Review

Graphite and Hybrid Nanomaterials as Lubricant Additives

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Abstract: Lubricant additives, based on inorganic nanoparticles coated with organic outer layer, can reduce wear and increase load-carrying capacity of base oil remarkably, indicating the great potential of hybrid nanoparticles as anti-wear and extreme-pressure additives with excellent levels of performance. The organic part in the hybrid materials improves their flexibility and stability, while the inorganic part is responsible for hardness. The relationship between the design parameters of the organic coatings, such as molecular architecture and the lubrication performance, however, remains to be fully elucidated. A survey of current understanding of hybrid nanoparticles as lubricant additives is presented in this review.

Keywords: hybrid; nanoparticle; lubricant; additives; friction

1. Introduction

Beginning with the first mechanical device, lubrication has been an essential design parameter for any mobile parts involved in machinery, mechanical tools, and transport means. A variety of materials, in the forms of gas, liquid or solid, were interposed between two surfaces in order to improve the smoothness of relative movement and to prevent damages to the surfaces [1,2]. Although there are no restrictions on the type of material required to reduce friction force between two rubbing surfaces, lubrication mechanisms are chosen to meet specific requirements. For example, a gaseous film is suitable for low contact stress while solid films are usually applied to contacts with slow sliding speed.

Liquid lubrication is generally regarded as a technological nuisance since filters, pumps and cooling systems are required to maintain the performance of a lubricant over a period of time.

For many years, various liquid oils and greases have been used as lubricants to make one surface slide smoothly over another, such as bearings or pistons in their chambers or wheels on their axes. When two surfaces come into contact, the numerous asperities on both surfaces experience elastic deformation. Further increase in the contact pressure causes the asperities to deform plastically and the thickness of the fluid film to decrease. Additionally, contacts between asperities become the dominating contact mechanism where the average film thickness falls below the average surface roughness [3]. Two basic principles of traditional lubrication are: (i) introduction of fluid pressure to separate the surfaces so as to avoid contacts; and (ii) addition of sacrificial surface chemical films to protect the surfaces from shear and abrasion [3]. This is attributed to the properties of oils and greases possessing a complex colloidal structure, which implies that throughout their mass, the density is maintained perfectly constant due to the amphiphilic nature of the components within them.

It is worth noting that each liquid has its individual chemical composition, and consequently the way a liquid functions as a lubricant depends on how its chemical structure governs its density and viscosity behaviour [4]. This yields, from a mechanical point of view, numerous advantages as the surface interactions are significantly reduced when colloidal lubricants are introduced to prevent wear and friction between two solid surfaces. However, it is well known that pure petroleum-based hydrocarbon blends or lubricants based on synthetic hydrocarbon-type mixtures do not meet all requirements for lubricants used in modern engines or in other applications. A widely accepted solution is the addition of a relatively small amount of additive compounds that provide significantly improved performance of base oil with regard to either oxidative degradation or to tribological and other performance characteristics [5].

Initially, nanomaterials, specifically graphite, were only applied as dry lubricants in very harsh environments such as high temperature applications, where organic lubricants are considered to be unsuitable [6]. More recently, numerous studies demonstrate a fine control over the size, shape, and surface functional groups of nanoparticle [7]. The potential of nanoparticles in colloidal systems yields a high number of applications in all fields varying from lubrication [8–11] to oil extraction [12], from biomedical applications [13] to drug delivery systems [14], and the focus of this review will fall on the tribological applications of nanoparticles. Addition of nanoparticles in lubricating oil could significantly reduce the interfacial friction and improve the load-bearing capacity of the parts, which has been regarded as having great potential as lubricant additives [15–18]. The representative study shown here was performed by Peng and colleagues in which the tribological properties of diamond and SiO_2 nanoparticles added in paraffin were examined [19]. Friction and wear were measured between two surfaces made of bearing steel using a ball-on-ring tester to evaluate the performance of lubricants. It was found that friction coefficient changes not only as a function of the concentration of nanoparticles, but also the measurement time. When pure liquid paraffin is used, friction coefficient increases with the increasing measuring time, which is attributed to the adhesion between the contact surfaces. As a contrast, friction coefficient decreases monotonously as the testing time increases, becoming stable after a certain period, when diamond or SiO_2 nanoparticles were added to the base fluid.

Different explanations were proposed for the lubrication mechanism of nanoparticles, including the ball bearing effect [20,21], protective film [22], mending effect [23] and polishing effect [21]. Lee and

colleagues categorized them based on: (i) the direct effect of nanoparticles on enhanced lubrication-the nanoparticles form a protective film on the surface, and cause role of ball bearing effect between the two surfaces in contact; (ii) the presence of nanoparticles on surface enhancement—nanoparticles deposited on the surface could compensate for the loss of mass, whilst the roughness of the lubricating surfaces is reduced by the existence of nanoparticles [24].

By introducing nanoparticles in colloidal systems, the term "nanofluids" was first coined by Choi in 1995 [7,25] on the pretext that a liquid suspension with nanostructures can significantly alter the properties and behaviour of that liquid. However, the nature of nanofluid can be considerably influenced by the properties of nanoparticle. Up to this point the most widely studied and used nanoparticles are made of metals such as Au [26], Ag, Cu [27], and metal oxides [28] such as SiO_2 [29], TiO_2 [30], ZrO_2 [31], and various iron oxides. Ideally, the nanoparticles, once introduced within the base liquid, can be dispersed evenly throughout the liquid as the nature of the colloid is arranged and have a uniform density and dispersion regardless of what the lubricant is subjected to, which results in an increased lubrication [7,32]. Some studies show other behavioural patterns such as formation of films on the surface, which could increase anti-wear ability and decreases contact-temperature [22,33,34]. Performance of lubricants is strongly dependent on their behaviour under nanoscale confinement, including stiffness, yield strength, melting point, surface energy, and viscosity, all of which can be different in ultrathin shearing film, which is under tribological conditions [18].

Introducing nanoparticles in lubricants is a complicated task because size, shape, concentration and of course the materials itself are all very important factors to influence the lubrication performance of a specific system. Due to their high surface energy, studies [35,36] indicate that nanoparticles, regardless of their size, tend to aggregate, cluster, or coagulate once introduced in most liquids, especially when they are subjected to variations in temperature or pressure and do not move uniformly within the colloidal system. Some nanoparticles are difficult to disperse in the liquid phase—the base oil. For example, inorganic fullerenes are mineral particles with a spherical or cylindrical shape and a size ranging between 50 and 150 nm. They do not present any affinity with oil and their dispersion is consequently difficult without surfactants. The hardness of nanoparticles is another factor for consideration. In general, nanoparticles greater than 100 nm tend to be very hard, while those less than 10 nm tend to be soft, which results in significantly increased surface smoothness and lubrication behaviour [37].

Nature of the entire system (e.g., temperature, pH, density) significantly influences both the interactions between nanoparticles and those between nanoparticles and the surrounding medium, which in turn allows tailoring nanofluids for required application. Effect of solution pH on the interaction between two mica surfaces coated with cerium oxide (CeO_2) has been reported to be profound [38]. Surface potential of the nanoparticles was altered by changes in solution pH, which results in the dispersion or aggregation of the nanoparticles depending on their surface chemistry. Increasing thermal conductivity of fluid is highly desirable in many fields such as power generation, transportation. Numerous studies suggest that a high thermal conductivity enhancement can be achieved with nanofluids, even though the fraction of nanoparticles is low [39]. As for the surface, Kalin and colleagues [40] showed that chemical reaction takes place between the a-C:H coatings and oil additives, which is dependent on temperature. The extreme pressure additive interacts with

the diamond-like carbon surface and forms a tribochemical layer with a four-times lower sulphur/phosphorous ratio than the additive formulation at high temperature.

Concentration of nanoparticles in a lubricant is, of course, a very important parameter. Low concentration of nanoparticles is sufficient to improve the friction and wear behaviour: A concentration of less than 2 wt% was found as an optimum one for a range of systems [41]. High concentrations can very easily do more damage in terms of wear. Both wear scar diameter and friction coefficient were found to be dependent on the concentration of additives [19]. Studies on different fractions of nanoparticles in various circumstances have been performed, and none of them shows an addition of nanoparticles of more than 1% [22,33,42–44]. Heat is produced as a consequence of friction, such that lubricants are required to have higher temperature degradation points. Addition of inorganic nanoparticles significantly improves their lifetime and performance, although nanomaterials tend to manifest a sharp decrease in their melting point at around or below 50 nm.

To address the above-mentioned issues associated with nanolubricants, hybrid nanoparticles in which inorganic nanoparticles are incorporated with organic molecules are seen as a promising approach [45]. The organic outer layer can reduce aggregation of nanoparticles to a large extent, which makes them to form a stable dispersion, even at high particle loading. Jamming effect associated with the hybrid nanoparticles could improve the lubricant's viscosity upon increase in temperature, without compromising thickness, structure, and stability of the lubricating film between rubbing surfaces. Although core/shell nanoparticles are widely used in a range of applications including biomedical and pharmaceutical system, electronics, and catalysts, their application as lubricant additives are rather limited. To this end, the present work attempts to summarize the published results in this aspect.

2. Results and Discussion

While dispersion of nanoparticles in liquid phase and its influence over the tribological properties of a lubricant are still not fully understood, a certain level of knowledge has been established through recent research. Details of representative lubrication mechanisms of nanoparticles can be summarized as: (i) Mending effect: Nanoparticles deposited on a surface forming a physical tribofilm that compensates for the loss of mass during friction. Liu *et al.* [23] found that copper nanoparticles in an SN500 base oil tend to cluster/assemble, and the heat generated during friction results in the deposition of copper nanoparticles to surface defects which reduces the wear and friction during high pressure or load; (ii) Ball bearing/rolling effect: Spherical diamond nanoparticles, used as additive in paraffin oil, were found to penetrate into the rubbing surfaces, bear the loading, and separate the two surfaces to prevent their direct contact [21]. Bhushan and colleagues [46] reported that a decreased friction coefficient was observed when C_{60} films slide against a steel ball. This could be that some C_{60} are transferred and compacted on the steel ball and behave like ball bearing in the contact area. However, for particles to act like miniaturized ball bearings, they must be significantly larger than the characteristic roughness of the surface if they are to be able to roll over the surface asperities [47]; (iii) Film effect: Nanoparticles tend to interact with surfaces or friction pairs to form a surface protective film. For example, alkyl thiol-functionalized copper nanoparticles showed different anti-wear ability as a function of their size; smaller particles were more likely to interact with the surfaces of the friction pairs to form a surface protective film, which contributes primarily to the

increased anti-wear performance [22]. Deposition of products of tribochemical reactions produced by nanoparticles during the friction process can also result in an anti-wear boundary film, which reduces the shearing stress [48].

Other mechanisms had been proposed including colloidal effect and third-body friction model. Chiñas-Castillo and Spikes [34,49] examined how colloidal solid nanoparticles behave in lubricating oils, and showed that colloidal nanoparticles in thin film contacts can penetrate elastohydrodynamic (EHD) contacts by mechanical entrapment, and form patchy films. The colloids were also found to form a boundary film in rolling contacts at slow speeds that was at least one or two times of the particle size. Furthermore, the boundary film formed by the nanoparticles inside the contact is solid-like and it is unable to re-form on the surface at high speeds. The third-body model of WS_2 and MoS_2, so-called inorganic fullerene-like (IF), nanoparticles were evaluated by Rappoport and co-workers [50]. They proposed that under severe contact conditions, when the thickness of the lubricant film is less than the size of the nanoparticles, the third body consists of not only the base oil and wear debris, but also the delaminated nanosheets of those IF nanoparticles. Very often, the aforementioned mechanisms could be found in one system, e.g., Rappoport *et al*. [15,50,51] reported that these three mechanisms: The rolling effect, the prevention of direct contact and the third-body material transfer, act concomitantly in one system where lubrication is enhanced with inorganic fullerene-like nanoparticles. Wu and co-workers examined the effect of CuO, TiO_2, and nano-diamond nanoparticles as additives on the tribological properties of two lubricating oils [42]. They attributed the reduced friction coefficients to viscosity effect at low temperature and rolling effect at high temperature, and anti-wear performance to the deposition of CuO nanoparticles on the worn surface, which results in improved tribological properties.

### 2.1. Conventional Carbon-Based Lubricants

2.1.1. Graphite and Diamond

Carbon based lubricants, more precisely graphite and diamond, have been used since 1950s [21,52]. Graphite, like other lamellar solids such as molybdenum disulphide (MoS_2), is known to be a good solid lubricant which provides greater cleanliness compared to oil lubricants, and can provide lubrication at extreme temperature, under vacuum conditions or in the presence of strong radioactivity [1,53]. The low-friction performance is attributed to their low resistance to shear between neighbouring atomic layers of these materials. Some essential characteristics of lamellar solids that limit the usefulness of graphite as lubricating additives include: (i) The lamellar structure can be deformed, even at low level of shear stress; (ii) The lamellar solid adhere to the worn surface strongly; and (iii) There is no composition or other forms of chemical degradation of the lamellar solid at the operating temperature and in the environment [1].

In the hot forging process of carbon steel, colloidal graphite dispersed in water or oil has been applied as lubricant to keep the die interface temperature below 600 °C even though the workpiece is heated to between 1000 °C and 1200 °C. Forging industry is strived to find alternatives to graphite-based lubricants mainly because the following factors: (i) bad working environment; (ii) earth leakage due to the electric conductivity of oil; (iii) its tendency to facilitate pitting corrosion in some

stainless steel, and to prompt galvanic corrosion between dissimilar metals; and (iv) low recovery rate due to poor oil separation [54]. Calcium stearate, water soluble high molecular weight polymer, high molecular weight carboxylate, water soluble glass, and super high-molecular weight polyethylene have been sought as lubricants for warm and hot forming of carbon steels and high alloyed steels [1].

Another major challenge of using graphite as a lubricant is to maintain a continuous supply of graphite between two sliding surfaces, which can be achieved much easier in the case of fluid lubricants. An innovative design is incorporating graphite into the matrix of one of the sliding components to form composite. Considerable work has been done on the development of metal matrix-graphite particle composites which exhibit low friction, low wear rate, and excellent anti-seizing properties. It was found that hybrid composites of copper and graphite particulate possess properties of copper such as excellent thermal and electrical conductivities, as well properties of graphite, *i.e.*, solid lubricating and small thermal expansion coefficient [55]. Liu and colleagues evaluated the tribological performance of particle composites of aluminium alloy 2014-graphite as a function of the volume fraction of graphite particles [56], reporting that wear resistance can be improved with the addition of graphite, which results in a reduced coefficient of friction (Figure 1). A systematic review of the tribological behaviour of metal matrix composites containing graphite particles system was conducted by Rohatgi and colleagues, in which they surveyed a range of metals including copper, aluminium alloy, and magnesium alloy [57]. The review highlighted that friction and wear rate in those composites are substantially reduced compared with those in matrix alloys, as a result of the incorporation of graphite particles.

Figure 1. Weight loss and coefficient of friction as a function of volume fraction of graphite in aluminum alloy 2014-graphite particle composites, measured under 15 N, 1 m·s^{-1} for 5 min [56].
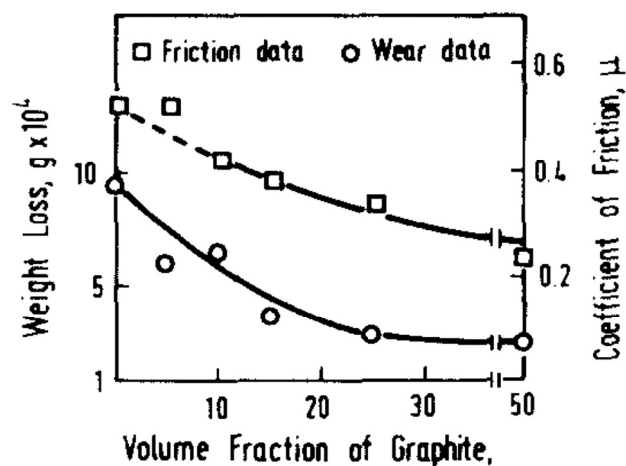
2.1.2. Nanotubes

The range of novel properties offered by nanotubes has far exceeded expectations: The unique structure could significantly improve their electrical, thermal, and mechanical properties [58,59]. Nanotubes demonstrate great potential as lubricant additives. The dimension of nanotubes allows them to be easily active in the contact area, without dangling bonds confers them a chemical inertness. Chen

and colleagues [60] examined the tribological applications of carbon nanotubes in a metal-based composite coating, in which effects of carbon nanotubes (CNTs) on the frictional properties of these composites were evaluated. It was found that a Ni-P-CNT composite coating exhibit higher wear resistance and lower friction coefficient in comparison with traditional electroless composite coatings such as Ni-P-SiC and Ni-P-graphite. The authors attributed the favourable effects of CNTs on the tribological performance to their excellent mechanical properties and unique hollow topological structure. A series of studies were performed to examine the tribological properties and resistance to wear and corrosion of nanocomposites based on CNTs [61–65].

Single wall carbon nanotubes (SWNTs) were used as additives in synthetic poly-α-olefin (PAO) base oil, examined in the regime of boundary lubrication [64]. It was found that the addition of SWNTs, even only at 1 wt%, resulted in a substantial decrease of friction and a reduction of wear of both antagonist surfaces. The frictional coefficient is very low (0.07) from the first cycle and remains stable during the test, which was attributed to the formation of carpet-like wear debris made up of amorphous carbon and catalyst particles. In the case of multi-walled carbon nanotubes (MWNTs), frictional performance of PAO base oil was found to be influenced by the contact pressure. The friction coefficient of a dispersion of MWNTs at 0.1 wt% in PAO is 0.15 when the contact pressure is 0.83 GPa, but 0.06 when pressure is increased to 1.42 and 1.72 GPa [66]. It is worth noting that the addition of MWNTs to PAO leads to a reduction of wear at all contact pressure examined, which illustrates the good anti-wear properties of MWNTs.

The same with other objects of nanoscale, nanotubes have a high surface energy and tend to aggregate in colloidal systems, and, as a result, presents a challenge in dispersing them uniformly [67]. Although the percolation threshold may be low for multi-walled carbon nanotube (MWCNT) composites, their performance strongly depends on the degree of dispersion, since the dispersion of MWCNTs is much more difficult than that of spherical particles. Recent studies have shown that the dispersibility of carbon nanotubes can be significantly improved if the nature of the interaction can be controlled. The amphiphilic characteristics of ionic fluids can be easily tuned by controlling the cations and/or counter-anions, making them excellent candidates for solving the dispersibility problem associated with most nanomaterials [68,69]. By covalently modifying carbon nanotubes with imidazolium cation-based ionic liquids, their dispersibility has been reported to improve [70]. Once uniform dispersity is obtained, the nanotubes-incorporated lubricant presents significantly improved properties. A study by Wang *et al*. suggests that the nanotubes exhibit a bearing-like behaviour at the interface [71]. At the same time, as most tribological characteristics are enhanced, specific samples with lower dispersibility show a decrease in performance, which confirms that controlling the surface interactions at nanoscale is the key to enhance the corresponding macroscopic characteristics.

Peng *et al*. functionalized MWCNTs with self-assembled surfactant layers by sonicating the MWCNTs in anionic sodium dodecyl sulfate (SDS) aqueous solution [72]. Subsequently, they evaluated the performance of the functionalized MWCNTs as additives for water-based lubricant with a four-ball tester. Figure 2 presents that SDS-functionalized MWCNTs exhibit good anti-wear and friction reduction properties as well as enhanced load-carrying capacity. A novel poly(ionic liquid)s (PILs)-grated multi-walled carbon nanotubes (MWCNTs-*g*-PILs) were used as lubricant additives, and found to improve anti-wear and friction-reducing properties of based lubricant. Pei and colleagues attributed such performance to the good dispersity and the rigid CNT core-flexible PILs shell structure

by way of a roller bearing effect between the two sliding surfaces [73]. The same strategy was used to prepare Room Temperature Ionic Liquid (RTIL)/Multi-Walled Carbon Nanotubes (MWNTs) composite which showed good friction-reduction and anti-wear properties in friction process [74].

Figure 2. (**a**) SEM image of the oxidized multi-walled carbon nanotubes (MWCNTs); (**b**) TEM image of the oxidized MWCNTs; (**c**) Friction coefficient as a function of MWCNT concentration (200 N); (**d**) Wear scar diameter (mm) as a function of MWCNT concentration (200 N) [72].
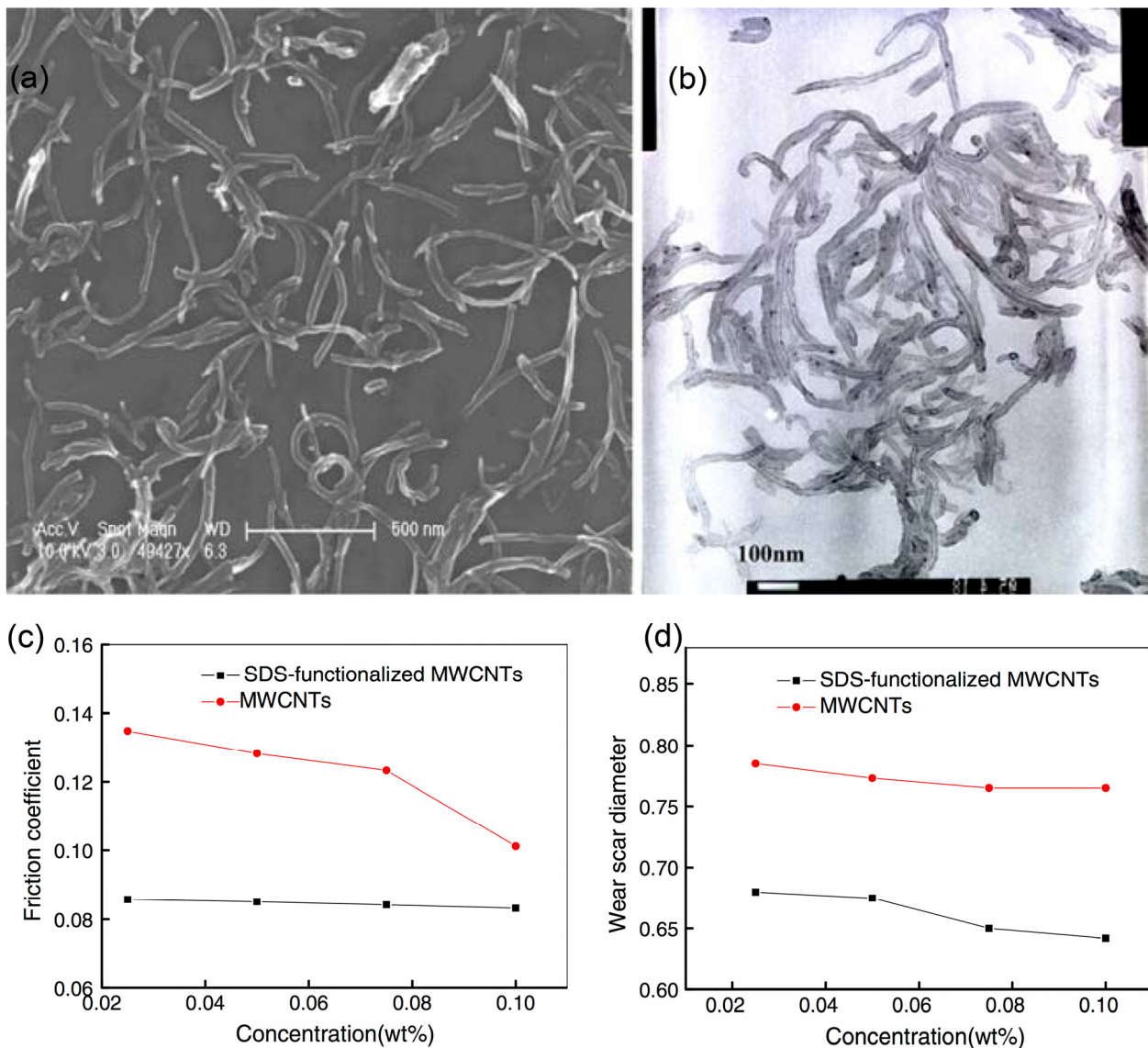

2.2. Metal-Based Nanoparticles with Capping Agents

Numerous metal nanoparticles, including Cu, CuO, Fe, and TiO_2 are widely used in tribological applications as lubricant additives [28,41,42,75–77]. The many slip planes presented by the face-centred structure of these soft metals allow low shear strength along the sliding direction. Although some studies show an improvement in friction and wear characteristics, over time and in harsher conditions, this is not sufficient to overcome the challenges faced by tribology. As summarized by Liu and Wang [78], the lubricating film is composed of soft metals that to a certain extent show

self-repairing properties under low friction speed. However, their potential as lubricant additives is limited by: (i) The self-repairing properties which disappear under high sliding speed or load; (ii) The inability to remove heat generated by the friction process; (iii) In lack of re-lubrication; and (iv) Complex application techniques.

Copper nanoparticles are widely used as lubricant additives because they could deposit on the sliding surfaces, improve tribological properties of the base oil and display good anti-friction and wear reduction characteristics. Therefore, copper nanoparticles are chosen as a representative system reviewed here to discuss the available routes of using metal nanoparticles as lubricant additives. Similar to any other types of nanoparticle, Cu nanoparticles are inherently unstable and easy to aggregate, which ultimately leads to precipitation when added to base oil. Their poor stability, solubility, and dispersibility in lubricating oils are the major obstacles for the application of metal nanoparticles as lubricant additives. Despite these uncertainties regarding the interaction between the nanoparticles and the colloid, the enhancement of the lubricant is undoubted. Research performed by Choi *et al.* shows clear evidence of augmented properties of lubrication brought by the presence of Cu nanoparticles, as shown in Figure 3 [77]. Lower friction coefficients and reduced wear are the first to see the improvement, and when nanoscale analysis is performed with AFM and EDS, the deposition of nanoparticles in scars and grooves illustrate why the friction reduction occurred.

Figure 3. SEM images of the friction surface of the fixed disc after the friction test (**a**) in raw oil; (**b**) in nano-oil with Cu 25 nm; (**c**) in nano-oil with Cu 60 nm [77].
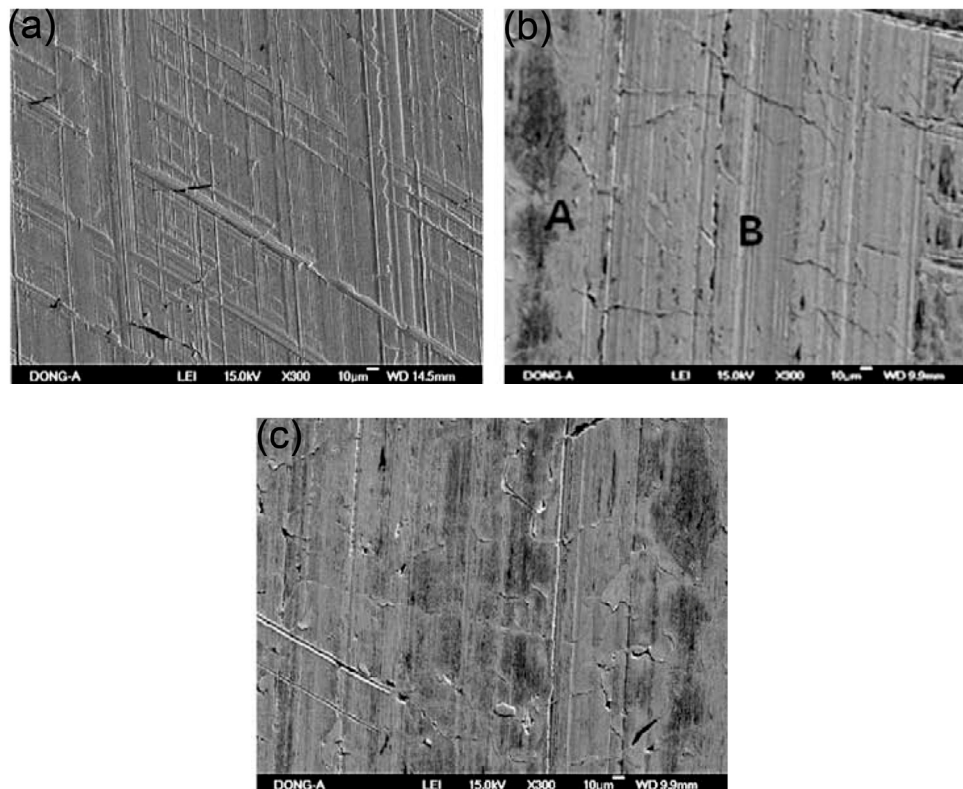
Common methods to address the aforementioned technical challenges include reduction of relevant metal salts or thermal decomposition of metal organometallic precursors in the presence of a suitable capping agent. This is because the unprotected inorganic nanoparticles in liquid media are thermodynamically unstable and they tend to spontaneously coalescence. The capping agents provide stabilization of nano-sized objects in various liquid media to suit applications' need. The organic molecules used as capping agent usually have a polar group, which can adsorb on the surface of the inorganic core (the NPs) chemically; and a long alkyl chain, which enables inorganic NPs soluble in organic media to expand their potential application fields. The resulting core-shell NPs are clusters materials protected by monolayer. For a range of nanoparticles, such as WO_3, the surface-capping layer can not only effectively prevent agglomeration between nanoparticles, but also prevent the surface adsorbed water around WO_3 nanoparticles [2]. A general requirement for the outer layer is that it should be solvated by the surrounding medium, *i.e.*, it should be hydrophilic when aqueous solution was used, or hydrophobic in the case of organic solvents [5]. A range of strategies have been used to coat Cu nanoparticles.

A common approach is the addition of a dispersant to protect nanoparticles, as well improve their dispersity [79]. Surfactants are amphiphilic, surface active substances that are added in a base liquid to reduce surface tensions. They are composed of two parts: A polar hydrophilic headgroup and an apolar long hydrocarbon chain, which allow them to self-assemble into micelle-like structures to reach an energy balance. Once the surface of nanoparticles is occupied by the hydrophobic end of the surfactants, their tendency to cluster/aggregate will be reduced considerably. Different kinds of dispersants have been used, including sodium dodecyl sulphate [80,81], poly(vinylpyrrolidone) [79,82], and cetyltrimethylammonium bromide (CTAB) [83]. The effects of these dispersants on the particle size and the size distribution of Cu nanoparticles were compared by Cheng and colleagues [84]. A series of characterization techniques were used, and it was found that effect follows the order PEG-2000 > SDBS > PEG-600 > SDS > PEG-6000.

Long-chain alkyl thiols, specifically, *O,O′*-dialkyldithiophosphates (DDP) are the widely used capping agents [22,85,86]. DDP-capped copper NPs can be readily dispersed in common nonpolar solvents and mineral oils to result in a transparent solution. And their liquid paraffin solution is very stable: Remains unchanged for several months in ambient conditions [22]. It was found that the size and concentration of copper nanoparticles have substantial influence on their tribological properties [22]. The results show that DDP-capped Cu nanoparticles with grain sizes of 2 and 5 nm could effectively improve the anti-wear (AW) behaviour of liquid paraffin (LP). In contrast, DDP-capped Cu nanoparticles of 12 nm decrease the AW performance of LP. This was explained by way of the smaller the size of copper nanoparticles, the lower the melting point and the higher the reactivity of the nanosized copper core. Therefore, copper nanoparticles of smaller size are more readily to interact with rubbing surfaces to form a protective film, which results in an increased AW function.

Other capping agents used to functionalize the surface of nanoparticles include stearic acid and oleic acid, which can increase the tribological properties substantially in comparison to the bare nanoparticles in oil, according to the studies performed by different groups [19,30,87–89]. Xu *et al*. prepared surface-coated copper nanoparticles with FCC structure, and characterized their tribological properties using ball-on-disc tester and ring-on-block tester [90]. They showed that the surface-coated

Cu nanoparticles could significantly improve the wear resistance and load-carrying abilities of oil, as well as reduce the friction coefficient. In a separate study, Viesca and co-workers examined the performance of carbon-coated copper nanoparticles as additives in polyalphaolefin (PAO6) [91]. It was found that the carbon-coated copper nanoparticle did not behave better than bare copper nanoparticles.

Although addition of surfactant is an effective approach to reduce the aggregation/agglomeration of nanoparticles, there are several issues associated with this method [92]: e.g., addition of surfactant molecules may contaminate the lubricant (base liquid); surfactants may produce foams when being heated. The other approach, functionalizing the surface of nanoparticles with capping agents, is more complex; however, the prepared nanoparticles introduce no contamination to the medium, and the prepared nanofluid possesses low viscosity, high stability, and good fluidity.

A representative system of surfactant capped nanoparticle used as lubricant additives was given by Gara and Zou in which oleic acid was used as surfactant to improve dispersity and stability of ZnO nanoparticles [88]. It was found that oleic acid alone contribute to friction reduction, for *ca.* 10%, and a combined effect of oleic acid and ZnO nanoparticles could reach 20% maximum. Such a comparison shows that the presence of oleic acid contributes more to the dispersity of nanoparticles and stability of nanofluids than to friction reduction. The same approach has also been applied on SiO_2 and diamond nanoparticles in order to improve the tribological properties of paraffin [19]. Gu and colleagues [93] mixed lubricating oils containing CeO_2 and TiO_2 nanoparticles with suitable surfactants such as Tween-20, Tween-60, Span-20 and sodium sodecylbenzenesulfonate. Their results not only show the weight proportion of the surfactants when the optimal tribological properties can be achieved, but also indicate that the addition of CeO_2 could reduce the required amount of TiO_2 nanoparticles.

Although fumed silica particles made by a costly route have good dispersity in organic solvents, those made by precipitation method are difficult to be well dispersed. Most coupling agents cannot make silica nanoparticles to disperse well in organic solvent, because the unsaturated dangling bonds and hydroxyl groups on silica surface are extremely active. Therefore, silane coupling agents were used to interact with silica nanoparticles via strong covalent bonds to make sure the nanoparticles can be dispersed well and steadily in many organic mediums [94].

Attempts have been made to disperse other soft metals into base liquid to improve their lubrication properties. Until recently, results were discouraging as the dispersion of particles was not uniform. Due to quantum confinement effects, the behaviour of nanoparticles made of soft metals such as In, Zn and Bi is expected to present a higher level of lubrication. According to Zhao *et al.* [95], the simplest way of solving both the lubrication and dispersion problems is by synthesizing the nanoparticles through a direct solution-dispersion method. This technique involves loosing large molten metal droplets into an aggressively stirred hot oil bath, which stimulates the metal droplets to disperse into smaller particles. Once an energetic balance is reached, a thin oxide layer forms over the particles, which prevents them from clustering while at the same time allowing the suspension to reach monodispersity. Tests show a significant improvement to tribological properties by using this technique involving everything from wear reduction to lower friction coefficients, however the exact mechanism by which the nanoparticles act is still subject to questioning. Replacing organic capping agents by tiny particles of solid material is another available route, although is not straightforward, and has only been regarded as a feasible option in recent studies.

2.3. Polymer Coated Nanoparticles

Over the recent decades, surface anchored polymeric chains have demonstrated great potential as boundary lubricants [96]. In 1994, it was reported that neutral polymer brushes at well solvated conditions could act as extremely efficient boundary lubricants when the surface to which they are attached are sliding against each other, under moderate compression [97]. This is because, due to entropic factors, the swollen brush layer is more energetically favourable than to interpenetrate each other. Further studies by Raviv and co-workers [98,99], in which frictional properties of charged polymer brushes in water were used, indicate that polyelectrolyte brushes provide a much more efficient boundary lubrication than neutral polymer brushes. An additional factor that contributes to the load-bearing behaviour of charged polymer brushes is the osmotic pressure of the trapped counter-ions within the brush layer, even though these ions are unlikely to provide lubrication. Numerous works have been reported on the tribological properties of anchored polymer brush on planar surfaces [100–104]. Other than water, surface anchored polymer brushes show excellent lubrication performance in organic solvents [97,105], ionic liquids [106] and model oil systems [107,108]. Surface anchored poly(dodecyl methacrylate) brushes were characterized in a range of lubricating fluids of different chemical natures, and it was found that polymer brushes are capable of maintaining low coefficients of friction (on the order of 0.01) over thousands of reciprocating cycles when immersed in appropriate based fluids [107]. The P12MA was also found to provide better wear resistance when coating thickness was higher, which was attributed to a greater cushioning of the asperities by the polymeric brushes.

Naturally, with the aforementioned properties of polymer brushes on planar surface, nanoparticles coated with polymer brushes could be an ideal candidate for lubricant additives. Unlike the common nanoparticles which tend to aggregate irreversibly, polymer coated nanoparticles (PGNs) are stabilized by steric interactions between polymeric chains. The PGNs consist of an inorganic core (nanoparticle), functionalized with an outer layer of organic oligomers. They are different to the aforementioned hybrid nanoparticles that the grafted polymers are easily deformed, and therefore able to fill the space between the inorganic cores to form the suspending fluid "phase". The unique combination offers a versatile platform to design nanoparticles with tunable properties by changing parameters of the organic corona (molecular weight, chemistry, charge group, density), and the inorganic core (shape, size) [109–112].

The core/shell nanoparticles have attracted more and more attention, with applications in the fields of electronics, biomedical, pharmaceutical, optics, and catalysis [113,114]. A large range of core/shell nanoparticle systems have been surveyed by Chaudhuri and Paria [113], in which stability of nanoparticles in dispersant is one of the focuses. Theoretical, computational, and experimental works have been carried out to establish the correlation between the design parameters of PGNs (particle concentration, polymer density, polymer length, *etc.*) and properties, such as microstructure, particle mobility, and viscous response [109,115–117]. Although it is widely accepted that the base fluid that contains nanostructured-materials could significantly alter the forces between rubbing surfaces [25], research on the tribology-related properties of PGNs is at early stage [118].

Voevodin *et al*. [119] studied the lubricating properties of PGNs, in particular at the contact surfaces of the switches on microelectromechancial systems (MEMS). Previous attempts to lubricate

MEMS switch contacts involved self-assembled monolayers of thiolates, but these were found to be thermally unstable. By using metallic (Au or Pt) nanoparticles and an ionically tethered low viscosity corona, surface roughness was increased, reducing contact area and thus reducing van der Waals force-mediated friction. Since the cores were metallic, they were able to dramatically improve the resistance of the switches to wear without compromising conductivity, increasing durability of the switch in the most extreme environments by over two orders of magnitude.

In a representative study, Kim and Archer used two synthesis routes to prepare organic coatings on silica nanoparticles as hybrid lubricants [45]. The nanoscale organic hybrids (NOHMs) were prepared by tethering a base-stabilized organic silane to SiO_2 NPs suspended in H_2O, while xylene sulfonic acid was used to create an ionically tethered corona around the NOHMs. The latter sample is named as XNIMs, as presented in Figure 4. The silica NPs densely grated with amphiphilic organic molecules can form homogeneous nanofluids when dispersed in poly-α-olefin (PAO) oligomers, at both low and high particle loadings. A PAO-XNIMs composite with 60 wt% XNIMs has been shown to lower interfacial friction coefficients, enhanced wear and mechanical properties, and superior thermal stability in comparison with control systems. A series of physical and chemical analysis of the wear track shows that the antiwear benefits of the hybrid NPs stem from their ability to deposit in the wear track and reinforce the interface between approaching solids at high sliding speed. Comparison between the two types of NPs shows that the effect of organic coating is not just limited to preventing the aggregation of NPs, but also to enhance other lubricant-related performance.

Figure 4. Schematic diagram of synthesis routes of (**A**) PAO-Nanoscale organic hybrids (NOHMs) (path 1a using 5:1 toluene/2-propanol as a solvent); and (**B**) PAO-XNIMs (path 1b using toluene as a solvent) blending [45].
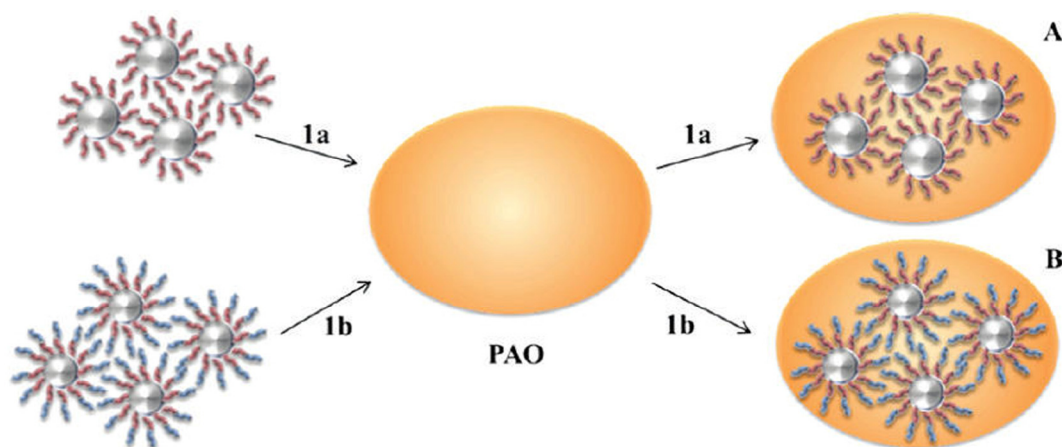
As a summary, some representative systems of hybrid nanomaterials as lubricant additives, including the nanoparticle core, dispersant, outer layer (capping agent), dispersion method, size and shape, are presented in Table 1.

Table 1. Representative systems of hybrid nanomaterials as lubricant additives.

Nanoparticle	Capping agent	Shape	Base liquid	Size/nm	Reference
Nickel-based $Ni(HCOO)_2 \cdot 2H_2O$	Oleylamine Oleic acid	Face-centered Cubic	Poly-alpha-olefin (PAO6)	7.5, 13.5, 28.5	[9]
ZnS	Octadecylamine	Rod-like	Dodecane	Length ~ 5 Width ~ 1	[18]
Cu	Dialkyldithiophosphate (DDP)	Spherical	Liquid paraffin	5	[22]
Cu	DDP	Face-centered Cubic	Liquid paraffin	8	[75,78]
TiO$_2$	Stearic acid	Spherical	Liquid paraffin	10	[30]
Gold, silver	Oleate, amine	Spherical	Hexadecane	5–20	[49]
Nano-diamond, SiO$_2$	Oleic acid	Spherical	Liquid paraffin	110, 92	[19]
SiO$_2$	Base-stabilized organic silane	Spherical	PAO	Core size: 12	[45]
Multi-walled carbon nanotubes	Imidazolium cation-based ionic liquid	Tube	Ionic liquid ((Bmim) (PF$_6$))	Diameter: 20–40	[71]
Multi-walled carbon nanotubes	Poly(ionic liquids)	Tube	Base lubricant LP104	Diameter: 20–40	[73]
Multi-walled carbon nanotubes	Room temperature ionic liquid (HEHImPF$_6$)	Tube	Toluene, dichloromethane ionic liquid P106	N/A	[74]
Cu, Ag, LaF$_3$	DDP	Spherical	Non-polar solvents, mineral oil	5, 4, 2	[85]
Cu	SDS, PVP, CTAB, AAS	Spherical	PEGASUS 1005	60, 130	[79]
Cu	Tween, SDS	Spherical	Aqueous solutions	4.8–12.1	[81]
Cu	CTAB	Spherical	Toluene	1–45	[83]
Cu	EDTA	Spherical	50CC oil	40	[90]
Cu	Carbon-coating	Spherical	PAO6	25	[91]
ZnO	Oleic acid	Spherical	Paraffin oil	40–100	[88]
CeO$_2$, TiO$_2$	Tween, Span, sodium sodecylbenzenesulfonate	Spherical	500SN	10.4, 15.2	[93]
SiO$_2$	Silane coupling agents	Spherical	Mobile oil	15–20	[94]
Megnetite	Poly(methyl methacrylate)	Spherical	THF, DCM, toluene	Core size: 13	[110]
Iron oxide	Poly(ethylene glycol)	Spherical	Aqueous solutions	23–82	[112]
Silica	Poly(ethylene oxide)	Spherical	Aqueous solutions	Core size: 12, 16	[116,118]
Silica	Poly-L-lysine	Spherical	Aqueous solutions	Core size: 22	[117]

3. Conclusions

We have selectively summarized the tribological applications of hybrid nanoparticles as lubricant additives. In order to prevent their aggregation in base fluids, there are a number of strategies available to functionalize conventional bare nanoparticles.

Although surfactants provided a relatively simple way to prevent nanoparticles from agglomerating, they do not offer a guarantee that the nanoparticles will disperse uniformly throughout the colloid. There are several issues associated with the addition of surfactants to the base liquid. Naturally, integration of elongated polymeric chains with nanoparticles would be an ideal strategy. This cannot

be performed by surfactants as they are neither strong nor stable enough. The magnitude of the interactions between two surfaces mediated by a lubricant that contains hybrid nanoparticles has been found to be strongly affected by the size, aspect ratio and concentration of nanoparticles due to their enhanced steric contribution, packing efficiency and tendency for aggregation. The nature of the polymeric coating could make the hybrid nanoparticles sensitive to external stimuli, such as salt concentration, pH or the presence of other materials. It is believed that, with the large libraries of nanoparticles, various parameters for tethered polymers including its chemistry, molecular weight, and density, hybrid nanoparticles will find broad applicability in formulations of new types of lubricant additives for different base oils with engineered purpose, without compromising higher tolerances demanded by most high-performance machineries.

Acknowledgments

Author Contributions

Zhenyu J. Zhang and Dorin Simionesie surveyed the literature; Zhenyu J. Zhang, Dorin Simionesie and Carl Schaschke prepared the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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