MoS_2 Nanomaterials as Lubricant Additives

Subjects: Mechanics

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Improving the lubricating properties of base oils through additives is a crucial objective of tribological research, as it helps to reduce friction and wear of materials. Molybdenum disulfide (MoS_2) is a 2D nanomaterial with excellent tribological properties that is often used as a lubricant additive. Several studies have been conducted on the preparation and utilization of MoS_2 and its nanocomposites as lubricant additives.

nano-MoS2 dispersion stability anti-wear friction reduction lubrication mechanism

1. Introduction

Friction and wear have always been the top issues in different industrial fields. While modern industry is developing rapidly, global energy consumption also maintains rapid development. In mechanical systems, energy waste due to friction and wear accounts for about 1/3–1/2 [1][2], and friction and wear of machineries and equipment will seriously affect the normal operation and life cycle of its components [3] and may even produce more dangerous consequences under the process of operation [3]. Mechanical systems in industrial production are usually lubricated with lubricants, which can not only significantly reduce friction and wear and improve lubrication efficiency, but also have important significance for energy saving and environmental protection [4]. Currently, lubricants commonly used in various industries and research experiments are composed of base oils and various lubricant additives [5]. Traditional anti-wear and extreme pressure additives such as molybdenum dialkyl dithiocarbamate (MoDTC) and zinc dialkyl dithiophosphate (ZDDP) can greatly reduce friction and wear by generating beneficial products in situ from the reaction between the additive and the metal friction pair surface [6][7]. However, traditional lubrication additives are facing serious challenges with the development of the industry. In order to fulfill the needs of different fields such as ultra-low friction, wear, and extreme conditions, new requirements are placed on lubricants such as resistance to high temperature and pressure [8]. Lubricant additives can give new properties to the lubricant and make up for the shortcomings of the base oil, thus greatly improving the tribological properties of the lubricant.

The utilization of nanomaterials as additives in lubricants presents a promising avenue to enhance the performance of mechanical systems, surpassing that of the traditional lubricant additives. Nanomaterials are tiny particles, with at least one dimension ranging between 1–100 nanometers, which allows them to easily penetrate the contact zone [9]. Due to their high surface activity, they can strongly adsorb onto the friction surface and form a stable protective film that prevents direct contact between solid surfaces, effectively reducing friction. These nanomaterials include metals [10], metal oxides [11], metal sulfides [12], carbon-based materials [13], nitrides [14], and their composites. During friction processes, nanomaterials can be physically or chemically adsorbed onto the contact surfaces of friction pairs, thus improving lubricant tribological properties, a subject that has been extensively researched in the field of tribology [15][16][17]. Transition metal dichalcogenides (TMDs), due to their structural similarity to graphene, have attracted significant attention from global scholars in recent years for their ability to significantly enhance lubrication and anti-wear properties in lubricants.

MoS_2 is a typical representative of transition metal disulfides and is used as an anti-wear and friction-reducing additive in solid lubricants, lubricants, and greases, or as a lubricating component in coatings [18]. MoS_2 is an excellent solid lubricant and has gained the reputation of “king of lubrication” because of its good lubrication performance even under special working conditions like ultra-high temperature and ultra-vacuum. MoS_2 also has certain problems, such as humidity and oxygen enrichment that can degrade its performance [19][20][21][22]. Low humidity and low oxygen environments need to be constructed for them to perform. However, MoS_2 can overcome the effects of moisture and oxygen by developing specific structures or morphologies. Although some progress has been made in improving MoS_2’s resistance to moisture and oxidation [20], there is still much work to be undertaken.

MoS_2 was initially used in the mid-19th century during the California Gold Rush as a lubricant for horse-drawn carriage bearings. MoS_2 as a lubricant has been the subject of a great deal of scientific research, with reviews and books on the subject published as early as the 1960s [23][24]. Although its use as a dry film lubricant was established in the mid-20th century, its effective use in oils took longer to perfect.

2. Structure and Synthesis

2.1. Structure of MoS_2

A single layer of MoS_2 is composed of three atomic layers. It consists of a molybdenum layer sandwiched between two sulfur atom layers, forming a sandwich-like structure. MoS_2 belongs to the hexagonal or rhombohedral crystal system, with six sulfur atoms distributed around each molybdenum atom and three molybdenum atoms oiled around each sulfur atom, Mo and S are bonded to each other by covalent bonding, whereas the triatomic layer of S-Mo-S is bonded to each other by van der Waals forces, with a layer-to-layer spacing of about 0.615 nm (PDF#37-1492).

2.2. Synthesis Method of Nano-MoS_2 Nanomaterials

MoS_2 is a substance with excellent lubricating properties and has gained widespread attention in the field of tribology. The last few years have seen rapid advancements in the preparation technology and processes of MoS_2, which have laid a solid foundation for its basic research and application and significantly promoted its development. The synthesis method of MoS_2 is the cornerstone for its development and application and holds significant scientific and economic significance. Similar to graphene, the preparation method for two-dimensional layered MoS_2 starts with the mechanical stripping method, and several other preparation methods have been developed through continuous research and exploration. The preparation methods of MoS_2 include mechanical exfoliation, hydrothermal, solvothermal, liquid-phase precipitation method, and more.

2.2.1. Mechanical Exfoliation

The earliest method used to prepare MoS_2 was micromechanical exfoliation, i.e., the use of adhesive tape to strip thin sheets of MoS_2 from a block of MoS_2. This method was first proposed by Frindt et al. [25] in 1965, and several tens of layers of MoS_2 were successfully obtained by this method. Although the MoS_2 obtained by this method has a high degree of crystallinity, the preparation is inefficient and reproducible, which makes it difficult to realize large-scale applications. For this reason, researchers have explored the ultrasound-assisted exfoliation method.

2.2.2. Hydrothermal

The hydrothermal is a method to complete the material synthesis and preparation by heating and pressurizing the reaction system (or self-generated steam pressure) in a specially designed closed reactor (e.g., autoclave) with water as the reaction medium to create a relatively high-temperature and high-pressure reaction condition. The advantage of this method is that the synthesized products are characterized by complete grain development, small and uniform particle size distribution, and light particle agglomeration, and it is one of the most commonly used methods for the preparation of two-dimensional materials, including MoS_2 and its nanocomposites [26][27].

It can be seen that the hydrothermal method usually involves pre-preparing an aqueous solution containing the raw material, placing it in a sealed autoclave reactor reacting it for some time at a temperature of about 200 °C, and then cooling it naturally to room temperature. The precipitate after the reaction is collected for some additional post-treatment (e.g., calcination) to optimize the product. However, the hydrothermal method requires high-temperature and high-pressure reaction conditions, high dependence on equipment, expensive autoclaves for fabrication, safety issues during the reaction process, and the inability to observe the reaction while synthesizing the nanomaterials, which makes it difficult to realistically control the parameters [28], thus limiting the development of the method to some extent.

2.2.3. Solvothermal

Solvothermal is a high-pressure growth method that does not require any catalyst. It is developed from the hydrothermal method, which is similar but differs in using organic solvents or non-aqueous solvents (such as N, N-dimethylformamide (DMF) [29][30], ethylene glycol [31]) instead of water as the reaction medium. This method is used to prepare materials that cannot grow in aqueous solution and are easily oxidized, hydrolyzed, or sensitive to water, such as III-V semiconductor compounds, nitrides, and sulfur compounds.

Li et al. [30] used ammonium tetrathiomolybdate ($(NH_4)_2MoS_4$) as a precursor for Mo and S and reacted it in DMF at 210 °C for 36 h to obtain MoS_2 nanosheets. In some cases it is also necessary to use DMF and water as a mixed solvent. hao et al. [29] reported that the proper DMF/water ratio is very important for the construction of MoS_2 nanocomposites, because the use of DMF as a solvent does not allow for the self-assembly of the hybrid material into the desired structure, and the use of pure deionized water does not result in homogeneous MoS_2 nanoparticles.

Solvothermal has some limitations. Although they are usually less demanding than hydrothermal, they still require high temperature and pressure conditions in most cases. Additionally, the synthesis process usually lasts longer [32][33][34] and consumes more energy. Comparing the two methods, the simple hydrothermal method usually has no negative impact on the material properties, whereas solvothermal methods usually have a greater impact on material properties due to differences in solvents. However, the solvothermal method is more likely to result in a better morphology than the hydrothermal method.

2.2.4. Liquid-Phase Precipitation

Liquid-phase precipitation is a process in which a solution containing the desired reactants is generated by controlling the acidity and temperature of the reaction. By adjusting these factors, a large number of particles can be generated, and the use of surfactants prevents agglomeration of the particles, resulting in uniformly dispersed nanoparticles. This method is low-cost, easy to operate, and has a mild reaction process, making it suitable for industrial production.

Hou et al. [35] prepared MoS_2 nanoparticles using a simple method. They dissolved $Na_2MoO_4{\cdot}H_2O$ and CH_3CSNH_2 in deionized water, added a surfactant, and adjusted the pH to 1.0 using H_2SO_4. The mixture was stirred for 5 min at 90 °C, resulting in the formation of MoS_3. The product was washed, dried, and desulphurized at 800 °C under a hydrogen atmosphere, which led to the formation of MoS_2 nanoparticles with a size range of 150–300 nm. Hu et al. [36][37] utilized thioacetamide (CH_3CSNH_2, TAA) as the sulfur source and dissolved it in distilled water along with $Na_2MoO_4{\cdot}2H_2O$. The resulting solution was heated to 82 °C for 5 min, then HCl or H_2SO_4 was rapidly poured into the reaction system and the reaction was continued for 5 min. The product was then washed and dried to give the desired MoS_3 precursor. Hu and colleagues [38][39] utilized $Na_2S{\cdot}9H_2O$ as a source of sulfur, which was then dissolved in deionized water along with $Na_2MoO_4{\cdot}2H_2O$. While stirring the mixture at room temperature, they added HCl or H_2SO_4 dropwise to the reaction system. The obtained precipitate was washed and dried to obtain the desired MoS_3 precursor. The MoS_3 precursors obtained under both conditions were subjected to calcination under a high-purity hydrogen atmosphere at a selected temperature for 50 min to obtain MoS_2 nanoparticles.

3. Stability of MoS_2 Nanomaterial Dispersion

In recent years, MoS_2 nanoparticles have received increasing attention as lubricant additives for their excellent tribological properties. In practice, poor dispersion of the additive causes agglomeration and precipitation, which can adversely affect the friction system. However, due to the small particle size of MoS_2 nanoparticles with high surface energy, such nanoparticles have a strong tendency to agglomerate and are prone to aggregate and form agglomerates with larger sizes, thus making it difficult to form a stable lubricant suspension, which has become a challenging problem for the application of nano-MoS_2 as a lubricant additive [40][41][42], seriously hindering the application of nano-MoS_2 materials in practice. Therefore, optimizing the dispersion stability of MoS_2 in oil solutions and slowing the tendency of particle agglomeration in suspensions can be regarded as prerequisites for studying other properties.

3.1. Physical Methods

Physical dispersion of nanomaterials in the base lubrication medium can be achieved by mechanical techniques such as mechanical agitation, ultrasonic treatment [43][44][45][46], ball milling [47][48], and high-pressure homogenization [49], with ultrasonic treatment being one of the most commonly used physical methods.

Ultrasonic dispersion is a relatively mature technology, which is used in textile, printing and dyeing, chemical, biological, pharmaceutical, and many other industries and fields. The mechanism of ultrasonic dispersion occurs when ultrasonic waves propagate in a dispersing medium, wherein the pressure by the speed of sound oscillatory changes, which produces a series of rapid compressions of the liquid so that the suspended particles are instantly broken and dispersed. However, overheated ultrasonic mixing should also be avoided, as the chance of particle collision increases with the increase in mechanical energy in the thermal phase, leading instead to further agglomeration. It was mentioned earlier that ultrasonic treatment helps in stripping the bulk material into nanoscale products without any other reactants [25][50] and also helps in homogeneous dispersion of MoS_2 material in solution or solvent [51][52].

3.2. Chemical Methods

Graphene-like topic nanomaterials cannot be dissolved in most solvents due to the strong π-π bonds, and neither direct dispersion nor simple ultrasonic dispersion can make MoS_2 stably dispersed in lubricating oils. Currently, surface modification or composite materials with other materials are commonly used to improve the dispersion of MoS_2 in lubricating oils.

Adding surfactants as dispersants is a relatively easy method. Organic dispersants are adsorbed by these particles suitably to create a state of repulsion between the particles, thus counteracting the natural attraction between the particles [53]. There are many common dispersants such as Span 80, tween 80, oleic acid (OA), sodium dodecyl sulfate sodium dodecyl benzene sulfonate, etc. Hou et al. [54] investigated the effect of different dispersants (OA and Span 80) on the dispersion stability of MoS_2 nanomaterials in PAO6 to provide a theoretical basis for the stability of the MoS_2 nano-lubricant. Oleic acid and Span 80 successfully modified the MoS_2 nanomaterials, and the MoS_2 nano-lubricant was able to remain somewhat stable at room temperature for a period of 7 days. The paper also points out that concentration, sonication time, and morphology (spherical and sheet) all have a certain effect on the dispersion stability of MoS_2 in base oils as well.

Surface modification is a commonly used method for MoS_2 surface modification. Through surface grafting modification, specific functional groups in surfactants are grafted on the surface of nanoparticles to improve their oil solubility, so that the nanoparticles can be stably dispersed in lubricating oils, which has become an important direction in the research on the practicalization of nano-lubricant additives [55][56][57]. OA is an unsaturated fatty acid, which is often used as a chemical modifier for MoS_2 [58][59].

Meng et al. [60], in order to mitigate the agglomeration and deposition of MoS_2 nanofluid, conducted an experiment wherein surface modification of MoS_2 nanosheets was carried out by using homemade surface modifiers based on triethanolamine (TEA) and stearic acid (SA), and modified MoS_2 nanosheets with better dispersion stability were obtained. The effects of the surface modification on the tribological properties of the modified MoS_2 nanofluids were investigated using a four-ball friction and wear tester and molecular dynamics simulation. The diffusion rate, interlayer spacing, interlayer adsorption energy, and shear stress of MoS_2 nanosheets before and after modification were calculated. The interlayer spacing of the modified MoS_2 nanosheets increased due to the interaction between the MoS_2 nanosheets and the surface modifier. Especially at atmospheric pressure, the interlayer adsorption energy and interlayer shear stress were decreased. The modified MoS_2 nanosheets not only have better dispersion stability but also have excellent tribological properties.

Due to the strong attraction between metal atoms and polar functional groups (-OH, -O-, $-NH_2$, etc.) in MoS_2, it helps to graft surfactant molecules containing such groups onto the nanoparticles [61][62][63], which not only reduces the agglomeration of nanoparticles but also avoids the separation of the nanoparticles and grafted functional groups due to frictional stress, which effectively improves the dispersive stabilization and lubrication properties of the nanoparticles. With the deepening of the research, a single decentralized method can no longer meet the demand, and the combination of methods has become the choice of many researchers.

The composite material realizes the result of “1 + 1 > 2” for two or more materials. The composite of MoS_2 with a dibasic material to improve its dispersion in the base oil and then improve its lubrication performance is also one of the research hotspots of MoS_2 in recent years.

The hexagonal boron nitride (*h*-BN) nanosheets prepared by Kumari et al. [64] via alkali-assisted hydrothermal stripping were used for the growth of a MoS_2 sheet by chemical reduction in the presence of cetyltrimethylammonium bromide (CTAB). The CTA molecules on the surface of the composite nanomaterials avoided their re-stacking through the spatial site resistance of the long alkyl chains, and furthermore, the alkyl chains of the CTA molecules in the *h*-BN-MoS_2-CTAB had van der Waals interactions with the hydrocarbons in the 5W30 engine oil, resulting in the formation of a heterogeneous structure of *h*-BN-MoS_2-CTAB. Thus, the dispersion of *h*-BN-MoS_2-CTAB in 5W30 engine oil was stable for one month.

Therefore, although physical methods are one of the simplest and most economical ways to disperse MoS_2 into lubricants, the nanoparticles are prone to re-agglomerate due to degradation problems under frictional conditions. Surfactant-modified MoS_2 has better dispersion properties, but the presence of other atoms or functional groups may lead to significant degradation of its intrinsic properties. The composites obtained by compositing with other two-dimensional nanomaterials not only obtain good stability of the products, but also can choose the composite two-dimensional materials according to the need for their own defects to make up for the corresponding defects, and at the same time, the composite nanoparticles are able to realize self-dispersion in lubricating oils, which is a very promising method.

4. Tribological Behavior and Lubrication Mechanism of MoS_2 Nanomaterials

4.1. Tribological Properties of Nano-MoS_2

It is widely recognized that the tribological properties of 2D nanomaterials are closely related to their size and morphology [65][66][67][68]. In recent years, with the continuous development of the synthesis process, researchers have prepared MoS_2 particles with various morphologies, such as nanoflower [69], nanospherical [70], hollow core-shell [71], nanorod [72], and nanowire [73].

Hu et al. [65] investigated the effect of nanospheres, nanosheets, and bulk 2H-MoS_2 additives on the tribological properties of liquid paraffin (LP) using a four-ball friction and wear tester. The results showed that all the MoS_2 additives used could improve the tribological properties of LP, and the lubrication effect of nano-MoS_2 particles in LP was better than that of micrometer MoS_2 particles. The LP containing nanospheres had the best friction reduction and anti-wear properties when the MoS_2 content was 1.5 wt%. This was attributed to the chemical stability of the layer-closed spherical structure of the nanospheres. This study further deepens the understanding of the relationship between the tribological properties and morphology of MoS_2.

4.2. Tribological Properties of MoS_2 Composites

When single MoS_2 particles are used as lubrication additives, the MoS_2-based friction film adsorbed on the contact surface of the friction pair due to the experimental process is easily destroyed under certain extreme friction conditions and easily removed from the friction interface. A feasible way to improve the tribological performance of pure MoS_2 additives is to develop MoS_2 nanocomposites, which, as mentioned in the previous section, can not only enhance the dispersion stability of the material in the base oil but also realize the synergistic enhancement effect during the friction process.

Carbon-based solid lubrication materials have been one of the focuses of research in the field of new materials for friction reduction and anti-wear, with broad application value and prospects. Scholars at home and abroad have shown strong interest in the research of carbon materials and MoS_2 composites, especially graphene. Xu et al. [74] outlined the development of graphene/MoS_2 nanocomposites in recent years, and discussed the synthesis method, dispersion behavior, tribological properties, and lubrication mechanism of the composites, and put forward the challenges that graphene/MoS_2 nanocomposites will face in the field of tribology. It is also pointed out that modified graphene/MoS_2 nanocomposites have good prospects in the field of tribology. Hu et al. [75] prepared rice husk charcoal/MoS_2 (RHC/MoS_2) nanoparticles by the precipitation method and modified the synthesized products with surface modifiers. The tribological properties of the nanoparticles in polyethylene glycol (PEG) before and after modification were tested by a ball-and-disc friction and wear tester. When the experimental tests were conducted at 80 N and 300 rpm for 30 min, the nanoparticle additions before and after modification were 0.5 wt%, and the wear rates were reduced by 88.6% and 97.8%, respectively, compared with pure PEG. The modified RHC/MoS_2 particles are more effective in improving the anti-wear and friction reduction performance of PEG.

Combinations with other nanomaterials are still remarkable, such as *h*-BN [64][76], graphitic phase carbon nitride (g-C_3N_4) [77], and MSH [78][79]. Kumari et al. [64] used the design idea of generating ultra-low friction at the interface of two asymmetrically stacked 2D/2D heterostructures with different lattices to prepare *h*-BN-MoS_2-CTAB by alkali-assisted hydrothermal stripping. *h*-BN-MoS_2-CTAB, which was added to the engine oil (5W30) as a 30 ppm compound, resulted in a reduction of friction and wear of a steel friction pair by 44% and 96%.

4.3. Lubrication Mechanism

4.3.1. Rolling Mechanism

According to researchers, spherical nanoparticles can roll between two sliding surfaces and help reduce friction and wear. Stabilized spherical nanoparticles can also improve extreme pressure performance and lubricant load-carrying capacity [80][81][82]. The rolling effect of spherical nanoparticles depends on the thickness of the film. When the nanoparticle diameter is close to the thickness of the membrane, the shape of the nanoparticles will remain unchanged and the ball-bearing mechanism will dominate [83][84].

When the nanoparticles are spherical in shape, they can act as a kind of ball-bearing during friction [85][86][87], thus improving the lubrication performance. Alazemi et al. [88] synthesized CS-MoS_2 particles and added them to engine oil (SAE 5W30) and studied the tribological properties of the lubricant blend using a friction and wear meter. When 1 wt % CS-MoS_2 particles were kindly added to the engine, there was a significant reduction in friction and wear (15–35%) compared to the original reference oil at various disk speeds. Raman spectroscopic investigations of wear scars after tribological tests showed that the CS-MoS_2 particles were highly chemically stable. The improved tribological performance of the CS-MoS_2 and engine oil blend lubricant was attributed to the fact that the CS-MoS_2 particles prevented direct contact between the sliding surfaces and acted as particulate ball bearings on the nanoscale.

4.3.2. Shear Slip

MoS_2 has good lubricating properties due to its unique crystal structure. Within each molecular layer of MoS_2, sulfur atoms are strongly bonded to molybdenum atoms through covalent bonds, while sulfur atoms between the layers are connected to molybdenum atoms through weak van der Waals forces. As a result, a low-shear plane is formed. When a small amount of shear force is applied between the molecules, the molecular layer breaks easily and a slip plane is created.

Xie et al. [89] pointed out that the tribological mechanism of lamellar nanocomposites is different from that of spherical nanocomposites. They concluded that the lamellar nanocomposites were able to provide lower COF and lower wear rate due to the shearing effect of weak van der Waals bonds between molecular layers. Compared to spherical nanocomposites, sheet nanocomposites are less likely to roll on the friction surface.

4.3.3. Tribofilm Formation

Numerous studies have shown that nanoparticles tend to migrate toward the friction surface during the friction process due to two factors. One is that the localized high temperature caused by friction may cause the undulation of nanoparticles on the friction surface to be greater than that of nanoparticles in the nanofluid. Due to this undulation, random migration is more active and ultimately increases the chances of nanoparticles migrating to the friction surface. Secondly, the acceleration of escaping electrons generated during friction enhances the electric field at the friction surface, the presence of which may lead to the aggregation of nanoparticles at the friction surface [90].

Wu et al. [91] investigated the effect of different percentages of polyisobutylene amine succinimide (PIBS) on the tribological properties of MoS_2 nanosheets. At low percentages of PIBS and without any PIBS, the nanosheet aggregates gathered in front of the contact area tend to enter the contact area and form a uniformly distributed friction film in the contact area, effectively reducing the coefficient of friction (COF) and the amount of wear. When lubricated with a high percentage of PIBS, the discrete particles tend to move and spread around/away from the contact region due to lateral flow, and thus the particles cannot enter the contact region resulting in poor lubrication performance.

4.3.4. Cooperative Lubrication

The lubrication ability of nano MoS_2 can be enhanced by utilizing the synergistic effect of nano MoS_2 with other materials [89][92][93]. MSH-reinforced MoS_2 hybrid nanocomposites synthesized by Guan et al. [78] as lubricant additives produced a strong two-layer friction film on the friction surface during sliding due to the synergistic effect of MSH and MoS_2; the upper layer was rich in MoS_2, which had an excellent friction-reducing effect, and the neighboring layer, which consisted of the reaction products of the MSH and the lubricant additives with the substrate, strongly ensured the stability of the first layer, which resulted in the reduction of friction and wear.

4.3.5. Other Mechanisms

Apart from the aforementioned mechanisms, other mechanisms have also been demonstrated such as repair and inlay, elastic deformation, and stripping. During the friction process, nanoparticles fill and repair the microcracks on the surface by desorption or deposition, which eventually results in a smoother and more even friction surface. It is worth noting that the “self-healing” mechanism is not just about the accumulation of nanoparticles on the friction surface. As the size of the nanoparticles reduces, their melting point also decreases drastically. Under the high temperature of the friction surface, these nanoparticles can easily melt or sinter in the microcracks in the contact zone, forming ordered nanoparticles and closely bonding with the friction surface [90].

4.3.6. Diversification of Lubrication Mechanism

It is worth noting that in most practical friction processes, nanoparticles do not act through a single lubrication mechanism, but rather two or more mechanisms act simultaneously [90]. The combination of different mechanisms leads to some extent to the complexity of mechanism studies. Kumari et al. [94] showed that when fully dispersed MoS_2-ODT was used as an additive in polyol lubricant base oils, the uninterrupted supply of MoS_2-ODT nanosheets on the friction contact surfaces resulted in the formation of MoS_2 films at the friction interface, and the easy shear driven by weak van der Waals interactions between the MoS_2 lamellae and the high mechanical strength of MoS_2 combined to improve friction performance.

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