Friction **7**(2): 93–116 (2019)
https://doi.org/10.1007/s40544-019-0261-y

ISSN 2223-7690
CN 10-1237/TH

REVIEW ARTICLE

Metal-containing nanomaterials as lubricant additives: State-of-the-art and future development

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Received: 18 August 2018 / Revised: 27 October 2018 / Accepted: 28 November 2018

Abstract: This review focuses on the effect of metal-containing nanomaterials on tribological performance in oil lubrication. The basic data on nanolubricants based on nanoparticles of metals, metal oxides, metal sulfides, nanocomposities, and rare-earth compounds are generalized. The influence of nanoparticle size, morphology, surface functionalization, and concentration on friction and wear is analyzed. The lubrication mechanisms of nanolubricants are discussed. The problems and prospects for the development of metal-containing nanomaterials as lubricant additives are considered. The bibliography includes articles published during the last five years.

Keywords: coefficient of friction; metal-containing nanomaterials; nanolubricants; nanoparticles; wear

1 Introduction

Recently, the use of nanomaterials as lubricant additives (also known as nanolubricants) has become an important research area [1–18]. The nanolubricant approach is used to overcome the drawbacks of conventional anti-wear and anti-friction additives associated with the need for chemical reactions with substrates, and hence the induction period for obtaining a tribo-film on the friction surface. The main advantages of nanoparticles (NPs) are their size in the nanometer range, which is well adapted for the ideal filling of the friction interface, allowing the combination of several properties, including anti-wear (AW) and extreme pressure (EP) additives, as well as friction modifiers (FM). Owing to their low melting point and high chemical reactivity, NPs can deposit on microdefects of friction surfaces and, to some extent, play the role of "self-repairing" [19]. In addition, NPs have higher thermal conductivity than the base fluid, which facilitates the release of the heat generated by friction and contributes to the stability of the tribo-pairs. An essential advantage of nanolubricants is that they do not require triboactive elements such as phosphorus and sulfur to improve the tribological properties of the base oil, exhibiting excellent friction and wear reduction characteristics. NPs are of considerable interest for improving the properties of biodegradable lubricants. Finally, most NPs are environmentally friendly, as they minimize the use of hazardous materials and additives [16, 20], which is useful for environmental and economic sustainability. In addition, eco-friendly NPs may also facilitate the reduction of energy consumption in production processes, thus leading to a reduction of the carbon footprint. Nanolubricants meet the requirements of green tribology, which is a new area for a large number of tribologists [21, 22].

To date, a large number of nanomaterials used as additives to lubricating oils, in particular, carbon materials [23, 24], carbon nanotubes [25], graphene oxide [26–28], boron nitrides [29, 30], and silicon oxide [31], have been obtained. However, the most extensive studies have been carried out with metal-containing nanomaterials, whose NPs contain, e.g., metals, their oxides, and sulfides [32–34]. Importantly, some of the nanomaterials studied are commercial products [35–39],

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but most studies are concerned with self-made NPs. Various chemical and physical methods are used to obtain NPs [40–44], and they continue to improve. An interesting example is the use of self-propagating high-temperature synthesis for the production of various tribological nanomaterials [45].

It is well known that lubrication can be divided into three different regimes: boundary lubrication, mixed lubrication, and elastohydrodynamic/hydrodynamic lubrication (Fig. 1) [9, 46, 47].

Among them, friction and wear are particularly high in boundary and mixed lubrication, which leads to high machine wear and energy loss [48, 49]. Consequently, lubricant additives are highly important in boundary lubrication owing to the higher coefficient of friction (COF) [16, 50]. Actual problems of reducing friction and wear require an adaptable lubricant for various operating conditions. Accordingly, a large amount of research has focused on the concept of nanolubrication in internal combustion engines as the main strategy for reducing COF and the wear of contact surfaces, which ultimately leads to improved tribological characteristics [51].

To date, despite a significant number of experimental studies on NPs as lubricant additives, several aspects of their tribological behavior have not yet been fully understood. This review will summarize the latest advances in the field of nanolubricants based on metal-containing nanomaterials over the past few years. The rapid growth of this area makes this review timely. No exhaustive analysis of the entire array of current experimental data will be attempted; rather, the focus will primarily be on the composition, the factors influencing the tribological characteristics, and the mechanisms of friction of metal-containing nanolubricants.

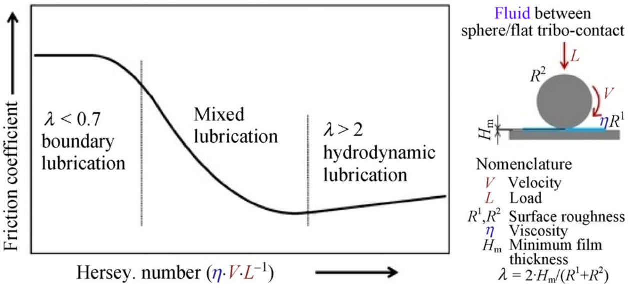

Fig. 1 Stribeck curve and lubrication regime [9]. H_m (minimum thickness of liquid film developed from the base fluid between the surfaces, clearance of the surfaces) could be calculated from the operating parameters (load and velocity) and material parameters (elastic modulus and pressure–viscosity relations).

2 Composition of metal-containing nanolubricants

In most of the studies carried out, it is noted that the addition of NPs to the lubricant can increase its tribological characteristics, which largely depend on the composition of the lubricant [39, 47, 52–58]. According to the data in Ref. [15], metal-containing nanomaterials account for 72% of the nanolubricants studied.

2.1 Metals

Metallic NPs have unique chemical and physical properties as lubricant additives [59–71]. Nano-metals with low shear stress, high extension, and low melting point have been used as FMs owing to their excellent friction-reducing, anti-wear, and self-repairing ability.

Among metallic NPs, Cu-containing nanolubricants have received particular attention owing to their remarkable properties [59–71]. Copper NPs usually have small particle size, low melting point, and the desired ductility; therefore, they are well perceived as an excellent AW and EP agent in comparison with similar products [72, 73]. Copper NPs as an additive can significantly improve the tribological properties of lubricants, which allows the necessary lubrication of equipment. A typical example is the use of two commercially available base oils with synthetic engine oil SAE 5W40 grades dispersed with 0.2 wt% Cu NPs [74]. A significant reduction in friction and wear on the order of less than 13% was observed, and was tribological performance of base oils. Cu nanolubricants form boundary films on friction surfaces, thus increasing tribo efficiency by reducing friction and wear.

In another interesting example, the tribological properties of nanolubricants based on Fe, Cu, and Co NPs, which were added individually and in pairs into mineral oil, were estimated [59]. Cu-containing nanolubricants significantly reduced friction and wear compared to other NPs when added individually. In particular, the presence of Cu, Fe, and Co NPs reduced friction by 49%, 39%, and 20%, respectively, compared to lubricants without additives. When they were added in pairs, nanolubricants containing Fe–Cu and Co–Cu exhibited a decrease in friction of up to 53%, whereas Fe–Co resulted in a 36% decrease.

It is of interest to use Ag and Au NPs as nano-additives to lubricant compositions [75, 76]. In particular, the use of Ag NPs modified by thiolated ligands, 4-(tert-butyl)benzylthiol, and dodecanethiol in the base oil reduced friction by up to 35% and wear by up to 85% in boundary lubrication [77].

It is also interesting to study the friction-reducing and anti-wear behavior of multialkylated cyclopentanes oil with Mo and W NPs as additives under vacuum conditions (~10^{-4} Pa) [78, 79]. The oil exhibited transient high friction in vacuum, resulting into strong adhesion wear of the steel friction pairs, which can be effectively eliminated by Mo and W nano-additives.

The lubrication mechanisms of metal NPs can be grouped as follows: (a) Tribo-films or adsorption films are formed. These films change the surface properties and separate the two friction surfaces, thus giving promising tribological characteristics. (b) The added NPs are rolled within two sliding surfaces, resulting in a reduction in friction and wear. (c) NPs are compacted on the wear track owing to the heat and pressure generated during the friction process. This phenomenon is called sintering or repair effect.

An overview of the typical representatives of metallic NPs used as lubricant additives is given in Table 1.

Table 1 Metallic NPs as lubricant additives.

Nanolubricant details				Tribometer	Conditions			Tribological test results		Ref.
Nano-materials	Grain size	Concentration	Base oil		Load	Speed	Tem-perature	Wear reduction, %	Friction reduction, %	
Bi	7–65 nm	900 mg/L	Light base oil	Four-ball tester	392 N	1,200 rpm	75 °C	—	From 0.091 to 0.052	[80, 81]
		310 mg/L	Heavy base oil	Pin-on-disc setup					From 0.074 to 0.047	
Cu		3 wt%	Chevron Taro 30 DP 40 and Teboil Ward	Pin-on-disc setup	0.1–180 mN	0.02 mm/s	25 °C	0.023–0.018 mg	From 0.15 to 0.11	[82]
	45 nm	0.20 wt%	SAE grade 5W-40	Four ball tribotester	40 N	1,200 rpm	75 °C	2.94–13.30%	From 2.58 to 4.76%	[64]
		0.15 wt%	Mineral oil SN 650	Optimol SRV 4 tester	400 N	200 rpm	rt	32%	34%	[83]
	2–6 nm	1.5 wt%	Paraffin oil	Four-ball machine	300 N	1,450 rpm		0.665–0.460 mm		[84]
	10–60 nm	0.02 wt%	Paraffin oil	Four-ball machine	300 N	1,450 rpm	20 °C		26%	[85]
	2–5 nm		Paraffin oil	Four-ball friction and wear tester				Reduced the COF of steel pair		[86]
Fe, Cu, Co		0.5 wt%	SAE 10 mineral oil	Four ball tribotester	150 N	1,420 min^{-1}		Up to 20% (Co), 39% (Fe), 49% (Cu)		[59]
Ni	7.5–13.5 nm and 28.5 nm	0.05 wt%	PAO	Four-ball friction and wear tester	300 N	1,450 rpm		0.47–0.54	0.78–0.68	[87, 88]
Pd	2 nm	2 wt%	Paraffin	Ball-on-disk tribometer	1–20 N	10 cm/s		Reduced COF		[89]
Sn and Fe	30–60 nm and 20–70 nm	1 wt%	Multialkylated cyclopentanes	Four-ball tribometer	300 N	1,450 rpm	25 °C	Sn is effective on friction reduction; Fe is effective on anti-wear performance, low COF around 0.1		[90]
Mo W	20–50 nm 30–60 nm	0.1–0.5 wt% 1.0 wt%	Multialkylated cyclopentanes	Four ball fatigue tester	294 N	1,450 rpm	rt	Low COF of approximately 0.1		[78]

2.2 Metal oxides

Various metal oxides are used as lubricant additives, including TiO_2, CuO, Fe_3O_4, ZnO, Co_3O_4, and Al_2O_3 [34, 55, 91]. Their lubrication mechanisms are analogous to those of metal-containing nanomaterials, including the formation of tribo-film or adsorption film, the rolling effect, and the sintering or repair effect. A typical example is the use of spherical CuO and TiO_2 NPs as lubricant additives, exhibiting good friction reduction and anti-wear behavior, particularly for CuO [56]. The friction reduction can be explained by the effect of viscosity at low temperature and the rolling effect at high temperature, and the anti-wear mechanism is associated with the deposition of CuO NPs on the friction surface, which can reduce shearing stress and improve tribological properties.

Several studies are devoted to the use of TiO_2 NPs as lubricant additives [92–96]. In particular, a sample of palm oil biolubricant with 0.1 wt% of a TiO_2 nano-additive had the lowest COF and wear scar diameter.

The use of oxide NPs (ZnO and CuO) as lubricant additives should be noted [97–104]. For example, biolubricants using vegetable oils (soybean and sunflower) with ZnO and CuO NPs as additives are biodegradable and have better performance in boundary lubrication.

Magnetic Fe_3O_4 NPs with an average particle diameter of 11.7 nm were dispersed in alpha-olefin hydrocarbon synthetic lubricating oil with a solid weight fraction of 0 to 10 wt% [105, 106]. This resulted in a reduction in COF and the diameter of the wear scar by 45% and 30%, respectively, at the optimal value, i.e., 4 wt% of the concentration of the NPs. The rolling mechanism is responsible for the reduction of COF, whereas the magnetic NPs act as the spacer between the asperities and reduce the diameter of the wear scar.

It is of interest to use copper [107–111] and cerium oxide NPs [112] as lubricant additives to improve tribological characteristics. A nanolubricant based on palm oil with the addition of copper oxide NPs exhibited 20.12% and 8.73% lower COF compared to mineral-based engine oil (SAE 40) and palm kernel oil, respectively [113]. However, it represented 10.13% and 1.74% higher wear scar diameter than SAE 40 and palm kernel oil, respectively.

The typical representatives of nanolubricants based on metal oxide NPs are listed in Table 2.

2.3 Metal sulfides

Although MoS_2 has been widely used as an important lubricant additive for a long time, it has been demonstrated that MoS_2 NPs as FMs in liquid lubricants are superior to MoS_2 microparticles, owing to the chemical stability of the layer-closed spherical structure of NPs. Both MoS_2 and WS_2 NPs, which are layered compounds with a hollow polyhedral structure known as fullerene-like NPs (IF-NPs), have proven to be good FMs when dispersed in lubricants [130].

It is of interest to study the anti-friction behavior of FeS NPs with a size ranging from 20 to 200 nm as a lubricating oil additive in engine oil [131]. COF decreases remarkably with the addition of these NPs; furthermore, a persistent antifriction effect under dry condition is observed. It is important that the diffusion of S atoms in the near-surface region forms a sulfur diffusing area, resulting in a durable friction-reduction behavior on the friction pair.

Examples of the use of metal sulfide NPs in nanolubricants are presented in Table 3.

2.4 Nanocomposites

Owing to the synergetic effect of more than one NP type, composites usually exhibit superior performance compared to individual NPs [136–138]. Thus, Cu/CeO_2, Al_2O_3/SiO_2, ZrO_2/SiO_2, and (Zn-Ni)/nano Al_2O_3 composite NPs were used as energy-efficient lubricant additives [139]. Lubricant additives such as nano-Ag/multi-wall carbon nanotubes [140] and silver NP-decorated graphene [141] should be mentioned.

It is of interest to study the tribological properties of composite nanomaterials based on zinc oxide NPs and nanolamellar tungsten and molybdenum disulfide [142, 143]. According to tribological measurements, the addition of ZnO NPs did not significantly alter the COF of nanolamellar metal disulfides at 25 ℃ in air, whereas it positively affected wear resistance at 400 ℃.

Cu NPs and Ag NPs were used as metal cladding modifiers of nanolamellar MoS_2 [144, 145] and WS_2 [137] particles. It was demonstrated that such nanocomposite lubricants changed the COF of the original

Table 2 Metal oxide NPs as lubricant additives.

Nanolubricant details				Tribometer	Conditions			Tribological test results		Ref.
Nano-materials	Grain size	Concen-tration	Base oil		Load	Speed	Tem-perature	Wear reduction, %	Friction reduction, %	
TiO_2	20–25 nm	0.25 wt%	Mineral oil	Four ball tribo-tester	14.7 N	0.05 m/s	rt	—	21%	[55]
	30 nm	2 wt%	Oil-in-water lubricant	Rtec MFT-5,000 multi-functional high temperature tribometer	50 N	10–70 mm/s	80 °C	—	16.3%	[114]
	30 nm	0, 0.5, 2, 4 and 6 wt%	Oil-in-water lubricant	Ball-on-disk tester	50 N	50 mm/s	80 °C	Wear was significantly reduced		[115]
	20 nm	4 wt%	Water based oil	Ball-on-disk tribometer	5 N	50 mm/s	rt	34%	20%	[116]
	20 nm	0.1–1.6 wt%	Water-based cutting fluids	Four-ball tribotester	147 N	1,440 rpm		34.8%	from 0.17 to 0.04	[117]
	< 100 nm	volume fractions of 0.0001 to 0.005	SAE30 engine oil						40%	[118]
		0.1 wt%	Biolubricant palm oil-based trimethy-lolpropane ester	Four-ball machine tribotester	160 kg	1,200 rpm	rt	11%	15%	[119]
	10–25 nm	1.5 wt%	multi-grade engine oil Castrol Active 4T SAE 20W 40	Pin-on-disc tribometer	40, 60 and 90 N	0.5, 1.0 and 1.5 m/s		Wear was significantly reduced		[120]
	50–100 nm	0.1, 0.2, 0.3, 0.4, 0.5 wt%	API-1509 base oil	Four-ball tribometer and ball-on-disk tribometer	100 N		75 °C	Friction and wear reduction compared to the base oil		[121]
		from 0.1 to 2.0 wt%	Vaseline oil	Four-ball tribometer	200 N	1,460 rpm			29.4%	[122]
SnO_2		from 0.5 to 5 wt%	PAO	Bruker universal mechanical tribometer	25 N		rt	43.7%	65.4%	[123]
Al_2O_3	78 nm	0.1 wt%	Base oil	Four-ball tribometer	200 N	1,200 rpm	75 °C	41%	17–24%	[58]
	40–80 nm	0–1 wt%	SAE20W40 lubricating oil	Pin-on-disc tribotester	160 N	1,200 rpm		The minimum COF was obtained with 0.8 wt% of medium NPs size 60 nm		[124]
Al_2O_3 and CuO	< 50 nm	0.5, 1.0, and 2.0 wt%	SAE 75W85 and PAO8	Optimol SRV 4 tester	from 0 to 7,200 N	500 rpm	25 °C		up to 18% and 14%	[125]
Al_2O_3 and TiO_2	8–12 nm 10 nm	0.25 wt%	5W–30	Piston ring/cylinder liner contact tester	120–250 N	0.5 m/s	100 °C	21% 29%	45% 50%	[47]
ZnO and CuO	11.71 nm 14.35 nm	0.5 wt%	Mineral, PAO, sunflower, soybean	High frequency reciprocating test rig	10 N		50 °C	ZnO is effective with mineral oil. CuO is effective with synthetic oil.		[126]
ZnO		0.5 wt%	60SN base oil	Four-ball machine				9.9%	31.2%	[127]
	4.04 nm	1.20 wt%	Lubricant base oils	Pin-on-disc tribotester	392 N	1,200 rpm	75 °C	31.2%	9.9%	[128]

(Continued)

Nanolubricant details				Tribometer	Conditions			Tribological test results		Ref.
Nano-materials	Grain size	Concen-tration	Base oil		Load	Speed	Tem-perature	Wear reduction, %	Friction reduction, %	
ZrO_2	<100 nm	0.5 wt%	$20^{\#}$ machine oil	Four-ball tester	392 N	1,450 rpm	rt	3.98%.	5.36%	[129]
Fe_3O_4 magnetic NPs	11.7 nm	4 wt %	alpha olefin hydrocarbon synthetic lubricating oil	Four-ball tester	392 N	1,200 ± 20 rpm	75 °C	30%	45%	[101]
Fe_3O_4	45.8–50.1 nm	1.5 wt%	#40 engine oil	Four-ball tester	400 N	1,450 rpm		COF could be reduced by 58.16%, 47.96%, and 34.69%, and the wear could be reduced by 13.87%, 11.17%, and 10.18% for the oils containing Fe_3O_4 NPs with hexagonal, octahedral, and irregular morphologies, respectively.		[105]

Table 3 Metal sulfide NPs as lubricant additives.

Nanolubricant details				Tribometer	Conditions			Tribological test results		Ref.
Nano-materials	Grain size	Concentration	Base oil		Load	Speed	Tem-perature	Wear reduction, %	Friction reduction, %	
FeS	20–200 nm	0 to 2 wt%	Commercial API SL/CF 10W-40 engine oil	Pin-on-disc system	50 or 150 N	150 rpm		COF decreases remarkably under oil lubrication and dry conditions		[131]
MoS_2	350 and 150 nm	1 wt%	Blend of PAO 4 and PAO 40	High Frequency Reciprocating Rig	10 N		80 °C		From 0.20 to 0.06	[132]
	50–100 nm	2.0, 1.5, 1.0, 0.5, 0.25, and 0 wt%	Dioctyl sebacate	High-frequency reciprocating ball-on-disc tribometer	7.84 N	0.1 m/s	60 °C	35%	~37%	[133]
	Diameters below 100 nm and lengths up to 20 μm	2 wt%	PAO	Ball-on-disc tribometer	35 N	from 3.2 to 0.002 m/s	rt		From 30 to 50%	[134]
	Average diameter ~50 nm; single layer thickness ~3 nm	≈1 wt%	SE 15W-40	Disc-on-disc frictional testing machine	1,500 N	500 rpm	rt	Enhance significantly tribological performance		[135]
	90 nm	0.53 wt% 0.58 wt%	vegetable (coconut) oil and a mineral oil (500 N base-oil)	Pin-on-disc tribometer and a four-ball tester	100–200 N	100–300 rpm	30–120 °C	Enhance significantly tribological performance		[35]

lubricant and significantly improved its wear resistance.

In Ref. [138], the tribological behavior of decorative thin-film nanocomposities consisting of gold NPs dispersed in the TiO_2 dielectric matrix was studied, and it was demonstrated that the clustering of gold, the increase in grain size, and the crystallization of the TiO_2 dielectric matrix correlated with changes in tribological parameters.

Typical examples of lubricants based on nanocomposities are given in Table 4.

2.5 Rare-earth compounds

Among the rare-earth compounds studied, the most widely used elements were La and Ce. Such compounds can be used either individually as lubricant additives or in other NPs such as TiO_2. Their lubrication

Table 4 Nanocomposite NPs as lubricant additives.

Nanolubricant details				Tribometer	Conditions			Tribological test results		Ref.
Nanomaterials	Grain size	Concentration	Base oil		Load	Speed	Temperature	Wear reduction, %	Friction reduction, %	
TiO_2/SiO_2	50 nm	0.75 wt%	Palm oil	Four-ball extreme pressure and piston ring-cylinder liner sliding tribotesters	160 N	500 rpm	70 °C	10.4%	~17–25%	[146]
Al_2O_3/SiO_2	70 nm	0.05, 0.1, 0.5, 1 wt%	PAO 6	Pin-on-disk tribometer	147 and 200 N	1,200 and 1,450 rpm	75 °C		~20%	[139–141]
Graphene and MoS_2	Two-dimensional size is ~2 μm	1.0 wt%	Hydraulic oil	Ball-on-disk reciprocating friction tester	3 N	1.2–38.4 mm/s	25–125 °C		Up to as low as 0.04	[147]
Re:IF-MoS_2	100 nm		PAO-6	Rotational disc tribometer	0–100 N	3,000 rpm	25, 50 and 80 °C	The best results in boundary, mixed and elasto-hydrodynamic lubrication regimes		[130]
WS_2-Cu	50-80 nm			Ball-on-disk High Temperature Tribometer	5 and 10 N	5 cm/s	Rt	Reduce wear of the friction body when using both commercial and nanolamellar molybdenum disulfide		[145]
MoS_2, WS_2 and ZnO				Ball-on-disk High Temperature Tribometer			25 °C	ZnO NPs additive did not practically change COF		[143]
WS_2 and ZnO	50–150 nm 24 nm			Ball-on-disk High Temperature Tribometer	5 N	5 cm/s	25 and 400 °C	ZnO NPs did not significantly change COF of nanolamellar WS_2 at 25 °C in air, whereas they positively impact on wear resistance of nanolamellar WS_2 at 400 °C		[141]
MoS_2 and SiO_2	The layer thickness of MoS_2 is 90 nm. The SiO_2 NPs have an average particle diameter of 30 nm.	0.2, 0.5, 0.7 and 1.0 wt%	EOT5# engine oil	Ball-on-flat tribometer	1, 3, 5, and 8 N	0.03 m/s		Exhibit excellent lubrication properties		[39]
Cu/MoS_2 Ag/MoS_2			LITOL and VNIINP	Ball-on-disk High Temperature Tribometer	5 N	5 cm/s		Changed COF of the initial grease and essentially improved its wear resistance		[144]
Al_2O_3/TiO_2 nanocomposites	75 nm	0, 0.05, 0.1, 0.5 and 1 wt%	pristine lubricating oil	Friction-abrasion testing machine	147 and 200 N	1,200 and 1,450 rpm	75 °C	Exhibit significantly better tribological performance of the lubricating oil		[148, 149]
Nano-Cu/ Graphene oxide nanocomposite	5–10 nm	0.05 wt%	paraffin oil	Four-ball tribometer	200 N	1,200 rpm	rt	Greatly reduce friction and wear as lubricant		[150]

(Continued)

Nanolubricant details				Tribometer	Conditions			Tribological test results		Ref.
Nanomaterials	Grain size	Concentra tion	Base oil		Load	Speed	Tem-perature	Wear reduction, %	Friction reduction, %	
TiO_2, CuO, Al_2O_3, MWNTs	< 21 nm < 50 nm < 50 nm 6–9 nm by 5μm	0.01 to 0.10 wt%	greases Mobilgrease 28 (PAO syntethic fluid) and Uniflor 8623B (Perfluoropolyether)	Four-ball tribotester	40 kgf	600 rpm	75 ˚C	Up to 20% reduction using TiO_2. CuO showed up to a 14% reduction. Both MWNTs and Al_2O_3 increased wear		[151]
Oleic acid/La-TiO_2	20 nm	0.25 wt%	rapeseed oil	Four-ball friction and wear tester	392 N	1,200 rpm		NPs could markedly improve anti-wear and friction-reducing capacities of rapeseed oil.		[152]

mechanisms primarily include the formation of a tribo-film or an adsorption film. In particular, the tribological properties of the rare-earth compounds $CeVO_4$, Y_2O_3, $La(OH)_3$, and LaF_3 NPs used as FMs in lubricants have been widely studied [153–155]. Cerium oxide (≈ 90 nm) should also be noted, which was blended in paraffin oil and used as a nanolubricant [156]. Rare-earth compounds can obviously prolong oil life, enhance machine antiwear capacity by 2–4 times, and improve the load-carrying capacity of lubricating grease by 10%–100%. Moreover, the synergistic lubrication effect of rare-earth compounds and other additives is more pronounced [157].

Nanolubricants based on rare-earth compounds are listed in Table 5.

3 Factors influencing the tribological properties of nanolubricants

The size, morphology, surface functionalization, and concentration of NPs are among the most influential factors on the tribological properties of nanolubricants.

3.1 Effect of nanoparticle size

The tribological characteristics of nanolubricants directly depend on NP size. In particular, it determines their internal mechanical and physico-chemical properties,

Table 5 Rare-earth compounds as lubricant additives.

Nanolubricant details				Tribometer	Conditions			Tribological test results		Ref.
Nanomaterials	Grain size	Concentration	Base oil		Load	Speed	Tem-perature	Wear reduction, %	Friction reduction, %	
CeO_2	10 nm	Up to 50 wt%	Mixed oil of 350SN and 650SN (1:1, weight ratio)			1,450 rpm	25 ˚C	Tribological properties were significantly improved.		[158]
Hydroxides NPs (Mg/Al/Ce LDHs)	190.1 nm	0.5 g LDHs per 100 ml oil	Diesel engine oil (CD 15W-40)	MS-10JR four-ball friction tester	392 N	1,200 rpm	Rt		Decreased to 0.083 (27.2%)	[153]
LaF_3	10–30 nm	0.08 wt%	Fluoro silicone oil	Four-ball machine	300 N	1,450 rpm	25 ˚C	When the load is 500, 600 and 700 N, the wear scar diameter is reduced by 17%, 43% and 42%, respectively		[159]
	10–30 nm	0.40 wt%	Liquid paraffin	MS-10JR four-ball friction tester	300 N	1,450 rpm	25 ˚C	Excellent anti-wear and good friction-reducing ability. COF rises to 0.108.		[154]
Stearic acid-capped/$CeBO_3$	8 nm	2.0 wt%	Rapeseed oil	Four-ball tribo-tester	392 N	1,500 rpm	Rt	Outstanding in enhancing friction-reduction and anti-wear capacity of rapeseed oil		[160]

which, in turn, affect their tribological properties. For materials in the size range of 100 nm or higher, hardness increases as particle size decreases owing to an increase in the number of dislocation pileups for crystals (Hall–Petch regime). In this regime, hardness increases linearly with the inverse square root of particle size. At critical grain sizes, usually below 10 nm, nanomaterials become softer as size decreases (inverse Hall–Petch regime). If NP hardness exceeds the hardness of the tribo-pair material, the result is indentation and scratching. For example, the high hardness (8–9 Mohs) of nano-Al_2O_3 compared to the metal substrate leads to abrasive wear and re-agglomeration of the NPs [125]. Therefore, in the design of a nanolubricant, it is necessary to consider the relationship between the size and hardness of NPs.

In the choice of a suitable NP size, an important parameter is the ratio of the root-mean-square roughness of the lubricant surface to the NP radius. That is, NP-based lubrication systems must remain in the contact zone during loading and shearing to protect friction surfaces. If their size is overly large compared to the characteristic roughness length scale of the shearing surfaces, the NPs will not deposit on the contact zone, which will lead to poor lubrication. However, when the characteristic roughness length scale is significantly larger than the NP radius, the valleys between asperities of the shearing surfaces can be filled with NPs.

Finally, the homogeneity of the nanolubricant composition, which largely controls its tribological characteristics, depends heavily on colloidal stability. Dispersion stability is a function of NP size, which is the main requirement for the correct composition of the nanolubricant. An important parameter for determining dispersion stability is sedimentation rate, which can be calculated using the Stokes law:

$$\upsilon_z = \frac{2(\rho_{\mathrm{NP}} - \rho_{\mathrm{F}})gr^2}{9\mu}$$

where υ_z is the settling velocity, ρ_{NP} is NP density, ρ_{F} is the density of the fluid, g is gravity, r is NP radius, and μ is the viscosity of the fluid.

According to the Stokes law, smaller size implies better dispersion stability and tribological behavior.

In Ref. [161], a nanolubricant based on CuO NPs was added to synthetic oil at three concentration and size levels: 0.1, 0.25, and 0.5 wt%, and 2.5, 4.4, and 8.7 nm, respectively [161]. It was demonstrated that a low NP concentration reduces wear and contributes to a smooth surface, whereas a large plastic deformation is observed at a high concentration. Furthermore, the smallest NP size corresponded to the smallest COF. In general, the best results were obtained for a nanolubricant with a concentration of 0.1 wt% and an NP size of 2.5 nm.

3.2 Effect of nanoparticle morphology

The shape of NPs used as lubricant additives is another important parameter for nanolubricant design, because it directly determines the pressure experienced by the NPs during loading. There are five types of NP shapes: granular, onion, sheet, spherical, and tube. According to the statistics (Fig. 2), most NP shapes are spherical, followed by granular, sheet, onion, and nanotube.

After nucleation, crystalline particle structures tend to evolve so that surface energy may be minimized, which leads to a spherical shape. Onion morphology is described as a spherical shape on the outside and a lamellar structure inside. If the onion morphology is stable, it is closer to spherical morphology. Otherwise, it will exfoliate and become a sheet-like morphology. The advantages of onion structure lie in the absence of dangling bonds and spherical shape.

Onion, leaf, and spherical morphologies exhibit excellent tribological characteristics. Spherically shaped NPs exhibit high load capacity and EP characteristics owing to their ball bearing effect, which can change friction characteristics from sliding to rolling, thus reducing friction [148, 149]. The spherical shape of

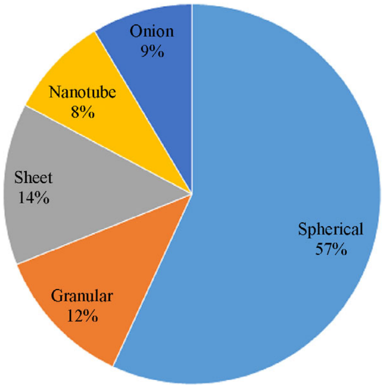

Fig. 2 Statistics of NP morphology [15].

NPs leads to point contact with the counter surface. Line contact is associated with nanosheets, whereas planar contact is a feature of nanoplatelets.

It is of interest to investigate the tribological properties of single-crystalline α- and β-MnO_2 nanorods as nanoadditives in green lubricants [162]. The minimum friction torque was observed for α-MnO_2-added palm oil, followed by β-MnO_2-added palm oil, and pure palm oil (Fig. 3(a)). Even though β-MnO_2 nanorods exhibited a decrease in COF by approximately 15%, α-MnO_2 nanorods are even better nanoadditives, with a reduction of up to 30% (Fig. 3(b)). Such an increase in anti-wear capacity arises primarily from the interplay between the rolling action and the formation of a protective layer by the corresponding quasi-1D MnO_2 polymorphs.

Another example illustrating the significance of a nanostructure is the layered structure of NPs of transition metal dichalcogenides, which is more suitable for reducing friction by forming a tribo-film [163, 164]. Figure 4 shows the molecular structure of MoS_2 as an example of a layered crystal structure.

Compared to typical transition metal dichalcogenides, IFs have been developed that are layered compounds with a hollow polyhedral structure [165]. They exhibit excellent tribological behavior under severe contact conditions and tend to form tribo-films on friction surfaces [127]. Such solid IF-NPs can use additional “exfoliation” lubrication mechanisms. In addition to their layered structure, sulfur plays an important role in the interaction between particles and lubricant molecules.

Although materials such as MoS_2 have been studied for some time, various other 2D nanomaterials have appeared as an alternative to friction modification [165, 166].

3.3 Effect of surface functionalization

The functionalization of the NP surface is used to regulate the colloidal stability of the NP dispersion and to increase the lubricity of most layers of NPs. It is well known that non-functionalized NPs tend to aggregate in inert non-polar liquids such as hydrocarbon. Aggregation is usually prevented by protecting

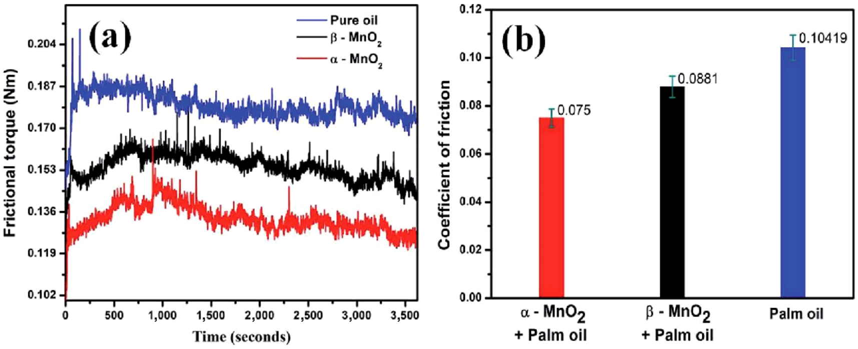

Fig. 3 (a) Frictional torque with respect to time observed using four-ball test technique, (b) COF of pure palm oil, β-MnO_2-added palm oil, and α-MnO_2-added palm oil.

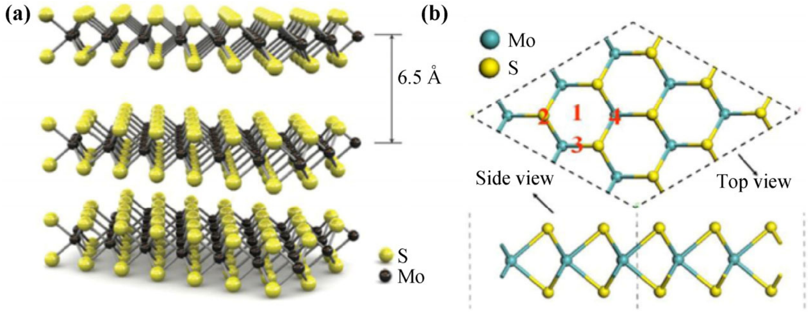

Fig. 4 (a) Three-dimensional representation of the structure of MoS_2. Single layers, 6.5 Å thick, can be extracted using scotch tape-based micromechanical cleavage. (b) Optimized structures of MoS_2 monolayer with four adsorption sites: (1) hollow site, (2) top site of the S atom, (3) Mo-S bridge site, and (4) top site of the Mo atom [165].

NPs by steric or electrostatic stabilization, which typically involves coating the NPs with a polymer or surfactant. As a rule, the functionalization of the NP surface is necessary to increase the colloidal stability and homogeneous distribution of NPs in the base oil.

It should be noted that functionalized NPs have better lubricating properties compared to bare NPs because the latter experience material transfer when they come into direct contact with shearing surfaces and prevent cold-welding of the shearing surfaces. In addition, functionalized NPs prevent the transfer of material between them and cold-welding between the shearing surfaces. Of great importance is the fact that functionalized NPs have a hybrid structure with a rigid inner core and a soft outer shell. This synergistic combination provides NPs with a rigid internal shape and a slippery fluid-like surface (Fig. 5, left). Ultimately, such NPs allow higher load carrying capacity, without reducing lubricity (Fig. 5, right) [167].

Finely dispersed Cu NPs covered by surfactants were used as an additive to fully-formulated engine oils [81]. The tribological process of formation of protective films on the metal surface includes the accumulation of polar molecules by absorption to produce an FM film and mechanochemical processes comprising a combination of redox reactions and a third body formation. The oil-soluble Cu NPs obtained by surface modification with tetradecyl hydroxamic acid have been used as environmentally friendly oil additives that could remarkably improve anti-wear and friction reduction performance. Cu NPs can deposit and fill up micropits and grooves on steel friction surfaces under a higher load, and consequently they significantly reduce steel pair wear by self-repairing worn surfaces [80]. One should note triangular copper nanoplates prepared with cetyltrimethylammonium bromide as the capping agent [82]. As an additive for lubricants, nanoplates are responsible for the formation of a film deposit at the interface of a friction pair and a 12% drop in COF of the lubricant and an 82.2% drop in wear loss. Cu NPs surface-capped by dioctylamine dithiocarbamate [83] or alkanethiols [84] were used as an additive in liquid paraffin. They have excellent anti-wear and friction-reduction properties owing to the deposition of Cu NPs, with a low melting point on the worn steel surface, which results in the formation of a self-repairing protective layer on it.

Ni-based nanolubricants with oleylamine and oleic acid as surface-capping agents in poly-alpha-olefin as a base oil [87] or a synergistic lubricant system with a solid liquid [168] exhibit good anti-wear behavior even at low Ni concentrations (0.05 wt%). This is because surface-capped Ni NPs in nanolubricants can release highly active Ni nanocores as well as O- and N-containing organic modifying agents, which can easily form a boundary lubricating film on sliding steel surfaces.

Two types of thiolated ligands, namely, 4-(*tert*-butyl)benzylthiol and dodecanthiol, were used to modify oil-suspended Ag NPs in the ranges 1–3 nm and 3–6 nm [77]. The organic surface layer successfully suspended Ag NPs in PAO base oil with concentrations up to 0.19–0.50 wt%, depending on the particle type. Using Ag NPs in the base oil reduces friction by up to 35% and wear by up to 85% in boundary lubrication. NPs modified with a ligand of the first type resulted in lower COF than NPs modified with a second-type ligand, whereas larger NPs (3–6 nm) had better wear

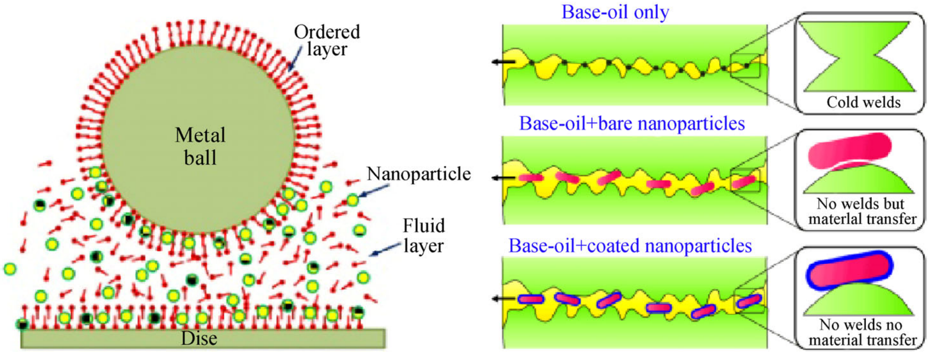

Fig. 5 (left) Core-shell structure of NP on the disc; (right) comparison of the effect of three types of lubrication conditions on cold-welding and material transfer behavior of a tribo-pair.

protection than smaller NPs (1–3 nm). It is important that the molecular structure of the organic ligand can exert a dominant influence on friction behavior, whereas NP size may be more influential in wear protection. Wear protection in boundary lubrication is due to the formation of a 50–100 nm thick silver-rich tribo-film on the worn surface.

It is of interest to study the tribological properties of CuO NPs dual-coated with sodium oleate and alkylphenol polyoxyethylene ether [163, 164]. The COF and wear scar diameter of deionized water in the presence of dual-coated CuO NPs are significantly reduced, and excellent tribological properties under a certain load are obtained at the optimum concentration of the dual-coated CuO NPs. CuO nanorods stabilized with ionic liquids exhibit excellent friction reduction (15%–43%) and improved anti-wear properties (26%–43%) compared to PEG 200 and 10W-40 engine oil [169]. The increase in the lubricity of CuO nanorods is due to their good dispersion stability and rolling mechanism. One should note the use of tiny CuO NPs with low concentrations as EP additives in synthetic oil [56]. NPs with an average size of 5 nm were coated with oleic acid and added to poly-alpha-olefin oil using a toluene dispersant. It was demonstrated that it is possible to reduce COF and wear using tiny NPs, as well as to reduce the percentage of the CuO addition in the lubricating oil. The wear and friction properties of a suspension of CuO (50 nm) NPs modified with oleic acid in liquid paraffin were studied [170]. After modification, the lowest COF (0.123) was obtained at 3% CuO and the highest value (0.158) at 0.2% CuO. Nanolubricants based on castor and paraffin oil with CuO NPs, modified with a surfactant sodium dodecyl sulfate, as an additive in the regime of boundary lubrication were studied in Ref. [171]. The maximum wear reduction was 28.3% and 22.2%, whereas COF was reduced by 34.6% and 17.3% at optimum NP concentration in the former and latter oils, respectively. A significant improvement in the weld load was observed for both nanolubricants.

Oleic acid surface-modified ZnO NPs dispersed in 60SN base oil [100], poly-alpha olefin, or diisooctyl sebacate [127] significantly reduced friction and wear. Interestingly, when the amount of oleic acid added was 8 wt% and ZnO NPs was 0.5 wt%, COF and the average diameter of the wear scars were minimal, and the nanolubricant exhibited the best friction-reducing and anti-wear properties. It is of interest to use nanolubricants based on multiwalled carbon nanotubes and ZnO NPs with a volume fraction of 0.005% and 0.02%, respectively, dispersed along with Gum Arabic surfactant in SAE 20W40 engine oil [172].

It should be noted that TiO_2 NPs modified by tetra(2-ethylhexyl)-thiuramdisulfide and di(2-ethylhexyl)-thiophonedisulfide can be completely well-dispersed in the base oil, with no significantly negative effect on anti-friction properties [121, 122]. It is important that functionalized TiO_2 NPs exhibit better anti-wear and friction-reducing properties in base oil compared to non-coated TiO_2 NPs. Aqueous suspensions containing various concentrations of TiO_2 NPs (50 nm), in which sodium polyacrylate is used as the dispersant, have good anti-wear and friction reduction properties as well as load-carrying capacity [173].

Oleic acid was used as a surfactant to improve the stability of oil-based SnO_2 nanofluid, reducing COF by up to 65.4% and the wear volume loss by up to 43.7% [123]. A tribosintered or embedded patchy film containing tin was observed inside the wear track, which protected the surface from wear and lowered COF. In addition, SnO_2 NPs can roll or slide between two friction surfaces to prevent adhesive wear. CeO_2 NPs (≈90 nm) were used as additives in castor oil with four different concentrations in the range 0.1%–1.0% *w*/*v*, with sodium dodecyl sulfate as a dispersant [174]. The maximum reduction in the wear scar diameter was 37.4% at the optimum concentration of CeO_2.

Solid sphere-like MoS_2 NPs improve the tribological properties of dioctyl sebacate (DOS) more than commercial micro-MoS_2 [133]. It is important that MoS_2 NPs bind to DOS molecules, promoting the solidification of DOS on the surface of MoS_2 NPs and the formation of fiber-like solids aggregated into a net-like structure (Fig. 6). A large number of DOS molecules are captured in the net-like structure, forming an adsorption film that reduces friction and wear.

3.4 Effect of nanoparticle concentration

Concentration is another important factor that affects the lubrication characteristics of nanolubricants [35]. Typically, the addition of NPs is effective in reducing friction and wear, even at concentrations below 1 wt% [59] and above 2 wt% [170], indicating that NPs do

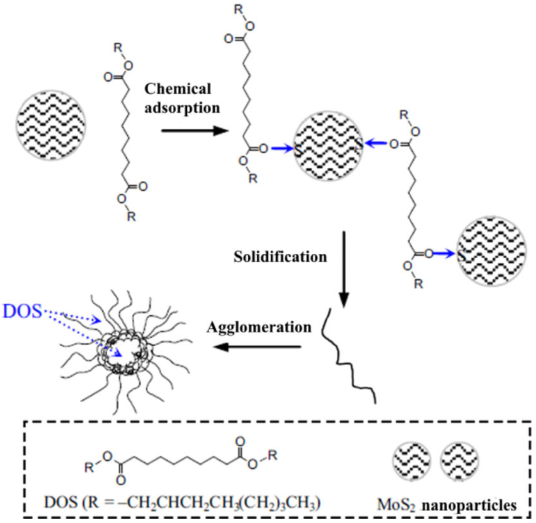

Fig. 6 Formation of adsorption layer using MoS_2 NPs [133].

not have an ideal concentration. In addition, there is no predictable relationship between the concentration and the effect of the nanoadditive on friction and wear. It should be noted that there is an optimum concentration at which COF is minimal. However, it is highly dependent on the system because the lubricant composition must be adjusted for each operating condition [175]. For example, the same MoS_2 NPs show different suitable concentrations for two different base lubricants, i.e., 0.58 wt% for mineral oil and 0.53 wt% for coconut oil [35]. Furthermore, a fixed optimal concentration of 0.5 wt% of CuO NPs and ZnO NPs was established for mineral, synthetic, and vegetable oils [126]. A study of the tribo-performance of cerium oxide (≈90 nm) NPs in paraffin oil with a concentration change from 0.1 to 1.0% *w*/*v* demonstrated that a concentration of 0.25% *w*/*v* is optimal in anti-wear and anti-friction tests [171]. At this concentration, the maximum reduction in the wear scar diameter was 26.1% and the average COF was reduced by 29.6%. For nanolubricants based on sunflower oil and two types of the nanoadditives, that is, CuO and CeO_2, with different concentrations from 0.10% to 0.50% *w*/*v*, a concentration of 0.10% *w*/*v* for the nanoadditives is optimal owing to least wear scar and COF [176]. A higher NP concentration degrades the base oil performance. Hafnium doped into diamond-like thin films exhibited low COF and excellent wear resistance at the optimum 0.42% Hf concentration [177].

It was suggested [178, 179] that NPs reduce the real area of contact, and consequently reduce the friction in boundary lubrication. That is, the particles in contact will keep the surfaces apart around the particles, leading to a decrease in the real contact area (Fig. 7) and thus to a decrease in COF.

When more concentrated nanolubricants are used, more particles will come into contact, which explains the monotonic decrease in COF compared to the particle concentration in the tests.

The obtained results demonstrate that each type of NP should be analyzed considering both the previously mentioned factors (size, morphology, surface functionalization, and concentration) and the application conditions (temperature, load, and slip speed), as well as the nature of the base lubricant.

4 Lubrication mechanisms

The investigation of lubrication mechanisms is considered a decisive parameter for a complete understanding of nanolubricant tribology. However, the definition of active mechanisms remains a subject of discussion in several studies on metal-containing nanoadditives to lubricating oils. A number of mechanisms have been proposed using surface analysis techniques to explain the increase in lubrication. These mechanisms include ball bearing, the formation of a protective film, mending, and polishing.

To study the lubrication mechanisms for lubricating oils enriched with NPs, a number of methods for characterizing surfaces have been used [59, 124, 126, 127, 180, 181]. However, it was noted that owing to the existence of different lubrication mechanisms by nanolubricants, these surface analysis tools are not sufficient to distinguish the role of NPs among

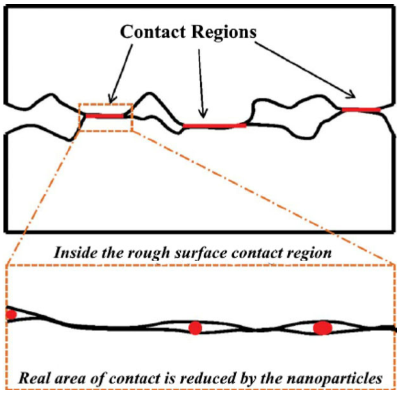

Fig. 7 Mechanism of reduction of the real area of contact by NPs.

these mechanisms. The combinations of lubrication mechanisms include the direct action of NPs (ball bearing/tribo-film formation) and secondary surface enhancement (mending/polishing). For example, the examination of the performance of a four-stroke diesel engine with the addition of Al_2O_3 NPs to the engine oil (SAE15W40) demonstrated signs of ball bearing and surface polishing, which are responsible for the improvement of the tribological properties of the oil [182].

4.1 Ball bearing effect

Spherical and quasi-spherical NPs generally function as tiny ball bearings that roll into the contact zone and change sliding friction to a mixture of sliding and rolling friction (Fig. 8).

In particular, the rolling friction of sphere-like CuO NPs at the contact surface could improve the tribological properties of the base lubricant [126, 184]. Introducing a nanolubricant may result in superior product quality owing to the rolling action of NPs between sliding surfaces, thus preventing surface contact [185]. Analysis of ZnO composite submicrospheres with Al_2O_3 NPs as additives for lubricating oils has demonstrated that rolling friction becomes dominant instead of sliding friction, and these composite particles squeezed into grooves on the friction surfaces can reduce wear [186]. Copper oxide NPs convert sliding friction into rolling friction, thereby reducing the effective COF [128].

4.2 Protective film formation

The protective film on the tested surfaces is also called a tribo-film. Tribo-films and near-surface materials determine the tribological behavior of friction surfaces. Film formation is initiated by a reaction between the treated material and additives under environmental conditions or tribo-sintering [13, 187]. There are several experimental studies that describe the mechanism of tribo-film formation for excellent lubrication. The rate of tribo-film formation should be higher than the wear removal rate to protect worn surfaces [188–190]. Self-replenishment is necessary for maintaining a tribo-film with sufficient adhesion to the substrate and internal cohesion to withstand the friction during boundary lubrication. NPs play a vital role in the formation of tribo-films on contact interfaces to improve engine performance and combustion through various mechanisms [191]. Tribological characteristics are associated with the mechanical strength and thickness of the tribo-film produced on worn surfaces [192]. As presented in some studies [56, 59, 119, 170], the efficiency of metallic NPs is attributed to their deposition on worn surfaces forming a thin layer, generally softer than the substrate, capable of reducing friction through smaller sliding resistance and of protecting the substrate from wear by preventing metal-to-metal contact.

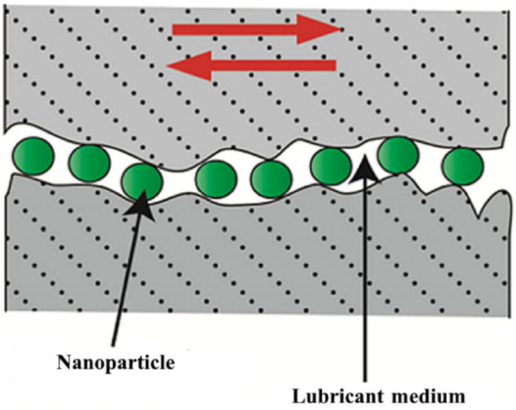

Fig. 8 Ball bearing mechanism by NP-based lubrication [183].

Figure 9 shows the patterns of tribo-film formation, which not only provides surface protection but also protects the material from crack propagation by reducing the friction between the asperities [13].

An investigation of the influence of Cu NPs on the tribological properties of attapulgite base grease demonstrated that under lubrication, a smoother and more compact tribo-film was formed on the friction surface [72, 73]. It primarily consisted of Cu, FeO, Fe_2O_3, FeOOH, CuO, and SiO_2, and the content of iron oxides and silicate oxide formed in tribo-film increases by the introduction of Cu NPs.

In addition, wear debris (Fe_3O_4 particles) deposited in the structure of tribo-film was observed in other studies [193]. The use of Cu-doped muscovite composite particles as lubricant additives leads to the formation of tribo-film primarily consisting of O, Si, Fe, Cu, as well as Al elements on the block worn surface, thereby further reducing friction and wear [194].

It should be noted that a smoother and more compact tribo-film is formed on the worn surface, which is responsible for further friction and wear reduction, by using nanolubricants based on vegetable

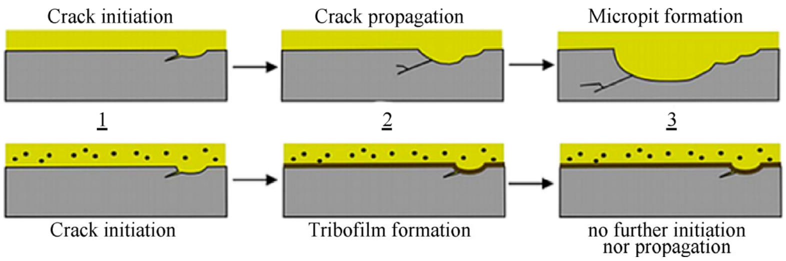

Fig. 9 Lubrication by base oil alone (top), and tribo-film formation and surface protection by NPs (bottom) [13].

lubricants with the addition of ZnO and CuO NPs [101].

It is of interest to study the formation of tribo-films using molecular dynamics simulation [195–197]. It was demonstrated that owing to the adsorption layer around NPs, nanolubricant molecules become more organized and compact compared to base oil. In addition, soft Cu NPs are deformed by the structural elements of the nanolubricant film, which provides good support for the lubricating film.

4.3 Mending effect

The mending or self-repairing effect is characterized by NPs deposition on friction surfaces and mass loss compensation. During this phenomenon, NPs deposit on the wear surface and fill the scars and grooves of the friction surface to reduce abrasion.

The study of the effects of the nanolubricants made of CuO and Al_2O_3 NPs on the surface quality of the forging process demonstrated that nanolubricants significantly improve surface roughness compared to conventional lubricants [198]. Suspensions of surface-modified CuO NPs in bio-based lubricant exhibited high EP characteristics in terms of load wear index and low cylinder liner wear owing to the surface mending effect of NPs [185].

4.4 Polishing effect

The polishing effect, also called smoothing effect, is manifested when the roughness of the lubricating surface is reduced by abrasive treatment with NPs. In tribological contacts, NPs can fill the gaps of rough asperities that can act as reservoirs of solid lubricants (NPs) in contact. This process of filling up rough valleys is called smoothing out process. This “artificial smoothing” or polishing mechanism results in improved tribological characteristics owing primarily to reduced surface roughness [183].

4.5 Friction mechanism of IF-nanoparticles

The lubrication mechanisms of IF-NPs as FMs include the following: rolling, sliding, and third body effects (Fig. 10) [183].

Rolling friction implies that NPs will roll between two sliding surfaces, which requires a spherical shape and a stable structure. In the case of sliding, the IF-NPs serve as a spacer and eliminate the metal/metal contact between the asperities of both surfaces under slightly higher loads. For the case of third body effect, the exfoliation of the IF-NPs and their external layers are gradually transferred to the roughness of the friction surfaces, providing easy shearing under high loads, where the third body can be considered a mixture of oil, NPs, and wear particles.

Poorly crystallized particles have better lubricating properties owing to their tendency to exfoliate, forming a tribo-film consisting of sheet-like particles on the surface. In particular, such sheet-like particles include MoS_2 nanoplatelets and Y_2O_3 [199]. To understand the lubrication mechanisms of sheet-like NPs, there are two types of interactions that play a decisive role in determining the frictional behavior [167]. For MoS_2, owing to its weak interlayer van der Walls forces, two

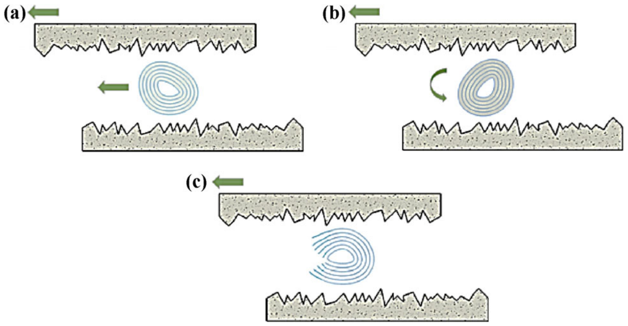

Fig. 10 Three main friction mechanisms of multilayered IF NP: (a) sliding, (b) rolling, (c) exfoliation [15].

adjacent layers are easily exfoliated under a shear force, and sliding movement of the adjacent layer leads to friction reduction. For other 2D NPs with relatively strong interlayer van der Walls forces, in particular Y_2O_3 [200], it is difficult for layers to exfoliate. Another interaction associated with the outer layer and the substrate is determined by the surface energy of the basal plane and the property of the environment. It should be emphasized that the number of layers and interlayer spacing affect tribological performance. When the number of layers decreases, other problems appear, for example, the puckering and wrinkle effects, inclination angles [199], and interlayer spacing [201].

5 Concluding remarks

Analysis of existing data on the use of metal-containing nanomaterials as lubricant additives indicates significant progress on several problems regarding nanolubricants; it also demonstrates that this is an active research field. It can be confidently concluded that the development of this interesting field of nanomaterials science has reached its peak in the accumulation of experimental facts and their theoretical interpretation and generalization, although this is only the tip of the iceberg in terms of the potential for their application. As objects of research, several new types of metal-containing nanomaterials were presented. The main emphasis in these studies is on the use of environmentally friendly technologies, the possibility of mass production, and efficiency, which will make these materials promising for future industrial applications. However, it is unfortunately impossible to determine the correlations between composition, size, morphology, surface functionalization, NP concentration, and nanolubricant properties, which in several respects impedes the development of a scientifically ground approach to structuring these nanomaterials and predicting their promising properties. To date, although a large number of experimental studies have been carried out on nanoparticle as additives for lubricating oils, several aspects of their tribological behavior have not yet been fully understood. Furthermore, it should be noted that new groups of researchers are involved in this field of nanomaterials science.

The following are important tasks in the development of the field, the accomplishment of which would give an opportunity to discover the general principles of nanolubricants:

- Maintaining their long-term dispersion stability. To stabilize NPs in various lubricating base oils, several combinations of surfactants/NPs should be investigated, as well as surface functionalization methods.
- Investigating their compatibility with lubricant additives, such as detergents, dispersants, antioxidants, viscosity improvers, and corrosion inhibitors.
- The relationship between their molecular structure and their tribological characteristics should be further discussed and applied as a guide for the molecular design of new nanolubricants.
- Regarding environmental protection, it is necessary to develop environmentally friendly nanolubricants that do not contain sulfur and phosphorus, without reducing wear and friction characteristics.
- The development of multifunctional lubricant additives with excellent anti-wear, friction-reduction, extreme pressure, and antioxidant properties will be the main trend in this field, and their joint mechanisms of action should be investigated.
- The tribological mechanism of nanolubricants should be studied and examined in more detail using modern analytical methods as well as molecular simulation.

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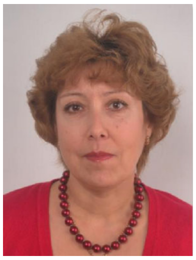

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