



Review

Frictional Properties of Two-Dimensional Nanomaterials as an Additive in Liquid Lubricants: Current Challenges and Potential Research Topics

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Abstract: This paper reports on the trend of studying and applying two-dimensional materials in tribology. Two-dimensional materials have improved the ability of lubricants when used as additives to reduce wear between surfaces through the formation of protective layers by sliding on metal surfaces. The morphology and chemical nature of 2D materials are among the important factors that influence their dispersion in the lubricant medium and determine the final performance of the lubricant for various applications. The mentioned materials in this work are *h*-BN, graphene, graphene oxide, and MoS₂ as part of the transition metal dichalcogenides. The most studied material to date is graphene and its analogs, such as graphene oxide, which, under controlled conditions, can present superlubricity, with COF values less than 0.01. Some methodologies applied to modify two-dimensional materials and examples of the application and characterization of their performance in tribology are mentioned. This review also shows the benefits of using 2D nanomaterials and the synergy generated when two or more of them are combined to not only achieve superlubricity but also improve corrosion resistance and mechanical properties at the interfaces found in contact.

Keywords: additive; bidimensional material; graphene oxide; molybdenum disulfide; boron nitride



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1. Introduction

Annually, the economic losses due to friction and wear between metal parts are huge since friction is a key factor that causes the wear of parts and the reduction of their useful life to the loss of energy. The total energy consumption used to overcome friction in the mining industry globally is estimated to be around 38% [1]. Meanwhile, in the transportation industry, it is estimated that one-third of fuel energy is used to overcome friction, causing 28% of the energy used to move a car to be lost [2]. For this reason, to reduce the problem posed, new lubricating materials are currently being explored to improve the reliability and useful life of manufactured products, thus reducing energy and resource losses.

A lubricant is a substance used to facilitate the relative motion of solid bodies by minimizing friction and wear between interacting surfaces. These can be classified in different ways as a function of their physical or chemical nature. Generally, they are grouped as solid (dry lubricants), gas (compressed air or other gases), liquid (oils), and semi-solid (grease) [3]. During the selection of lubricant, the factors to be considered will depend on the application of the lubricant; for example, on automobile engines, the shear stability, cloud point, dynamic and kinematic viscosity, volatility, pour point, foaming characteristics, element content, flash point, density, ash, water tolerance, corrosiveness color, homogeneity, and elastomer compatibility must be considered [4]. Generally, liquid and semi-solid lubricants are the most widely used due to their versatility and ease of use [3]. However, the huge consumption of external lubricants is a serious problem in practice, and the external supply of lubricants is unacceptable in some unusual situations, such as medical equipment, precision electronics, and optical instruments [5]. Therefore, solid lubricants also have some advantages in respect to liquid lubricants, as shown in Table 1.

Table 1. Advantages and disadvantages of using solid and liquid lubricants.

	Solid Lubricants	Liquid Lubricants
Advantages	<p>More effective than fluid lubricants at high loads and high speeds.</p> <p>Highly stable in extreme conditions (high operating temperatures, reactive, and high radiation environments).</p> <p>High resistance to abrasion in high dust environments.</p> <p>Minimal degradation (no migration of lubricants)</p> <p>Good long-term storage.</p> <p>No viscosity effects.</p> <p>Corrosion protection.</p>	<p>Long endurance lives.</p> <p>Resupply possible.</p> <p>Low mechanical noise.</p> <p>High heat dissipation (ease to use in recirculating systems).</p> <p>Very low friction in elastohydrodynamic lubrication regime.</p> <p>No wear in hydrodynamic or elastohydrodynamic regimes.</p> <p>No wear debris.</p> <p>Excellent cleaning and flushing capability.</p>
Disadvantages	<p>Life determined by lube wear.</p> <p>Poor thermal characteristics (no heat dissipation).</p> <p>Reapplication difficult or impossible.</p> <p>Higher coefficients of friction and wear than for hydrodynamic lubrication.</p> <p>Poor self-healing properties.</p>	<p>Lubrication is temperature dependent (viscosity, creep, and vapor pressure).</p> <p>Seals or barrier coating needed to prevent creep.</p> <p>Friction dependent on speed.</p> <p>Endurance life is dependent on lubricant degradation or loss.</p> <p>Additives are necessary for boundary lubrication regime.</p> <p>Long-term storage difficult.</p>

To solve the disadvantages of solid lubricants, small amounts of additives are introduced into the base material to improve the tribological performance of lubricants and modify their thermal properties and antioxidant capacity. Additives are the main categories as friction and wear modifiers, antioxidants, rust inhibitors, antifoam agents, extreme pressure/load-carrying compounds, viscosity index improvers, detergents, emulsifiers, and metal deactivators [6]. Nanotechnology has allowed the introduction of nanomaterials such as nanoparticles, which have attracted considerable attention as potential lubricant additives due to their excellent physical and chemical properties [7]. Developing additives with specific functions is one of the most effective ways to reduce friction and wear.

Two-dimensional nanomaterials such as graphene, h-BN, and transition metal dichalcogenides (TMDs) have had a great boom due to their properties and utility in fields such as electronics and optoelectronics, catalysis, energy storage devices such Li-ion batteries, sensors, solar cells, and reinforced ceramics, as well as biomedical and antipathogenic applications [8,9]. The use of graphene, h-BN, and transition metal dichalcogenides such as MoS₂ in applications as a lubricant or additive has been growing in the last ten years. A query was made through the Web of Science, using the keywords “graphene, h-BN, MoS₂ (separately), together with wear, friction, and tribology”, and the most relevant articles in the journals were identified, as shown in Figure 1.

Among the most relevant works is the review published by Xiao et al. [10], who talk about forming a tribofilm in the presence of 2D nanomaterials during the rubbing process. The formation of this tribofilm is one of the main reasons for improving lubricity. However, the formation mechanism has yet to be fully understood, as complex compounds are formed from a possible tribochemical reaction during rubbing. In the various works compiled in this work, multiple mechanisms have been proposed for forming tribofilms, including the microstructural transformation of the 2D material, slippage between layers, and synergistic effects.

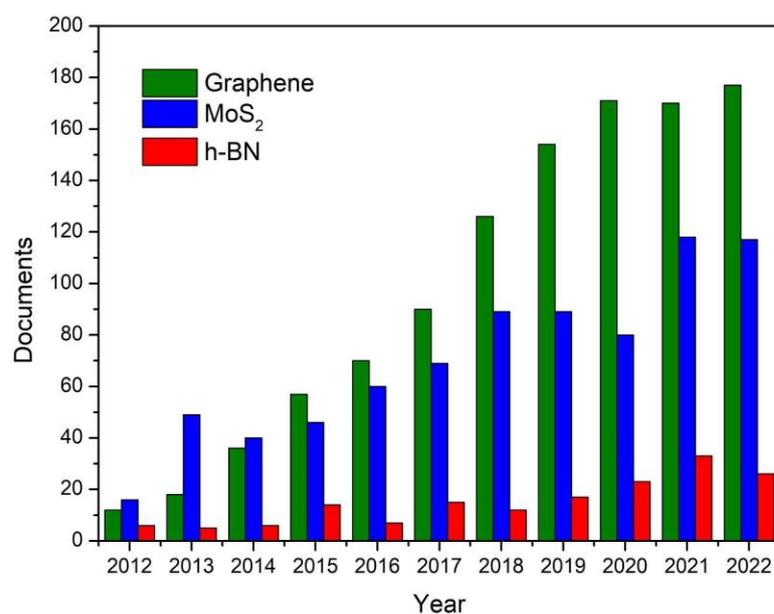


Figure 1. Documents published between 2012 and 2022 related to using graphene, MoS₂, and h-BN as lubricants.

Two of the characteristics that a 2D material must possess to have a good performance as an additive in lubricants are stability and good dispersion. There are three main ways to improve the dispersion stability of graphene in lubricants, including physical modification, which is within the microstructural transformation that Xiao discusses in his review paper; and chemical modification and structural regulation, which are also summarized in the work of Zhao et al. [11].

Taking advantage of the thin lamellar structure of 2D materials, specific surface area, surface energy, ease of cutting, and high chemical and thermal resistance, in addition to the ease of being modified through functionalization, 2D materials are promising for extreme working applications (temperature, pressure, and speed) [12,13].

This review provides relevant research from recent tribological studies using graphene, h-BN, and some main TDM and their uses as additives for liquid lubricants. The graph of Figure 1 shows the importance that research using graphene and MoS₂ has had in tribology over time, especially in the last five years. For its part, hexagonal boron nitride, although it does not show significant growth, was considered in this review, given its similarity to graphene, specifically in its structural characteristics. Additionally, here we present the advantages and disadvantages of using the different materials, mainly those graphene-based and TDM, whether they are used as additives in oil or water-based lubricants; the possibility of synergistically improving the resulting properties by combining two or more two-dimensional additives; and using computational tools such as molecular dynamics simulations to try to explain the lubrication mechanisms seen experimentally.

2. Graphene Family

Graphene-based materials are preferably used as lubricant additives and reducers of energy losses due to friction. When the dimensions of the materials are taken to the nanoscale, exceptional physical–mechanical properties are obtained, which differ significantly from the “bulk” properties. The new properties are due to its lamellar structure composed of thin layers with a thickness of at least one atomic layer [14]. Furthermore, these materials have a high aspect ratio and serve as coatings that minimize friction and wear [15]. Graphene is the thinnest material known to the scientific community. Carbon atoms are linked in a 2D hexagonal panel-like structure, giving graphene unique tribological, mechanical, electrical, and thermal properties [16]. The tribological properties of graphene and its derivatives as lubricant additives were reported for the first time in

2011. In addition to being used as additives in oil-based lubricants, they are also beneficial in water-based media. Graphene is also an excellent lubricant due to its low surface energy. When recovered on other substrates, its thickness is little, and its surface energy sustains less adhesion and friction with coated surfaces [17]. Chemical modification is an alternative to improve the dispersibility of graphene in lubricants by selecting functional terminations [18]. Gupta et al. [19] obtained graphene oxide with hydroxyl terminations dispersed in PEG. They reported smaller coefficient of friction (COF) values and better wear performance because the integrity of the graphene sheets was maintained.

Graphene has been widely used in scientific research and industrial applications to reduce friction energy consumption and improve wear resistance. Oxidized graphene or graphene oxide (GO) is the most studied chemically modified 2D material; many works have shown that friction in graphene is decidedly enhanced by oxidation [20]. Figure 2a,b show a SEM micrograph in the STEM mode of a graphene oxide sheet and a schematic configuration of this material with its interlayer distance is shown in Figure 2c. A homogeneous thin layer can be seen with characteristic wrinkles generated by the oxygen groups adhered to the surface (Figure 2a,b). Zhao et al. [21] synthesized super-exfoliated reduced graphene oxide with a high specific surface area ($1665 \text{ m}^2/\text{g}$) and an interlayer spacing of 4.25 \AA . The material presented excellent tribological characteristics. The COF could be reduced by 70%, and the volume of wear could be by more than 60%. These reductions were attributed to the high degree of exfoliation, the stability of the dispersion, and the evolution of the oriented displacement. Furthermore, Ge et al. [22] found that the amino groups ($-\text{NH}_2$) were better than oxygenated groups ($-\text{OH}$ and $-\text{COOH}$) in terms of GO superlubricity performance due to larger adhesive force between functional groups and contact surfaces.

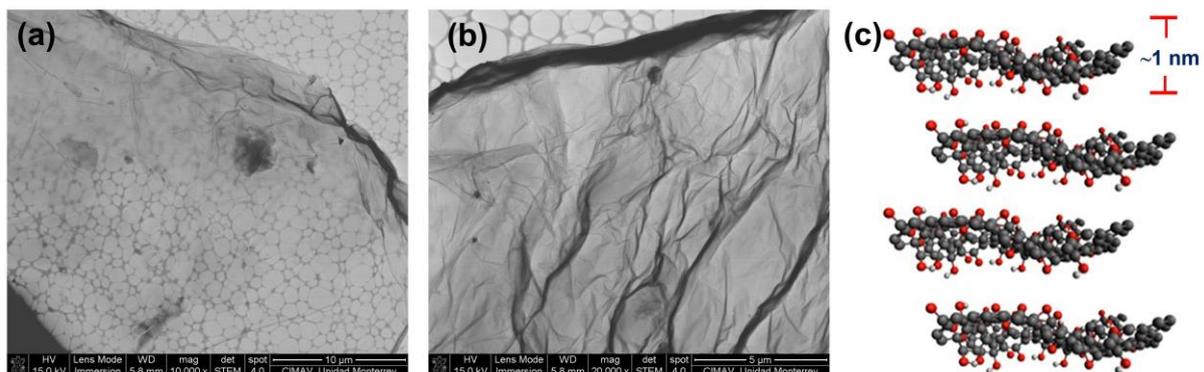


Figure 2. SEM-STEM micrograph of graphene oxide obtained at (a) $10,000\times$ and (b) $50,000\times$. (c) Atomic structure of layered graphene oxide (GO) and interlayer distance.

On the other hand, Kong et al. [23] reported the effects of graphene thickness and particle size on its frictional performance, finding better tribological properties with a higher number of layers and smaller particle sizes. This behavior is associated with the interlaminar shear slip in multilayer graphene that favors friction reduction. In addition, a smaller graphene size is less prone to structural defects and wrinkles. It is also more easily absorbed into the sliding surface for a lubricating film that provides less wear.

The lubrication mechanism of graphene or its derivatives is associated with forming a protective film from friction in the contact area, thus significantly reducing wear [24]. Materials with laminar structures are joined between layers by van der Waals forces generating relatively low shear stress. Therefore, adjacent layers easily slide over each other under little shear stress (providing a lubricating effect) [10,11]. Using excessive amounts of graphene as an additive could increase surface roughness, which generates the opposite effect of lubrication [23]. The thickness and size of the graphene used as an additive in lubricants directly influence the resulting tribological properties. Kong et al. [23] added multilayer graphene to PAO4 as a lubricant additive. The multilayer graphene with small

particle size exhibited an excellent reduction of friction (37%) and wear (47%) concerning the oil-based lubricant.

Furthermore, the wear track was flatter and brighter with multilayer graphene. The above was attributed to the interlaminar shear slip that occurs in graphene with multiple layers, thus allowing a more significant reduction in friction and resistance to wear. Graphene, with its smaller particle size, is less prone to structural defects and folds and is more easily absorbed into the sliding surface to form a lubricating film. Graphene, as an additive in lubricants, works according to three mechanisms. First, graphene nanosheets will be in contact with surfaces, generating shear forces due to motion in the tribo-system, giving a lubricating effect [25]. Secondly, nanosheets can form a protective layer and transfer film in the liquid lubricant environment. As the friction progresses, the graphene flakes break into smaller sheets transferred to the contact area, providing a support effect. Finally, the nanofoils are deposited and fill the worn surfaces, repairing them and improving the lubrication's performance. Figure 3 shows an illustration of tribofilm formation by the exfoliation mechanism corresponding to bidimensional materials.

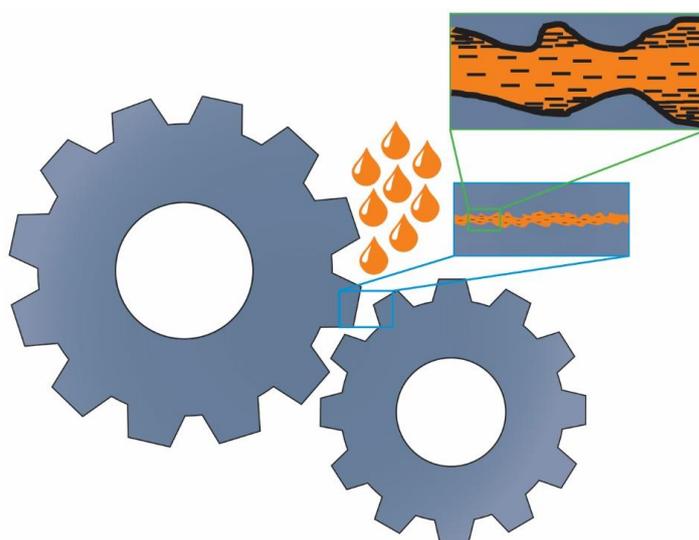


Figure 3. Illustration of tribofilm formation for bidimensional materials.

3. Hexagonal Boron Nitride (*h*-BN)

Hexagonal boron nitride is a solid lubricant belonging to the group of inorganic lubricants with a lamellar structure. The crystal lattice of *h*-BN contains hexagonal rings that form thin parallel planes. Its structure allows the sliding of parallel planes. Due to the weak bond between the planes, the shear stress is low in the sliding direction, but the compressive stress (perpendicular to shear) is high. The elevated adhesion strength of *h*-BN causes a strongly adhering lubricating film to form on the substrate's surface. In addition, its thermal stability and chemical inertness give it an advantage over graphite and MoS₂ as a solid lubricant [26].

Recently, research on lubricants has focused on water-based ones due to their low contamination and high resistance to fire. New lubricants with good anti-friction and anti-wear performance have been explored [27]. Hexagonal boron nitride nanosheets are a typical two-dimensional material with less than a 2% mismatch in their crystal structure compared to that of graphene. Therefore, *h*-BN nanosheets share many properties with graphene, such as mechanical strength, good optical properties, and high thermal conductivity. However, they have better resistance to oxidation and greater chemical stability than graphene, making them attractive for applications in aggressive environments [27].

There are very few studies of 2D nanomaterials as liquid lubricant additives where super lubrication (COF < 0.01) is achieved. However, several 2D nanomaterials are commonly used in industrial production processes to reduce friction and wear, improve a compo-

ment's lifetime, and increase energy transfer efficiency [28]. An et al. [27] fabricated *h*-BN nanosheets by using Pebax as a functionalizing agent through a solvent-free mechanical exfoliation process; it was used as an additive with a low concentration (0.3 mg/mL) in a water-based lubricant, and they were able to obtain coefficients of friction below 0.01, reaching super lubrication. When the Pebax-BN/water dispersion is added to the lubricant, the Pebax-BN nanosheets accumulate on the surface of the substrate to form a protective layer that reduces adhesion wear. For its part, the slight separation of the *h*-BN layers could also decrease friction coefficients. Table 2 shows recent research on the tribological performance of nanocomposites associated with graphene and hexagonal boron nitride as lubricant additives.

Table 2. Tribological performance of nanocomposites based on graphene and h-BN as lubricant additives.

2D Nanomaterial	Synthesis Method	Mating Surfaces (Conditions)	Tribological Properties		Ref.
			COF	Wear	
Graphene quantum dots (GQDs)	Hydrothermal and dialysis route	AISI 52100-GCr15 steel (ball on disc, 20 Hz, 100 N, 60 min)	0.23 (0.5 to 8 mg/mL)	6 $\mu\text{m}^3/\text{Ns}$ (wear rate)	[29]
rGO	unknown	GCr 15 bearing steel (ball on plate, 5 mm/s, 40 N)	0.105–0.11 (0.1 to 0.8 mg/mL)	$7.2 \times 10^{-7} \text{ mm}^3/\text{Nm}$	[23]
Super-exfoliated GO (SRGO)	Modified Hummer's method	AISI 52100 steel (ball on disc, 3 mm/s, 0.6–1.6 GPa)	<0.08 (0.5 wt%)	$80 \times 10^3 \text{ nm}^3$ (wear volume)	[21]
Hexagonal boron nitride nanosheets (<i>h</i> -BNNs)	Solvent-free mechanical exfoliation	Si_3N_4 and Al_2O_3 balls (ball on disc, 1–8 Hz, 1–8 N, 30 min)	<0.01 (0.3 mg/mL)	21.3 (wear rate $\mu\text{m}^2/\text{Nm}$)	[27]
rGO	Hummer's method	100Cr6 steel (ball on disc, 4 cm/s, 1–5 N)	0.06 (0.1 mg/mL)	$2 \times 10^{-7} \text{ mm}^3/\text{Nm}$	[19]
Graphene	Microwave-assisted ball milling	(four-ball friction tester, 1200 rpm, 392 N)	0.1 (0.11 mg/mL)	0.35 mm (wear scar diameter)	[30]
Graphene platelets	Reflux reaction with stearic and oleic acids	GCr15A bearing steel (MS-10A four-ball machine, 1450 rpm, 147 N, 60 min)	0.12 (0.075 wt%)	0.2% (wear rate)	[15]
GO nanosheets	Hummer and Offeman's method	GCr15 bearing steel (UMT-2-ball-plate, 120 rpm, 10 N, 10 min)	0.127 (0.1 wt%)	0.275 mm (wear scar diameter)	[31]

4. Transition Metal Dichalcogenides (TMDs)

TMDs are a family of compounds formed by a transition metal and a chalcogen element (S, Se, or Te). These owe their lubricating properties to their 2D microstructure made up of sheets, as shown in Figure 4b, with strong covalent bonds and weak van der Waals forces between the intermediate layers of the material. As shown in Figure 4a, a single layer of a TMD comprises three atomic layers with the transition metal and chalcogens interleaved, making them easy to cut under sliding contact with a low friction coefficient value [10,32].

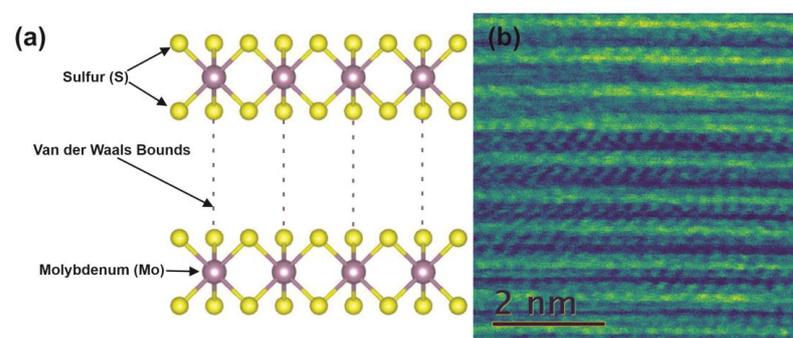


Figure 4. (a) Illustration of the crystal structure of MoS_2 and (b) experimental HRTEM of stacked MoS_2 .

When TMDs nanoparticles such as MoS₂ are dispersed in different base liquids, they will significantly improve their thermal conductivity and tribological performance, making these materials widely applied as additives in the oil [33].

5. Molybdenum Disulfide (MoS₂)

Within the family of TMDs, MoS₂ has been widely studied for its potential use in lubricants since it acts as an anti-wear additive (AW), reducing friction (FM) [34]. As a result of these properties, numerous applications for MoS₂ nanoparticles have been studied as lubricant additives, ranging from their use in motor oil [35,36] to metalworking fluids [37,38]. In recent decades, the influence of the different morphologies of MoS₂ on the tribological properties of oils has been extensively studied, finding that forms such as nanosheets [39–43], fullerene-like nanoparticles [44–46], flowers-like [47–49], and nanotubes [50,51] present good tribological properties in oils.

The synthesis of three different nanoparticles (fullerene-like, nanotubes, and rhenium-doped MoS₂) was reported by Tomala et al. [33], showing that all the synthesized particles improved the lubricating properties. Nevertheless, the morphology and composition of the resulting tribofilm and lubrication mechanisms are significantly different. The same effect was reported by Yi et al. [52] in liquid paraffin, using the flower-like morphologies, microspheres, and nanosheets of MoS₂, showing that the MoS₂ particle concentration influences the friction-reducing effects of the oil. Under high-pressure conditions, the nanosheets presented better friction and wear reduction performance than the other two morphologies, with a 41.1% reduction in the coefficient of friction and a 76.8% reduction in wear. The origin of this outstanding anti-wear and friction reduction effect of the MoS₂ nanosheets was studied. This effect was attributed to material transfer mechanisms by exfoliation by observing the formation of a MoS₂ tribofilm in the wear tracks. So, the exfoliation of MoS₂ nanosheets into individual ultrathin nanosheets was responsible for the excellent performance under heavy load. This effect was also reported by Zhang et al. [53], as their tribological tests indicated that nanosheets present excellent antifriction and anti-wear properties when used as an additive, especially when the concentration is 1.0–2.0 wt%; they also attributed the antifriction mechanism through which the nanosheets adhered to the wear surface to the formation of a continuous tribofilm on the rubbing surface that prevented direct contact between tribo-parts.

The use of ultrathin nanosheets was also reported by Yi et al. [36], who studied the anti-wear and friction reduction capacity in SAE 10W40 formulated motor oil (Mobile, USA) and the formation of tribofilm at the interface and their friction mechanism. They found that the ultrathin nanosheets improved the effect of the oil by reducing the COF by 41.87% and the wear by 18.22% at a temperature of 100 °C. The formation of a 25-to-40 nm thick tribofilm was also found. However, it contained zinc sulfide, phosphate, molybdenum sulfide, molybdenum oxide, iron sulfides and oxides, etc., which were present in the formulated oil. Figure 5 shows different morphologies of MoS₂, where nanoflowers, nanosheets, and ribbons are seen. According to the previously mentioned reports, it is easier to form a tribofilm with nanosheets or, where appropriate, with ribbon-like morphologies (Figure 5b,c) since the sliding of the individual layers will require less energy than in the case of nanoflowers (Figure 5a).

Despite their great potential as an additive in lubricants, many MoS₂ nanoparticles have poor dispersion, so they tend to agglomerate, thus making it necessary to use dispersants [38]. However, it has been reported that structures such as MoS₂ nanotubes and IF-MoS₂ lost their lubricating capacity due to dispersants in oil-based lubricant [51], which did not allow the nanoparticles to form tribofilm on the surfaces with rubbing. The synergistic and antagonistic effects of MoS₂ nanotubes and anti-wear (AW) and extreme pressure (EP) additives of representative oils under different tribological contact conditions were also studied [51]. From this study, they found that MoS₂ nanotubes have an excellent anti-wear performance. Regardless of the additive present and the tribological contact conditions under reciprocating slip conditions, the presence of dispersant can lead to a decrease in anti-wear performance. However, using dispersants to achieve stable dispersions is almost

inevitable since, when dispersing MoS₂ nanotubes in some oils, they form agglomerates that limit the stability of the lubricant and affect its rheological properties.

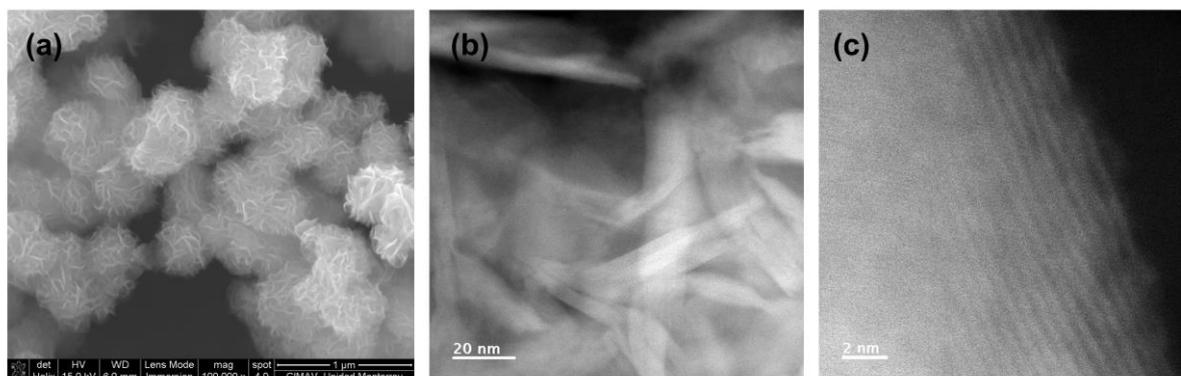


Figure 5. SEM-STEM and HRTEM micrograph with morphologies of (a) nanoflowers, (b) nanosheets, and (c) ribbons.

6. Oil-Based Lubricant Additives

The performance of a lubricant depends enormously on the additives that make it up. However, commonly used additives cause severe contamination when burned or disposed of. Therefore, the need arises to develop fewer polluting additives. An alternative is to use materials based on graphene or graphene oxide, composed only of C, H, and O, that are considered to be environmentally friendly [54]. Most compounds in the graphene family have strong π - π interactions and are difficult to dissolve in most solvents. Its high aggregation and precipitation capacity in lubricants have hampered its application. Researchers have tried to improve the solubility and dispersion of graphene compounds without sacrificing their graphitic characteristics [10]. In this way, the additive enters easily, preventing rough surfaces from coming into direct contact. Lin et al. [15] reported in 2011 that the chemical modification in a reflux reaction with stearic and oleic acids of graphene platelets generates increased dispersion in oil-based lubricants. The results indicated that, with only 0.075% by weight of the modified nano silver, the machine's wear resistance and load capacity were improved, and this was attributed to the small particle size and thin laminar structure. In 2016, Chen et al. [54] evaluated the tribological properties of few-layer GO sheets as an additive in an oil-based hydrocarbon. They found that adding GO sheets decreased COF and wear, expanding the operating temperature range of the lubricant.

7. Water-Based Lubricant Additives

Water-based lubricants are economical and environmentally friendly. However, they have drawbacks regarding friction reduction and load-carrying capacity. To overcome these problems, surface modifications and the addition of nanoparticles have been carried out as the most promising options due to their low cost, good lubricating performance, and low contamination. GO contains multiple functional groups (carboxylic, hydroxyl, and epoxide groups), making it dispersible in water [10]. Song et al. [31] prepared graphene oxide nanosheets as a water-based lubricant additive; the nanoparticles were tested in pure water, and a higher anti-wear ability and lower COF (0.127) were found. The behavior was related to the formation of a thin physical tribofilm on the substrate that not only supported the load generated by the steel ball but also prevented direct contact between the surfaces.

On the other hand, Qiang et al. [29] synthesized graphene quantum dots (GQDs) by hydrothermal treatment and evaluated the tribological performance as an additive in a water-based lubricant. Large hydrophilic groups were found that improved their dispersibility. In addition, it acquired a higher tribological performance compared to graphene oxide and with a smaller amount of material. A decrease of 42.5% in the COF and 58.5% in the wear rate was found compared to water. On the other hand, Liu et al. [55] conducted a comparative study between graphene oxide and diamond nanoparticles as

water-based additives on ceramic surfaces. Different effects were found for each type of nanoparticle; firstly, GO nanosheets decreased by increasing the COF from 0.6 to 0.1 compared to deionized water. After a long test period (steady state), it reached an ultra-low friction coefficient (0.01). In the case of diamond nanoparticles, friction was reduced by forming a regular grain area on the contact surfaces. Still, COF reduction did not occur in the steady state due to its larger size and hardness than GO.

8. Future Perspectives

Various investigations have shown the need for modification and functionalization treatments to enhance liquid lubricants. Most traditional dry (bulk) lubricants are being transformed into highly attractive functional nanomaterials, such as graphene (a single layer of graphite), h-BN monolayers, and TMDs. Besides the simplicity of production and the implementation of large-scale green synthesis processes respectful of the environment [56], the new generation of lubricants must have thermal and chemical stability and anticorrosion properties as a time function. The additives addition is a simple, effective, and economical way to improve the performance of lubricants under extreme conditions [18]. It is crucial to deepen the study of the formation mechanisms of the tribofilm in 2D materials to establish and better understand this type of lubrication. In most cases, the results are achieved through the synergistic effects of multiple mechanisms.

Researchers have now begun to explore combinations of two or more 2D materials as lubricant additives. The structure, morphology, concentration, and individual properties of each additive can significantly impact the tribological behavior of the resulting lubricant. For example, Mutyala et al. [57] combined graphene and MoS₂ to form a solid lubricant to reduce friction and wear in steel hydrogenated DLC contacts subjected to high contact pressures and sliding speed under dry nitrogen conditions; the reduction in friction and wear was found to be 16 and 29 times, respectively. As a subproduct, the formation of amorphous carbon mixed with graphene layers at the sliding interface was confirmed. Furthermore, Yang et al. [58] synthesized a solid–liquid composite formed with a molybdenum disulfide film and graphene hybrid gear oil. The excellent anti-friction and anti-wear properties were attributed to the solid–liquid synergism and transfer film, enhancing the interfacial load-bearing capacity.

Zaharin et al. [59] prepared a Ti₃C₂/graphene hybrid. They reported an improvement in the tribological properties of four samples of marine nanolubricants made up of 0.01% by weight of graphene, CNT, MXene, and Ti₃C₂/graphene hybrid. The Ti₃C₂/graphene hybrid improved the coefficient of friction by 11.16% and 6.55%, respectively. The remarkable improvement could be attributed to the ability of Ti₃C₂/graphene to penetrate tribological contact due to its nanoscale thickness. The new family of 2D materials, MXenes, also offers excellent properties in the lubrication areas. The oriented design or modulation of properties is a key point in developing lubricant additives based on next-generation 2D nanomaterials.

On the other hand, molecular dynamics (MD) simulations have been a powerful tool for understanding experimentally observed lubrication mechanisms. Xu et al. [60] studied the frictional behavior of atomically supported graphene, h-BN, and MoS₂ thin nanofilms with and without heating, using microscopy (AFM) and MD simulations. The AFM tapping mode showed that the interaction strength of the substrate increased with heating. Instead, the substrate surface roughness reproduced experimental observations in the simulations and revealed that the evolution of the real contact area in different interfacial interactions has divergent behaviors. In addition, hysteretic friction occurred because of a lower roughness of the substrate, unlike in other studies. Surface roughness and interaction strength were the key parameters to control out-of-plane deformation in nanofilms. Furthermore, Li et al. [61] studied the lubrication mechanism in a graphene-based system and a water-based lubricant by MD simulation. They included the effect of different factors, such as the number of water molecules, load, surface roughness, and sliding speed. It was found that the reduction in friction is due to the improvement of the insulation between the friction pairs by graphene presence and the water replenishment.

The synergistic lubrication mechanism works so that water molecules protect the structural integrity of graphene by inducing its motion to release lateral stresses, thus improving water movement and promoting their rolling-like bearings.

Considering recent research, one directly related to 2D materials as potential lubricants could follow to understand lubrication mechanisms and develop self-lubricating composites with optimized properties. Self-lubrication provides an opportunity to experience a considerable challenge in the processing and manufacturing of new ways to incorporate nanostructured materials from known lubricants, considering stability as another study point in 2D materials.

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References

1. Holmberg, K.; Kivikytö-Reponen, P.; Härkisaari, P.; Valtonen, K.; Erdemir, A. Global energy consumption due to friction and wear in the mining industry. *Tribol. Int.* **2017**, *115*, 116–139. [[CrossRef](#)]
2. Holmberg, K.; Andersson, P.; Erdemir, A. Global energy consumption due to friction in passenger cars. *Tribol. Int.* **2012**, *47*, 221–234. [[CrossRef](#)]
3. Bart, J.C.J.; Gucciardi, E.; Cavallaro, S. Lubricants: Properties and characteristics. In *Biolubricants*; Elsevier: Cambridge, UK, 2013; pp. 24–73. [[CrossRef](#)]
4. Raza, A.; Ahmed, A.; Kalam, M.A.; Fattah, I.M.R. Bio-Based Lubricant in the Presence of Additives: Classification to Tribological Behaviour. In *Green Tribology*; CRC Press: Boca Raton, FL, USA, 2021; pp. 27–70. [[CrossRef](#)]
5. Gong, H.; Yu, C.; Zhang, L.; Xie, G.; Guo, D.; Luo, J. Intelligent lubricating materials: A review. *Compos. Part B Eng.* **2020**, *202*, 108450. [[CrossRef](#)]
6. Singh, A.; Verma, N.; Mamatha, T.G.; Kumar, A.; Singh, S.; Kumar, K. Properties, functions and applications of commonly used lubricant additives: A review. *Mater. Today Proc.* **2020**, *44*, 5018–5022. [[CrossRef](#)]
7. Shahnazar, S.; Bagheri, S.; Abd Hamid, S.B. Enhancing lubricant properties by nanoparticle additives. *Int. J. Hydrog. Energy* **2016**, *41*, 3153–3170. [[CrossRef](#)]
8. Zhu, W.; Kamali, A.R. Green preparation of nanostructured β -MoO₃/hexagonal-shaped MoS₂/graphene with enhanced lithium-ion storage performance. *J. Alloys Compd.* **2023**, *932*, 167724. [[CrossRef](#)]
9. Kamali, A.R.; Feighan, J.; Fray, D.J. Towards large scale preparation of graphene in molten salts and its use in the fabrication of highly toughened alumina ceramics. *Faraday Discuss.* **2016**, *190*, 451–470. [[CrossRef](#)]
10. Xiao, H.; Liu, S. 2D nanomaterials as lubricant additive: A review. *Mater. Des.* **2017**, *135*, 319–332. [[CrossRef](#)]
11. Zhao, J.; Gao, T.; Li, Y.; He, Y.; Shi, Y. Two-dimensional (2D) graphene nanosheets as advanced lubricant additives: A critical review and prospect. *Mater. Today Commun.* **2021**, *29*, 102755. [[CrossRef](#)]
12. Gao, Q.; Liu, S.; Hou, K.; Li, Z.; Wang, J. Graphene-Based Nanomaterials as Lubricant Additives: A Review. *Lubricants* **2022**, *10*, 273. [[CrossRef](#)]
13. Nyholm, N.; Espallargas, N. Functionalized carbon nanostructures as lubricant additives—A review. *Carbon* **2023**, *201*, 1200–1228. [[CrossRef](#)]
14. Yu, B.; Wang, K.; Pang, X.; Wu, G.; Pu, J.; Zhao, H. Tribological properties of alkylated reduced graphene oxide as lubricant additive. *Tribol. Int.* **2022**, *165*, 107273. [[CrossRef](#)]
15. Lin, J.; Wang, L.; Chen, G. Modification of graphene platelets and their tribological properties as a lubricant additive. *Tribol. Lett.* **2011**, *41*, 209–215. [[CrossRef](#)]
16. Wang, W.; Zhang, G.; Xie, G. Ultralow concentration of graphene oxide nanosheets as oil-based lubricant additives. *Appl. Surf. Sci.* **2019**, *498*, 143683. [[CrossRef](#)]
17. Xie, H.; Dai, J.; Zhou, D. Tribological behaviors of graphene oxide partly substituted with nano-SiO₂ as lubricant additives in water for magnesium alloy/steel interfaces. *Int. J. Miner. Metall. Mater.* **2022**, *29*, 1425–1434. [[CrossRef](#)]

18. Liang, Z.; Wang, S.; Zhu, K.; Chen, Y.; Wei, F.; Chen, D. Enhancing the tribological properties and corrosion resistance of graphene-based lubricating grease via ultrasonic-assisted ball milling. *Colloids Surf. A Physicochem. Eng. Asp.* **2022**, *633*, 127889. [[CrossRef](#)]
19. Gupta, B.; Kumar, N.; Panda, K.; Kanan, V.; Joshi, S.; Visoly-Fisher, I. Role of oxygen functional groups in reduced graphene oxide for lubrication. *Sci. Rep.* **2017**, *7*, 45030. [[CrossRef](#)] [[PubMed](#)]
20. Guo, W.; Yin, J.; Qiu, H.; Guo, Y.; Wu, H.; Xue, M. Friction of low-dimensional nanomaterial systems. *Friction* **2014**, *2*, 209–225. [[CrossRef](#)]
21. Zhao, J.; Huang, Y.; Li, Y.; Gao, T.; Dou, Z.; Mao, J.; Wang, H.; He, Y.; Li, S.; Luo, J. Superhigh-exfoliation graphene with a unique two-dimensional (2D) microstructure for lubrication application. *Appl. Surf. Sci.* **2020**, *513*, 145608. [[CrossRef](#)]
22. Ge, X.; Chai, Z.; Shi, Q.; Li, J.; Tang, J.; Liu, Y.; Wang, W. Functionalized graphene-oxide nanosheets with amino groups facilitate macroscale superlubricity. *Friction* **2023**, *11*, 187–200. [[CrossRef](#)]
23. Kong, S.; Wang, J.; Hu, W.; Li, J. Effects of Thickness and Particle Size on Tribological Properties of Graphene as Lubricant Additive. *Tribol. Lett.* **2020**, *68*, 112. [[CrossRef](#)]
24. Meng, Y.; Xu, J.; Ma, L.; Jin, Z.; Prakash, B.; Ma, T.; Wang, W. A review of advances in tribology in 2020–2021. *Friction* **2022**, *10*, 1443–1595. [[CrossRef](#)]
25. Shin, J.H.; Kim, S.H.; Kwon, S.S.; Park, W.I. Direct CVD growth of graphene on three-dimensionally-shaped dielectric substrates. *Carbon* **2018**, *129*, 785–789. [[CrossRef](#)]
26. Cho, D.H.; Kim, J.S.; Kwon, S.H.; Lee, C.; Lee, Y.Z. Evaluation of hexagonal boron nitride nano-sheets as a lubricant additive in water. *Wear* **2013**, *302*, 981–986. [[CrossRef](#)]
27. An, L.; Yu, Y.; Bai, C.; Bai, Y.; Zhang, B.; Gao, K.; Wang, X.; Lai, Z.; Zhang, J. Simultaneous production and functionalization of hexagonal boron nitride nanosheets by solvent-free mechanical exfoliation for superlubricant water-based lubricant additives. *NPJ 2D Mater. Appl.* **2019**, *3*, 28. [[CrossRef](#)]
28. Wang, H.; Liu, Y. Superlubricity achieved with two-dimensional nano-additives to liquid lubricants. *Friction* **2020**, *8*, 1007–1024. [[CrossRef](#)]
29. Qiang, R.; Hu, L.; Hou, K.; Wang, J.; Yang, S. Water-Soluble Graphene Quantum Dots as High-Performance Water-Based Lubricant Additive for Steel/Steel Contact. *Tribol. Lett.* **2019**, *67*, 64. [[CrossRef](#)]
30. Wang, S.; Liang, Z.; Liu, L.; Cao, Y.; Cheng, Y.; Chen, D. Preparation of chemically functionalized graphene with excellent dispersibility and tribological properties as lubricant additives by microwave-assisted ball milling. *J. Mol. Liq.* **2021**, *344*, 117929. [[CrossRef](#)]
31. Song, H.J.; Li, N. Frictional behavior of oxide graphene nanosheets as water-base lubricant additive. *Appl. Phys. A Mater. Sci. Process.* **2011**, *105*, 827–832. [[CrossRef](#)]
32. Essa, F.A.; Zhang, Q.; Huang, X.; Ali, M.K.A.; Elagouz, A.; Abdelkareem, M.A.A. Effects of ZnO and MoS₂ Solid Lubricants on Mechanical and Tribological Properties of M50-Steel-Based Composites at High Temperatures: Experimental and Simulation Study. *Tribol. Lett.* **2017**, *65*, 1–29. [[CrossRef](#)]
33. Tomala, A.; Vengudusamy, B.; Ripoll, M.R.; Suarez, A.N.; Remškar, M.; Rosentsveig, R. Interaction Between Selected MoS₂ Nanoparticles and ZDDP Tribofilms. *Tribol. Lett.* **2015**, *59*, 26. [[CrossRef](#)]
34. Gulzar, M.; Masjuki, H.H.; Kalam, M.A.; Varman, M.; Zulkifli, N.W.M.; Mufti, R.A.; Zahid, R. Tribological performance of nanoparticles as lubricating oil additives. *J. Nanoparticle Res.* **2016**, *18*, 223. [[CrossRef](#)]
35. Srinivas, V.; Thakur, R.N.; Jain, A.K.; Saratchandra Babu, M. Tribological Studies of Transmission Oil Dispersed with Molybdenum Disulfide and Tungsten Disulfide Nanoparticles. *J. Tribol.* **2017**, *139*, 041301. [[CrossRef](#)]
36. Yi, M.; Qiu, J.; Xu, W. Tribological performance of ultrathin MoS₂ nanosheets in formulated engine oil and possible friction mechanism at elevated temperatures. *Tribol. Int.* **2022**, *167*, 107426. [[CrossRef](#)]
37. Singh, N.; Sinha, S.K. Tribological performances of hybrid composites of Epoxy, UHMWPE and MoS₂ with in situ liquid lubrication against steel and itself. *Wear* **2021**, *486–487*, 204072. [[CrossRef](#)]
38. Xie, H.; Jiang, B.; He, J.; Xia, X.; Pan, F. Lubrication performance of MoS₂ and SiO₂ nanoparticles as lubricant additives in magnesium alloy-steel contacts. *Tribol. Int.* **2016**, *93*, 63–70. [[CrossRef](#)]
39. Wu, H.; Qin, L.; Dong, G.; Hua, M.; Yang, S.; Zhang, J. An investigation on the lubrication mechanism of MoS₂ nano sheet in point contact: The manner of particle entering the contact area. *Tribol. Int.* **2017**, *107*, 48–55. [[CrossRef](#)]
40. Wu, P.R.; Li, W.; Feng, Y.M.; Ge, T.; Liu, Z.; Cheng, Z.L. Fabrication and tribological properties of oil-soluble MoS₂ nanosheets decorated by oleic diethanolamide borate. *J. Alloys Compd.* **2019**, *770*, 441–450. [[CrossRef](#)]
41. Wu, H.; Johnson, B.; Wang, L.; Dong, G.; Yang, S.; Zhang, J. High-efficiency preparation of oil-dispersible MoS₂ nanosheets with superior anti-wear property in ultralow concentration. *J. Nanoparticle Res.* **2017**, *19*, 339. [[CrossRef](#)]
42. Rajendhran, N.; Palanisamy, S.; Periyasamy, P.; Venkatachalam, R. Enhancing of the tribological characteristics of the lubricant oils using Ni-promoted MoS₂ nanosheets as nano-additives. *Tribol. Int.* **2018**, *118*, 314–328. [[CrossRef](#)]
43. Wu, H.; Wang, L.; Johnson, B.; Yang, S.; Zhang, J.; Dong, G. Investigation on the lubrication advantages of MoS₂ nanosheets compared with ZDDP using block-on-ring tests. *Wear* **2018**, *394–395*, 40–49. [[CrossRef](#)]
44. Rosentsveig, R.; Gorodnev, A.; Feuerstein, N.; Friedman, H.; Zak, A.; Fleischer, N.; Tannous, J.; Dassenoy, F.; Tenne, R. Fullerene-like MoS₂ nanoparticles and their tribological behavior. *Tribol. Lett.* **2009**, *36*, 175–182. [[CrossRef](#)]

45. Cizaire, L.; Vacher, B.; Le Mogne, T.; Martin, J.M.; Rapoport, L.; Margolin, A.; Tenne, R. Mechanisms of ultra-low friction by hollow inorganic fullerene-like MoS₂ nanoparticles. *Surf. Coat. Technol.* **2002**, *160*, 282–287. [[CrossRef](#)]
46. Rabaso, P.; Ville, F.; Dassenoy, F.; Diaby, M.; Afanasiev, P.; Cavoret, J.; Vacher, B.; Le Mogne, T. Boundary lubrication: Influence of the size and structure of inorganic fullerene-like MoS₂ nanoparticles on friction and wear reduction. *Wear* **2014**, *320*, 161–178. [[CrossRef](#)]
47. Tang, G.; Zhang, J.; Liu, C.; Zhang, D.; Wang, Y.; Tang, H.; Li, C. Synthesis and tribological properties of flower-like MoS₂ microspheres. *Ceram. Int.* **2014**, *40*, 11575–11580. [[CrossRef](#)]
48. Zhang, X.; Huang, X.; Xue, M.; Ye, X.; Lei, W.; Tang, H.; Li, C. Hydrothermal synthesis and characterization of 3D flower-like MoS₂ microspheres. *Mater. Lett.* **2015**, *148*, 67–70. [[CrossRef](#)]
49. Zhou, X.; Xu, B.; Lin, Z.; Shu, D.; Ma, L. Hydrothermal synthesis of flower-like MoS₂nanospheres for electrochemical supercapacitors. *J. Nanosci. Nanotechnol.* **2014**, *14*, 7250–7254. [[CrossRef](#)]
50. Tomala, A.; Ripoll, M.R.; Gabler, C.; Remškar, M.; Kalin, M. Interactions between MoS₂ nanotubes and conventional additives in model oils. *Tribol. Int.* **2017**, *110*, 140–150. [[CrossRef](#)]
51. Tomala, A.; Ripoll, M.R.; Kogovšek, J.; Kalin, M.; Bednarska, A.; Michalczewski, R.; Szczerek, M. Synergisms and antagonisms between MoS₂ nanotubes and representative oil additives under various contact conditions. *Tribol. Int.* **2019**, *129*, 137–150. [[CrossRef](#)]
52. Yi, M.; Zhang, C. The synthesis of MoS₂ particles with different morphologies for tribological applications. *Tribol. Int.* **2017**, *116*, 285–294. [[CrossRef](#)]
53. Zhang, X.; Xue, Y.; Ye, X.; Xu, H.; Xue, M. Preparation, characterization and tribological properties of ultrathin MoS₂ nanosheets. *Mater. Res. Express* **2017**, *4*, 115011. [[CrossRef](#)]
54. Chen, Z.; Liu, Y.; Luo, J. Tribological properties of few-layer graphene oxide sheets as oil-based lubricant additives. *Chin. J. Mech. Eng.* **2016**, *29*, 439–444. [[CrossRef](#)]
55. Liu, Y.; Wang, X.; Pan, G.; Luo, J. A comparative study between graphene oxide and diamond nanoparticles as water-based lubricating additives. *Sci. China Technol. Sci.* **2013**, *56*, 152–157. [[CrossRef](#)]
56. Kamali, A.R. *Green Production of Carbon Nanomaterials in Molten Salts and Applications*; Springer: Singapore, 2022.
57. Mutyala, K.C.; Wu, Y.A.; Erdemir, A.; Sumant, A.V. Graphene—MoS₂ ensembles to reduce friction and wear in DLC-Steel contacts. *Carbon* **2019**, *146*, 524–527. [[CrossRef](#)]
58. Yang, Y.; Fan, X.; Yue, Z.; Li, W.; Li, H.; Zhu, M. Synergistic lubrication mechanisms of molybdenum disulfide film under graphene-oil lubricated conditions. *Appl. Surf. Sci.* **2022**, *598*, 153845. [[CrossRef](#)]
59. Zaharin, H.A.; Ghazali, M.J.; Rasheed, A.K.; Khalid, M.; Otsuka, Y. Tribological Performance of Hybrid Ti₃C₂/Graphene Additive on Outboard Engine Oil. In *Lecture Notes in Mechanical Engineering*; Springer: Singapore, 2022; pp. 146–153. [[CrossRef](#)]
60. Xu, C.; Ye, Z.; Egberts, P. Friction hysteretic behavior of supported atomically thin nanofilms. *NPJ 2D Mater. Appl.* **2023**, *7*, 1. [[CrossRef](#)]
61. Li, C.; Tang, W.; Tang, X.Z.; Yang, L.; Bai, L. A molecular dynamics study on the synergistic lubrication mechanisms of graphene/water-based lubricant systems. *Tribol. Int.* **2022**, *167*, 107356. [[CrossRef](#)]

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