and wear. A “slide-roll” physical lubrication model was proposed in the research.

4.5 Surface repairing effect

The rubbing surfaces are generally smooth, of which the asperities can contact with each other directly

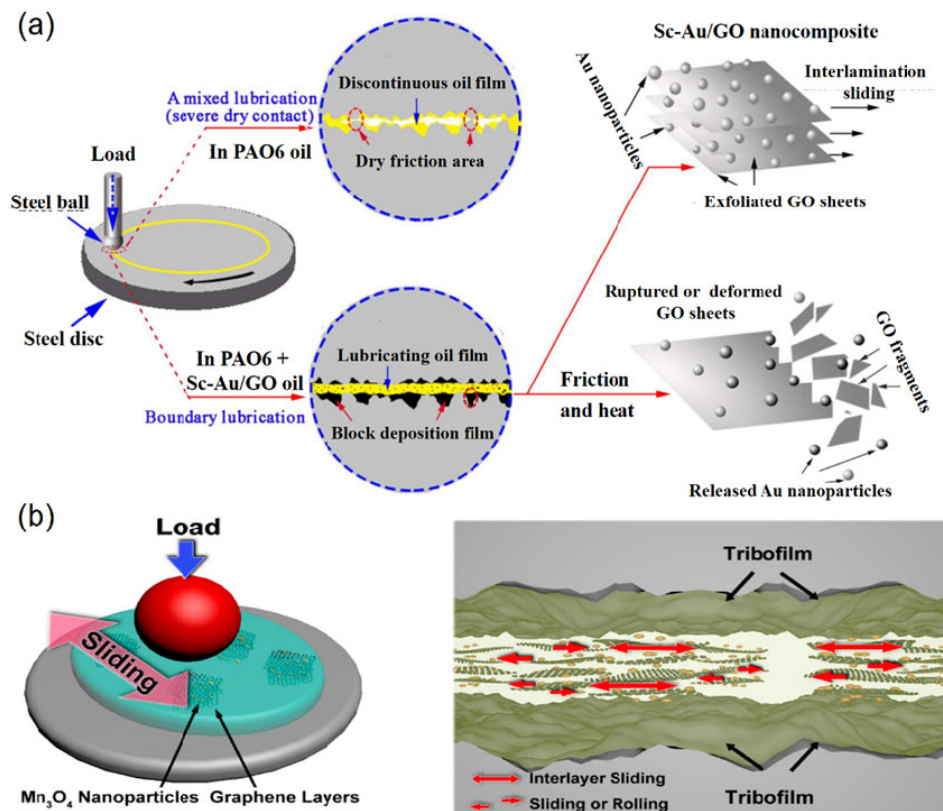


Fig. 13 (a) Synergistic effect model of $\text{Au}@r\text{GO}$ nanocomposites. Reproduced with permission from Ref. [166], © American Chemical Society, 2017. (b) The synergistic effect model of $\text{Mn}_3\text{O}_4@\text{Graphene}$ nanocomposites. Reproduced with permission from Ref. [81], © American Chemical Society, 2019.

at boundary lubrication, thereby leading to high friction coefficient and wear rate. Nanoparticles can repair the friction-induced surface defects and improve the tribological properties, as shown in Fig. 14. Via surface repairing effect, the roughness of friction surfaces reduces considerably and the tribological properties are enhanced remarkably. Ali et al. [139] investigated the antifriction and antiwear properties of Al_2O_3 and TiO_2 nanoparticles in engine oil. The results indicated that the high compressive pressure and temperature during friction promoted the sintering of nanoparticles on the surfaces and mended the scars and grooves, which resulted in the improvement of tribological properties. Çelik et al. [181] used SEM and EDS to analyze the characteristics of worn surfaces and found that h-BN nanoparticles completely filled the asperities by mending effect, thereby reducing the roughness of the worn surface and enhancing the antifriction and antiwear properties. The researches carried out by Gulzar et al. [182] revealed the excellent friction-reduction and wear-resistance properties of $\text{TiO}_2@\text{SiO}_2$ nanocomposites. Based on the surface analyses via SEM, EDS, and AFM, they confirmed that the mending and polishing effect of $\text{TiO}_2@\text{SiO}_2$ nanocomposites enhanced the friction surface. The surface repairing effect of nanoparticles is also mentioned in the research carried out by Choi et al. [183]. Deposited copper nanoparticles were detected on the grooves, and no nanoparticles were deposited on the asperities, which meant that copper nanoparticles mended the grooves and smoothed the friction surfaces. The research confirmed the surface repairing effect and led to an outstanding tribological performance. In contrast to the filling

effect of nanoparticles, the asperities of the surfaces can be polished. Chu et al. [184] found that the addition of diamond nanoparticles played an essential role in resisting scuffing. The polishing effect of nanodiamond particles increased the surface hardness and the rubbing surfaces change to be very smooth.

5 Conclusions and outlook

It is of great significance to use nanomaterials as additives in lubricants for energy conservation, emission reduction, and environmental protection. According to the component elements of nanoparticles, there are three categories of nano lubricant additives: nanometal-based, nanocarbon-based, and nanocomposite-based additives, which have been systematically discussed in this review. With physically and/or chemically dispersed methods, a stable dispersion of nano additives in lubricants can be obtained. Moreover, via controlling the structure, nanoparticles can exhibit good self-dispersion properties. The review has also discussed the characteristic of different dispersed methods through contrastive analysis. By adding nano additives in lubricants, the tribological properties of lubricants can be significantly improved. Furthermore, the lubrication mechanisms of lubricant additives include the formation of tribofilm, rolling bearing effect, transformation of microstructure, synergistic, and repairing effects. Finally, to facilitate the use of nanomaterials as lubricant additives, future studies should take into consideration the following:

Firstly, traditional organic and inorganic lubricant additives always contain sulfur and phosphorus

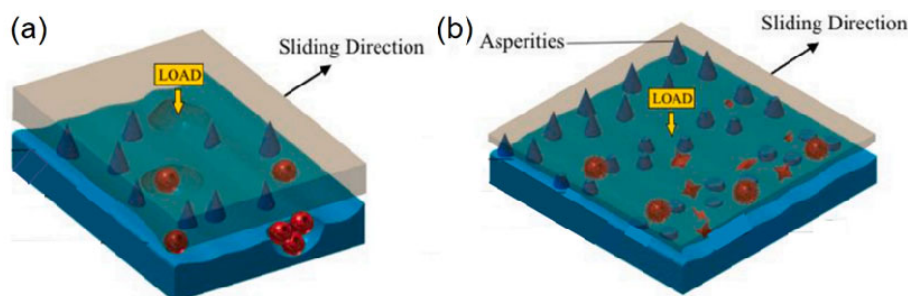


Fig. 14 (a) Model of surface repairing effect: mending effect and (b) polishing effect. Reproduced with permission from Ref. [69], © Elsevier, 2020.

components, which easily releases SAPS and cause environmental pollution. Thus, it is essential to develop green and stable lubrication nanomaterials, and among these materials, nanocarbon-based, especially for graphene and graphene-like nanomaterials are regarded as potential candidates. Secondly, dispersion stability as the premise of practical applications is of great importance. But there are still difficulties in enhancing the dispersion stability of nanolubricant additives. Nanoparticles with physical treatment are prone to reaggregation. Chemical modification may conceal the natural characteristics of nanoparticles and chemical modifiers are prone to be degraded during friction. Therefore, further researches should be conducted to improve dispersion methods. And it seems to be the development trend of self-dispersed methods, which needs no modifiers and displays good dispersion stability. Furthermore, the agglomeration behavior of nanoparticle/lubricant dispersion during the friction process has not been studied yet, because the exploration methods of dispersion stability are mainly from offline processes such as optical microscopes and ultraviolet (UV) spectrophotometry, which cannot reveal the real state of nanoparticles in the lubricant. Therefore, Online exploration of dispersion is urgently needed. Finally, it is very important to study new lubricant additives under extreme friction conditions. With the rapid development of advanced industrial equipment, the work conditions of machinery meet extreme conditions such as high-pressure, high speed, and high temperature. Many high-efficiency lubricant additives will decompose at 150 °C and their flash points are not more than 100 °C. The applications of lubricant additives are still limited to a temperature of 1,000 °C and a load of 3,000 N. Therefore, exploring new lubricant additives with high tribological performance especially under extreme conditions will be the focus of basic researches and applications in future.

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