Friction **11**(5): 647–684 (2023)
https://doi.org/10.1007/s40544-022-0667-9
ISSN 2223-7690
CN 10-1237/TH
Review Article

Nanomaterials for lubricating oil application: A review

Linlin DUAN, Jian LI, Haitao DUAN*
State Key Laboratory of Special Surface Protection Materials and Application Technology, Wuhan Research Institute of Materials Protection, Wuhan 430030, China
Received: 18 March 2022 / Revised: 11 May 2022 / Accepted: 13 June 2022

Abstract: Friction and wear are ubiquitous, from nano-electro-mechanical systems in biomedicine to large-scale integrated electric propulsion in aircraft carriers. Applications of nanomaterials as lubricating oil additives have achieved great advances, which are of great significance to control friction and wear. This review focuses on the applications of nanomaterials in lubricating oil and comprehensively compares their tribological characteristics as lubricating oil additives. Statistical analysis of tribology data is provided and discussed accordingly; moreover, the interaction between nanomaterials and sliding surface, lubricating oil, other additives, and synergistic lubrication in nanocomposites are systematically elaborated. Finally, suggestions for future research on nanomaterials as lubricating oil additives are proposed. Hence, this review will promote a better fundamental understanding of nanomaterials for lubricating oil application and help to achieve the superior design of nanoadditives with outstanding tribological performances.

Keywords: nanomaterial; additive; friction modifier; lubrication; wear

1 Introduction

Friction and wear are everywhere and critical to carbon release. With great friction comes a great demand for energy to overcome it. However, at present, the energy source of industry and transportation is mainly fossil fuels, which generate a considerable part of greenhouse gases emission. On a global scale, 100 million terajoules are annually consumed as a result of tribological contacts, which is contributing to the greenhouse gas emission with 7,000 million tons annually [1–3]. It is a great challenge to the achievement of carbon neutrality on account of the inevitability of friction [3]. Accordingly, governing friction and reducing wear are of great significance in modern technologies and up to now, one of the most effective approaches in the industry is the lubrication by lubricating oil [4, 5], which are usually stable in diverse environment.

Additives in base oil could achieve prominent friction reduction and excellent anti-wear properties in friction pairs [6, 7]. The additive existing could be divided into four types: organic friction modifiers, functional polymers, oil-soluble organic additives, and nanomaterials [5]. As a novel class of materials, nanomaterials have found applicability across the tribology field, and they provide excellent lubrication performance as lubricating oil additives [8, 9]. There has been growing attention to the exploration of nanomaterials as lubricating oil additives in recent years despite a great number of researches have been undertaken over the past decades [10–13]. The number of times cited and publications during 2001–2022 are shown in Fig. 1.

By reviewing several hundreds of papers published by scholars from different groups, we found that plenty of studies has shown remarkable tribological properties improvement in lubricating oil dispersed with different types of nanomaterials. However, each study is based on exclusive conditions, such as sizes and morphologies of nanomaterials, surface functionalization, compatibility, concentrations, test

* Corresponding author: Haitao DUAN, E-mail: duanhaitao@rimp.com.cn

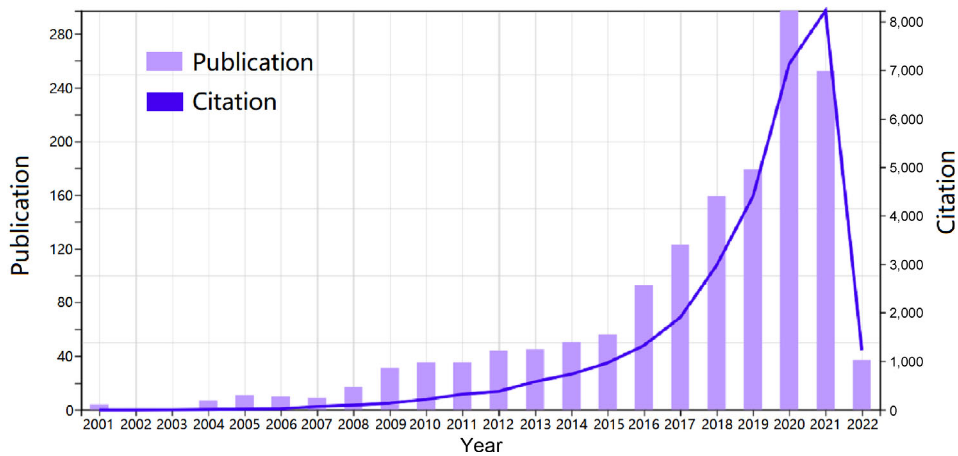

Fig. 1 Numbers of times cited and publications during 2001–2022. The data were compiled from the Web of Science database on March 16, 2022. (The topic words for retrieval are nano, additive, and oil.)

parameters, friction pair, base oil types, etc. For appointed working conditions and base oil, it is still difficult to decide on a suitable nanomaterial additive. In order to overcome the issue mentioned, practically all known nanomaterial additives in lubricating oil are systematically discussed in this review.

This review focuses on the applications of nanomaterials in lubricating oil and the comparisons of tribological characteristics and mechanisms of different nanomaterial additives, highlights the existing problems and prospects of nanomaterials as lubricating oil additives, and aims to provide a recommendation to choose an applicable nanomaterial additive depending on different working conditions.

The structure and contents of this review are presented in Fig. 2. Section 1 opens with the

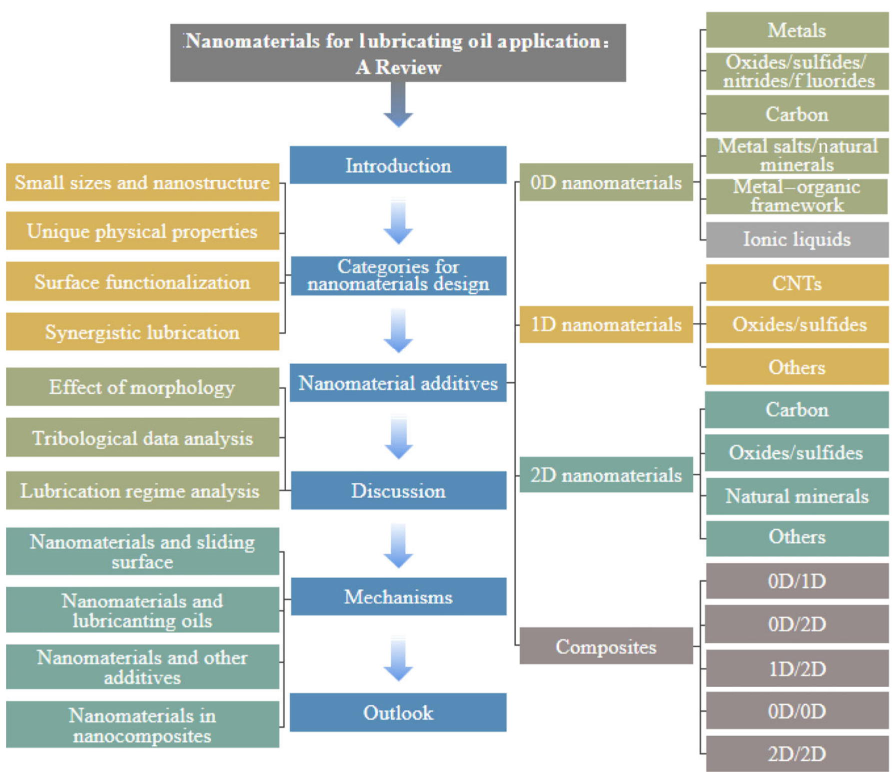

Fig. 2 Structures and contents of this review (Note: Ionic liquids (ILs) do not fall within the scope of nanomaterial in theory, and their existence in this review is explained in Section 1; all the abbreviations are disclosed in the text).

introduction, presenting the background of this paper. Then followed the categories for nanomaterials design as lubricating oil additives. Nanomaterial additives with zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and composites are presented in Section 3. The main classifications of nanomaterial additives with subcategories are also shown in Fig. 2. Sections 4 and 5 are the summary and discussion based on the data of Section 3 and the lubrication mechanisms of nanomaterial additives. Sections 3–5 are the main body of this paper, in which exhaustive analysis and comparison of the entire current experimental data about implementing nanomaterial additives for friction reduction are attempted, and Tables 1–4 and Fig. 12 are given to reveal the details of tribological tests. Tribological properties and lubrication regimes of nanomaterials in different dimensions are also summarized and analysed. Finally, challenges, suggestions, and outlook of nanomaterials application in lubricating oil are briefly summarized. (Note that ionic liquids (ILs) do not fall within the scope of nanomaterial in theory; however, owing to the unique physicochemical properties, oil-soluble ILs have been developed into the new focal and promising additives in lubricating oil. Therefore, the application of ILs in lubricating oil is briefly introduced in Section 3 to facilitate the comparison with nanomaterials.)

2 Categories for nanomaterials design as lubricating oil additives

Undeniably, nanomaterials have become one of the most attractive branches in physics, chemistry, biology, and material science [14, 15]. The evolution of nanomaterials has led to the development of lubricating oil additives. A wide variety of studies have been implemented to investigate the potential of nanomaterials and nanocomposites as lubricating oil additives [16]. What are the original intentions of using nanomaterials as lubricating oil additives? How can design nanomaterials achieve excellent tribological performances? Categories for nanomaterials design are summarized and illustrated in Fig. 3.

1) Small sizes and nanostructure. The characteristic size of nanomaterials in the nanometer range from 1 to 500 nm [5]. By Brownian motion, small-size or functionalized nanomaterials could be dispersed in oil [5, 6] and pass through filters undisturbedly [5]; but even more, they can enter the contact interface easily to reduce the friction and prevent friction pairs from being worn, as a result of tribo-film formation, rolling mechanism, or surface repairing, etc. [17, 18] Moreover, the nanostructure of sphere, tube, or layer is another key consideration in nanomaterials design because it is directly associated with the pressure that nanomaterials are subjected to during loading [19]. Especially, spherical nanomaterials could offer a high capacity of load and pressure.

2) Unique physical properties. It is well-known that a substance in small sizes may show specific properties that bulky ones do not. Most nanomaterials have distinguished properties including large specific surface area [20], high mechanical strength, and load capacity [21], which contribute to improving the performance of lubricating oil. Owing to the large specific surface areas, nanomaterials with strong adsorption could allow the combination of several substances to obtain good dispersion in lubricant or form nanocomposites [22]. Besides, a part of layer nanomaterials with weak interlayer interactions could

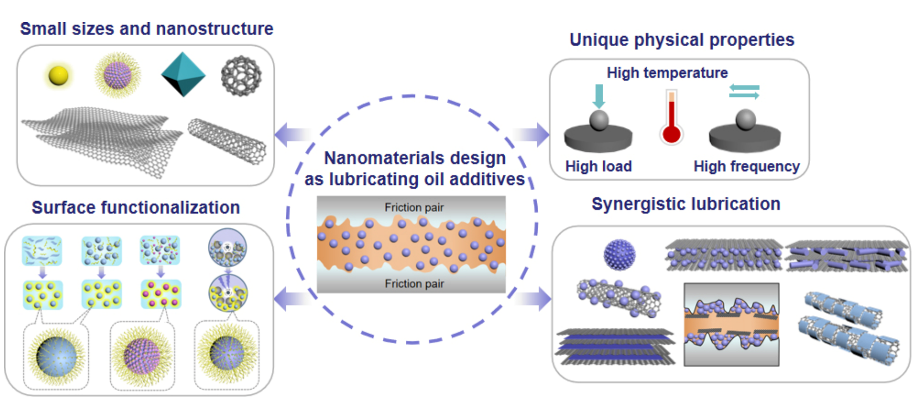

Fig. 3 Categories for nanomaterials design as lubricating oil additives.

offer low interfacial shear force, which is beneficial to friction reduction [23]. On the other hand, most nanomaterials have high thermal conductivity [8], which promotes the release of frictional heat and contributes to the stability of the friction systems. In comparison with organic oil additives, nanomaterials are also considered thermal stable at increasing temperatures, which is necessary for the durability of lubricating oil [24].

3) Surface functionalization. By serving as a host substrate for various functional chemical groups and species, nanomaterial offers the opportunity to graft targeted groups and develop novel types of composite nanomaterials that display enhanced or new performances in comparison to the parent counterparts [25]. Therefore, it is highly desirable to control the size, functionalization, and composition of the incorporated nanomaterials, as such ability should achieve the relevant properties of the nanomaterials to be tuned systematically [26]. Note that surface functionalization of nanomaterials can effectively enhance their dispersion stability and homogeneous distribution in base oil, and well-dispersed nanofluids have lower yield stress to reduce the starting resistance. However, most non-functionalized nanomaterials are considered prone to aggregation in nonpolar oil [27], which cannot be changed by the mechanical stirring process. The categories of surface functionalization are multifarious, and primary methods are summarized by four processes shown in Fig. 4: (1) Precursor of nanomaterial reacts with the modifying agent under appointed process, and nanomaterial preparation and surface functionalization occur simultaneously; (2) the as-prepared nanomaterials are mixed with the modifying agent; after reaction process, functionalized nanomaterials are generated; (3) coupling agent/crosslinking agent (or others) is used to connect the as-prepared nanomaterials and modifying agent; (4) the as-prepared nanomaterials are mixed with modifying agent; after dielectric barrier discharge plasma-assisted ball milling, functionalized nanomaterials are generated.

4) Synergistic lubrication. One potential method to improve the tribological properties of nanomaterials and exploit the mentioned advantages for extensive applications would be the preparation of nanocomposites, which can exhibit the synergistic effect in thin film boundary [28]. The obtained results show that benefitting from the synergistic lubricating effect, the combination of two or more nanomaterials has better tribological behavior than individual nanomaterial. Due to the different synergistic mechanisms, nanocomposites could display superior friction reduction and anti-wear properties, antioxidation

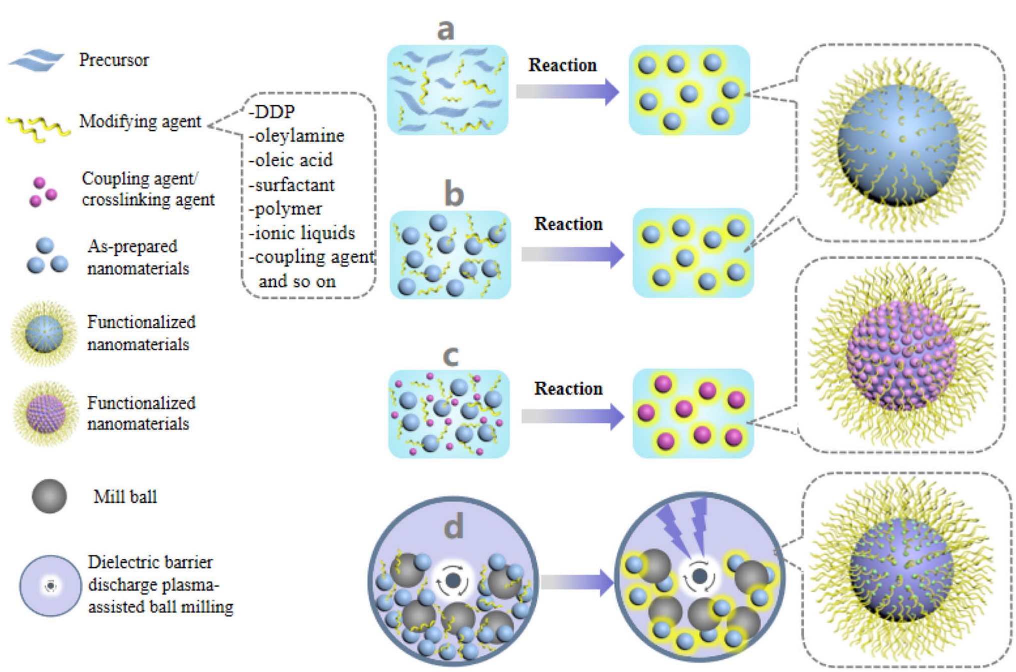

Fig. 4 Four preparation methods of functionalized nanomaterials (DDP: dialkyldithiophosphate).

property, oil dispersibility, and higher load-carrying capacity [29]. Nanomaterial additives can also integrate the merit of organic compound additives and solid lubricant additives [30].

3 Nanomaterial additives with different dimensions

3.1 0D nanomaterials

To date, a large number of nanoparticles were used as oil additives to improve tribological properties, in particular, the particles of Cu, Ni, Fe, Sn, Co, spherical oxides and sulfides, irregular shaped natural mineral nanoparticles, carbon spheres (CSs) and so on (all of them are regarded as 0D nanomaterials in this review, which have all dimensions at nanoscale). Metal-containing nanomaterials accounted for a considerable proportion in Section 3.1. A summary and comparison of 0D nanomaterials as lubricating oil additives is shown in Table 1. Besides, as mentioned above, the application of ILs in lubrication oil is briefly introduced in Section 3.1.

3.1.1 Metals

As lubricating oil additives, nano-metals have unique physical and chemical properties, such as no corrosive effect [31], chemical inertness [32], low shear stress, and low melting point [13, 22]. Therefore, their excellent friction-reducing, anti-wear, and self-repairing ability have been well perceived.

Copper nanoparticles have received distinctive attention as a result of their remarkable properties [33–35], and they can significantly improve the tribological characteristics of lubricating oil. Compared with Co and Fe nanoparticles, Cu nanoparticle lubricant additives could reduce the energy loss [36] and were more effective for friction and wear reduction when added individually [37]. However, it is worthy to note the type of oil. In nonpolar oil, Cu nanoparticles were remarkable as friction modifiers and anti-wear agents for each concentration and load, attributing to the deposition of Cu nanoparticles on the rubbing surfaces. However, the lubricating layer of polar oil on the metal-to-metal contact surface could be destroyed by Cu nanoparticles [38].

It is of interest to use Ni nanoparticles as nano-additives [31]. Chen et al. [39] reported that Ni nanoparticles synthesized in polyalphaolefins (PAO) could be tuned to diverse nano-sizes and had good dispersibility. Owing to the release of Ni nanocores with high activity and a stable protective layer formed by smaller-size Ni nanoparticles, the as-synthesized nanolubricants mixed with Ni nanoparticles exhibited good friction and anti-wear behaviors. This is a method for preparing oil-soluble metal nanoparticles, which can achieve good dispersion of nanoparticles in oil.

The changes of tribological properties by adding metal nanoparticles have been of great attraction to researchers. Except Cu and Ni nanoparticles, various metal nanoparticles were used as lubricating oil additives, including Ag [40], Sn [41], Fe [41], Co [37], Pb [42], Au [43], Bi [44], Mo [45], W [45], and Ga [46].

An innovative and simple study is that gallium-based liquid metal (GLM) nanodroplets functionalized with DDP were prepared by polydopamine (PDA)-coating, which combined the advantages of nanoparticles and traditional additives. Dopamine is a biomolecule owning two functional groups (catechol and ethylamine), which possesses the ability to self-polymerize to form PDA [47]. The experimental conditions were mild and convenient for operating, and excellent friction reduction and anti-wear performances were obtained [45]. The preparation method of functionalization is in accord with Fig. 4(c). The related processes and results are given in Fig. 5.

On the other hand, it must be accepted that untreated nanoparticles tend to aggregate in nonpolar oil. Improving the dispersion of nanoparticles in lubricating oil by surface functionalization with organic molecules is necessary (organic molecules include DDP [48], polyethylene glycol (PEG) [49], oleylamine, oleic acid, thiolated ligands, etc.). Of great importance is that functionalized nanoparticles have better friction reduction and anti-wear properties compared to the untreated.

Friction and wear are also affected by the hardness of nanoparticle additives. When Sn, Fe, and Cu nanoparticles were used as additives that had lower hardness than friction pair, a film with low hardness could be formed on the contact area [34, 40]. After

Table 1 Summary and comparison of 0D nanomaterials as lubricating oil additives.

Nanomaterial detail					Working condition					Test result			Ref.
Type	Nanomaterial	Functionalization	Size	Concentration	Base oil	Tribometer	Friction pair	Load (N)	Speed	Dispersion stability	COF reduction (%)	Wear reduction (%)	
Metals	Cu	—	25 nm	0.1 vol%	Raw oil	Disc-on-disc tribotester	Grey cast iron	3,000	1,000 rpm	Add dispersant	44	—	[36]
		—	10–30 nm	3 wt%	Paraffinic mineral	Pin-on-disk and four-ball tribometer	AISI 52100 and AISI 1020/AISI 1020	392	0.5 m/s	Add dispersant	60	16	[38]
		DDP	5 nm	0.1–1 wt%	Liquid paraffin	Four-ball tribometer	Steel	392	1,450 rpm	Several months	—	58	[35]
		PEG	44.7 nm	0.2–1 wt%	SF15W-40	Ball-on-disk tribometer	GCr15 bearing steel/45# carbon steel	15	0.13 m/s	Good	14	66	[49]
	Fe	—	50–80 nm	0.25 wt%	SAE 10 mineral oil	Four-ball tribometer	100 Cr6 bearing steel	150	1,420 rpm	—	39	23	[37]
	Co	—	50–80 nm	0.25 wt%	SAE 10 mineral oil	Four-ball tribometer	100 Cr6 bearing steel	150	1,420 rpm	—	20	11	[37]
	Ni	Oleylamine and oleic acid	7.5 nm	0–0.4 wt%	PAO6	Four-ball tribometer	GCr15 steel	300	1,450 rpm	More than 1 month	−15	25	[40]
	Pd	Tetrabutylammonium	2 nm	0–10 wt%	Tetrabutylammonium acetate	Ball-on-disk tribometer	AISI 52100	20	10 cm/s	Good	−100	91	[42]
	Ag	Thiolated ligands	1–6 nm	0.19–0.5 wt%	PAO	Cylinder-on-flat tribometer	AISI 8620 alloy steel/M2 bearing steel	50	0.1–1.2 m/s	Good	35	85	[39]
	Mo	—	20–50 nm	0–1 wt%	Multialkylated cyclopentanes	Vacuum four-ball tribometer	AISI 52100	294	1,450 rpm	—	15	20	[45]
	W	—	30–60 nm	0–1 wt%	Multialkylated cyclopentanes	Vacuum four-ball tribometer	AISI 52100	294	1,450 rpm	—	7	41	[45]
	Bi	—	7–65 nm	0–1 g/L	BS900/BS6500	Four-ball tribometer	AISI 52100	392	1,200 rpm	Good	50	30	[44]
	Ga	DDP	50–400 nm	2 wt%	PAO10	Ball-on-disk tribometer	AISI 52100	20	25 Hz	More than 5 days	57	96	[46]
Oxides	SiO_2	Poly-(lauryl methacrylate)	23.8 nm	1 wt%	PAO	Ball-on-flat tribometer	AISI 52 100 steel/CL35 cast iron	100	10 Hz	More than 55 days	30	96	[52]
		Polytetrafluoroethylene	500 nm	0.25–2 wt%	PAO6	Ball-on-disk tribometer	AISI 52100	100–500	25 Hz	More than 12 h	3	17	[53]
	TiO_2	Poly-(lauryl methacrylate)	15 nm	1 wt%	PAO	Ball-on-flat tribometer	AISI 52 100 steel/CL35 cast iron	100	10 Hz	More than 55 days	40	97	[52]
		Poly(alkyl methacrylate)	15–20 nm	0.1 wt%	Mineral oil	Pin-on-disk tribometer	AISI 52100	5	3 mm/s	More than 12 months	31	81	[51]
	CuO	—	< 50 nm	2 wt%	PAO8	Four-ball tribometer	AISI 52100	200	50 Hz	—	18	14	[55]
	Al_2O_3	Silane coupling agent	78 nm	0.1 wt%	Lubricating oil	Four-ball tribometer	GCr15 steel	147	1,450 rpm	More than 50 days	18	42	[56]
	ZnO	—	20 nm	0.5 wt%	PAO6	Block-on-ring tribometer	AISI 1045/AISI D3 steel	165	2 m/s	—	21	55	[58]
	ZrO_2	—	20–30 nm	0.5 wt%	PAO6	Block-on-ring tribometer	AISI 1045/AISI D3 steel	165	2 m/s	—	22	55	[58]
	CeO_2	Oleylamine	10 nm	0.1–2 wt%	PAO	Four-ball tribometer	GCr15 steel	100–400	1,200 rpm	Good	—	66	[62]
	Y_2O_3	Methyl methacrylate	24.5 nm	0–1 wt%	Liquid paraffin	Four-ball tribometer	GCr15 steel	392	1,450 rpm	More than 1 week	11	21	[27]

(Continued)

Nanomaterial detail					Working condition					Test result			
Type	Nanomaterial	Functionalization	Size	Concentration	Base oil	Tribometer	Friction pair	Load (N)	Speed	Dispersion stability	COF reduction (%)	Wear reduction (%)	Ref.
Sulfides	MoS_2	Surfactant	0.5–3 μm	0.25 wt%	Liquid paraffin	Ball-on-disk tribometer	GCr15 steel	200	25 Hz	Good	59	90	[64]
		—	3 nm	0.1–1 wt%	PAO	Ball-on-disk tribometer	AISI 52100	50–300	25 Hz	More than 2 weeks	38	> 90	[65]
	PbS	Oleic acid	8 nm	0.2 wt%	Liquid paraffin	Four-ball tribometer	GCr15 steel	300	1,450 rpm	Good	30	31	[69]
	ZnS	DDP	3 nm	0.1 wt%	Liquid paraffin	Four-ball tribometer	—	300	1,450 rpm	Good	—	46	[68]
Nitrides	BN	—	70 nm	5 wt%	Canola oil	Pin-on-disk tribometer	Oxygen-free electronic copper/ 2024 aluminum	10	36 mm/s	—	40	70	[74]
Fluoride	LaF_3	DDP	6 nm	0–1.6 wt%	Liquid paraffin	Four-ball tribometer	GCr15 steel	300	1,450 rpm	—	10	55	[72]
	CeF_3	—	25 nm	1 wt%	500SN	Four-ball tribometer	GCr15 steel	500–1250	1,480 rpm	Add dispersant	25	7	[73]
Carbon	ND	—	5–10 nm	0.2 wt%	ISO VG 46	Flat-on-flat tribometer	Steel/copper	106	2 Hz	More than 100 days	—	70	[79]
		Oleic acid	21–269 nm	0.05 wt%	Lubricating oil	Ball-on-disk tribometer	Al_2O_3/SKD11 steel	20	—	More than 10 days	23	—	[78]
	CS	—	190–250 nm	0.5 wt%	5W-40	Ring-on-disk tribometer	Tungsten steel/ PEEK	1,500	150 rpm	More than 3 weeks	33	24	[82]
		Nitrogen–phosph-orus	121 nm	0.2 wt%	500SN	Ball-on-disk tribometer	Steel/steel	100	25 Hz	More than 25 days	64	90	[83]
	CD	Ionic liquids	1.73 nm	0.1–0.5 wt%	PEG	Four-ball tribometer	AISI 52100	392–600	1,200 rpm	More than 3 months	70	45	[84]
		Polyethyleneimine	5 nm	0.07 wt%	PEG	Ball-on-disk tribometer	AISI 52100	40	10 mm/s	More than 1 month	54	80	[86]
	C_{60}	—	25 nm	0.02 wt%	SE15 W-40	Four-ball tribometer	GCr15 steel	300	2,003 rpm	—	40	—	[89]
Metal salts	Calcium borate	Lauric acid	50–100 nm	0.1–0.5 wt%	MVIS 250	Four-ball tribometer	GCr15 steel	100–500 N	1,450 rpm	—	10	41	[95]
	$CaCO_3$	—	40 nm	1 wt%	PAO	Ball-on-block tribometer	AISI 52100	100	20 Hz	—	7	89	[96]
Natural minerals	Serpentine	—	290–365 nm	0.2–0.8 wt%	CD 15W-40	Ball-on-disk tribometer	AISI 52100/ AISI 1045	10–200	10–30 Hz	—	18	73	[103]
MOFs	ZIF-67	—	—	1 wt%	100 SN	Four-ball tribometer	GCr15 steel	147	1,200 rpm	—	—	48	[108]
	ZIF-8	—	Nano and micro	1 wt%	150 SN	Four-ball tribometer	Steel	294	—	More than 24 h	63	—	[112]
	Zr-MOFs	DDP	36.2 nm	0.6 wt%	500 SN	Ball-on-disk tribometer	Bearing steel	—	—	More than 2 months	44	52	[113]
ILs	Trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate			5 wt%	PAO	Ring-cylinder tribometer	Engine piston steel/ cast iron	160	10 Hz	—	60	> 99	[118]
	Trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl) phosphinate			5 wt%	10W	Ring-cylinder tribometer	Engine piston steel/ cast iron	160	10 Hz	—	—	> 99	[119]
	$[(C_8H_{17})_3NC_{16}H_{33}]^+[C_4H_{10}O_2PS_2]^-$ $[(C_8H_{17})_3PC_2H_4SC_2H_5C_{16}H_{33}]^+[C_4H_{10}O_2PS_2]^-$			0.5 wt%	PAO10	Ball-on-disk tribometer	AISI 52100	300	25 Hz	—	~52	~93	[123]

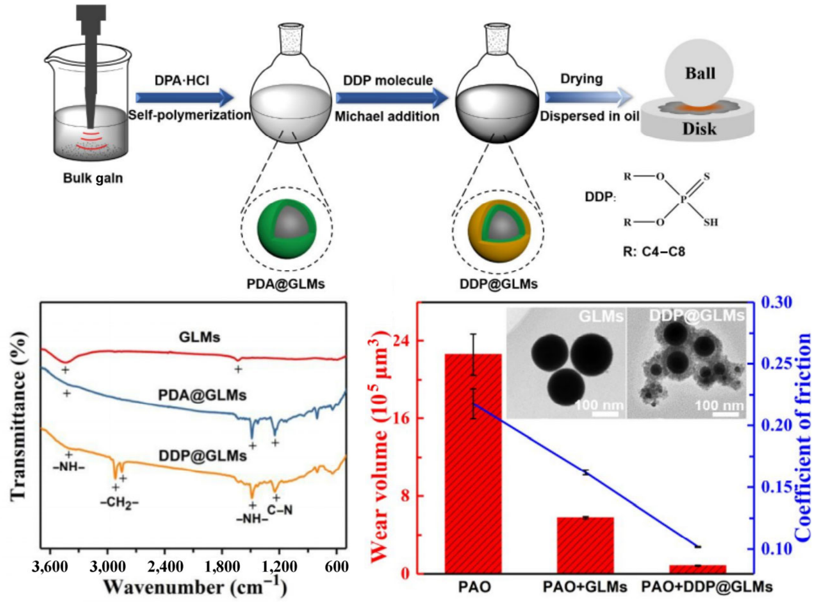

Fig. 5 Preparation process, FT-IR spectra, and results of tribological tests of DDP@GLMs. Reproduced with permission from Ref. [46], © American Chemical Society 2020.

comparing the tribological behaviors, it was concluded that hard nanoparticles showed obviously different tribological behaviors, and the friction mechanisms of hard (such as Mo and W) or soft (such as Pb, Sn, Ag, Cu, Ni, Fe, and Co) nanoparticles were also different [44]. For soft metallic nanoparticles, their antiwear property becomes more significant as the hardness and shear modulus increase, but has little effect on the improvement of friction reduction. Because their mechanisms of antiwear and friction-reducing are both attributed to the formation of metallic boundary films on the worn surfaces. For harder metallic nanoparticles, there are two effects that need to be considered: the promotion by nanoparticles to form a protective film or behave as rollers; their disturbance of continuity and stability of oil film. Tribological behaviors depend on which effect is dominant [44].

Another problem that needs to be considered is the negative effect of metal particles on the oxidation stability of lubricating oil. In engines, one of the most significant factors in the deterioration of lubricating oil probably is the presence of metals. Many tests were devised to evaluate the effect of different metals on lubricating oil deterioration. However, Fe, Cu, and Pb are considered well-recognized catalysts for the deterioration. Not only the copper salts are the effective catalysts, but also copper in bulk form [50]. Besides, up to now, the increasingly metal-base catalysts that could effectively catalyze the oxidative degradation of oil are reported. Therefore, not only the tribological properties but also the effect of metal particles on the oxidation stability of lubricating oil needs to be considered.

3.1.2 *Oxides/sulfides/nitrides/fluorides*

Among the study of oxides, sulfides, nitrides, and fluorides, the most widely used were oxides and sulfides. According to the number of references, oxides and sulfides nanomaterials account for 83% of Section 3.1.2.

Due to high surface activity, low cost, and load-bearing capacities, SiO_2 and TiO_2 have been widely used as additives in lubricating oil [51]. Typically, SiO_2- and TiO_2-grafted oil-soluble polymer brush [52] were dispersed in PAO steadily, and no change was observed after being kept at 100 °C for 55 days. Significant reductions of oil-soluble SiO_2 and TiO_2 in wear volume of flat and ball were achieved. The preparation method of functionalization is in accord with Fig. 4(c). The same dispersibility was also observed by using polytetrafluoroethylene (PTFE)@SiO_2 [53]. It was also found that the smaller-size SiO_2 exhibited outstanding tribological performances under lower frequency, larger-size SiO_2 performed better friction reduction properties under higher frequency, and lubricating oil additives with the uniform size displayed better tribological properties [54].

Other oxides and sulfides include CuO [55], Al_2O_3 [56], ZnO [57, 59], Fe_3O_4 [60], ZrO_2 [61], CeO_2 [62], WO_3 [63], Y_2O_3 [27], ZnS [68], PbS [69], and CuS [70]. To obtain a good dispersion, dispersants [64] and surface functionalization were widely used [65–67]. The comparison of them is given in Table 1.

Sulfides have a common disadvantage because of the active element S, which can lead to oxidation corrosion of mechanical systems and environmental pollution [12]. However, because of the outstanding tribological properties, MoS_2 has been extensively discussed as an important lubricating additive for a long time. Four different types of fullerene (C_{60})-like MoS_2 were synthesized and tested, and it was revealed that they all possessed excellent friction reduction properties in severe boundary lubrication [9]. However, the tribological performance of C_{60}-like MoS_2 varies with the internal structure. High load-carrying capacity is obtained by using perfectly spherical and crystallized C_{60}–MoS_2 particles, attributing to a higher contact pressure needed to achieve the collapse of structure. However, outstanding tribological properties are observed when using poorly crystalline C_{60}–MoS_2 nanoparticles, because they could be easily exfoliated to produce sheets and assembled layer upon layer to form a tribo-film. Similarly, the presence of point defects and hollow structures in the particles also facilitate easier exfoliation and faster tribo-film formation [71]. This result also indirectly shows the different tribological characteristics between MoS_2 sheets and particles.

As for the fluorides and nitrides, a reported test showed that LaF_3 [72], CeF_3 [73], and boron nitride (BN) [74] nanoparticles could improve the load-carrying capacity, friction reduction, and anti-wear property.

3.1.3 *Carbon*

In most studies of nanomaterials in oil lubrication, carbon-based nanomaterials have been emphasized, such as nanodiamond (ND), C_{60}, carbon dots (CDs), CSs, carbon nanotubes (CNTs), graphene (G) and graphene oxide (GO). In Section 3.1.3, 0D carbon-based nanomaterials are discussed, and the others will be presented in following sections.

As the nontoxicity and chemical stability of ND, their utilization in boundary lubrication and durability to extreme pressure have always been attractive during the past several years. The viscosity, rheological relation, dynamic, friction torque, secondary addition, and thermal behavior of ND-dispersed lubricant were both investigated [75–80], which provided the foundation for exploring the mechanisms of tribological performances.

Carbon sphere (CS) possessing the regular spherical structure has a diameter of more than 100 nm, in contradistinction to metal nanoparticles [81–83]. Ultrasmooth submicron CSs were demonstrated as an efficient lubricating oil additive, and the particle sizes ranged from 100 to 500 nm [81]. Generally, the size of CS will affect the friction performances. However, for nitrogen–phosphorus co-doped CSs, the relatively large size of CS did not affect their

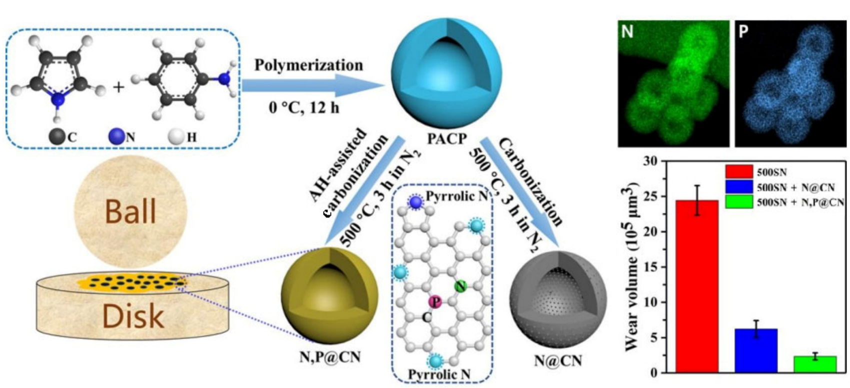

Fig. 6 Nitrogen and phosphorus co-doped CSs (denoted as CN) were prepared via the carbonization of poly (aniline-co-pyrrole) (PACP), and the prepared CSs with N, P elements showed enhanced anti-wear and friction-reducing performance as 500SN additives. Reproduced with permission from Ref. [83], © American Chemical Society 2020.

excellent performance [83]. The preparation method of functionalization is in accord with Fig. 4(a), and the graphic abstract is shown in Fig. 6.

Several studies have also been devoted to the application of CDs as lubricating oil additives, as a consequence of their small size (< 10 nm), which is important to solve the problem of dispersion stability. Moreover, good compatibility of CDs with base oil can be directly obtained in the synthesis process [84]. Subsequently, oleylamine [85], polyelectrolyte [86, 87], and poly(ionic liquid) brush-grafted CDs [88] were studied. The preparation methods of functionalization are both in accord with Fig. 4(c). In addition, other 0D carbon materials were also demonstrated, such as C_{60} [89], onion-like carbons [90], and so on [91, 92].

Thermal and rheological properties of lubricants mixed with different carbon nanostructures were evaluated and compared [93]. The results showed that all the thermal conductivities of sample oils were greater than that of the base oil. CS particles exhibited the most positive influence on the thermal conductivity and flash point. But G nanosheets had the greatest improvement effect on pour point. Moreover, all the viscosity of sample oils rises with the increasing concentration of nanomaterials and decreasing temperature, but different structures had little effect.

3.1.4 *Metal salts/natural minerals*

Among the metal salts studied, the most widely used over the past decade were borates. Oil-soluble calcium borate nanoparticles modified by oleic acid and lauric acid were prepared [94, 95], and the functionalization methods were described in Fig. 4(a). Modified calcium borates had good properties of anti-wear and friction reduction, and during the sliding process, a wear resistance film composed of depositions and tribo-chemical reaction products was formed. $CaCO_3$ nanoparticles were also studied, but their tribological properties depended on the experimental conditions. Only under lower load, higher frequency, and lower temperature, the tribo-chemical reaction product (CaO) was produced, and a film was formed on the worn surface [96].

Overbased calcium sulfonates and/or salicylates have been widely applied [97]. For example, overbased calcium sulfonate detergents are colloidal sols, in which nanosized $CaCO_3$ particles are stabilized in oil by calcium alkylbenzene sulfonate molecules [98]. They are widely applied in the automotive and marine engine to neutralize acidic products and prevent the build-up of deposits [97]. As oil additives, they could also improve the tribological properties of oil [99]. In addition to the mentioned above, there are also some other metal salts applied in lubricating oil [100–102].

Serpentine oil additives had been comprehensively studied, such as the chemical compositions, mechanical properties [103], auto-restoration mechanism [104], and thermal treated properties [105]. Especially in boundary and mixed lubrication, by adding serpentine additives, the tribo-film with excellent mechanical properties composed of SiO_2, Al_2O_3, Fe_3O_4, and other compounds was formed, which was attributed to the crystalline structure and reinforced phase of those chemical reaction products [106]. Generally, the resource-rich natural minerals are composed of many complex components and possess a high chemically active. The chemical reactions and physical–chemical depositions could occur easily under friction conditions, which may be beneficial for tribological properties of oil. However, there may be some by-products generated in the process of tribo-chemical reaction due to the complex components in natural minerals. The effect of these by-products on oil has not been pointed out.

3.1.5 *Metal–organic framework (MOF)*

MOFs are prepared by reticular synthesis via the link of inorganic and organic units with strong chemical bonds. Robust crystalline structures can be yielded when linked to metal-containing units [107]. In particular, the geometry, size, and functionalization of MOFs can be precisely controlled and designed. Hence, there has been significant interest recently in the application of MOFs in lubricating oil. However, there are only a few studies concerning MOFs as lubricating oil additives were reported.

Zeolitic imidazolate frameworks (ZIFs) are a subclass of MOFs, which have the large surface area, pore volume, and high chemical and thermal stability. ZIF-8 (2-methylimidazole zinc salt) and ZIF-67 (3-methylimidazole cobalt salt) firstly used as additives in lubricating oil showed excellent anti-wear property and load-carrying ability [108]. Then, the friction and wear performances of ZIF-8, ZIF-71 (4,5-dichloroimidazole zinc salt), and MAF-6

(2-ethylimidazole zinc salt) as additives were evaluated [109], and the influence of size on tribological performances were analysed [110–112].

It was found that MOF-based oil additives mainly focused on ZIFs. However, during the friction process, the collapsed structures of ZIFs were observed, and the structure stability was also influenced by acidic environment originating from the oxidation of base oil [113]. It is of interest to investigate DDP-modified Zr-based MOFs (Zr-MOFs) by self-assembly as lubricating oil additives [113]. Because of the coordinatively unsaturated metal sites, Zr-MOFs can be easily functionalized. Combining with the advantages of traditional zinc dialkyldithiophosphate (ZDDP), reduction in both coefficient of friction (COF) and wear volume were achieved, and the oxidation induction time of oil mixed with Zr-MOFs@DDP was expanded much longer. Related functionalization processes and the results of Zr-MOFs@DDP are given in Fig. 7.

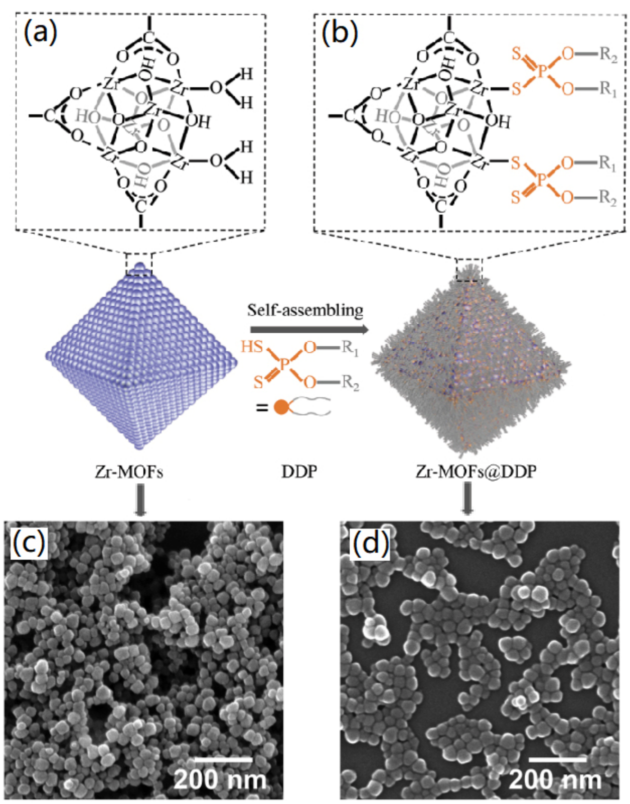

Fig. 7 Schematic illustration for surface functionalization of Zr-MOFs@DDP. Chemical structures and scanning electron microscopy (SEM) images of Zr-MOFs and Zr-MOFs@DDP were shown in (a, b) and (c, d), respectively. Reproduced with permission from Ref. [113], © Elsevier B.V. 2021.

As one of the most attractive functional nanomaterials, MOFs show superiority in many fields, including liquid separation, gas storage, sensors, drug delivery, supercapacitor, and catalysis [114, 115] because of their design ability of molecules and frameworks. MOFs are promising as lubricating oil additives and worth being explored in tribology, and thus more interdisciplinary researches are needed to be carried out.

3.1.6 ILs

ILs composed of cations and anions possess unique characteristics, including great adsorption capacity, low volatility, and high thermal stability [116]. From 2001 to 2011, ILs were primarily explored as base lubricants. However, the achievement of miscibility in 2012 promoted the development of ILs as lubricating oil additives [117].

Qu et al. [118] has been devoted to the research of oil-soluble ILs as lubricant additives for a long time. In 2012, with good solubility in nonpolar oil, the IL trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate was investigated as oil additive. The wear rate was surprisingly reduced by 3 orders of magnitude, which was attributed to a protective boundary tribo-film. Similarly, the IL trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl) phosphinate was also investigated [119]. The ranking of effectiveness in anti-wear behavior for the anions of ILs was summarized [120], and the synergistic effect between phosphonium–alkylphosphate IL and ZDDP was revealed [121]. In addition, multifunctional oil-soluble ILs were synthesized and evaluated, exhibiting excellent properties of solubility, anti-corrosion, anti-rust, anti-wear, and higher load-carrying capacity [122]. ILs also exhibited superior tribological performances than ZDDP [123, 124]. However, the miscibility, molecular structure, ion pairing of ILs, and the polarity of base oil all have an impact on oil film thickness and tribological performance [125, 126].

The viscosity of lubricating oil is also affected by the viscosity of ILs, and then affects the tribological behaviors. The viscosity of ILs varies substantially despite a relatively narrow range of density (1.0–1.6 g/mm^3) because the rheological behavior is significantly affected by the cationic and anionic structures. Accordingly, due to the diversity of cationic/anionic and the complexity of their molecular structures, a definite law of influence on the viscosity has not been established (the existing influence factors include length, structure, and symmetry of alkyl chain, H-bonding between the ions, and so on) [117]. Viscosity has different effects in different lubrication regions, and suitable ILs can be designed according to particular working conditions.

Various oil-soluble ILs have been synthesized and optimized in the past ten years, and the development of oil-soluble ILs has solved a lot of problems, including corrosion, thermal instability, toxicity, high cost, and so on [127, 128]. On the other hand, it is highly effective to enhance the anti-wear behavior of base oil, which is confirmed by lots of experimental results. Hence, the unique characteristics of ILs as lubricating oil additives indicate the potential for future industrial applications [117].

3.2 1D nanomaterials

1D nanomaterials have two dimensions at nanoscale with large length-to-diameter aspect ratios. Section 3.2 summarizes the research progress on 1D nanomaterials as lubricating oil additives. CNTs, oxides, sulfides, halloysite clay nanotubes (HNTs), and cellulose nanocrystals are primarily included in Section 3.2. An overview of 1D nanomaterials used as lubricant additives is listed in Table 2.

3.2.1 CNTs

As one form of 1D nanomaterials, CNTs or multi-walled CNTs (MWCNTs) have been widely explored for their excellent friction behaviors. With distinctive structure characteristics of coaxial cylindrical graphene with various layers, it can relatively move along the concentric axis of cylindrical graphene [129]. Theoretical modeling has predicted an ultralow interfacial shear force between layers of double-walled CNTs. Nevertheless, for non-concentric layers, the presence of defects in structure would remarkably increase the shear force, and it monotonically increases with the length of CNTs. On the other hand, the chemical inertness of bare CNTs causes little adsorption on the considered surfaces.

Significant progress in CNTs was achieved in recent years. To overcome the chemical inertness of CNTs, extensive surface functionalization was conducted by stearic acid [130], Co [131], carboxyl [132], and so on [133], and the density of modifier on surface has an impact on their friction behaviors [130, 134]. Noteworthily, MWCNTs modified with polymeric aryl phosphates (PAPs) could dramatically improve the friction reduction (~60%) and anti-wear performances (~95%) with 0.08 wt% contents [135]. The detailed data of tribological properties are illustrated in Fig. 8.

The mechanism and rheological behavior of CNTs were also studied [134–136]. Meaningfully, CNT additives were investigated in the engine [137]. Conclusions showed that CNT additives in engine oil resulted in a reduction (7%) in the motoring torque; moreover, during normal operation, the dispersion of CNTs in engine was effectively improved by oil shear, and the agglomerates of CNTs were quickly removed by oil filtration system.

3.2.2 Oxides/sulfides

Progress was made in the preparation of metal dichalcogenide nanotubes, in analogy to CNTs, they can also exhibit good tribological performances attributing to layered cylindrical shape. $Mo_6S_{4.5}I_{4.5}$ [138] and $Mo_6S_3I_6$ [139] nanowires presented outstanding friction reduction properties, and COF both reached a value of 0.04. MoS_2 was formed in contact area during the friction process. However, these two results were almost identical, so the different chemical formulas were suspicious.

By sulfurization, MoS_2 nanotubes could be synthesized from $Mo_6S_2I_8$ nanowires, and it was found that MoS_2 nanotubes remarkably decreased the COF and wear loss [140]. Similarly, *in-situ* tribo-chemical sulfurization was occurred by using MoO_3 nanotubes as additives in base oil in the existence of sulfur-containing lubricant additive, and followed a MoS_2-rich tribo-film formation [141, 142]. The load-carrying capacity of this tribo-film was much higher than that of the common MoS_2 nanotubes [141]. Owing to the continuous sulfurization of MoO_3 nanotubes during sliding contact, common MoS_2 nanotubes progressively degraded and lost lubricity because of oxidation. *In-situ* sulfurization of MoO_3 nanotubes broke the temperature sensitivity limit of MoS_2 nanotubes and caused superb tribological performance up to 200 °C [142]. On the other hand, it

Table 2 Summary and comparison of 1D nanomaterials as lubricating oil additives.

Nanomaterial detail					Working condition					Test result			Ref.
Type	Nanomaterial	Functionalization	Size (in diameter, nm)	Concentration	Base oil	Tribometer	Friction pair	Load	Speed	Dispersion stability	COF reduction (%)	Wear reduction (%)	
CNTs	Co-based single-wall CNTs	—	—	0.5 wt%	SAE 20	Pin-on-disk tribometer	100Cr6 steel/ 41MoCr4-2 steel	4 N	0.15 m/s	72 h	19	48	[131]
	MWCNTs	Stearic acid	—	0.45 wt%	Liquid paraffin	Pin-on-disk tribometer	Carbon steel	500–1,000 N	384 rpm	More than 2 months	~9	~52	[130]
	MWCNTs	Stearic acid	—	0.025 wt%	Liquid paraffin	Ball-on-disk tribometer	Plain steel	50g	0.84 m/s	—	~87	~89	[136]
	MWCNTs	Polymeric aryl phosphates	11–14	0.08 wt%	PAG	Ball-on-disk tribometer	AISI 52100	50 N	25 Hz	More than 20 days	~60	~95	[135]
	MWCNTs	–COOH	—	0.025 wt%	PPG2000	Ball-on-disk tribometer	AISI 52100	300 N	50 Hz	More than 4 months	6	86	[132]
	CNTs of fly ash	—	20–30	0.1 wt%	500SN	Ball-on-disk tribometer	100 Cr steel/ polished steel	4 N	0.5 cm/s	—	18	—	[133]
Oxides	CuO	Ionic liquids	8–18	0.075 mg/mL	PEG 200	Four-ball tribometer	Steel ball	392 N	1,200 rpm	Good	40	43	[143]
	MoO_3	—	100–200	5 wt%	PAO	Ball-on-disk tribometer	AISI 52100	25 N	25 Hz	—	40	—	[141]
	MoO_3	—	100–150	2 wt%	PAO8	Ball-on-disk tribometer	Steel/steel	100 N	50 Hz	—	20	11	[142]
Sulfides	MoS_2	—	100–500	5 wt%	PAO	Ball-on-disk tribometer	Steel	10 N	0.5 cm/s	—	56	89	[140]
		—	100–150	2 wt%	PAO8	Ball-on-disk tribometer	Steel/steel	100 N	50 Hz	—	30	21	[142]
		—	100–150	5 wt%	PAO4	Ball-on-disk tribometer	AISI 52100	25 N	10 Hz	—	55	80	[230]
	WS_2	—	10–15	2 wt%	PEG	Four-ball tribometer	GCr15 steel	245 N	1,200 rpm	Add dispersant	~54	34	[144]
	CuS	Oleic acid	—	1 wt%	Liquid paraffin	Pin-on-disk tribometer	Pig iron/bearing steel	300 N	300 rpm	Add dispersant	66	96	[145]
Others	$Mg_2B_2O_5$	—	120–180	5 wt%	HD 80W-90	Ball-on-disk tribometer	Bearing steel/ 45# steel	3,000 N	300 rpm	—	23	—	[150]
	BaB_2O_4	Oleic acid	20	1 wt%	—	—	—	600 N	6,000 rpm	—	~78	—	[152]
	WSe_2	—	10–50	7 wt%	HVI500	Ball-on-disk tribometer	—	2 N	150 rpm	—	50	—	[151]
	HNTs	—	30–70	0.05 wt%	Polymeric lubricant	Four-ball and block-on-ring tribometer	AISI 52100; AISI D2/AISI 1018	3,000 N	200 rpm	—	71	70	[148]
	HNTs	—	30–70	1 wt%	PAO8	Ball-on-disk tribometer	Steel	100 N	50 Hz	—	28	3	[149]
	Cellulose nanocrystal	Stearoyl chains	—	2 wt%	PAO	Ball-on-disk tribometer	GCr15	60 N	200 rpm	More than 5 h	30	41	[153]

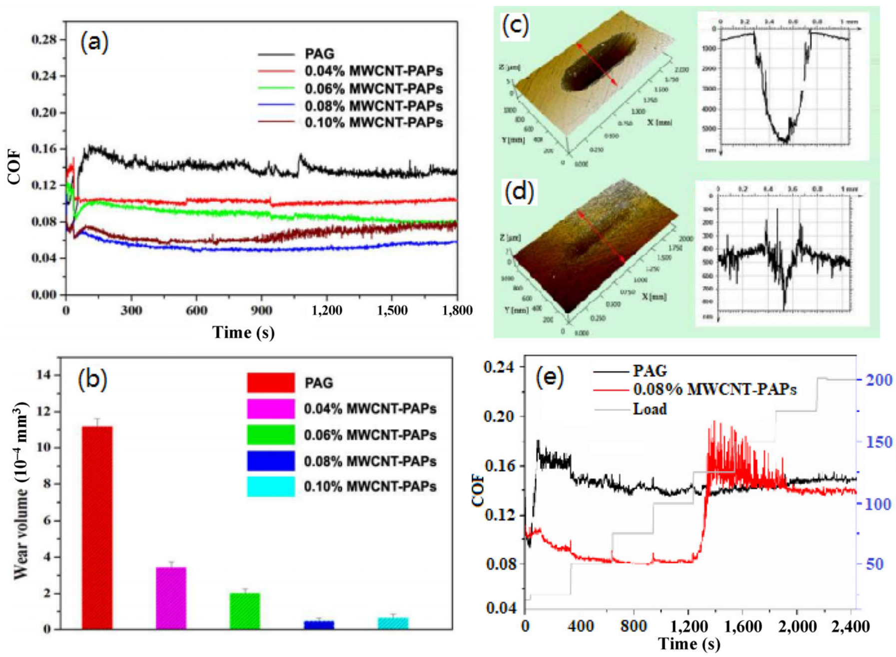

Fig. 8 (a) COFs and (b) wear volumes lubricated by MWCNT-PAPs with different concentrations (50 N, 25 Hz, and 150 °C); (c, d) three-dimensional (3D) optical microscopic images of the disc worn surfaces lubricated by polyalkylene glycol (PAG) and PAG with 0.08 wt% MWCNT-PAPs, respectively; (e) variations of COF with time under different loads (25 Hz, 150 °C). Reproduced with permission from Ref. [135], © Elsevier Ltd. 2017.

can be concluded that the oxidation stability of MoS_2 is poor. WS_2 [144] and CuS nanorods [145] were also prepared and investigated, and their anti-oxidation behaviors were not good either [17]. Probably, the method of *in-situ* tribo-chemical sulfurization is helpful to overcome this problem, but the sulfur element cannot be avoided.

3.2.3 *Others*

As naturally occurring materials, HNTs with adequate hydroxyl groups [146, 147] are considered effective additives in lubricating oil. It was proved that HNT additives could significantly improve the load-carrying capacity and raise the seizure load [148]. Meaningfully, a comparison of carbon nanoparticles (CNPs), TiO_2, MoS_2, MoO_3, and HNTs was performed, indicating that the friction reduction properties of using HNTs under the same concentration in oil were equal to MoS_2 [149]. These results are displayed in Fig. 9.

The improvement of load-carrying capacity and tribological performances of HNTs may be attributed to the C_{60}-like hollow nanostructure with a smaller Young's Modulus, which leads to the easier exfoliation of outer layers to form a protective tribo-film on the surface. Moreover, a rolling bearing mechanism may be also present under different working conditions [148]. On the other hand, as clay mineral nanomaterials, HNTs are not hazardous to the environment. The affluence in natural resources and the ability to minimize the quantity of sulfur and phosphorus in oil facilitate HNTs to be the promising, effective, and green additives in oil.

Besides, single crystalline magnesium borate ($Mg_2B_2O_5$) nanowires [150] and WSe_2 nanorods [151] as additives in lubricating oil both presented high load-carrying capacity that maybe benefit from the structure of column. BaB_2O_4 nanorods [152] and cellulose nanocrystals [153] were also studied.

3.3 2D nanomaterials

With ultrathin longitudinal dimensions, 2D nanomaterials could decrease the shear resistance between the contact sliding surfaces, and thus optimize the applied conditions [23]. Moreover, strong covalent bonds and weaker layer–layer interactions in 2D nanomaterials ensure the mechanical stability of nanostructure [11]. In Section 3.3, recent progress in research on 2D nanomaterial additives in oil is

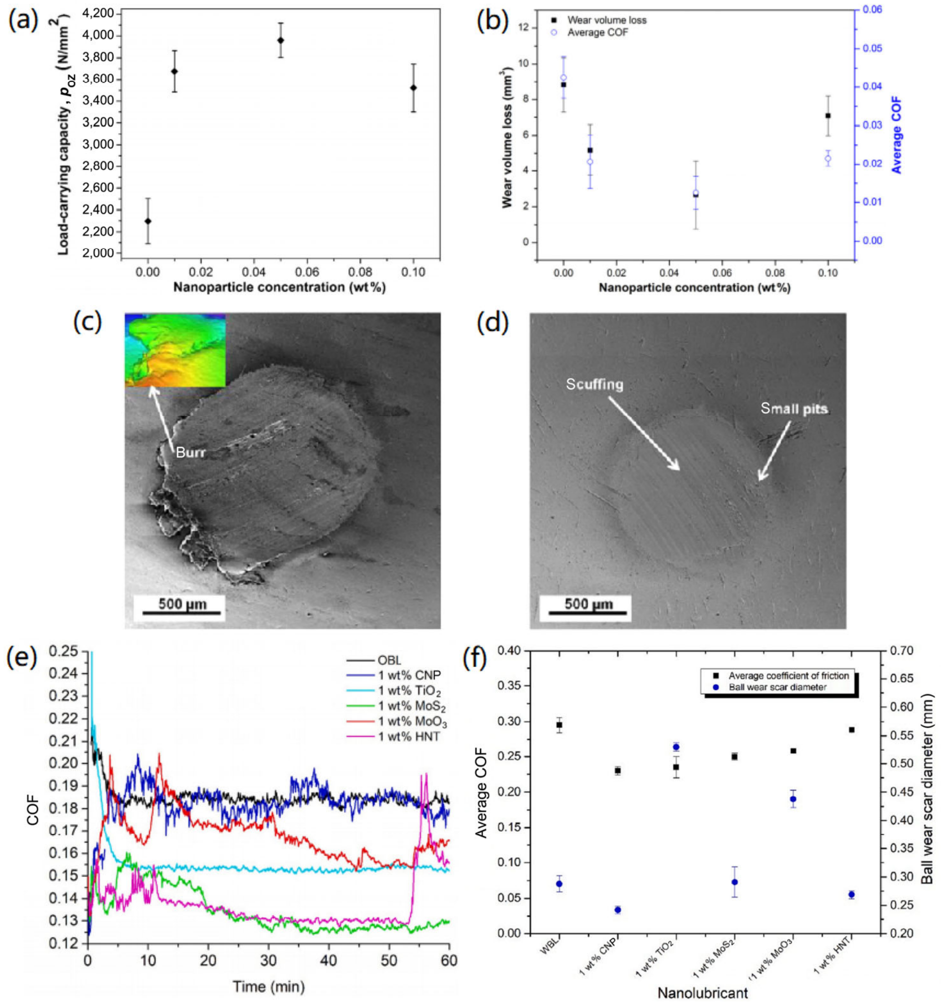

Fig. 9 (a) Load-carrying capacity of HNTs in polymeric lubricant obtained by the four-ball tests at extreme pressures; (b) wear volume losses and average COFs for HNTs in polymeric lubricant with varying concentrations obtained by the block-on-ring tests (2,000 N, 200 rpm); (c, d) SEM images of worn steel balls by the four-ball tests at extreme pressures: polymeric lubricant and 0.05 wt% HNT nanolubricant; (e) COFs for PAO dispersed with different nanomaterials obtained by ball-on-disk test (100 N, 50 Hz); (f) average COFs and wear scar diameters (WSDs) for different nanomaterials obtained by ball-on-disk test (100 N, 50 Hz). Reproduced with permission from Ref. [148] for (a–d), © Elsevier B.V. 2017; Ref. [149] for (e, f), © Elsevier B.V. 2021.

summarized, typically including G, GO, MoS_2, layered double hydroxide (LDH), black phosphorus (BP), and covalent organic frameworks (CFs). An overview of 2D nanomaterials used as lubricating oil additives is listed in Table 3.

3.3.1 *Carbon*

In the past few years, a great deal of graphene-based layered nanomaterials including G, GO [154], fluoro graphene (FG) [155], and reduced graphene oxide (rGO) have been added to base oil to improve the anti-wear and friction reduction behaviors for their high specific surface area, small-size nanosheets with only nanometers thickness [156], and the ability to facilely enter the contact surface. However, due to a large number of demands for acid aqueous solution and water, the synthesis process of graphene-based nanomaterials is not economical and environment-friendly [15, 21].

Pristine graphene-based layered nanomaterials are not dispersible in most oil because of chemical inertness that could be avoided by physical or chemical modification. They were functionalized by oleic acid [157], ILs [158], dodecylamine [159], phosphonium–organophosphate [160] and so on. There are also several kinds of methods to improve dispersity.

Table 3 Summary and comparison of 2D nanomaterials as lubricating oil additives.

Nanomaterial detail				Working condition					Test result			
Type	Nanomaterial	Functionalization	Concentration	Base oil	Tribometer	Friction pair	Load	Speed	Dispersion stability	COF reduction (%)	Wear reduction (%)	Ref.
Carbon	G	Oleic acid	0.02–0.06 wt%	PAO9	Four-ball tribometer	GCr15 steel	400 N	1,450 rpm	—	17	14	[157]
		Ionic liquids	0.02 mg/mL	PEG 200	Ball-on-disk tribometer	100Cr6 steel/316LN	2 N	3 cm/s	Good	~27	78	[158]
		Dodecylamine	0.1 wt%	5W-30	Ball-on-disk tribometer	SS304	10 N	0.5–3 mm/s	More than 32 days	~40	—	[159]
		Phosphonium–organophosphate	0.25–0.75 wt%	150 N	Ball-on-disk tribometer	GCr15	20–100 N	3/25 Hz	More than 30 days	50	85	[160]
	3D porous G	—	0.1 wt%	PAO6	Ball-on-disk tribometer	GCr15/316ASS	100 N	10 Hz	More than 30 h (add dispersant)	73	98	[162]
	Ultrathin G	—	0.025 mg/mL	Engine oil	Four-ball tribometer	Chrome alloy steel	392 N	600 rpm	1 month	80	33	[161]
	G	—	0.05 wt%	SAE 10W-30	Pin-on-disk tribometer	GCr15/bronze CuSn10P1	10 MPa	0.3 m/s	—	65	61	[164]
	Graphite	—	0.01 wt%	Paraffin oil	Four-ball tribometer	GCr15	245 N	1,500 rpm	—	~80	~33	[166]
		—	0.3 vol%	Canola oil	Pin-on-disk tribometer	2024 aluminum alloy/ 440C stainless steel	15 N	25 mm/s	—	73	99	[167]
	Reduced graphite oxide	—	0.5 wt%	PAO6	Ball-on-disk tribometer	AISI 52100	2 N	2.4 mm/s	4 days	44	90	[168]
	GO	Oleic acid	1 wt%	PAO	Ball-on-disk tribometer	AISI 52100/AISI 1045	40 N	20/30 Hz	More than 7 days	75	94	[154]
	rGO	Fluorine	0.3 mg/mL	GTL8	Ball-on-disk tribometer	Silicon nitride/ polished 316L	10 N	2 Hz	—	21	87	[155]
Oxides	Fe_3O_4	Oleic acid	1.5 wt%	#40	Four-ball tribometer	GCr15	392 N	1,450 rpm	More than 48 h	18	11	[176]
Sulfides	MoS_2	—	0.25 wt%	White oil	Block-on-ring tribometer	AISI 52100/AISI 1045	326 N	1 m/s	Add dispersant	29	34	[175]
		—	0.5–5 wt%	Paraffin oil	Ball-on-disk tribometer	Steel	10–60 N	200 rpm	—	39	27	[173]
		Ni	0.5 wt%	SN 500	Four-ball tribometer	AISI 52100	392 N	1,200 rpm	More than 240 h	21	42	[171]
		—	1.5 wt%	Liquid paraffin	Four-ball tribometer	AISI 52100	250 N	1,450 rpm	Add dispersant	~15	58	[170]
		Cetyltrimethylammonium bromide	0.4 wt%	Liquid paraffin	Four-ball tribometer	GCr15	300 N	1,450 rpm	More than 2 days	35	~0.1	[174]
Natural minerals	LDHs	Sodium laurate	1 g/100 mL	CD15W-40	Four-ball tribometer	GCr15	392 N	1,200 rpm	—	11	9	[182]
		—	5 g/1 L	CD15W-40	Four-ball tribometer	GCr15	392 N	1,200 rpm	—	49	33	[178]
		—	1 wt%	GTL8	Ball-on-disk tribometer	AISI 52100	50 N	50 Hz	More than 12 h	11	~10	[177]
		—	1 wt%	PAO10	Cylinder-on-disk tribometer	AISI 52100	350 N	3 Hz	—	~20	63	[181]
	Anthracite sheets	Sorbitol fatty acid ester	0.03 wt%	PAO40	Four-ball tribometer	GCr15	150 N	1,200 rpm	More than 90 days	45	96	[184]
	Palygorskite	Molybdenum	0.5 wt%	ULTRA-S 150N	Four-ball tribometer	GCr15	400 N	1,200 rpm	More than 7 days	~20	63	[183]
Others	ZrP	—	0.1 wt%	Mineral oil	Pin-on-disk tribometer	AISI 52100/glass slide	0.15–1 N	10–600 rpm	—	65	—	[185]
	CFs	—	0.05–1 wt%	PAO10	Ball-on-disk tribometer	Steel	100 N	25 Hz	More than 48 h	39	89	[187]
	BP	Oleic acid	0–0.1 wt%	PAO6	Ball-on-disk tribometer	GCr15	2.9 N	0.1 m/s	—	20	~49	[188]
		—	—	Liquid paraffin	Ball-on-disk tribometer	GCr15/titanium alloy	8–15 N	150 rpm	—	30	45	[189]

Highly-deoxygenated and less defective G was prepared by exfoliation of graphite oxide based on the focused solar electromagnetic radiation. It was also observed that COF reduction, anti-wear, and extreme pressure properties were all enhanced [161]. 3D porous G and high molecular weight polyisobutylene succinimide (T161) as hybrid additives were proposed [162]. The hybrid additives could effectively reduce the COF and wear rate of 316 ASS by 73.1% and 97.8%. The results are displayed in Fig. 10.

Moreover, the methods of ball milling, electrochemically exfoliation [163], liquid phase exfoliation [164], and arc-discharge [165] were also used to prepare high-performance additives. Interestingly, tribological performances of graphite nanosheets [166, 167] and highly exfoliated reduced graphite oxide [168] gained by ball milling were both wonderful, and the functional groups could also be grafted on the surface of G by ball milling [169]. The preparation methods of functionalization are both in accord with Fig. 4(d). Obviously, ball milling is a promising way to produce high-performance carbon-based layered nanomaterials as lubricating oil additives.

G is a kind of flexible 2D nanomaterial. Because of the flexibility, their tribological performances are greatly affected by working conditions. Especially, under the mixed lubrication, exfoliated G sheets tended to be trapped in the wear area and induced the "puckering" effect. Then, their high mechanical strength resulted in a higher COF than base oil.

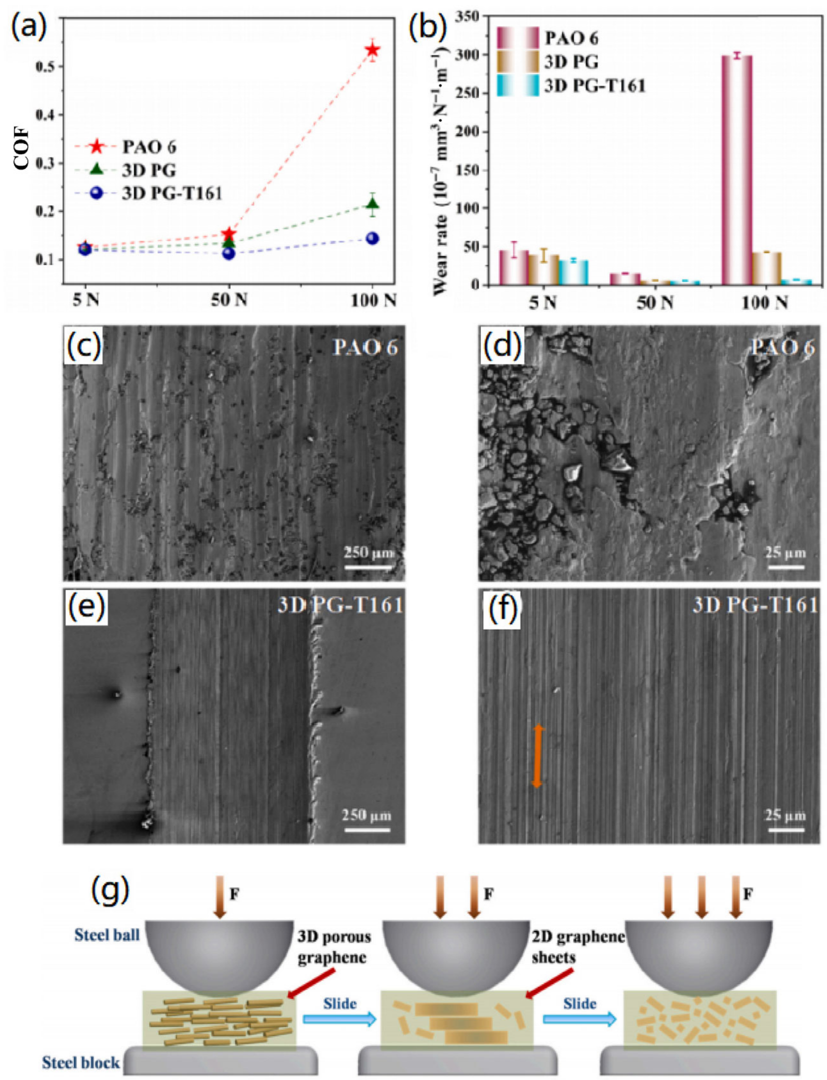

Fig. 10 (a, b) Changes in average COF and wear rate; (c–f) SEM images of wear track surfaces; and (g) schematic diagram. Reproduced with permission from Ref. [162], © Elsevier Ltd. 2021.

Moreover, along with frictional time, the uniformity and dispersion were worsened, and their aggregation intensified. Accordingly, the adsorption film formation was difficult to occur, which was detrimental to their tribological performances [163].

3.3.2 Oxides/sulfides

MoS_2 with a sandwiched S–Mo–S nanostructure has attracted considerable attention. As mentioned above, MoS_2 can be synthesized into different nano-shapes, such as nanoparticles, C_{60}-like, nanotubes, and nanosheets. Despite different geometries, MoS_2 nanosheets possess better tribological properties as a result of the ability to easily form linear tribo-film and supernatant performance [171]. Except for Fe_3O_4 nanoflakes, there are few oxides with layer nano-structure as lubricating oil additives were studied.

MoS_2 nanosheets synthesized by ball-milling the mixture of MoO_3 and S could strongly adsorb the surface of substrates to form stable tribo-films [170]. Ultrathin MoS_2 nanosheets prepared by the typical synthesis route [172], solid-state reaction [173], or electrochemically exfoliation [163] were both confirmed to enhanced anti-friction and anti-wear properties as lubricating oil additives. MoS_2 nanosheets with high concentration exhibited significant superiority over ZDDP in reduction of friction and wear in high load [175]. Coral-like MoS_2 prepared by a hydrothermal method could reduce the COF but not wear scar diameter [174].

3.3.3 Natural minerals

As a kind of natural mineral, LDHs can also be fabricated by chemical synthesis in lab, which are composed of metal ions located at the hexagonal crystal center of laminates and hydroxide ions occupying the apexes [177]. The metal ions in LDHs include Mg^{2+}, Al^{3+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, etc. Due to the unique crystal nanostructures, diversity of chemical composition and size, as well as shape-memory, LDHs have been widely investigated in various fields. It is also interesting to explore the potential tribological properties as additives in lubricating oil. Co–Al–CO_3-LDHs [178], Mg/Al-LDHs, Zn/Al-LDHs, and Zn/Mg/Al-LDHs [179] were studied and compared, and Mg/Al-LDHs possessed the best lubrication. Moreover, LDHs with different metal ions and geometry features (spherical, plate-like, and flower-like) were discussed [180]. It was found that instead of different chemical compositions, morphology had a greater influence on the tribological behaviors, and flower-like LDHs with the high specific surface area were demonstrated to exhibit the best performance. Calcined [181] and modified LDHs [182] were also studied.

In addition, layered palygorskite and anthracite sheets as natural inorganic minerals were also studied [183, 184].

3.3.4 Others

Zirconium phosphate (ZrP) with plate-like nanostructures was found to be effective as additive [185]. CFs are covalent crystalline porous polymers that achieve the assembly of organic units to create designed skeletons [186]. Triazine-based CFs as additives in oil exhibited high thermal stability, excellent dispersity, and tribological performances [187]. Several families of CFs have been constructed, but there are still challenges in exploring their application of additives in lubricating oil. Besides, a few studies have also shown the application of BP nanosheets in tribology. BP nanosheets prepared by ball milling could improve the load-carrying capacity, friction reduction, and anti-wear properties [188, 189].

3.4 Nanocomposites

Due to the synergetic effect, nanocomposites usually possess superior tribological performance compared to the individual. According to the nanocomposites composited with different dimensions, they are divided into five major sections: composition of 0D nanomaterials composited with 1D nanomaterials (0D/1D), and others are marked as 0D/2D, 1D/2D, 0D/0D, and 2D/2D. Because few reports related 1D/1D, there is no detailed introduction in this review. A summary and comparison of nanocomposites as lubricating oil additives is shown in Table 4.

3.4.1 0D/1D

The nanocomposites of MoS_2 nanoparticles composited with different types of carbon nanomaterials were synthesized [28], and it was confirmed that MoS_2@CNT (0D/1D), MoS_2@G (0D/2D), and MoS_2@C_{60} (0D/0D) showed better stability compared with MoS_2 nanoparticles when dispersed in PAG and noticeably

Table 4 Summary and comparison of nanocomposites as lubricating oil additives.

Nanomaterial detail				Working condition					Test result			
Type	Nanomaterial	Functionalization	Concentration	Base oil	Tribometer	Friction pair	Load (N)	Speed	Dispersion stability	COF reduction (%)	Wear reduction (%)	Ref.
0D/1D	Cu/CNTs	PDA	0.2 wt%	Rapeseed oil	Ball-on-disk tribometer	GCr15/45# steel	1–12	500 rpm	More than 10 days	34	24	[194]
	Ni/CNTs	Octadecylamine	0.2 wt%	500N	Ball-on-disk tribometer	GCr15/stainless steel	5	0.1 m/s	More than 5 days	44	56	[193]
	ZnO/CNTs	—	0.25 wt%	10W40	Ball-on-disk tribometer	Steel/bronze	35–55	5–15 Hz	Add dispersant	32	74	[191]
	MoS_2/CNTs	—	1 wt%	PAG	Ball-on-disk tribometer	AISI 52100	100	25 Hz	More than 14 days	~33	~98	[190]
	Ni/magnesium silicate hydroxide	Oleic acid	0.5 wt%	PAO10	Ball-on-disk tribometer	AISI 52100/45# steel	100	500 rpm	More than 10 h	15	78	[192]
0D/2D	MoS_2/G	—	1 wt%	PAG	Ball-on-disk tribometer	AISI 52100	100	25 Hz	More than 14 days	~25	~98	[190]
		—	0.2 wt%	10W-40	Four-ball tribometer	Steel	392	1,200 rpm	More than 15 days	25	58	[205]
	MoS_2/ montmorillonite	—	0.2–1 wt%	Bis(2-ethyl hexyl) sebacate	Ball-on-disk tribometer	GCr15	7.84	0.1 m/s	—	49	76	[195]
	Ag/MoS_2	—	2 wt%	Pure formulated oil	Ball-on-disk tribometer	AISI 52100	5	0.13–16 cm/s	—	20	37	[208]
	Ni/MoS_2	—	0.5 wt%	SN 500	Four-ball tribometer	AISI 52100	392	1,200 rpm	More than 240 h	21	42	[171]
	Ni/GO	Oleic acid	0.08 wt%	Liquid paraffin	Four-ball tribometer	GCr15	50–300	300–1,500 rpm	More than 10 days	32	42	[198]
	Cu/GO	Stearic acid	0.05 wt%	Liquid paraffin	Four-ball tribometer	GCr15	200	1,200 rpm	More than 10 days	27	53	[201]
		PDA	0.1 wt%	Soybean oil	Ball-on-disk tribometer	GCr15/45# steel	5	300 rpm	More than 8 days	47	26	[202]
		Ionic liquid	0.08 wt%	PEG 200	Four-ball/ ball-on-disk tribometer	GCr15	392/ 1–8	1,200 rpm/2 Hz	—	41	47	[207]
	Au/GO	Oleylamine	0.1 wt%	PAO6	Ball-on-disk tribometer	AISI 52100/AISI 40300	10	0.1 m/s	More than 10 days	34	73	[199]
	SiO_2/GO	Coupling agent	3 wt%	PEG	Ball-on-disk tribometer	AISI 52100	10	25 Hz	More than 7 days	23	73	[200]
	TiO_2/F-rGO	—	3 mg/10 mL	GTL8	Ball-on-disk tribometer	Si_3N_4/316 steel	3–10	2 Hz	More than 2 weeks	34	88	[196]
	SiC/G	—	0.06 wt%	PAO4	Four-ball tribometer	Steel	490	600 rpm	More than 7 days	~36	20	[203]
	Ag/BP	Oleic acid	0.075 wt%	PAO6	Ball-on-disk tribometer	AISI 52100/AISI 40300	10	200 rpm	—	73	92	[206]
	Cu/WS_2	PDA	0.9 wt%	PAG	Ball-on-disk tribometer	AISI 52100	100	25 Hz	More than 7 days	34	98	[204]
	Mn_3O_4/G	—	0–1 wt%	PAO6	Ball-on-disk tribometer	GGr15	2	2.4 mm/s	—	75	97	[12]
	CS/G	Nitric acid	0.2625, 0.275, and 0.3 wt%	20W-40	Four-ball tribometer	Chromium steel	392	1,200 rpm	30 days	18	8.4	[241]
1D/2D	CNTs/MoS_2	Oleylamine	0.1 wt%	NLG2	Ball-on-disk tribometer	Steel X45Cr13/steel X155CrVMo12-1	90	5 mm/s/ 0.5 m/s	—	25	20	[209]
0D/0D	MoS_2/C60	—	1 wt%	PAG	Ball-on-disk tribometer	AISI 52100	100	25 Hz	More than 14 days	~25	~97	[190]
	Al_2O_3/SiO_2	Coupling agent	0.5 wt%	Mineral oil	Four-ball tribometer	—	147	1,450 rpm	More than 3 months	50	22	[210]
	Serpentine/La$(OH)_3$	—	0.5 wt%	15W-40	Four-ball tribometer	GCr15	200	400 rpm	Add dispersant	25	42	[213]
	C_3N_4/Cu	—	0.5 wt%	Liquid paraffin	Ball-on-disk tribometer	440-C chromium steel/45# steel	20–100	100 rpm	Add dispersant	35	30	[212]
	Al_2O_3/TiO_2	Oleic acid	0.25 wt%	5W-30	Tribotest rig	—	20–230	0.5–1.2 m/s	More than 55 days	50	30	[211]
	TiO_2/C_3N_4	—	0.00625 mg/mL	Vegetable oil	Four-ball tribometer	High carbon and high chromium alloy	400	600 rpm	More than 48 h	23	17	[214]
2D/2D	MoS_2/G	—	0.5 wt%	Esterified bio-oil	Four-ball tribometer	ASTM E52100	100–500	400–1,450 rpm	More than 10 days	65	28	[218]
		—	1 wt%	Perfluoropolyether	—	—	—	—	More than 14 days	57	91	[219]
	Boehmite/GO	Coupling agent	0.03 mg/mL	VHVI8	Ball-on-disk/ four-ball tribometer	100Cr6 steel	10/392	5 cm/s /600 rpm	More than 48 h	14	73	[220]
	BN/G	Oleic acid	1 wt%	500 N	Four-ball tribometer	AISI 52100	200–1,200	1,770 rpm	—	~34	22	[221]

improved tribological behaviors compared with that of PAG or PAG containing separate each part. Similarly, MoS_2@CNT (0D/1D), MoS_2@GO (0D/2D), and MoS_2@rGO (0D/2D) were also compared [190].

ZnO/CNTs nanocomposites with varied mass ratios and concentrations revealed that nanocomposites exhibited enhanced friction reduction and higher anti-wear capability than pure oil, individual ZnO, and CNTs [191]. Interestingly, magnesium silicate hydroxide nanotubes composited with Ni nanoparticles could form a smoother tribo-film through tribo-chemical reactions, which were devoted to friction reduction (15%) and enhanced anti-wear ability (78%) [192]. Besides, the composition of CNTs composited with Ni [193] or Cu [194] nanoparticles was also studied, and the results are listed in Table 4.

3.4.2 0D/2D

The 0D nanomaterials in composites most frequently used are metal and oxide/sulfide nanoparticles, including Ni, Cu, Ag, MoS_2, TiO_2, and SiO_2.

Montmorillonite is a resourceful laminar mineral with low cost that is of great potential as lubricating oil additives. MoS_2/montmorillonite composites achieved the improvement of COF and wear loss [195], suggesting the application prospects as lubricant additives. Significantly, a sandwichlike nanostructure of Mn_3O_4 nanoparticles and G sheets (Mn_3O_4@G) was prepared [12]. Even at a low concentration of 0.075 wt% and a high temperature of 125 °C, the COF and wear depth were reduced by 75% and 97%, respectively. Moreover, TiO_2/F-rGO nanocomposites with a close link between particles and sheets displayed a low COF and excellent anti-wear capacity attributed to the synergistic lubricating effect, as shown in Fig. 11. It is worth noting that BP dotted with Ag nanoparticles prepared via a facile approach significantly enhanced the tribological performances, and the COF and wear rate were reduced by 73% and 92%, respectively.

Combining the advantages of 0D and 2D nanomaterials, these spherical nanoparticles between nanolayers could transform sliding friction into rolling friction, acting as the protective casing to effectively reduce friction and enhance anti-wear behaviors. Therefore, a great deal of nanomaterials composited

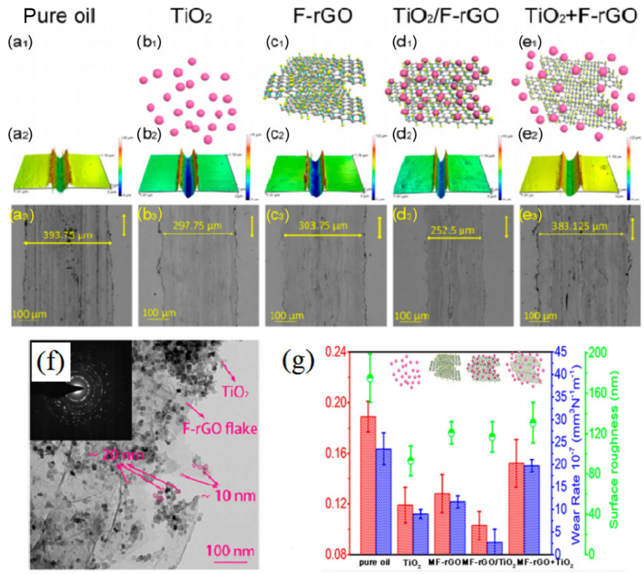

Fig. 11 (a_1-e_1) Schematic diagram of different nanoadditives; (a_2–e_2) Optical micrographs and (a_3–e_3) SEM images of wear tracks lubricated with pure oil, TiO_2 nanoparticles, F-rGO nanosheets, TiO_2/F-rGO nanocomposites, and a mixture of TiO_2 nanoparticles and F-rGO nanosheets; (f) TEM image of TiO_2/F-rGO nanocomposites; (g) tribological results. Reproduced with permission from Ref. [196], © American Chemical Society 2020.

with 0D and 2D have been carried out over the last ten years, e.g., MoS_2/montmorillonite, Ag/MoS_2, CSs/MoS_2 [197], Ni/MoS_2 [171], Ni/GO [198], Au/GO [199], SiO_2/GO [200], Cu/GO [201, 202], SiC/G [203], Cu/WS_2 [204], CS/G [156], and so on [205–208]. The detailed data are shown in Table 4.

3.4.3 1D/2D

With the innovative synthetic strategy, hybrid MoS_2@CNT nanocomposites were obtained, and the compatibility in nonpolar oils was achieved by coating with oleylamine [209]. In this kind of nanostructure, the outer surface of CNT was sheathed with 1 to 3 MoS_2 nanosheets that achieved unique synergy lubrication.

3.4.4 0D/0D

Compared with individual nanoparticles with functionalization or preparation in special ways, 0D/0D nanocomposites are of weaker ability. The COF and wear reduction of mostly 0D/0D nanocomposites were less than 50%, e.g., the COF and wear of Al_2O_3/SiO_2 nanoadditives were reduced by 50% and 22% [210], Al_2O_3/TiO_2 were 50% and 30% [211],

C_3N_4/Cu were 35% and 30% [212], serpentine/La$(OH)_3$ were 25% and 42% [213], and TiO_2/C_3N_4 were 23% and 17% [214]. It is worth noting that the COF and wear of MoS_2/C_{60} were reduced by approximately 25% and 97%, respectively; however, under the same conditions, because C_{60} with a smaller surface area could not protect MoS_2 nanoparticles from oxidation during the sliding process and their aggregation would weaken their synergistic effect [28].

3.4.5 2D/2D

The layer morphology allows deposition into the sliding area, protecting sliding surfaces from direct contact. Further, due to the different properties of 2D nanomaterials, composite nanosheets may overcome the limitations of individuals [215–217, 221].

MoS_2/G composite nanosheets as additives were discussed [218, 219], and their outstanding tribological performances were attributed to stable surface boundary films formed during the sliding. Besides, boehmite/GO [220] and BN/G [221] nanocomposites were prepared and explored as lubricating oil additives, both exhibiting better friction reduction and anti-wear properties than the homogeneous individual nanosheet.

The poor oxidation resistance of MoS_2 is a problem for its application. Combination with other nanomaterials with stronger oxidation resistance is an effective method. For all nanomaterials with poor oxidation resistance, there are four methods: (1) As mentioned above, select one material with stronger oxidation resistance to prepare composites, and combine their advantages. The one with poor oxidation resistance could be protected by the cover of another material. Accordingly, tribological characteristics may be changed with the various material addition. (2) Add traditional antioxidants into oil to enhance the oxidation resistance. It is convenient and effective. (3) Antioxidants are used as surface modification groups to coat nanomaterials that are easy to be oxidized, by which the good dispersion of nanomaterials can also be achieved. (4) *In-situ* tribo-chemical sulfurization of oxides. Select oxides as additives in base oil containing sulfur element, and *in-situ* tribo-chemical sulfurization occurs during sliding. This method was proved to be effective, and the tribological properties of tribo-film are better, but the sulfur element cannot be avoided.

4 Discussion

Due to a large number of articles and complexity of retrieval, it is impossible to cover entire published articles in this review, but most of the research results and statistics have reference value for nanomaterial design. According to many experimental results, the tribological characteristics of most nanomaterials are summarized below. However, due to the complexity of the friction process and the diversity of influencing factors, the conclusions are not absolute, which may be different from special nanomaterial and working conditions.

4.1 Relationship between morphology and tribological performance

Tribological performance is found to be affected by many factors. Morphology of nanomaterials plays an important role, which directly determines the pressure to which the nanoparticles are subjected to during loading.

As for 0D nanoparticles, the size of spherical structure is critical to tribological performance of nanoparticles. The smaller nanoparticles could more significantly improve the tribological performances than the larger ones, but the mixed nanoparticles with different sizes display better tribological performance than those with uniform size. Moreover, it has been confirmed by a large number of studies that load-carrying capacity can be significantly improved by 0D and 1D nanoparticles that maybe benefit from the structure of sphere and column.

2D nanomaterials with weak interlayer interactions could offer low interfacial shear force, which is beneficial to friction reduction. But for non-concentric layers, the presence of defects in structure would remarkably increase the shear force. By comparison, sheet-like structures generally outperform other morphologies [222]. As discussed in Section 3, nanosheets possess the ability to easily form linear tribo-film and supernatant performance [171]. The best example is that poorly crystalline onion-like MoS_2 nanoparticles own better lubricating properties than those of perfectly crystallized spherical particles because of their stronger exfoliation ability to produce sheets rapidly and assembled layer upon layer to form a tribo-film [223].

The morphology is also found as a critical role in dispersion stability of nanomaterials in oil. Ordinarily, the smaller-size nanomaterials are more easily dispersed in oil than the larger ones, but it will be changed when functionalization on nanomaterials' surface is conducted. Typically, the porous or flower-like nanomaterials with the relatively high specific surface area have a good dispersion in lubricating oil, which has been widely reported.

It is worthy to note that the influence of morphology is not absolute, and the aforementioned is just a summary of the most of existing experimental results. For example, the size of poorly crystalline onion-like MoS_2 nanoparticles do not impact their tribological performance, because they can be uniformly exfoliated into sheets to form tribo-film [9]; larger LDH nanosheets with a higher degree of crystallinity show the best and stable tribological performance than the smaller ones, because a tribo-film with superior mechanical property is formed during sliding as a result of high crystallinity [177]; aggregates are responsible for some tribo-films formation in point contact but not the nanoparticles with good dispersion in oil [190].

Briefly, although the morphology plays an important role, the tribological properties are affected by many factors, which should not be determined by the structure separately, considering that influence factors at the same time is necessary.

4.2 Statistical analysis of tribological data

Statistical analysis of friction reduction and anti-wear properties of four types of nanomaterials with different nanostructured features (0D, 1D, 2D, and nanocomposites) are directly shown in Fig. 12, including the data in Tables 1–4. The following comparison and discussion can be drawn.

1) It is relatively easy for nanomaterial additives to enhance the anti-wear property of base oil, but a significant reduction of COF may require more efforts. On the one hand, these results may be attribute to the reason that nanomaterials as lubricant additives can play as "a protective coating" or "bearing ball" between friction pairs, separating the sliding surfaces to avoid the direct contact to significantly enhance the anti-wear performance. On the other hand, the problem of COF reduction may be imputed to the physicochemical properties of lubricating oil and surface chemistry. The value of COF is closely connected to the pressure–viscosity coefficient and contact pressure [222], which can be easily explained by the Stribeck curve. The low COF value can be obtained under lubricants

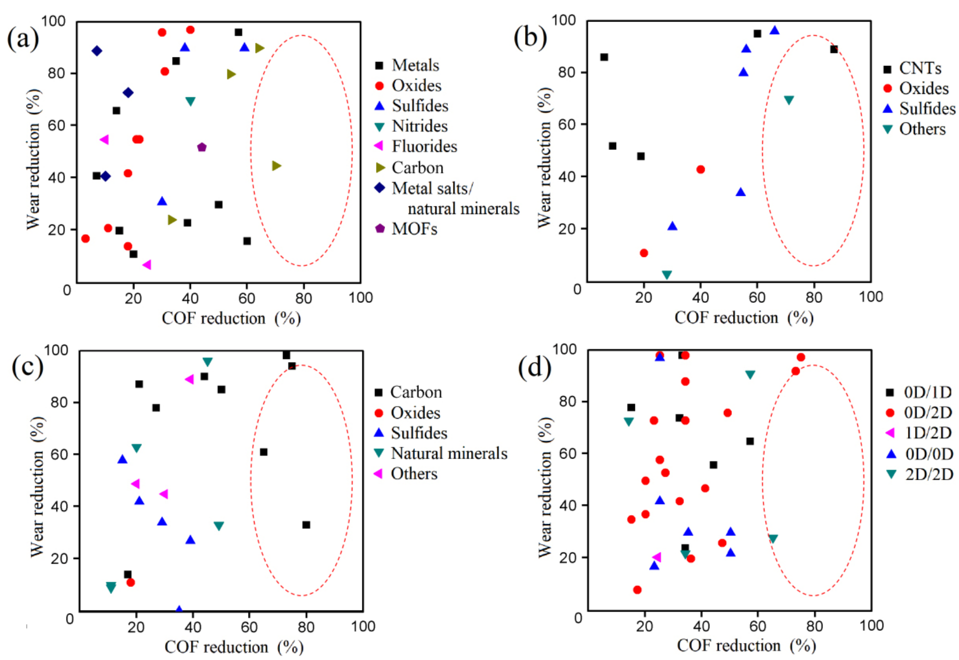

Fig. 12 Statistical analysis of friction reduction and anti-wear properties of four types of nanomaterials with different nanostructured features: (a) 0D nanomaterials; (b) 1D nanomaterials; (c) 2D nanomaterials; and (d) nanocomposites.

with a low pressure–viscosity coefficient, and the reduction of apparent viscosity can lead to the ordering of molecules. Generally, the pressure–viscosity coefficient of lubricating oil is relatively large, so it is challenging for lubricating oil to realize low COF value under relatively high contact pressure. Luo's group [224] that has been devoted to superlubricity believe that the ultralow COF is absolutely not obtained by using traditional steel/steel pairs under the same conditions, which is attribute to the surface chemistry. However, statistics show that the proportion of steel/steel pairs used in studies on nanomaterials as lubricating oil additives is 85%.

2) The nanomaterials that possess the ability to synchronously improve friction reduction and anti-wear properties of lubricating oil are mostly carbon-based nanomaterials, such as G and CNTs. The lubrication state of lubricating oil is mostly boundary lubrication, where the oil molecules are strongly adsorbed on the surfaces with only two or three molecular layers to form lubricant film. Benefitting from the developments of exfoliated technology, ultrathin or few-layered G and single-wall CNTs can be achieved by overcoming the strong interatomic-layer bonding. Ultrathin carbon-based nanomaterials could enter the thin oil film without damage to provide a lower shear stress sliding interface and play important roles in oil intermolecular interactions that are helpful to reduce friction. Besides, G is also considered to be an effective nanoadditive to improve the superlubricity system.

3) Compared with individual nanomaterials under the same experimental conditions, most nanocomposites own obvious superiority in tribological performances. However, according to the data of different reported articles that differ from preparations and friction conditions, generally, better tribological performances are not exhibited when nanocomposites are used as lubricating oil additives. It is shown that the different working conditions have great influences on tribological performances of nanomaterials [225], moreover, future experimental verifications and mechanism research are needed.

4.3 Lubrication regime analysis

It is well known that the Stribeck curve is widely used to determine the lubrication regime (Fig. 13), including boundary lubrication, mixed lubrication, and elasto-hydrodynamic lubrication, which can also be used to identify the role that nanomaterials play during friction [22]. Most nanomaterial additives could substantially improve the lubrication performance in all the lubrication regimes [226, 227], and generally, the impacts on boundary lubrication and mixed lubrication are relatively greater [36, 228].

In boundary lubrication, there is a little rolling effect, and the tribological performances are determined by a protective film, whose formation can be promoted by nanomaterial additives [39, 54]. Therefore, the mechanical properties of nanomaterials play a crucial role in the mechanical properties of protective film. Specifically, under low frequency or high load, the strength of film is more necessary; but under high-frequency condition, the ductility becomes more important [54]. It also explains why spherical nanoparticles can significantly improve the load-carrying capacity of oil. Besides, tribological performances of nanomaterials are affected by the viscosity of base oil in boundary lubrication. The more effective performances by adding nanoparticles were observed in base oil with lower viscosity. Because COF decreases as the oil viscosity increases, the lubricant with higher viscosity is more difficult to be squeezed out of the contact area. A longer squeezing time achieves a shorter time for the asperities to contact and results in a smaller COF [229].

By adding some nanomaterial additives, in boundary lubrication, there are not only physical effects that

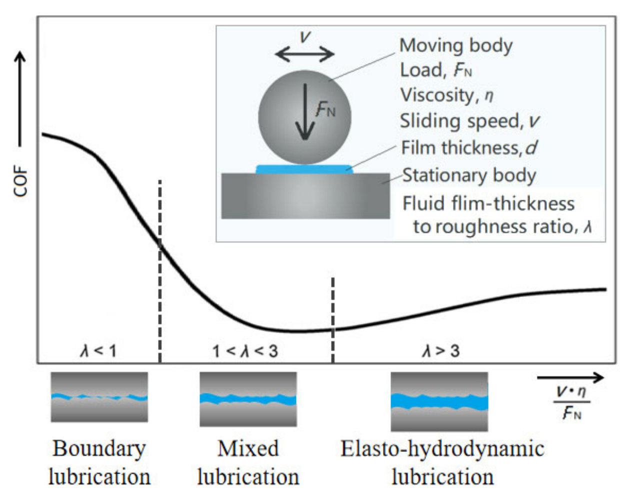

Fig. 13 Diagram of lubrication regimes in Stribeck curve.

arise, but also tribo-chemical reactions. During the sliding, tribo-chemical reactions between nanomaterials and the iron atoms and/or iron oxide species occur, and their products could adhere to the steel surfaces and form a tribo-film with a low shearing strength [65, 227].

In elasto-hydrodynamic lubrication, the dominant factor in determining the tribological performances is the flow feature of nanofluids, which can also be influenced by nanomaterial additives. A theory, based on some experimental results, was proposed: The nanoparticles induced a plug flow in the narrow area between sliding surfaces, leading to only a few layers of oil molecules sliding on each other, and then friction reduced [230, 231]. The aggregation phenomenon among nanoparticles was also found in the Hertz contact area [54]. However, results in some research cannot be explained by this theory, e.g., ZrP additives with higher concentration led to a lower COF [185]; under some working conditions, the parts of COF reduction by GO additives are almost the same in all the lubrication regimes [232]. It can be seen that the process of friction is quite complex, and the influence of nanomaterials on the properties of nanofluids needs to be further studied.

5 Mechanisms

5.1 Interaction between nanomaterials and sliding surface

The accepted lubrication mechanisms between nanomaterials and sliding surface are also discussed in many reviews that can be briefly summarized as follows: (1) Nanomaterials promote the formation of tribo-films, protection films, or adsorption films, which can separate the friction surfaces and change the surface property. (2) Physical function. The added nanomaterials in lubricating oil may result in promising tribological characteristics owing to the sliding and rolling effect within sliding surfaces depending on the normal and shear stress. Further, small-scale nanomaterials can fill the gaps on surfaces or polish the surfaces to reduce surface roughness, and it is called the polishing or smoothing effect. (3) Chemical function. Nanomaterials reformed because of certain reasons and deposited on the wear tracks during the sliding process. This function is called the repair effect. The main friction mechanisms are shown in Fig. 14.

In addition to the above mentioned, it is confirmed that nanomaterials are firmly associated with the interfacial interaction between nanomaterials and substrates. For instance, when the lubrication with the single layer is considered, the weak interlayer interactions are not the main factor in determining its lubrication performance, but the interaction between the layered nanomaterial and substrate surface is. Then the substrate properties have an increasing influence on the mechanical and dissipative properties of the layer nanomaterial [23]. It was reported that when exfoliated G was applied on surfaces such as mica, good contact with the substrate and strong adhesion were obtained. When applied on SiO_2 with atomically rough surfaces, the adhesive force between G and substrate was reduced, generating the "puckering" effect. Because the contact region was decreased after folding, G maintained the rough configuration, and the tribological performances were not improved [233]. However, GO with functional groups could be covalently grafted to the substrate surface to overcome abscission. In addition, with high out-of-plane flexibility, 3D nanostructural G is dominated by the contact substrate geometry, and tribological characteristics of G particularly depend on the roughness of sliding surface and interfacial adhesion by van der Waals forces. Hence, before, after, or in the process of sliding, the adhesion to substrate surface and morphology of nanomaterial are closely correlative to their tribological properties [23].

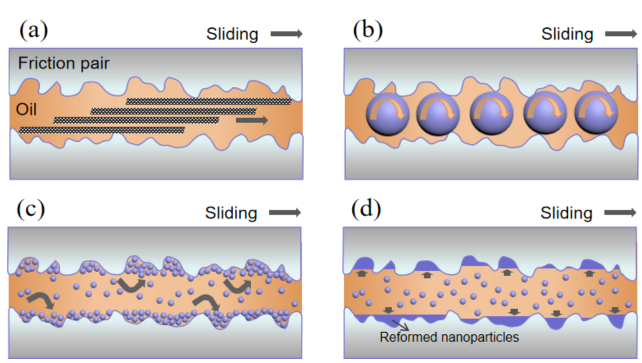

Fig. 14 Four main friction mechanisms: (a) sliding; (b) rolling; (c) polishing or smoothing; and (d) mending or self-repairing.

Similar to the aforementioned nanoparticles, the existence of 1D nanomaterial CNTs could also form the aggregations in the contact area, but during the sliding process, surface roughness of substrate led to a decrease in the number of aggregations, passing through the contact area. And an increasing film thickness, friction reduction, and wear drift were observed, originating from the transient propagation of CNT aggregation through the contact area affected by the interfacial interaction [135].

5.2 Interaction between nanomaterials and lubricating oil

The organization and distribution of nanomaterials in oil depend on their character of interaction forces such as van der Waals force, electrostatic force, Brownian motion, and steric interactions. The rheological performances and flow properties of colloidal fluids are governed by these forces together with dynamic interactions in oil owing to shear rate. For example, differing from graphite bulk [234], rGO is composed of loose layers with a lot of narrow cracks. This specific nanostructure reduces the van der Waals force between rGO interlayers, resulting in the decrease of resistance under shear force. The carbon layers with low cavities and defects can enhance the tribological behaviors [168]. The diagram of mechanisms is shown in Figs. 15(a_1) and 15(a_2).

The polar nature plays an important role in the interaction between nanomaterials and lubricating oil [235]. Polar compounds can be adsorbed onto metallic surfaces, and this attraction results in a thin oil film. However, metallic nanoparticles could also be adsorbed by polar molecules, preventing their ball-bearing function as lubricating oil additives or disrupting the oil film formation [38]. Accordingly, for the polar nature of different lubricating oil, surface functionalization on nanomaterials can effectively transform the interaction between nanomaterials and lubricating oil, such as enhancement of dispersion stability and homogeneous distribution; however, not all treatments associated with surface functionalization are positive [27, 53, 205]. The diagram of mechanisms is shown in Fig. 15(b). The conventional view is that tribological performances of nanomaterials as lubricating oil additives are in proportion to their dispersion stability in oil. However, when nanoparticles were added into oil as additives in point contact, tribo-film formation originated from the aggregates of nanoparticles but not the well-dispersed [190]. This new point may promote the advancement of novel lubricating oil additives design in different working conditions.

The relationship between nanomaterials and oil film is also one of the focus points discussed in the tribology fields. One of the major affecting factors to consider is the size of nanomaterials compared to the thickness of oil film. When the size of nanomaterials is larger than oil film thickness, nanomaterial behaviors are dominated by contact kinematics conditions. At low sliding velocity, nanomaterials easily enter into the contact surface where an adherent boundary oil film is from. However, this oil film disappears with

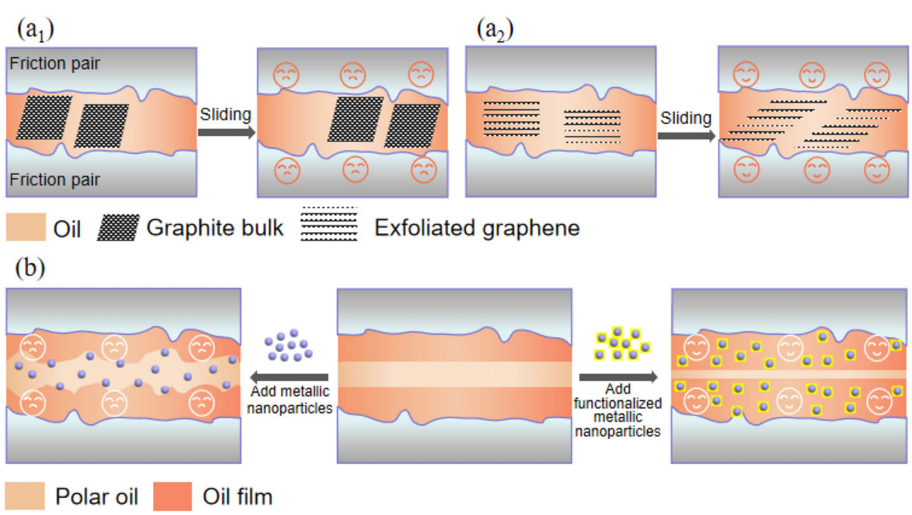

Fig. 15 Diagram of mechanisms.

the sustained increase of velocity, where the state of lubrication is changed from mixed lubrication to elasto-hydrodynamic lubrication. At higher sliding velocity, most materials in nanofluids are rejected to directly contact the surface, inducing a decrease in oil film thickness [135]. Therefore, substrate surface trapping mechanisms should be highlighted.

As already mentioned in Section 4, the viscosity of base oil also has an impact on the tribological performances of lubricant, especially in boundary lubrication. The thermal conductivity and viscosity of oil are both important properties, which can be directly affected by temperature and nanomaterial concentration. Generally, most oil samples mixed with nanomaterials have Newtonian behavior. The viscosity of nanofluids rises with the increasing concentrations of nanomaterials and decreasing temperatures [91], moreover, it is more sensitive to the concentrations [131]. At high temperatures and heat fluxes, heat transfer in lubricant assumes an important role. The presence of nanomaterials with high thermal conductivity could enhance the heat transfer from the contact surface, and lead to higher viscosity and load-carrying capacity even at a low concentration [91, 92].

5.3 Interaction between nanomaterials and other additives

With the development of oil additives, the coexistence of nanomaterials with conventional lubricating oil additives is unavoidable [236]. From the tribological data analyses of studies on lubricating oil mixed with nanomaterials and other additives, it is shown that in general, the tribological performances of base oil both added with nanomaterials and other additives are better than those of the bare nanomaterials, indicating the synergy between nanomaterials and other oil additives.

Dispersants are the most commonly used with nanomaterials in lubricating oil, because the dispersed stability of nanomaterials can be improved by adding them. This method could easily solve the agglomeration problem of nanomaterials in lubricating oil that is more simple, economical, and easier to achieve than surface functionalization on nanomaterials.

The interactions between MoS_2 nanotubes and several oil additives were investigated, which depended on the contact conditions and lubrication surfaces [30, 237]. The synergetic interaction was obtained between MoS_2 nanotubes with anti-wear additives under mixed rolling and sliding conditions. Besides, all the selected oil additives displayed a synergistic phenomenon with MoS_2 nanotubes under extreme pressure, indicating the importance of well-dispersed nanomaterial in boundary lubrication. However, higher antagonism was observed between the MoS_2 nanotubes and dispersants under reciprocating sliding. Those phenomena suggest that the effect of other oil additives on nanomaterials lubrication is also affected by working conditions and lubrication regime.

As shown in Fig. 10, there was an excellent synergistic effect between 3D G and T161. The edge and surface of 3D G were modified by long-chain T161 to form a steric layer, which enhanced the dispersion stability of 3D G and ensured the sustained supply of 3D G to promote the homogenization of oil film. Under lower contact pressure, 3D G could fill the tracks on the wear surface, and 3D porous nanostructures were mostly retained, resulting in the improvement of tribological performances.

5.4 Interaction between nanomaterials in nanocomposites

It must be accepted that there are different interactions between nanomaterials in nanocomposites, such as synergy and antagonism effects. Different types and nanostructures of nanomaterials differ in their characters and advantages. For instance, metallic nanoparticles own unique properties of non-corrosiveness and low melting point; the small size (< 10 nm) of CDs; large length-to-diameter aspect ratios of CNTs; and mechanical stability of carbon-based nanomaterials. In general, small-sized nanoparticles can improve the friction reduction and anti-wear properties, and large-sized nanoparticles exhibit better load-carrying capacity [111]. The coexistence of nanomaterials' advantages in achievable conditions is always expected by researchers.

Strong van der Waals forces and interactions are revealed due to the large surface area of a few graphene-based layers, and the tribological performance of oil mixed with graphene-based nanomaterials is limited by the aggregation of graphene sheets. Thus, there is no beneficial uniform coverage on the tribo-film. However, nanoparticles or nanotubes can effectively prevent graphene-based layers from stacking; moreover, they can roll between layers to reduce friction. The composites of 0D/2D and 1D/2D effectively combine the advantages of different nanostructures. The diagram of synergy effects with different dimensions are shown in Fig. 16.

Other parameters of nanomaterials in nanocomposites also need to consider, such as the concentration, the ability to deform, the affinity between different nanomaterials, and the mass ratio of different nanomaterials that can control the tribological performance of nanomaterials as lubricating oil additives.

6 Outlook

To date, a large number of applications in nanomaterials as lubricating oil additives have been carried out, indicating the prosperous development of this field. A preliminary suggestion is provided by this review for selecting appropriate nanomaterials to achieve superior tribological performances. However, analysis of experimental process and data indicates that there are still some challenges in applications. The following may be important future research suggestions in the development of nanomaterials as lubricating oil additives.

1) Trans-dimensional research. Nonconforming experimental data are obtained by using the same nanomaterials in different researches, which may be attributed to the different experimental processes, contact surfaces, and nanostructure of nanomaterials or others. Trans-dimensional research on tribology and molecular mechanism in depth is needed to explain the problem. Therefore, maybe several fields need to be paid attention to (i) the application of molecular dynamics simulation [238, 239] of tribological behaviors for nanomaterials and the combination of molecular simulation and tribological tests; (ii) the systematic research on the transformation regularities of oil film, contact surface, nanomaterials, and energy throughout the process of friction and the change regularities of tribological performances under different working conditions; (iii) the molecular interaction system between oil, contact surface, nanomaterials, and other conventional additives.

2) Design of nanoparticles. In general, scholars prefer the study of nanomaterials that have already been discovered. Therefore, changing the traditional pattern of research is important to reveal and achieve new nanomaterials with targeted tribological behaviors. For example, the geometry, nanosize, and functionalization of MOFs and CFs can be precisely controlled and designed, and it is interesting in studying their application in lubricating oil. However, the study of MOFs as lubricating oil additives began in 2011, and CFs began in 2017; there is few research carried out. And the same is true for ILs. Nanomaterial design is difficult but may be most effective to obtain better tribological performances.

3) Preparation with the superior method. Many severe preparation methods of nanomaterial have been carried out to pursue better tribological performances,

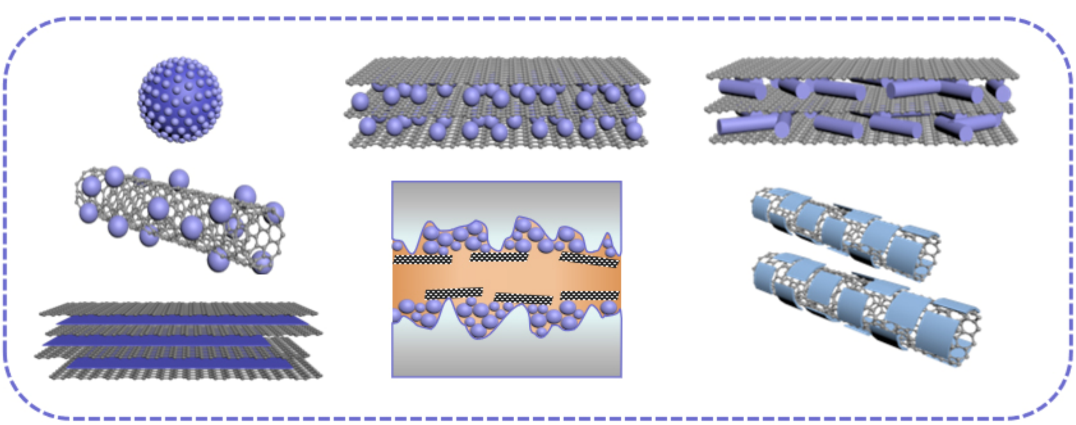

Fig. 16 Diagram of synergy effects with different dimensions.

but some drawbacks are displayed, such as high cost, small-scale production, poor repeatability, long time-consuming, and so on. It is hardly accessible in the current industry. One-step and low-cost methods that can achieve the preparation of nanomaterials with superior tribological performances are promising. On the other hand, due to the abundant resources and low cost, natural minerals are worth exploring in tribology. However, more efforts are required to optimize their tribological performance.

4) Research on synergistic mechanisms. Benefitting from the synergistic lubricating effect, the combination of two or more nanomaterials has better tribological behavior than individual nanomaterials under the same working conditions. On the other hand, the coexistence of nanomaterials with other conventional additives is positive and unavoidable. However, the synergistic lubricating effect and collaborative mechanism are not certainly confirmed at a molecular level, which is necessary for lubrication system design.

5) Environmental protection. It is important to minimize or eliminate the use of sulfur and phosphorus contained in lubricating oil additives. There is no doubt that eco-friendly nanomaterial is of great help to reduce energy consumption and carbon footprint. Eco-friendly nanomaterial additives are useful for environmental sustainability and meet the requirements of green tribology [240], which is a new area for tribologists.

Acknowledgements

This work was supported by the National Key R&D Program of China (No. 2018YFB2000301) and the National Natural Science Foundation of China (No. 51905385).

Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

References

[1] Holmberg K, Siilasto R, Laitinen T, Andersson P, Jäsberg A. Global energy consumption due to friction in paper machines. *Tribol Int* **62**: 58–77 (2013)

[2] Holmberg K, Erdemir A. Influence of tribology on global energy consumption, costs and emissions. *Friction* **5**(3): 263–284 (2017)

[3] Zhang S W. Recent developments of green tribology. *Surf Topogr Metrol Prop* **4**(2): 023004 (2016)

[4] Holmberg K, Andersson P, Erdemir A. Global energy consumption due to friction in passenger cars. *Tribol Int* **47**: 221–234 (2012)

[5] Spikes H. Friction modifier additives. *Tribol Lett* **60**(1): 5 (2015)

[6] Gulzar M, Masjuki H H, Kalam M A, Varman M, Zulkifli N W M, Mufti R A, Zahid R. Tribological performance of nanoparticles as lubricating oil additives. *J Nanoparticle Res* **18**(8): 223 (2016)

[7] Duan H T, Li W M, Kumara C, Jin Y L, Meyer H M, Luo H M, Qu J. Ionic liquids as oil additives for lubricating oxygen-diffusion case-hardened titanium. *Tribol Int* **136**: 342–348 (2019)

[8] Zhu S Y, Cheng J, Qiao Z H, Yang J. High temperature solid-lubricating materials: A review. *Tribol Int* **133**: 206–223 (2019)

[9] Rabaso P, Ville F, Dassenoy F, Diaby M, Afanasiev P, Cavoret J, Vacher B, le Mogne T. Boundary lubrication: Influence of the size and structure of inorganic fullerene-like MoS_2 nanoparticles on friction and wear reduction. *Wear* **320**: 161–178 (2014)

[10] Liu L C, Zhou M, Jin L, Li L C, Mo Y T, Su G S, Li X, Zhu H W, Tian Y. Recent advances in friction and lubrication of graphene and other 2D materials: Mechanisms and applications. *Friction* **7**(3): 199–216 (2019)

[11] Xiao H P, Liu S H. 2D nanomaterials as lubricant additive: A review. *Mater Des* **135**: 319–332 (2017)

[12] Zhao J, Li Y R, He Y Y, Luo J B. *In situ* green synthesis of the new sandwichlike nanostructure of Mn_3O_4/graphene as lubricant additives. *ACS Appl Mater Interfaces* **11**(40): 36931–36938 (2019)

[13] Wang J H, Zhuang W P, Liang W F, Yan T T, Li T, Zhang L X, Li S. Inorganic nanomaterial lubricant additives for base fluids, to improve tribological performance: Recent developments. *Friction* **10**(5): 645–676 (2022)

[14] Zeleňák V, Saldan I. Factors affecting hydrogen adsorption in metal–organic frameworks: A short review. *Nanomaterials* **11**(7): 1638 (2021)

[15] Duan L L, Wang Y M, Zhang Y T, Liu J D. Graphene immobilized enzyme/polyethersulfone mixed matrix membrane: Enhanced antibacterial, permeable and mechanical properties. *Appl Surf Sci* **355**: 436–445 (2015)

[16] Tang W W, Zhang Z, Li Y F. Applications of carbon quantum dots in lubricant additives: A review. *J Mater Sci* **56**(21): 12061–12092 (2021)

[17] Kogovšek J, Kalin M. Various MoS_2-, WS_2- and C-based micro- and nanoparticles in boundary lubrication. *Tribol Lett* **53**(3): 585–597 (2014)

[18] Zhao J, Huang Y Y, He Y Y, Shi Y J. Nanolubricant additives: A review. *Friction* **9**(5): 891–917 (2021)

[19] Yang H M, Li J S, Zeng X Q. Tribological behavior of nanocarbon materials with different dimensions in aqueous systems. *Friction* **8**(1): 29–46 (2020)

[20] Duan L L, Li H, Zhang Y T. Synthesis of hybrid nanoflower-based carbonic anhydrase for enhanced biocatalytic activity and stability. *ACS Omega* **3**(12): 18234–18241 (2018)

[21] Duan L L, Wang H X, Liu J D, Zhang Y T. Three-dimensional self-assembled graphene oxide/enzyme in the presence of copper phosphate. *Biomed Phys Eng Express* **1**(4): 045101 (2015)

[22] Uflyand I E, Zhinzhilo V A, Burlakova V E. Metal-containing nanomaterials as lubricant additives: State-of-the-art and future development. *Friction* **7**(2): 93–116 (2019)

[23] Spear J C, Ewers B W, Batteas J D. 2D-nanomaterials for controlling friction and wear at interfaces. *Nano Today* **10**(3): 301–314 (2015)

[24] Jin Y L, Li J, Cheng B X, Jia D, Tu J S, Zhan S P, Liu L, Duan H T. Thermal oxidation behavior of trimethylolpropane trioleate base oil when exposed to iron surfaces. *Ind Lubr Tribol* **72**(3): 473–478 (2019)

[25] Wang S Z, McGuirk C M, Ross M B, Wang S Y, Chen P C, Xing H, Liu Y, Mirkin C A. General and direct method for preparing oligonucleotide-functionalized metal–organic framework nanoparticles. *J Am Chem Soc* **139**(29): 9827–9830 (2017)

[26] Bhattacharjee S, Jang M S, Kwon H J, Ahn W S. Zeolitic imidazolate frameworks: Synthesis, functionalization, and catalytic/adsorption applications. *Catal Surv From Asia* **18**(4): 101–127 (2014)

[27] Yu L, Zhang L, Ye F, Sun M, Cheng X L, Diao G Q. Preparation and tribological properties of surface-modified nano-Y_2O_3 as additive in liquid paraffin. *Appl Surf Sci* **263**: 655–659 (2012)

[28] Gong K L, Lou W J, Zhao G Q, Wu X H, Wang X B. MoS_2 nanoparticles grown on carbon nanomaterials for lubricating oil additives. *Friction* **9**(4): 747–757 (2021)

[29] Bojarska Z, Kopytowski J, Mazurkiewicz-Pawlicka M, Bazarnik P, Gierlotka S, Rożeń A, Makowski Ł. Molybdenum disulfide-based hybrid materials as new types of oil additives with enhanced tribological and rheological properties. *Tribol Int* **160**: 106999 (2021)

[30] Tomala A, Ripoll M R, Kogovšek J, Kalin M, Bednarska A, Michalczewski R, Szczerek M. Synergisms and antagonisms between MoS_2 nanotubes and representative oil additives under various contact conditions. *Tribol Int* **129**: 137–150 (2019)

[31] Chou R, Battez A H, Cabello J J, Viesca J L, Osorio A, Sagastume A. Tribological behavior of polyalphaolefin with the addition of nickel nanoparticles. *Tribol Int* **43**(12): 2327–2332 (2010)

[32] Sarno M, Mustafa W A A , Senatore A, Scarpa D. One-step "green" synthesis of dispersable carbon quantum dots/poly (methyl methacrylate) nanocomposites for tribological applications. *Tribol Int* **148**: 106311 (2020)

[33] Ali M K A, Hou X J, Abdelkareem M A A. Anti-wear properties evaluation of frictional sliding interfaces in automobile engines lubricated by copper/graphene nanolubricants. *Friction* **8**(5): 905–916 (2020)

[34] Yu H L, Xu Y, Shi P J, Xu B S, Wang X L, Liu Q, Wang H M. Characterization and nano-mechanical properties of tribofilms using Cu nanoparticles as additives. *Surf Coat Technol* **203**(1–2): 28–34 (2008)

[35] Li B, Wang X, Liu W, Xue Q. Tribochemistry and antiwear mechanism of organic–inorganic nanoparticles as lubricant additives. *Tribol Lett* **22**(1): 79–84 (2006)

[36] Choi Y, Lee C, Hwang Y, Park M, Lee J, Choi C, Jung M. Tribological behavior of copper nanoparticles as additives in oil. *Curr Appl Phys* **9**(2): e124–e127 (2009)

[37] Padgurskas J, Rukuiza R, Prosyčevas I, Kreivaitis R. Tribological properties of lubricant additives of Fe, Cu and Co nanoparticles. *Tribol Int* **60**: 224–232 (2013)

[38] Guzman Borda F L, Ribeiro de Oliveira S J, Seabra Monteiro Lazaro L M, Kalab Leiróz A J. Experimental investigation of the tribological behavior of lubricants with additive containing copper nanoparticles. *Tribol Int* **117**: 52–58 (2018)

[39] Chen Y F, Zhang Y J, Zhang S M, Yu L G, Zhang P Y, Zhang Z J. Preparation of nickel-based nanolubricants via a facile *in situ* one-step route and investigation of their tribological properties. *Tribol Lett* **51**(1): 73–83 (2013)

[40] Kumara C, Luo H M, Leonard D N, Meyer H M, Qu J. Organic-modified silver nanoparticles as lubricant additives. *ACS Appl Mater Interfaces* **9**(42): 37227–37237 (2017)

[41] Zhang S W, Hu L T, Feng D P, Wang H Z. Anti-wear and friction-reduction mechanism of Sn and Fe nanoparticles as additives of multialkylated cyclopentanes under vacuum condition. *Vacuum* **87**: 75–80 (2013)

[42] Abad M D, Sánchez-López J C. Tribological properties of surface-modified Pd nanoparticles for electrical contacts. *Wear* **297**(1–2): 943–951 (2013)

[43] Beckford S, Cai J Y, Chen J Y, Zou M. Use of Au nanoparticle-filled PTFE films to produce low-friction and low-wear surface coatings. *Tribol Lett* **56**(2): 223–230 (2014)

[44] Flores-Castañeda M, Camps E, Camacho-López M, Muhl S, García E, Figueroa M. Bismuth nanoparticles synthesized by laser ablation in lubricant oils for tribological tests. *J Alloys Compd* **643**: S67–S70 (2015)

[45] Zhang S W, Li Y, Hu L T, Feng D P, Wang H Z. Antiwear effect of Mo and W nanoparticles as additives for multialkylated cyclopentanes oil in vacuum. *J Tribol* **139**(2): 021607 (2017)

[46] He B L, Liu S, Zhao X Y, Liu J X, Ye Q, Liu S J, Liu W M. Dialkyl dithiophosphate-functionalized gallium-based liquid-metal nanodroplets as lubricant additives for antiwear and friction reduction. *ACS Appl Nano Mater* **3**(10): 10115–10122 (2020)

[47] Duan L L, Wang H X, Hou J W, Zhang Y T, Chen V. A facile, bio-inspired synthetic route toward flower-like copper phosphate crystals with high specific surface area. *Mater Lett* **161**: 601–604 (2015)

[48] Zhou J F, Wu Z S, Zhang Z J, Liu W M, Xue Q J. Tribological behavior and lubricating mechanism of Cu nanoparticles in oil. *Tribol Lett* **8**(4): 213–218 (2000)

[49] Pan Q H, Zhang X F. Synthesis and tribological behavior of oil-soluble Cu nanoparticles as additive in SF15W/40 lubricating oil. *Rare Met Mater Eng* **39**(10): 1711–1714 (2010)

[50] Denison G H, Condit P C. Oxidation of lubricating oils. *Ind Eng Chem* **37**(11):1102–1108 (1945)

[51] Dassenoy F, Jenei I Z, Pavan S, Galipaud J, Thersleff T, Wieber S, Hagemann M, Ness D. Performance and lubrication mechanism of new TiO_2 nanoparticle-based high-performance lubricant additives. *Tribol Trans* **64**(2): 325–340 (2021)

[52] Wright R A E, Wang K W, Qu J, Zhao B. Oil-soluble polymer brush grafted nanoparticles as effective lubricant additives for friction and wear reduction. *Angew Chem Int Ed* **55**(30): 8656–8660 (2016)

[53] Wang N, Wang H G, Ren J F, Gao G, Zhao G R, Yang Y W, Wang J Q. High-efficient and environmental-friendly PTFE@SiO_2 core–shell additive with excellent AW/EP properties in PAO6. *Tribol Int* **158**: 106930 (2021)

[54] Liu X Y, Xu N, Li W M, Zhang M, Chen L F, Lou W J, Wang X B. Exploring the effect of nanoparticle size on the tribological properties of SiO_2/polyalkylene glycol nanofluid under different lubrication conditions. *Tribol Int* **109**: 467–472 (2017)

[55] Peña-Parás L, Taha-Tijerina J, Garza L, Maldonado-Cortés D, Michalczewski R, Lapray C. Effect of CuO and Al_2O_3 nanoparticle additives on the tribological behavior of fully formulated oils. *Wear* **332–333**: 1256–1261 (2015)

[56] Luo T, Wei X W, Huang X, Huang L, Yang F. Tribological properties of Al_2O_3 nanoparticles as lubricating oil additives. *Ceram Int* **40**(5): 7143–7149 (2014)

[57] Mousavi S B, Heris S Z, Estellé P. Experimental comparison between ZnO and MoS_2 nanoparticles as additives on performance of diesel oil-based nano lubricant. *Sci Rep* **10**(1): 5813 (2020)

[58] Elagouz A, Ali M K A, Hou X J, Abdelkareem M A A, Hassan M A. Frictional performance evaluation of sliding surfaces lubricated by zinc-oxide nano-additives. *Surf Eng* **36**(2): 144–157 (2020)

[59] Mousavi S B, Heris S Z. Experimental investigation of ZnO nanoparticles effects on thermophysical and tribological properties of diesel oil. *Int J Hydrogen Energ* **45**(43): 23603–23614 (2020)

[60] Zhou G H, Zhu Y F, Wang X M, Xia M J, Zhang Y, Ding H Y. Sliding tribological properties of 0.45% carbon steel lubricated with Fe_3O_4 magnetic nano-particle additives in baseoil. *Wear* **301**(1–2): 753–757 (2013)

[61] Battez A H, González R, Viesca J L, Fernández J E, Díaz Fernández J M, Machado A, Chou R, Riba J. CuO, ZrO_2 and ZnO nanoparticles as antiwear additive in oil lubricants. *Wear* **265**(3–4): 422–428 (2008)

[62] Du P F, Chen G X, Song S Y, Chen H L, Li J, Shao Y. Tribological properties of muscovite, CeO_2 and their composite particles as lubricant additives. *Tribol Lett* **62**(2): 29 (2016)

[63] Xiong S, Liang D, Kong F X. Effect of pH on the tribological behavior of Eu-doped WO_3 nanoparticle in water-based fluid. *Tribol Lett* **68**(4): 126 (2020)

[64] Sgroi M F, Asti M, Gili F, Deorsola F A, Bensaid S, Fino D, Kraft G, Garcia I, Dassenoy F. Engine bench and road testing of an engine oil containing MoS_2 particles as nano-additive for friction reduction. *Tribol Int* **105**: 317–325 (2017)

[65] Wu X H, Gong K L, Zhao G Q, Lou W J, Wang X B, Liu W M. MoS_2/WS_2 quantum dots as high-performance lubricant additive in polyalkylene glycol for steel/steel contact at elevated temperature. *Adv Mater Interfaces* **5**(1): 1700859 (2018)

[66] Liu L, Liu Z Q, Huang P, Wu Z, Jiang S Y. Protein-induced ultrathin molybdenum disulfide (MoS_2) flakes for a water-based lubricating system. *RSC Adv* **6**(114): 113315–113321 (2016)

[67] Osim W, Stojanovic A, Akbarzadeh J, Peterlik H, Binder W H. Surface modification of MoS_2 nanoparticles with ionic liquid-ligands: Towards highly dispersed nanoparticles. *Chem Commun* **49**(81): 9311–9313 (2013)

[68] Chen S, Liu W M. Characterization and antiwear ability of non-coated ZnS nanoparticles and DDP-coated ZnS nanoparticles. *Mater Res Bull* **36**(1–2): 137–143 (2001)

[69] Chen S, Liu W M. Oleic acid capped PbS nanoparticles: Synthesis, characterization and tribological properties. *Mater Chem Phys* **98**(1): 183–189 (2006)

[70] Kang X H, Wang B, Zhu L, Zhu H. Synthesis and tribological property study of oleic acid-modified copper sulfide nanoparticles. *Wear* **265**(1–2): 150–154 (2008)

[71] Lahouij I, Bucholz E W, Vacher B, Sinnott S B, Martin J M, Dassenoy F. Lubrication mechanisms of hollow-core inorganic fullerene-like nanoparticles: Coupling experimental and computational works. *Nanotechnology* **23**(37): 375701 (2012)

[72] Li Z W, Hou X, Yu L G, Zhang Z J, Zhang P Y. Preparation of lanthanum trifluoride nanoparticles surface-capped by tributyl phosphate and evaluation of their tribological properties as lubricant additive in liquid paraffin. *Appl Surf Sci* **292**: 971–977 (2014)

[73] Qiu S Q, Dong J X, Chen G X. Tribological properties of CeF_3 nanoparticles as additives in lubricating oils. *Wear* **230**(1): 35–38 (1999)

[74] Reeves C J, Menezes P L, Lovell M R, Jen T C. The size effect of boron nitride particles on the tribological performance of biolubricants for energy conservation and sustainability. *Tribol Lett* **51**(3): 437–452 (2013)

[75] Chou C C, Lee S H. Rheological behavior and tribological performance of a nanodiamond-dispersed lubricant. *J Mater Process Technol* **201**(1–3): 542–547 (2008)

[76] Chou C C, Lee S H. Tribological behavior of nanodiamond-dispersed lubricants on carbon steels and aluminum alloy. *Wear* **269**(11–12): 757–762 (2010)

[77] Peng D X, Kang Y, Chen C H, Chen S K, Shu F C. The tribological behavior of modified diamond nanoparticles in liquid paraffin. *Ind Lubr Tribol* **61**(4): 213–219 (2009)

[78] Lee G J, Park J J, Lee M K, Rhee C K. Stable dispersion of nanodiamonds in oil and their tribological properties as lubricant additives. *Appl Surf Sci* **415**: 24–27 (2017)

[79] Zhai W Z, Lu W L, Liu X J, Zhou L P. Nanodiamond as an effective additive in oil to dramatically reduce friction and wear for fretting steel/copper interfaces. *Tribol Int* **129**: 75–81 (2019)

[80] Raina A, Ul Haq M I, Anand A, Mohan S, Kumar R, Jayalakshmi S, Singh R A. Nanodiamond particles as secondary additive for polyalphaolefin oil lubrication of steel–aluminium contact. *Nanomaterial* **11**(6):1438 (2021)

[81] Alazemi A A, Etacheri V, Dysart A D, Stacke L E, Pol V G, Sadeghi F. Ultrasmooth submicrometer carbon spheres as lubricant additives for friction and wear reduction. *ACS Appl Mater Interfaces* **7**(9): 5514–5521 (2015)

[82] Wu C W, Wei C X, Jin X, Akhtar R, Zhang W. Carbon spheres as lubricant additives for improving tribological performance of polyetheretherketone. *J Mater Sci* **54**(6): 5127–5135 (2019)

[83] Ye Q, Liu S, Xu F, Zhang J, Liu S J, Liu W M. Nitrogen–phosphorus codoped carbon nanospheres as lubricant additives for antiwear and friction reduction. *ACS Appl Nano Mater* **3**(6): 5362–5371 (2020)

[84] Wang B G, Tang W W, Lu H S, Huang Z Y. Ionic liquid capped carbon dots as a high-performance friction-reducing and antiwear additive for poly(ethylene glycol). *J Mater Chem A* **4**(19): 7257–7265 (2016)

[85] Ye M T, Cai T, Zhao L N, Liu D, Liu S G. Covalently attached strategy to modulate surface of carbon quantum dots: Towards effectively multifunctional lubricant additives in polar and apolar base fluids. *Tribol Int* **136**: 349–359 (2019)

[86] Mou Z H, Wang B G, Lu H S, Quan H P, Huang Z Y. Branched polyelectrolyte grafted carbon dots as the high-performance friction-reducing and antiwear additives of polyethylene glycol. *Carbon* **149**: 594–603 (2019)

[87] Mou Z H, Zhao B, Wang B G, Xiao D. Integration of functionalized polyelectrolytes onto carbon dots for synergistically improving the tribological properties of polyethylene glycol. *ACS Appl Mater Interfaces* **13**(7): 8794–8807 (2021)

[88] Mou Z H, Wang B G, Lu H S, Dai S S, Huang Z Y. Synthesis of poly(ionic liquid)s brush-grafted carbon dots for high-performance lubricant additives of polyethylene glycol. *Carbon* **154**: 301–312 (2019)

[89] Yao Y L, Wang X M, Guo J J, Yang X W, Xu B S. Tribological property of onion-like fullerenes as lubricant additive. *Mater Lett* **62**(16): 2524–2527 (2008)

[90] He C, Yan H H, Li X J, Wang X H. One-step rapid fabrication of high-purity onion-like carbons as efficient lubrication additives. *J Mater Sci* **56**(2): 1286–1297 (2021)

[91] Gu Y F, Fei J, Zheng X H, Li M, Huang J F, Qu M, Zhang L J. Graft PEI ultra-antiwear nanolayer onto carbon spheres as lubricant additives for tribological enhancement. *Tribol Int* **153**: 106652 (2021)

[92] Ettefaghi E O L, Rashidi A, Ahmadi H, Mohtasebi S S, Pourkhalil M. Thermal and rheological properties of oil-based nanofluids from different carbon nanostructures. *Int Commun Heat Mass Transf* **48**: 178–182 (2013)

[93] Shahmohamadi H, Rahmani R, Rahnejat H, Garner C P, Balodimos N. Thermohydrodynamics of lubricant flow with carbon nanoparticles in tribological contacts. *Tribol Int* **113**: 50–57 (2017)

[94] Hao L F, Li J S, Xu X H, Ren T H. Preparation and tribological properties of a kind of lubricant containing calcium borate nanoparticles as additives. *Ind Lubr Tribol* **64**(1): 16–22 (2012)

[95] Huang Y, Han S, Liu S Z, Wang Y H, Li J S. Preparation and tribological properties of surface-modified calcium borate nanoparticles as additive in lubricating oil. *Ind Lubr Tribol* **66**(1): 143–150 (2014)

[96] Zhang M, Wang X B, Fu X S, Xia Y Q. Performance and anti-wear mechanism of $CaCO_3$ nanoparticles as a green additive in poly-alpha-olefin. *Tribol Int* **42**(7): 1029–1039 (2009)

[97] Bakunin V N, Suslov A Y, Kuzmina G N, Parenago O P, Topchiev A V. Synthesis and application of inorganic nanoparticles as lubricant components—A review. *J Nanopart Res* **6**(2–3): 273–284 (2004)

[98] Topolovec-Miklozic K, Forbus T R, Spikes H. Film forming and friction properties of overbased calcium sulphonate detergents. *Tribol Lett* **29**(1): 33–44 (2008)

[99] Costello M T, Kasrai M. Study of surface films of overbased sulfonates and sulfurized olefins by X-Ray Absorption Near Edge Structure (XANES) spectroscopy. *Tribol Lett* **24**(2):163–169 (2006)

[100] Jia Z F, Xia Y Q. Hydrothermal synthesis, characterization, and tribological behavior of oleic acid-capped lanthanum borate with different morphologies. *Tribol Lett* **41**(2): 425–434 (2011)

[101] Zhao C, Chen Y K, Jiao Y, Loya A, Ren G G. The preparation and tribological properties of surface modified zinc borate ultrafine powder as a lubricant additive in liquid paraffin. *Tribol Int* **70**: 155–164 (2014)

[102] Gao K, Chang Q Y, Wang B, Zhou N N, Qing T. The tribological performances of modified magnesium silicate hydroxide as lubricant additive. *Tribol Int* **121**: 64–70 (2018)

[103] Zhang B S, Xu Y, Gao F, Shi P J, Xu B S, Wu Y X. Sliding friction and wear behaviors of surface-coated natural serpentine mineral powders as lubricant additive. *Appl Surf Sci* **257**(7): 2540–2549 (2011)

[104] Qi X W, Jia Z N, Yang Y L, Fan B L. Characterization and auto-restoration mechanism of nanoscale serpentine powder as lubricating oil additive under high temperature. *Tribol Int* **44**(7–8): 805–810 (2011)

[105] Yu H L, Xu Y, Shi P J, Wang H M, Zhang W, Xu B S. Effect of thermal activation on the tribological behaviours of serpentine ultrafine powders as an additive in liquid paraffin. *Tribol Int* **44**(12): 1736–1741 (2011)

[106] Yu H L, Xu Y, Shi P J, Wang H M, Wei M, Zhao K K, Xu B S. Microstructure, mechanical properties and tribological behavior of tribofilm generated from natural serpentine mineral powders as lubricant additive. *Wear* **297**(1–2): 802–810 (2013)

[107] Furukawa H, Cordova K E, O'Keeffe M, Yaghi O M. The chemistry and applications of metal–organic frameworks. *Science* **341**(6149): 1230444 (2013)

[108] Shi Q, Chen Z F, Song Z W, Li J P, Dong J X. Synthesis of ZIF-8 and ZIF-67 by steam-assisted conversion and an investigation of their tribological behaviors. *Angew Chem Int Ed* **50**(3): 672–675 (2011)

[109] Yuan M, Zhao Y, Niu W X, Shi Q, Xu H, Zheng B, Dong J X. Tribological properties of typical zeolitic imidazolate frameworks as grease-based lubricant additives. *J Mater Eng Perform* **28**(3): 1668–1677 (2019)

[110] Sun W C, Shi Q, Xu H, Dong J X. Synthesis and tribological properties of zeolitic imidazolate framework-8 nanocrystals and microcrystals. *Asian J Chem* **27**(1): 81–84 (2015)

[111] Wang Y H, Shi Q, Xu H, Dong J X. The synthesis and tribological properties of small- and large-sized crystals of zeolitic imidazolate framework-71. *RSC Adv* **6**(22): 18052–18059 (2016)

[112] Wang F F, Liu Z, Cheng Z L. High performance of MOF-structured lubricating material with nano- and micro-sized morphologies. *Mater Lett* **248**: 222–226 (2019)

[113] Wu W, Liu J X, Li Z H, Zhao X Y, Liu G Q, Liu S J, Ma S H, Li W M, Liu W M. Surface-functionalized nanoMOFs in oil for friction and wear reduction and antioxidation. *Chem Eng J* **410**: 128306 (2021)

[114] Cao W, Liu Y, Xu F, Xia Q, Du G P, Fan Z Y, Chen N. Metal–organic framework derived carbon-coated spherical bimetallic nickel–cobalt sulfide nanoparticles for hybrid supercapacitors. *Electrochimica Acta* **385**: 138433 (2021)

[115] Rijnaarts T, Mejia-Ariza R, Egberink R J M, van Roosmalen W, Huskens J. Metal–organic frameworks (MOFs) as multivalent materials: Size control and surface functionalization by monovalent capping ligands. *Chem Eur J* **21**(29): 10296–10301 (2015)

[116] Hallett J P, Welton T. Room-temperature ionic liquids: Solvents for synthesis and catalysis. 2. *Chem Rev* **111**(5): 3508–3576 (2011)

[117] Zhou Y, Qu J. Ionic liquids as lubricant additives: A review. *ACS Appl Mater Interfaces* **9**(4): 3209–3222 (2017)

[118] Qu J, Bansal D G, Yu B, Howe J Y, Luo H M, Dai S, Li H Q, Blau P J, Bunting B G, Mordukhovich G, et al. Antiwear performance and mechanism of an oil-miscible ionic liquid as a lubricant additive. *ACS Appl Mater Interfaces* **4**(2): 997–1002 (2012)

[119] Yu B, Bansal D G, Qu J, Sun X Q, Luo H M, Dai S, Blau P J, Bunting B G, Mordukhovich G, Smolenski D J. Oil-miscible and non-corrosive phosphonium-based ionic liquids as candidate lubricant additives. *Wear* **289**: 58–64 (2012)

[120] Zhou Y, Dyck J, Graham T W, Luo H M, Leonard D N, Qu J. Ionic liquids composed of phosphonium cations and organophosphate, carboxylate, and sulfonate anions as lubricant antiwear additives. *Langmuir* **30**(44): 13301–13311 (2014)

[121] Qu J, Barnhill W C, Luo H M, Meyer H M III, Leonard D N, Landauer A K, Kheireddin B, Gao H, Papke B L, Dai S. Synergistic effects between phosphonium–alkylphosphate ionic liquids and zinc dialkyldithiophosphate (ZDDP) as lubricant additives. *Adv Mater* **27**(32): 4767–4774 (2015)

[122] Ma R, Zhao Q, Zhang E H, Zheng D D, Li W M, Wang X B. Synthesis and evaluation of oil-soluble ionic liquids as multifunctional lubricant additives. *Tribol Int* **151**: 106446 (2020)

[123] Duan H T, Li W M, Kumara C, Jin Y L, Meyer H M, Luo H M, Qu J. Ionic liquids as oil additives for lubricating oxygen-diffusion case-hardened titanium. *Tribol Int* **136**: 342–348 (2019)

[124] Huang G W, Yu Q L, Ma Z F, Cai M R, Zhou F, Liu W M. Oil-soluble ionic liquids as antiwear and extreme pressure additives in poly-α-olefin for steel/steel contacts. *Friction* **7**(1): 18–31 (2019)

[125] Somers A E, Khemchandani B, Howlett P C, Sun J Z, MacFarlane D R, Forsyth M. Ionic liquids as antiwear additives in base oils: Influence of structure on miscibility and antiwear performance for steel on aluminum. *ACS Appl Mater Interfaces* **5**(22): 11544–11553 (2013)

[126] Battez A H, Fernandes C M C G, Martins R C, Bartolomé M, González R, Seabra J H O. Two phosphonium cation-based ionic liquids used as lubricant additive: Part I: Film thickness and friction characteristics. *Tribol Int* **107**: 233–239 (2017)

[127] Zhou F, Liang Y M, Liu W M. Ionic liquid lubricants: Designed chemistry for engineering applications. *Chem Soc Rev* **38**(9): 2590–2599 (2009)

[128] Xiao H P. Ionic liquid lubricants: Basics and applications. *Tribol Trans* **60**(1): 20–30 (2017)

[129] Zhai W Z, Zhou K. Nanomaterials in superlubricity. *Adv Funct Mater* **29**(28): 1806395 (2019)

[130] Chen C S, Chen X H, Xu L S, Yang Z, Li W H. Modification of multi-walled carbon nanotubes with fatty acid and their tribological properties as lubricant additive. *Carbon* **43**(8): 1660–1666 (2005)

[131] Cursaru D L, Andronescu C, Pirvu C, Ripeanu R. The efficiency of Co-based single-wall carbon nanotubes (SWNTs) as an AW/EP additive for mineral base oils. *Wear* **290–291**: 133–139 (2012)

[132] Kumar H, Harsha A P. Enhanced lubrication ability of polyalphaolefin and polypropylene glycol by COOH-functionalized multiwalled carbon nanotubes as an additive. *J Mater Eng Perform* **30**(2): 1075–1089 (2021)

[133] Salah N, Abdel-Wahab M S, Alshahrie A, Alharbi N D, Khan Z H. Carbon nanotubes of oil fly ash as lubricant additives for different base oils and their tribology performance. *RSC Adv* **7**(64): 40295–40302 (2017)

[134] Dardan E, Afrand M, Isfahani A H M. Effect of suspending hybrid nano-additives on rheological behavior of engine oil and pumping power. *Appl Therm Eng* **109**: 524–534 (2016)

[135] Gong K L, Wu X H, Zhao G Q, Wang X B. Tribological properties of polymeric aryl phosphates grafted onto multi-walled carbon nanotubes as high-performances lubricant additive. *Tribol Int* **116**: 172–179 (2017)

[136] Chauveau V, Mazuyer D, Dassenoy F, Cayer-Barrioz J. *In situ* film-forming and friction-reduction mechanisms for carbon-nanotube dispersions in lubrication. *Tribol Lett* **47**(3): 467–480 (2012)

[137] Kałużny J, Merkisz-Guranowska A, Giersig M, Kempa K. Lubricating performance of carbon nanotubes in internal combustion engines—Engine test results for CNT enriched oil. *Int J Automot Technol* **18**(6): 1047–1059 (2017)

[138] Joly-Pottuz L, Dassenoy F, Martin J M, Vrbanic D, Mrzel A, Mihailovic D, Vogel W, Montagnac G. Tribological properties of Mo–S–I nanowires as additive in oil. *Tribol Lett* **18**(3): 385–393 (2005)

[139] Dassenoy F, Joly-Pottuz L, Martin J M, Vrbanic D, Mrzel A, Mihailovic D, Vogel W, Montagnac G. Tribological performances of $Mo_6S_3I_6$ nanowires. *J Eur Ceram Soc* **27**(2–3): 915–919 (2007)

[140] Kalin M, Kogovšek J, Remškar M. Mechanisms and improvements in the friction and wear behavior using MoS_2 nanotubes as potential oil additives. *Wear* **280–281**: 36–45 (2012)

[141] Rodríguez Ripoll M, Tomala A, Gabler C, Dražić G, Pirker L, Remškar M. *In situ* tribochemical sulfurization of molybdenum oxide nanotubes. *Nanoscale* **10**(7): 3281–3290 (2018)

[142] Tomala A M, Ripoll M R, Michalczewski R. Tribological synergy between classical ZDDP and innovative MoS_2 and MoO_3 nanotube additives at elevated temperatures. *Proc Estonian Acad Sci* **68**(2): 178–184 (2019)

[143] Gusain R, Khatri O P. Ultrasound assisted shape regulation of CuO nanorods in ionic liquids and their use as energy efficient lubricant additives. *J Mater Chem A* **1**(18): 5612–5619 (2013)

[144] Zhang L L, Tu J P, Wu H M, Yang Y Z. WS_2 nanorods prepared by self-transformation process and their tribological properties as additive in base oil. *Mater Sci Eng A* **454–455**: 487–491 (2007)

[145] Chen L J, Zhu D Y. Preparation and tribological properties of unmodified and oleic acid-modified CuS nanorods as lubricating oil additives. *Ceram Int* **43**(5): 4246–4251 (2017)

[146] Duan L L, Huang W, Zhang Y T. High-flux, antibacterial ultrafiltration membranes by facile blending with N-halamine grafted halloysite nanotubes. *RSC Adv* **5**(9): 6666–6674 (2015)

[147] Duan L L, Zhao Q Q, Liu J D, Zhang Y T. Antibacterial behavior of halloysite nanotubes decorated with copper nanoparticles in a novel mixed matrix membrane for water purification. *Environ Sci Water Res Technol* **1**(6): 874–881 (2015)

[148] Peña-Parás L, Maldonado-Cortés D, García P, Irigoyen M, Taha-Tijerina J, Guerra J. Tribological performance of halloysite clay nanotubes as green lubricant additives. *Wear* **376–377**: 885–892 (2017)

[149] Sifuentes E T, Kharissova O V, Maldonado-Cortés D, Peña-Parás L, Michalczewski R, Kharisov B I. A comparison of tribological properties of nanolubricants containing carbon nanotori and additional additives. *Mater Chem Phys* **272**: 124973 (2021)

[150] Zeng Y, Yang H B, Fu W Y, Qiao L, Chang L X, Chen J J, Zhu H Y, Li M H, Zou G T. Synthesis of magnesium borate ($Mg_2B_2O_5$) nanowires, growth mechanism and their lubricating properties. *Mater Res Bull* **43**(8–9): 2239–2247 (2008)

[151] Yang J H, Yao H X, Liu Y Q, Zhang Y J. Synthesis and tribological properties of WSe_2 nanorods. *Nanoscale Res Lett* **3**(12): 481–485 (2008)

[152] Liu N, Tian Y M, Yu L X, Li Q J, Meng F Y, Zheng Y H, Zhang G Y, Liu Z H, Li J, Jiang F M. Synthesis and surface modification of uniform barium borate nanorods for lubrication. *J Alloys Compd* **466**(1–2): L11–L14 (2008)

[153] Li K, Zhang X, Du C, Yang J W, Wu B L, Guo Z W, Dong C L, Lin N, Yuan C Q. Friction reduction and viscosity modification of cellulose nanocrystals as biolubricant additives in polyalphaolefin oil. *Carbohydr Polym* **220**: 228–235 (2019)

[154] Chen T D, Xia Y Q, Jia Z F, Liu Z L, Zhang H B. Synthesis, characterization, and tribological behavior of oleic acid capped graphene oxide. *J Nanomater* **2014**: 654145 (2014)

[155] Ci X J, Zhao W J, Luo J, Wu Y M, Ge T H, Xue Q J, Gao X L, Fang Z W. How the fluorographene replaced graphene as nanoadditive for improving tribological performances of GTL-8 based lubricant oil. *Friction* **9**(3): 488–501 (2021)

[156] Radhika P, Sobhan C B, Chakravorti S. Improved tribological behavior of lubricating oil dispersed with hybrid nanoparticles of functionalized carbon spheres and graphene nano platelets. *Appl Surf Sci* **540**:148402 (2021)

[157] Zhang W, Zhou M, Zhu H W, Tian Y, Wang K L, Wei J Q, Ji F, Li X, Li Z, Zhang P, et al. Tribological properties of oleic acid-modified graphene as lubricant oil additives. *J Phys D Appl Phys* **44**(20): 205303 (2011)

[158] Gusain R, Mungse H P, Kumar N, Ravindran T R, Pandian R, Sugimura H, Khatri O P. Covalently attached graphene–ionic liquid hybrid nanomaterials: Synthesis, characterization and tribological application. *J Mater Chem A* **4**(3): 926–937 (2016)

[159] Paul G, Shit S, Hirani H, Kuila T, Murmu N C. Tribological behavior of dodecylamine functionalized graphene nanosheets dispersed engine oil nanolubricants. *Tribol Int* **131**: 605–619 (2019)

[160] Gan C L, Liang T, Chen D L, Li W, Fan X Q, Tang G X, Lin B, Zhu M H. Phosphonium–organophosphate modified graphene gel towards lubrication applications. *Tribol Int* **145**: 106180 (2020)

[161] Eswaraiah V, Sankaranarayanan V, Ramaprabhu S. Graphene-based engine oil nanofluids for tribological applications. *ACS Appl Mater Interfaces* **3**(11): 4221–4227 (2011)

[162] Gu W C, Chu K, Lu Z B, Zhang G G, Qi S S. Synergistic effects of 3D porous graphene and T161 as hybrid lubricant additives on 316 ASS surface. *Tribol Int* **161**: 107072 (2021)

[163] Guimarey M J G, Viesca J L, Abdelkader A M, Thomas B, Battez A H, Hadfield M. Electrochemically exfoliated graphene and molybdenum disulfide nanoplatelets as lubricant additives. *J Mol Liq* **342**: 116959 (2021)

[164] Wang X B, Zhang Y F, Yin Z W, Su Y J, Zhang Y P, Cao J. Experimental research on tribological properties of liquid phase exfoliated graphene as an additive in SAE 10W-30 lubricating oil. *Tribol Int* **135**: 29–37 (2019)

[165] Ouyang T C, Shen Y D, Lei W W, Xu X Y, Liang L Z, Waqar H S, Lin B, Tian Z Q, Shen P K. Reduced friction and wear enabled by arc-discharge method-prepared 3D graphene as oil additive under variable loads and speeds. *Wear* **462–463**: 203495 (2020)

[166] Huang H D, Tu J P, Gan L P, Li C Z. An investigation on tribological properties of graphite nanosheets as oil additive. *Wear* **261**(2): 140–144 (2006)

[167] Omrani E, Siddaiah A, Moghadam A D, Garg U, Rohatgi P, Menezes P L. Ball milled graphene nano additives for enhancing sliding contact in vegetable oil. *Nanomaterials* **11**(3): 610

[168] Li Y R, Zhao J, Tang C, He Y Y, Wang Y F, Chen J, Mao J Y, Zhou Q Q, Wang B Y, Wei F, et al. Highly exfoliated reduced graphite oxide powders as efficient lubricant oil additives. *Adv Mater Interfaces* **3**(22): 1600700 (2016)

[169] Hou X B, Ma Y J, Bhandari G, Yin Z B, Dai L Y, Liao H F, Wei Y K. Preparation and tribological properties of graphene lubricant additives for low-sulfur fuel by dielectric barrier discharge plasma-assisted ball milling. *Processes* **9**(2): 272 (2021)

[170] Wu Z Z, Wang D Z, Wang Y, Sun A K. Preparation and tribological properties of MoS_2 nanosheets. *Adv Eng Mater* **12**(6): 534–538 (2010)

[171] Rajendhran N, Palanisamy S, Periyasamy P, Venkatachalam R. Enhancing of the tribological characteristics of the lubricant oils using Ni-promoted MoS_2 nanosheets as nano-additives. *Tribol Int* **118**: 314–328 (2018)

[172] Chen Z, Liu X W, Liu Y H, Gunsel S, Luo J B. Ultrathin MoS_2 nanosheets with superior extreme pressure property as boundary lubricants. *Sci Rep* **5**: 12869 (2015)

[173] Zhang X H, Xue Y P, Ye X, Xu H X, Xue M Q. Preparation, characterization and tribological properties of ultrathin MoS_2 nanosheets. *Mater Res Express* **4**(11): 115011 (2017)

[174] Liu L, Huang Z B, Huang P. Fabrication of coral-like MoS_2 and its application in improving the tribological performance of liquid paraffin. *Tribol Int* **104**: 303–308 (2016)

[175] Wu H X, Wang L P, Johnson B, Yang S C, Zhang J F, Dong G N. Investigation on the lubrication advantages of MoS_2 nanosheets compared with ZDDP using block-on-ring tests. *Wear* **394–395**: 40–49 (2018)

[176] Xiang L H, Gao C P, Wang Y M, Pan Z D, Hu D W. Tribological and tribochemical properties of magnetite nanoflakes as additives in oil lubricants. *Particuology* **17**: 136–144 (2014)

[177] Wang H D, Liu Y H, Liu W R, Wang R, Wen J G, Sheng H P, Peng J F, Erdemir A, Luo J B. Tribological behavior of NiAl-layered double hydroxide nanoplatelets as oil-based lubricant additives. *ACS Appl Mater Interfaces* **9**(36): 30891–30899 (2017)

[178] Bai Z M, Wang Z Y, Zhang T G, Fu F, Yang N. Synthesis and characterization of Co–Al–CO_3 layered double-metal hydroxides and assessment of their friction performances. *Appl Clay Sci* **59–60**: 36–41 (2012)

[179] Li S, Bhushan B. Lubrication performance and mechanisms of Mg/Al-, Zn/Al-, and Zn/Mg/Al-layered double hydroxide nanoparticles as lubricant additives. *Appl Surf Sci* **378**: 308–319 (2016)

[180] Wang H D, Wang Y, Liu Y H, Zhao J, Li J J, Wang Q, Luo J B. Tribological behavior of layered double hydroxides with various chemical compositions and morphologies as grease additives. *Friction* **9**(5): 952–962 (2021)

[181] Wang H D, Liu Y H, Guo F M, Sheng H P, Xia K L, Liu W R, Wen J G, Shi Y J, Erdemir A, Luo J B. Catalytically active oil-based lubricant additives enabled by calcining Ni–Al layered double hydroxides. *J Phys Chem Lett* **11**(1): 113–120 (2020)

[182] Wang X B, Bai Z M, Zhao D, Zhao F Y. Friction behavior of Mg–Al–CO_3 layered double hydroxide prepared by magnesite. *Appl Surf Sci* **277**: 134–138 (2013)

[183] Wang K P, Wu H C, Wang H D, Liu Y H, Yang L, Zhao L M. Tribological properties of novel palygorskite nanoplatelets used as oil-based lubricant additives. *Friction* **9**(2): 332–343 (2021)

[184] Liu H L, Huang Y J, Wang Y Z, Zhao X M, Chen D Q, Chen G H. Study of tribological properties and lubrication mechanism of surfactant-coated anthracite sheets used as lubricant additives. *Friction* **9**(3): 524–537 (2021)

[185] He X L, Xiao H P, Choi H, Díaz A, Mosby B, Clearfield A,

Liang H. α-zirconium phosphate nanoplatelets as lubricant additives. *Colloids Surf A Physicochem Eng Aspects* **452**: 32–38 (2014)

[186] Feng X, Ding X S, Jiang D L. Covalent organic frameworks. *Chem Soc Rev* **41**(18): 6010–6022 (2012)

[187] Wen P, Zhang C Y, Yang Z G, Dong R, Wang D M, Fan M J, Wang J Q. Triazine-based covalent-organic frameworks: A novel lubricant additive with excellent tribological performances. *Tribol Int* **111**: 57–65 (2017)

[188] Xu Y F, Yu J Y, Dong Y H, You T, Hu X G. Boundary lubricating properties of black phosphorus nanosheets in polyalphaolefin oil. *J Tribol* **141**(7): 072101 (2019)

[189] Wang Q J, Hou T L, Wang W, Zhang G L, Gao Y, Wang K S. Tribological properties of black phosphorus nanosheets as oil-based lubricant additives for titanium alloy-steel contacts. *R Soc Open Sci* **7**(9): 200530 (2020)

[190] Wu H X, Wang L P, Dong G N. Origin of the tribofilm from MoS_2 nanoparticle oil additives: Dependence of oil film thickness on particle aggregation in rolling point contact. *Friction* **9**(6): 1436–1449 (2021)

[191] Vardhaman B S A, Amarnath M, Ramkumar J, Mondal K. Enhanced tribological performances of zinc oxide/MWCNTs hybrid nanomaterials as the effective lubricant additive in engine oil. *Mater Chem Phys* **253**: 123447 (2020)

[192] Qin Y, Wu M X, Yang G, Yang Y, Zhao L M. Tribological performance of magnesium silicate hydroxide/Ni composite as an oil-based additive for steel–steel contact. *Tribol Lett* **69**(1): 19 (2021)

[193] Meng Y, Su F H, Chen Y Z. Nickel/multi-walled carbon nanotube nanocomposite synthesized in supercritical fluid as efficient lubricant additive for mineral oil. *Tribol Lett* **66**(4): 134 (2018)

[194] Wang Z Q, Ren R R, Song H J, Jia X H. Improved tribological properties of the synthesized copper/carbon nanotube nanocomposites for rapeseed oil-based additives. *Appl Surf Sci* **428**: 630–639 (2018)

[195] Cheng L H, Hu E Z, Chao X Q, Zhu R F, Hu K H, Hu X G. MoS_2/montmorillonite nanocomposite: Preparation, tribological properties, and inner synergistic lubrication. *Nano* **13**(12): 1850144 (2018)

[196] Zhao W J, Ci X J. TiO_2 nanoparticle/fluorinated reduced graphene oxide nanosheet composites for lubrication and wear resistance. *ACS Appl Nano Mater* **3**(9): 8732–8741 (2020)

[197] Alazemi A A, Dysart A D, Phuah X L, Pol V G, Sadeghi F. MoS_2 nanolayer coated carbon spheres as an oil additive for enhanced tribological performance. *Carbon* **110**: 367–377 (2016)

[198] Meng Y, Su F H, Chen Y Z. A novel nanomaterial of graphene oxide dotted with Ni nanoparticles produced by supercritical CO_2-assisted deposition for reducing friction and wear. *ACS Appl Mater Interfaces* **7**(21): 11604–11612 (2015)

[199] Meng Y, Su F H, Chen Y Z. Au/graphene oxide nanocomposite synthesized in supercritical CO_2 fluid as energy efficient lubricant additive. *ACS Appl Mater Interfaces* **9**(45): 39549–39559 (2017)

[200] Guo Y X, Guo L H, Li G T, Zhang L G, Zhao F Y, Wang C, Zhang G. Solvent-free ionic nanofluids based on graphene oxide–silica hybrid as high-performance lubricating additive. *Appl Surf Sci* **471**: 482–493 (2019)

[201] Meng Y, Su F H, Chen Y Z. Synthesis of nano-Cu/graphene oxide composites by supercritical CO_2-assisted deposition as a novel material for reducing friction and wear. *Chem Eng J* **281**: 11–19 (2015)

[202] Song H J, Wang Z Q, Yang J, Jia X H, Zhang Z Z. Facile synthesis of copper/polydopamine functionalized graphene oxide nanocomposites with enhanced tribological performance. *Chem Eng J* **324**: 51–62 (2017)

[203] Luo T, Chen X C, Wang P, Li C C, Cao B Q, Zeng H B. Tribology properties: Laser irradiation-induced SiC@graphene sub-microspheres: A bioinspired core–shell structure for enhanced tribology properties. *Adv Mater Interfaces* **5**(5): 1870021 (2018)

[204] Xu Z, Lou W J, Zhao G Q, Zheng D D, Hao J Y, Wang X B. Cu nanoparticles decorated WS_2 nanosheets as a lubricant additive for enhanced tribological performance. *RSC Adv* **9**(14): 7786–7794 (2019)

[205] Luo T, Chen X C, Li P S, Wang P, Li C C, Cao B Q, Luo J B, Yang S K. Laser irradiation-induced laminated graphene/MoS_2 composites with synergistically improved tribological properties. *Nanotechnology* **29**(26): 265704 (2018)

[206] Tang G B, Su F H, Xu X, Chu P K. 2D black phosphorus dotted with silver nanoparticles: An excellent lubricant additive for tribological applications. *Chem Eng J* **392**: 123631 (2020)

[207] Gan C L, Liang T, Li W, Fan X Q, Zhu M H. Amine-terminated ionic liquid modified graphene oxide/copper nanocomposite toward efficient lubrication. *Appl Surf Sci* **491**: 105–115 (2019)

[208] Zhang W Y, Demydov D, Jahan M P, Mistry K, Erdemir A, Malshe A P. Fundamental understanding of the tribological and thermal behavior of Ag-MoS_2 nanoparticle-based multi-component lubricating system. *Wear* **288**: 9–16 (2012)

[209] Altavilla C, Sarno M, Ciambelli P, Senatore A, Petrone V.

New ‘chimie douce’ approach to the synthesis of hybrid nanosheets of MoS_2 on CNT and their anti-friction and anti-wear properties. *Nanotechnology* **24**(12): 125601 (2013)

[210] Jiao D, Zheng S H, Wang Y Z, Guan R F, Cao B Q. The tribology properties of alumina/silica composite nanoparticles as lubricant additives. *Appl Surf Sci* **257**(13): 5720–5725 (2011)

[211] Ali M K A, Hou X J, Turkson R F, Peng Z, Chen X D. Enhancing the thermophysical properties and tribological behaviour of engine oils using nano-lubricant additives. *RSC Adv* **6**(81): 77913–77924 (2016)

[212] Yang J, Zhang H T, Chen B B, Tang H, Li C S, Zhang Z Z. Fabrication of the g-C_3N_4/Cu nanocomposite and its potential for lubrication applications. *RSC Adv* **5**(79): 64254–64260 (2015)

[213] Zhao F Y, Bai Z M, Fu Y, Zhao D, Yan C M. Tribological properties of serpentine, $La(OH)_3$ and their composite particles as lubricant additives. *Wear* **288**: 72–77 (2012)

[214] Ranjan N, Shende R C, Kamaraj M, Ramaprabhu S. Utilization of TiO_2/gC_3N_4 nanoadditive to boost oxidative properties of vegetable oil for tribological application. *Friction* **9**(2): 273–287 (2021)

[215] Mutyala K C, Wu Y A, Erdemir A, Sumant A V. Graphene–MoS_2 ensembles to reduce friction and wear in DLC–Steel contacts. *Carbon* **146**: 524–527 (2019)

[216] Wu H S, Zhang Y C, Long S, Zhang L Y, Jie X H. Tribological behavior of graphene anchored Mg–Al layered double hydroxide film on Mg alloy pre-sprayed Al coating. *Appl Surf Sci* **530**: 146536 (2020)

[217] Zhang Y, Yu P H, Qi Y, Chen F, Li Y D, Zhang Y L. Oleylamine/graphene-modified hydrotalcite-based film on titanium alloys and its lubricating properties. *Mater Lett* **193**: 93–96 (2017)

[218] Xu Y F, Peng Y B, Dearn K D, Zheng X J, Yao L L, Hu X G. Synergistic lubricating behaviors of graphene and MoS_2 dispersed in esterified bio-oil for steel/steel contact. *Wear* **342–343**: 297–309 (2015)

[219] Wu X H, Zhao G Q, Zhao Q, Gong K L, Wang X B, Liu W M, Liu W S. Investigating the tribological performance of nanosized MoS_2 on graphene dispersion in perfluoropolyether under high vacuum. *RSC Adv* **6**(101): 98606–98610 (2016)

[220] Zhang L, He Y, Feng S W, Zhang L, Zhang L, Jiao Z L, Zhan Y Q, Wang Y J. Preparation and tribological properties of novel boehmite/graphene oxide nano-hybrid. *Ceram Int* **42**(5): 6178–6186 (2016)

[221] Liu Y C, Mateti S, Li C Q, Liu X, Glushenkov A M, Liu D, Li L H, Fabijanic D, Chen Y. Synthesis of composite nanosheets of graphene and boron nitride and their lubrication application in oil. *Adv Eng Mater* **20**(2): 1700488 (2018)

[222] Dai W, Kheireddin B, Gao H, Liang H. Roles of nanoparticles in oil lubrication. *Tribol Int* **102**: 88–98 (2016)

[223] Lahouij I, Vacher B, Martin J M, Dassenoy F. IF–MoS_2 based lubricants: Influence of size, shape and crystal structure. *Wear* **296**(1–2): 558–567 (2012)

[224] Zhang C H, Li K, Luo J B. Superlubricity with nonaqueous liquid. In: *Superlubricity*, 2nd edn. Erdemir A, Martin J M, Luo J B, Eds. Amsterdam (the Netherlands): Elsevier Amsterdam, 2020: 379–403.

[225] Duan H T, Wu Y, Hua M, Yuan C Q, Wang D, Tu J S, Kou H C, Li J. Tribological properties of AlCoCrFeNiCu high-entropy alloy in hydrogen peroxide solution and in oil lubricant. *Wear* **297**(1–2): 1045–1051 (2013)

[226] Sarno M, Senatore A, Cirillo C, Petrone V, Ciambelli P. Oil lubricant tribological behaviour improvement through dispersion of few layer graphene oxide. *J Nanosci Nanotechnol* **14**(7): 4960–4968 (2014)

[227] Liu Y H, Xin L, Zhang Y J, Chen Y F, Zhang S M, Zhang P Y. The effect of Ni nanoparticles on the lubrication of a DLC-based solid–liquid synergetic system in all lubrication regimes. *Tribol Lett* **65**(2): 31 (2017)

[228] Ali M K A, Hou X J, Mai L Q, Cai Q P, Turkson R F, Chen B C. Improving the tribological characteristics of piston ring assembly in automotive engines using Al_2O_3 and TiO_2 nanomaterials as nano-lubricant additives. *Tribol Int* **103**: 540–554 (2016)

[229] Ku B C, Han Y C, Lee J E, Lee J K, Park S H, Hwang Y J. Tribological effects of fullerene (C_{60}) nanoparticles added in mineral lubricants according to its viscosity. *Int J Precis Eng Manuf* **11**(4): 607–611 (2010)

[230] Ghaednia H, Babaei H, Jackson R L, Bozack M J, Khodadadi J M. The effect of nanoparticles on thin film elasto-hydrodynamic lubrication. *Appl Phys Lett* **103**(26): 263111 (2013)

[231] Ghaednia H, Hossain M S, Jackson R L. Tribological performance of silver nanoparticle-enhanced polyethylene glycol lubricants. *Tribol Trans* **59**(4): 585–592 (2016)

[232] Senatore A, D’Agostino V, Petrone V, Ciambelli P, Sarno M. Graphene oxide nanosheets as effective friction modifier for oil lubricant: Materials, methods, and tribological results. *ISRN Tribol* **2013**: 425803 (2013)

[233] Cho D H, Wang L, Kim J S, Lee G H, Kim E S, Lee S, Lee S Y, Hone J, Lee C G. Effect of surface morphology on friction of graphene on various substrates. *Nanoscale* **5**(7): 3063–3069 (2013)

[234] Wan C X, Zhan S P, Jia D, Yang T, Chen H, Yao C Y, Duan H T. Tribological behavior of nanographite/polyimide composite under drying sliding condition. *Wear* **494–495**: 204271 (2022)

[235] Ge X Y, Halmans T, Li J J, Luo J B. Molecular behaviors in thin film lubrication—Part three: Superlubricity attained by polar and nonpolar molecules. *Friction* **7**(6): 625–636 (2019)

[236] Jin Y L, Duan H T, Cheng B X, Wei L, Tu J S, Liu J F, Li J. Synthesis of a multi-phenol antioxidant and its compatibility with alkyl diphenylamine and ZDDP in ester oil. *Tribol Lett* **67**(2): 58 (2019)

[237] Tomala A, Ripoll M R, Gabler C, Remškar M, Kalin M. Interactions between MoS_2 nanotubes and conventional additives in model oils. *Tribol Int* **110**: 140–150 (2017)

[238] Zhan S P, Xu H P, Duan H T, Pan L, Jia D, Tu J S, Liu L, Li J. Molecular dynamics simulation of microscopic friction mechanisms of amorphous polyethylene. *Soft Matter* **15**(43): 8827–8839 (2019)

[239] Zhan S P, Duan H T, Pan L, Tu J S, Jia D, Yang T, Li J. Molecular dynamics simulation of shock-induced microscopic bubble collapse. *Phys Chem Chem Phys* **23**(14): 8446–8455 (2021)

[240] Zhang S W. Green tribology: Fundamentals and future development. *Friction* **1**(2): 186–194 (2013)

Linlin DUAN She obtained her M.S. degree in 2016 from Zhengzhou University, China, and worked as research associate at Zhongyuan University of Technology, China, for several years. Now she is studying for a Ph.D. degree at State Key Laboratory of Special Surface Protection Materials and Application Technology, Wuhan Research Institute of Materials Protection, China. Her research topics focus on the preparation of organic–inorganic hybrid nanomaterials and the optimization of lubricating oil additives.

Haitao DUAN He obtained his Ph.D. degree in 2011 from State Key Laboratory of Special Surface Protection Materials and Application Technology, Wuhan Research Institute of Materials Protection, China. Now he is a professor and deputy general manager of Wuhan Research Institute of Materials Protection, China. He won the Young Scholar Award in Tribology and was selected into the National Youth Top-notch Talents Support Program. His research areas cover the basic theories of mechanical tribology and lubricating materials design.

Jian LI He obtained his M.S. degree in 1995 from Xi'an Jiaotong University, China. Now he is a professor and the vice-chief engineer of Wuhan Research Institute of Materials Protection, China. His research interests cover the lubricating materials, tribological testing technology, and surface coating.