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Advances in the Study of Quantum Dots as Lubricant Additives: A Review

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Author's contribution

The sole author designed, analysed, interpreted and prepared the manuscript.

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Review Article

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ABSTRACT

The study of quantum dots as lubrication additives has gained much attention in recent years, and has shown potential advantages in the field of lubrication due to their excellent physical and chemical properties, especially at the nanoscale. Quantum dots are nanoscale semiconductor particles with quantum effects, which are usually between 2 and 10 nanometres in size, with a large specific surface area and a special electronic structure. As lubricant additives, quantum dots enhance lubrication performance by improving the viscosity of the lubricant, lowering the coefficient of friction, reducing wear, and improving corrosion and oxidation resistance. At present, the research of quantum dots as lubrication additives is still in the exploratory stage, but with the development of nanotechnology, the application of quantum dots in the field of lubrication is promising, especially in the field of aerospace, automotive, machinery and equipment and other high-performance requirements, which has an important potential for application. This paper reviews the research and development progress of quantum dots lubricant additives, as well as many successful applications of quantum dots lubricant additives at present, and focuses on the friction reduction and anti-wear performance, superiority and lubrication mechanism of quantum dots as lubricant additives.

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Keywords: Quantum dots; lubricant additives; friction; wear; lubrication mechanism.

1. INTRODUCTION

“Friction exists in people's lives; on the one hand, people need friction to live and produce, and on the other hand, they need to overcome friction in order to reduce energy loss. Friction can cause wear and tear of components, affecting the smoothness and accuracy of the work, when the machine is running with relative movement of the surface will produce friction, due to the long time of relative movement, the surface is constantly consumed, changing its size, seriously affecting the performance of the work” [1]. “Friction will also cause energy consumption, so that the mechanical efficiency is reduced, according to statistics, at present, 30% to 50% of the world's energy is consumed in the friction loss, directly affecting the service life of machinery and productivity” [2], the progress of lubrication technology has become the key to ensure the stable operation of machinery and equipment.

“In today's world, with the rapid development of industrial technology and the increasing complexity of mechanical systems, the performance requirements for lubrication materials are also higher and higher, and the operational efficiency and life expectancy of machinery and equipment are increasing. In the aerospace, precision machinery and heavy equipment sectors, traditional lubricants have struggled to meet the demands of extreme operating conditions” [3]. Therefore, the research and development of new lubricant materials, especially lubricant additives with high performance, has become a hot topic in the field of materials science and tribology. As a newly focused research area, quantum dots, due to their unique physicochemical properties and size effect, have shown great potential for application in the field of lubrication in recent years.

“Quantum Dots (QDs) usually have an ideal spherical or quasi-spherical shape with an ultra-small particle size, which allows them to enter the friction surface to form a deposition or adsorption film, which helps to minimize friction and anti-friction [4]. Then, under severe friction conditions, the formation of deposited or adsorbed film will gradually transform into a strong friction film. In addition, the core of QDs-based nano-additives can act as a ball bearing to provide a nano-lubrication effect to further reduce the friction and wear of the friction pair” [5,6]. Thus, QDs-based nanomaterials as additives can significantly improve the lubrication performance of lubrication systems. Inspired by their extraordinary tribological functions, extensive efforts have been made to develop innovative QDs-based nano-additives.

The aim of this review is to discuss the latest research progress of quantum dots as lubrication additives, including their synthesis methods, surface modification techniques, performance in different lubrication systems, and their lubrication mechanisms.

2. CARBON-BASED QUANTUM DOTS

Carbon-based nanomaterials have received significant attention in the field of nano-lubrication additives due to their environmental friendliness, excellent self-lubricating properties, superior chemical and thermal stability, and remarkable mechanical properties. Nevertheless, these materials have some significant drawbacks in practical applications [7]. For example, nanographite, carbon nanotubes and graphene are still microscopic materials in some dimensions, which may lead to their insufficient embedding stability at friction interfaces. In addition, most carbon-based nanomaterials have chemically inert surfaces that are difficult to chemically modify to enhance their dispersion stability in lubricants. This makes them susceptible to aggregation during friction, which in turn exacerbates the wear of the friction surface due to severe abrasive wear and sometimes even degrades the tribological performance of the lubricant. These shortcomings somewhat weaken the tribological performance of conventional carbon-based nanomaterials and severely limit their commercialization potential [8,9].

2.1 Carbon Quantum Dots (CQDs)

Carbon quantum dots (CQDs), a new type of zero-dimensional carbon-based nanomaterials after fullerenes, carbon nanotubes and graphene, are receiving more and more attention in the fields of materials and chemical sciences due to their excellent properties such as low toxicity and environmental friendliness, homogeneous size distribution, easy preparation and functionalization, high chemical and thermal stability, and good designability [10]. It is becoming an extremely promising candidate for solving many difficult scientific and technological problems in the fields of biology, materials and chemistry [11].

2.1.1 CQDs as water-based lubrication additives

"It is well known that water-based lubricants can be used in a variety of industrial applications and manufacturing processes for different needs due to their many advantages such as low cost, high safety, good thermal conductivity, good cooling properties, environmental friendliness, and compatibility. Most CQDs exhibit good water dispersibility due to their surfaces being modified by abundant oxygenated and hydrophilic functional groups" [12,13]. Therefore, CQDs can be used directly as water-based lubricant additives without any dispersant.

Xiao et al. [14] prepared "sulfur-doped CQDs by a one-pot hydrothermal method using sodium citrate as the carbon source and sodium thiosulfate as the sulfur source; the prepared CQDs were then mixed with DI water as a water-based lubricant". The results showed that the CQDs were well dispersed and spherical in solution with an average diameter size distribution of 4.8 nm, as shown in Fig. 1. In addition, the tribological properties of the CQDs as additives in deionized water were evaluated in detail. The results of tribological tests showed that the maximum reduction of the average coefficient of friction was 30% and 14% for Si3N4-steel contact and Si3N4-Si3N4 contact, respectively. In addition to the excellent friction reduction performance, the addition of CQDs significantly improved the anti-wear performance of deionized water.

Liu et al. [15] synthesized carbon dots ionic liquid (CD-IL) with an average particle size of about 1.73 nm using a one-pot pyrolysis method, and the morphology of CDs-IL was uniformly spherical and poorly crystalline. It was shown by infrared experiments that the IL (1-aminopropyl-3-methylimidazolium bromide) molecule was covalently attached to the surface of CDs-IL through amide bonds. CDs-IL was directly added to the base fluid consisting of water and 2 wt% triethanolamine (a common rust inhibitor for water-based lubricants) to form a water-based lubricant with CDs-IL as an additive, and its tribological properties were evaluated. CDs-IL not only improved the load carrying capacity of the base fluid, but also significantly improved the friction reduction and antiwear properties of the base fluid. When the optimum value of CDs - IL was 0.05 wt.% and the load was 50 N, the load carrying capacity of the base fluid was increased from 70 N to at least 90 N, and the coefficient of friction and wear volume were reduced by 65% and 60%, respectively.

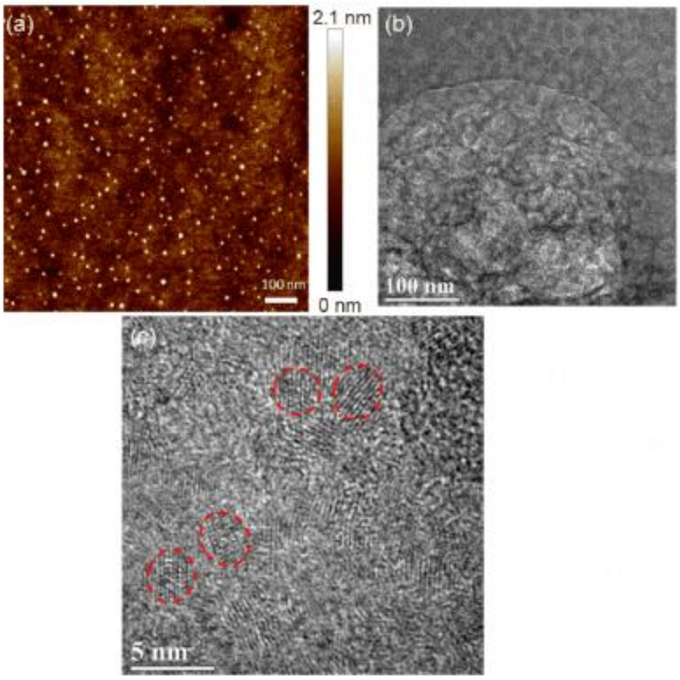

Fig. 1 (a) AFM image of CQDs; (b) high-resolution TEM image of CQDs; dashed circles in (c) indicate individual CQD particles [14]

In addition, Hu et al. [16] proposed “a simple and low-cost bottom-up method for the preparation of water-soluble carbon dots (CDs) by adjusting the degree of carbonization of ammonium citrate. Compared to graphene oxide, CDs have lower friction and significant wear reduction properties. In addition, CDs is also an effective corrosion inhibitor with a corrosion inhibition efficiency of up to 60.01% compared to deionized water. The results indicate that CDs prepared by one-pot pyrolysis of ammonium citrate can be used as an environmentally friendly nanoadditive to improve the lubrication and corrosion inhibition properties of water-based lubricants”.

In general, carbon quantum dots are well dispersed in water, and as water-based lubricant additives, carbon quantum dots exhibit excellent friction reduction and anti-wear properties, which can effectively reduce the coefficient of friction and wear rate. In addition, Carbon Quantum Dots can improve the load carrying capacity and corrosion inhibition of the lubrication system.

2.1.2 CQDs as oil-based lubricant additive

Ionic liquid (1-aminopropyl-3-methyl-imidazolium bromide) coated carbon dots (CDs-Br) with an average particle size of 1.73 nm and poor crystallinity were prepared by a one-pot pyrolysis method by Wang et al [17]. CDs-Br was changed to CDs-NTf2 by an anion exchange reaction of Br- with N(CF3SO2)2- (NTf2-).NTf2- gave CDs-NTf2 good dispersion stability in the synthetic lubricant polyethylene glycol (PEG). The tribological properties of CDs-NTf2 as a PEG lubricant additive were also investigated in detail. The results showed that the CDs-NTf2-based additive has excellent friction reduction and antiwear properties. In particular, the wear scar diameter and friction coefficient of the ball under PEG lubrication were reduced by 33% and 70%, respectively, when 0.3 wt% of CDs-NTf2 was added at 392 N, as shown in Fig. 7. When the test load was increased to 600 N, the wear scar diameter reduction rate further increased by 45%, and the CDs-NTf2-based additive could work for a long time without weakening the lubrication capability. The lubrication mechanism of CDs-NTf2-based additives is proposed, and it is shown that the synergistic lubrication effects of CDs-NTf2, including membrane lubrication of the IL base and nano-lubrication of the carbon core, such as rolling, patching, and polishing effects, may be responsible for their excellent tribological behaviour.

Shang et al. [18] synthesised “carbon quantum dots-ionic liquid hybrid nanomaterials (CQDs-IL) with a spherical shell structure by chemical grafting. Carbon quantum dots (CQDs) with an average diameter of 2.0 nm were firstly synthesized by a simple ‘bottom-up’ method, and then CQDs-OHMimBScB with an average diameter of 7.5 nm was synthesized by covalently grafting with 3-hydroxypropyl-3-methylimidazolium bis(salicylate) borate (OHMimBScB)”, as shown in Fig. 8. The synthesized CQDs-OHMimBScB hybrid nanomaterials have good solubility stability in PEG at concentrations up to 30% or more without any dispersant, and the prepared clear solutions are homogeneous for more than 6 months without obvious precipitation. The tribological properties of CQDs-OHMimBScB as lubricant additives were investigated by using a four-ball testing machine with different concentrations and test loads. Compared with PEG, OHMimBScB, CQDs and their blends, CQDs-OHMimBScB as a lubricant additive has better wide-load lubrication performance under boundary lubrication conditions, with maximum reductions of friction coefficients of 75.2%, 74.5%, 35.0% and 38.3%, and maximum reductions of wear of 92.2%, 57.1%, 52.5% and 50.9%. In addition, the friction reduction performance of CQDs-IL was also significantly improved at high loads and functional durations. The synergistic effect of the strong adsorption of CQDs nano-lubricant and IL and the co-deposition effect of carbon and borate elements at the interface after the friction chemical reaction effectively protects the surface from friction wear.

Inorganic-organic hybrid carbon quantum dots (CQDs-N) with a diphenylamine (DPA) structure attached to the surface were prepared by a low-temperature one-step pyrolysis method by Ye et al [19]. In order to investigate the antioxidant properties of CQDs-N, the oxidative stability of CQDs-N in PEG at different concentrations (0, 0.25, 0.5, 1, 1.5, 2 wt%) was evaluated by isothermal PDSC. In order to shorten the test time, the test temperature was chosen to be 180 °C with a certain time before OIT, and the temperature was increased and maintained for 4.6 min. As shown in Fig. 2, the antioxidant reaction of PEG without any additives failed to exhibit oxidative stability. In contrast, the OIT increased to 2.9, 5.2, 11.6, 17.0 and 23.7 min after the addition of different concentrations of CQDs-N (0, 0.25, 0.5, 1, 1.5, and 2 wt%) to the PEG, respectively. In addition, they found that the OIT was positively correlated with the concentration of CQDs-N, which indicated that the CQDs-N indeed conferred antioxidant properties to the PEG. And a possible antioxidant mechanism of CQDs-N in PEG was proposed as shown in Fig. 3. It is well known that the autoxidative degradation of base oils with organic hydrocarbons (RH) as the main component is a free radical chain reaction.RH undergoes a chain initiation reaction under the action of heat and light to generate alkyl radicals (R-).The rapid reaction of R- with O2 generates alkyl peroxy radicals (ROO-). It is this harmful radical ROO- that further forms the candle base oil, which reacts with RH to form R- and the initial product, hydrogen peroxide (ROOH). CQDs-N containing a diphenylamine (DPA) structure acts as a free radical scavenger. The N-H bond in the DPA of CQDs-N provides its own hydrogen atoms to ROO- through easy cleavage to prevent ROO- from attacking RH. In addition, the produced CQDs-N not only has antioxidant properties, but also has anti-wear and friction reduction properties as an additive to PEG. When the optimum concentration of CQDs-N was 1 wt%, the average coefficient of friction and wear scar diameter were significantly reduced by 75% and 34.8%, respectively. The produced N-doped carbon dots (CQDs-N) are spherical particles with narrow particle size distribution and excitation dependence, which is a multifunctional additive with dual properties of antioxidant and anti-wear and friction reduction.

The results showed that CQDs have good tribological and antioxidant properties and are a promising additive for industrial lubricants.

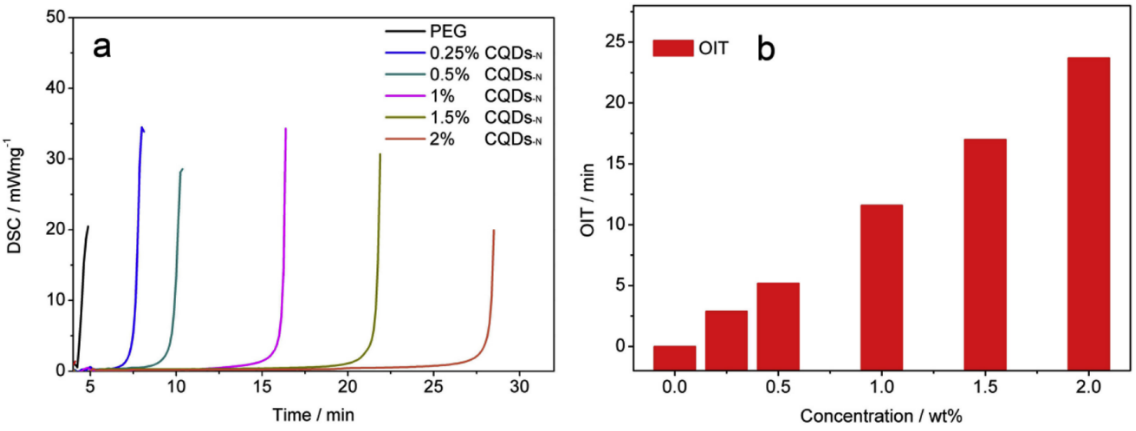

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Fig. 2 Antioxidant response and OIT of CQDs-N at various concentration in PEG measured [19]

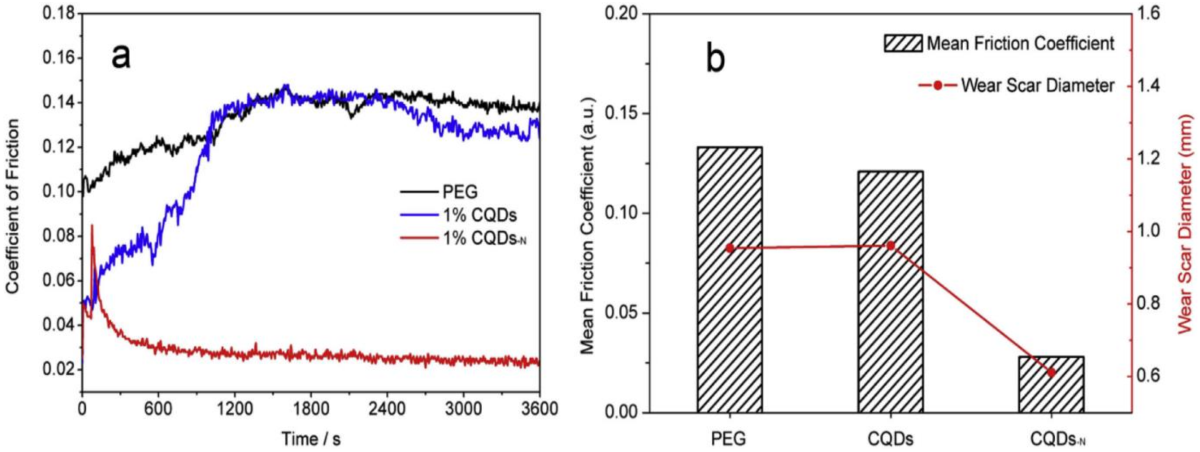

Fig. 3. (a)Friction coefficient curves, (b) mean friction coefficient and wear scar diameter lubricated by CQDs and CQDs-N (1 wt%) in PEG (load =392N; temperature =75 °C; rotate speed =1200 rpm; duration =60 min) [19]

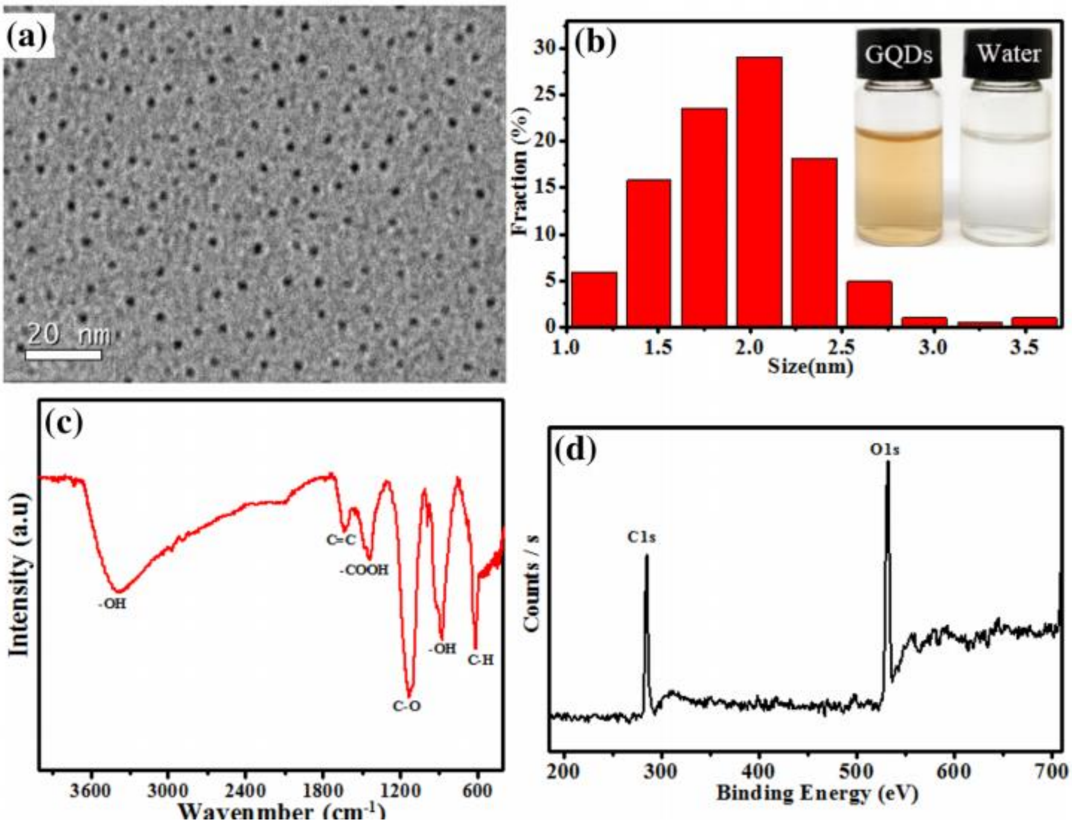

Fig. 4. (a) TEM image of GQDs, (b) size distribution of prepared GQDs, (c) FTIR spectra, (d) XPS measurement spectra of GQDs [20]

2.2 Graphene Quantum Dots

Qiang et al. [20] synthesised graphene quantum dots (GQDs) by a simple hydrothermal method and evaluated their tribological properties as additives for water-based lubricants. Transmission electron microscopy morphological observations showed that uniform, monodisperse GQDs could be obtained with an average diameter of about 2 nm (Fig. 4(a), (b)). Fourier-transfer infrared spectroscopy and x-ray photoelectron spectroscopy characterisation showed that abundant hydrophilic groups, including hydroxyl, epoxy and carbonyl groups, existed on the prepared GQDs, which resulted in good dispersion of GQDs in water (Fig. 4 (c), (d)). Compared with graphene oxide, GQDs showed better enhancement of tribological properties in water at lower concentrations. When the concentration of the aqueous dispersion of GQDs was 4 mg/mL, GQDs-4 had excellent tribological properties, with a 42.5% reduction in the coefficient of friction and a 58.5% reduction in the wear rate of GQDs-4 compared to the aqueous dispersion. These good properties indicate that the prepared GQDs can be used as a novel water-based lubricant additive, which greatly improves the tribological properties of water.

Liu et al. [21] successfully solved “the problem of using graphene oxide quantum dots (GOQDs) as nano-additives in aqueous ethylene glycol solution, which could reduce the coefficient of friction between silicon nitride and sapphire to 0.0068 (superlubricated state) with a wear period of only 6 s. Compared to lubrication in aqueous ethylene glycol solution without GOQDs, the wear period was shortened by 95.7%, and the amount of wear was reduced by 90.0%”. Under pure water lubrication, the average COF was around 0.24 at the beginning of the friction test and then gradually decreased to 0.21 (Fig. 5 (a)). Differently, under the lubrication of ethylene glycol (EG) solution, the COF could reach a high level of around 0.38 at the initial stage of the friction process, and then suddenly decreased to around 0.05 during the 30 s friction process, and then gradually decreased to the super-lubricated state after 150 s friction, and maintained at a low value of around 0.0073. However, lubricating the EG solution with GOQDs as nanoadditives reduced the initial COF during friction by 81.8% and shortened the break-in period before reaching superlubrication by 95.7% compared to EG lubrication (Fig. 5 (b)). The COF could be reduced to the superlubricated state with a very small COF of about 0.0068 during the break-in period of 6 s. The lubrication performance was investigated by variable speed friction test (Fig. 5 (c)). When the sliding speed was in the range of 0.025-0.25 m/s, both the EG solution and the EG solution with GOQDs as nanoadditives could reach the superlubricated state, and there was no significant difference in the COF between them. However, a significant increase in COF can be observed with a further decrease in sliding velocity. Under the lubrication conditions of 0.004 m/s, 0.002 m/s, 0.001 m/s and 0.0004 m/s, the COFs of GOQDs were 0.226, 0.233, 0.499 and 0.532, respectively, whereas with the addition of GOQDs as a nano-additive, the COFs could be reduced to 0.086, 0.149, 0.237 and 0.337, respectively. It shows that GOQDs have excellent friction reduction performance at lower sliding velocities, and the friction reduction performance can reach 61.9%. At the end of the friction test, the wear volume and wear scar diameter of the silicon nitride balls were examined using white light interference microscopy (Fig. 5 (d)). The addition of GOQDs reduced the wear scar diameter and wear volume of Si3N4 balls by 45.8% and 90.0%, respectively, after 10 min of friction. The results indicate that GOQDs have excellent antiwear properties as additives for EG.

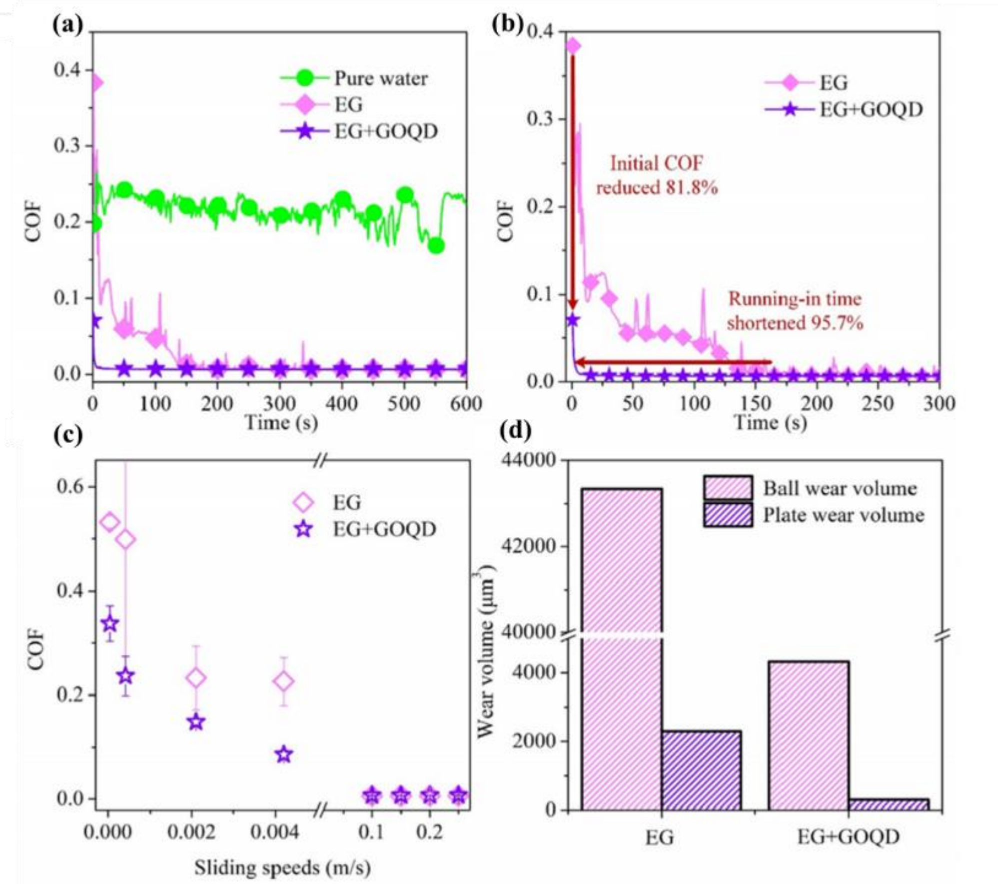

Fig. 5. (a) Evolution of lubrication COF with time (15N, 0.1m/s) for pure water, EG solution and EG solution with GOQDs as nanoadditives. (b) Comparison of the lubrication properties of EG solutions with EG solutions with GOQDs added (15N, 0.1m/s). (c) Comparison of COF under lubrication by EG solution with COF under lubrication by EG solution with GOQDs added at different sliding speeds under 15N normal load, where the error bars indicate the standard deviation of the mean COF under steady conditions in the friction test at different variable speeds. (d) Wear volumes of some wear tracks on the silicon nitride balls and sapphire plates after a 10 min (15 N, 0.1 m/s) friction test [21]

3. BLACK PHOSPHORUS QUANTUM DOT

"Two-dimensional (2D) layered nanomaterials, such as graphene, transition metal disulfides , hexagonal boron nitride, carbon nitride , MXene, and zirconium phosphate, have shown high potential in the field of aqueous-based lubricant additives" [22,23]. "The use of these nanomaterials as additives can effectively improve the friction reduction and antiwear properties of lubricants; however, they have some drawbacks, including poor dispersion stability, inhomogeneous particle size, and poor embedding stability between friction surfaces" [24].

"These drawbacks lead to the low tribological performance of conventional 2D nanomaterials, thus limiting the prospect of the materials' application in water-based lubrication. Therefore, there is a need to explore new 2D nano-additives with uniform particle size distribution, good dispersion stability in water and high stability on rough surfaces. Black phosphorus (BP), as a novel 2D layered nanomaterial, has received widespread attention due to its excellent physicochemical and mechanical properties, which have promising applications in the field of tribology" [25,26]. "Pioneering studies have shown that BP and its composites are useful as lubricant additives and can provide excellent lubrication due to their superior properties" [27,28]. However, BP-based materials are not commonly used as water-based lubricant additives due to their low dispersion stability in water. Ultra-miniaturisation, especially nano-miniaturisation, is an effective way to improve this property of BP-based materials.

Ren et al. [29] prepared black phosphorus quantum dots (BPQDs) with low cost and high yield by liquid-phase high-energy ball milling. Bulk BP powders were first synthesised from RP red phosphorus with >99% purity using high energy ball milling (HEBM) technique. Then 0.1 g of bulk BP powder was dispersed in 20 ml of ethanol and poured into a 50 ml sealed stainless steel ball mill bottle. About 100 g of stainless steel balls with diameters of 10 and 5 mm were used as grinding balls. The grinding process was carried out at 600 rpm for 6 h. Subsequently, the obtained dispersion was centrifuged at 10,000 rpm for 20 min and the supernatant containing BPQDs was gently poured out. Three polyhydroxy alcohols, ethylene glycol (EG), 1,3-propanediol (PG) and 1,4-butanediol (BG), were used as solvents to improve the stability of BPQDs. The ethanol solution of BPQDs was mixed with different kinds of polyhydroxy alcohols in the ratio of 1:1, and then evaporated under vacuum at 60 °C for 10 h. The obtained mixtures were labelled as BPQDs-EG, BPQDs-PG, and BPQDs-BG, respectively. In addition, the ethanol solution of BPQDs was also prepared in the ratios of 1:0.1, 1:3, and 1:5 with respect to the ratio of EG, respectively, for three different concentrations of BPQDs, and the effect of concentration on their lubricating properties was investigated. The corresponding aqueous suspensions were prepared by dispersing the BPQDs-PA suspensions in deionised water at a concentration of 20 wt.%, which were denoted as BPQDs-EGaq, BPQDs-PGaq and BPQDs-BGaq, as shown in Fig. 6.

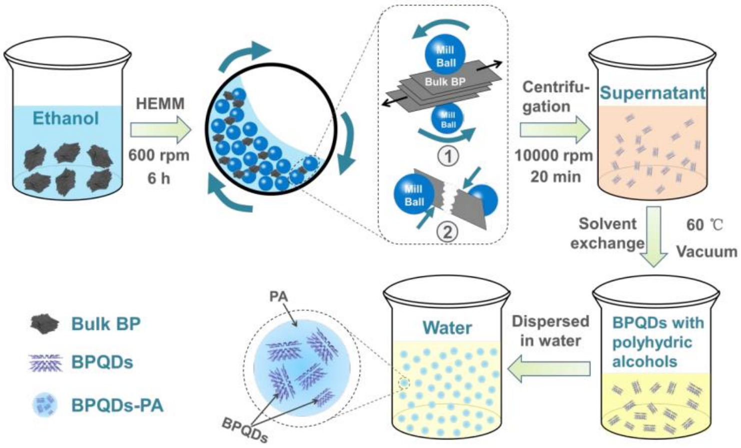

Fig. 6. Schematic representation of the synthesis process of BPQDs and aqueous solution of BPQDs with polyhydroxy alcohols (BPQDs- PA) [29]

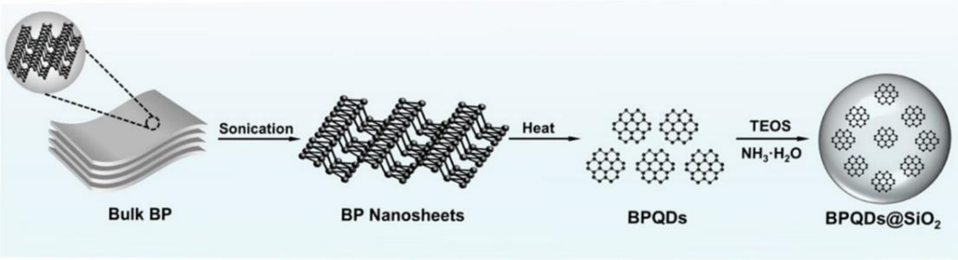

Fig. 7. Synthesis process of the BPQDs@SiO2 core−shell material [30]

It is found that a robust macroscopic superlubrication state (μ: 0.002) can be achieved by the lubrication of BPQDs-EGaq suspensions at the Si3N4/sapphire friction interface, even at a high contact pressure of 336 MPa. Compared to EGaq and micron-scale BP-EGaq, BPQDs-EGaq shows superior lubrication and anti-wear properties, which are mainly attributed to the rolling effect of BPQDs and the low shear strength of the interlayer. In addition, the oxidation product (PxOy) of BPQDs contributes to the effective realisation of macroscopic superlubricity.

Despite the good lubricating properties of BPQDs, they are susceptible to environmental degradation, leading to phosphate failure a problem that seriously hampers the application of BPQDs.Dong et al. [30] prepared BPQDs@SiO2 core-shell materials by sol-gel method, as shown in Fig. 7. BPQDs are uniformly distributed within the SiO2 shell and rarely free from the shell. The results show that the BPQDs@SiO2 lubricant has good dispersion, stability and lubricity. Add 0.05 wt% under friction conditions of 10 N and 150 r/min BPQDs@SiO2 Lubricating additives can reduce the average friction coefficient and wear rate by 45.7% and 83.0%, respectively. The tribological performance was better than that of ultrapure water and other lubricant additives when the load was increased, indicating that the BPQDs@SiO2 lubricant additive had excellent lubrication and stability.The lubrication mechanism of the BPQDs@SiO2 lubricant additive was mainly related to the polishing property of SiO2, the high extreme pressure performance of BPQDs and the friction chemical reaction film; the synergistic lubrication effect of SiO2 and BPQDs was revealed by the FE-SEM image, the depth map of the 3D image and high-resolution XPS analyses, the synergistic lubrication effect of SiO2 and BPQDs was revealed. The results show that the BPQDs@SiO2 core-shell material has good tribological properties, which is necessary to achieve the stable application of BPQDs in water.

4. MOLYBDENUM DISULPHIDE QUANTUM DOTS

Fullerene-like molybdenum disulfide nanoparticles can easily penetrate the contact area and form a uniform friction film for low friction wear [31,32]. The preparation of molybdenum disulfide nanoparticles as petroleum additives has been studied more; however, it is very difficult to prepare molybdenum disulfide quantum dots with a particle size of less than 5 nm as lubricant additives compared to nanosheets. Molybdenum disulfide quantum dots have smaller particle size and higher specific surface area, which are more favourable for dispersibility, and therefore have great potential as lubricant additives.

Ju et al. [33] prepared “molybdenum disulfide quantum dots in situ for the first time by combining ricinoleic acid and choline. Molybdenum disulfide quantum dots can be obtained by a simple one-step synthesis. The physicochemical and tribological properties of the obtained MoS2 quantum dots were systematically investigated. The MoS2 quantum dots in liquefied liquids with long-term dispersion stability showed superior lubrication properties under severe conditions compared to pure liquefied liquids, significantly reducing the coefficient of friction and wear volume of polymers at high temperatures and heavy loads. The formation of thin films based on XPS results is considered to be the main reason for the better tribological properties of MoS2 quantum dots in ILs than pure ILs”.

Guo investigated the tribological properties of molybdenum disulphide quantum dots as lubricant additives in paraffin oil [34]. A ball-and-disc friction test was carried out under boundary lubrication conditions to simulate the point contact between mechanical components, and the effect of molybdenum disulphide quantum dots on the tribological properties was investigated. In addition, the MoS2 quantum dots were continuously dispersed in paraffin oil, and there was no particle settling during the 10-day dispersion experiment. After the addition of MoS2 quantum dots to paraffin oil, the 0.3 wt.% MoS2 quantum dot oil sample had the lowest COF of 0.061, which was about 64% lower than that of the pure paraffin base oil. With the increase of MoS2 quantum dots, the friction time was significantly shortened, as shown in Fig. 8. The main type of wear on the wear surfaces lubricated by the phosphoric acid base oil containing molybdenum disulphide quantum dots was slight ploughing wear. The pure poly(naphthol) oils showed significant furrows and indentations with a maximum depth of 2.8 µm. molybdenum disulphide quantum dots played a decisive role in the improvement of the frictional properties. Potential lubrication mechanisms include the formation of a composite friction film consisting of MoS2, MoO3, FeS and Fe3SO4. In addition, the spherical molybdenum disulfide quantum dots may have a ball lubrication effect during the friction process.

5. NITROGEN CARBIDE QUANTUM DOTS

In the past few years, graphitic carbon nitride quantum dots (g-CNQDs), one of the innovative and environmentally friendly derivatives of graphitic carbon nitride (g-C3N4), which mainly consists of C and N, has become a new star in the materials, chemical and medical fields due to its environmentally friendly synthesis route [35], good chemical stability [36], excellent optical properties [37], and good biocompatibility [38]. A rapidly growing area of interest in the field of materials, chemistry and medicine. Therefore, g-CNQDs, like other qds-based materials, have received increasing attention in many fields such as photocatalysis, biomedicine, photovoltaics, and sensors. In addition, g-CNQDs have the unique characteristics unique to highly efficient lubricant additives such as good designability, good self-lubrication effect, high mechanical strength, good film-forming ability, low production cost, high yield, etc., and they have a broad application prospect in the field of water-based lubrication. Although g-CNQDs as nano-additives can predictably improve the lubricating properties of base lubricants, relevant research involving g-CNQDs-based lubricant additives is still in its infancy. Therefore, the development of new g-CNQDs nano-additives will further broaden the application scope of g-CNQDs and enrich the variety of water-based nano-additives.

Tang et al. [39] prepared g-C3N4 powder by thermal polymerisation of melamine molecules. Notably, the method is simple, low cost and high yield. They prepared g-CNQDs-12, g-CNQDs-24, g-CNQDs-36, and g-CNQDs-48, respectively, where 12, 24, 36, and 48 refer to hydrothermal reaction times in hours, as shown in Fig. 9.

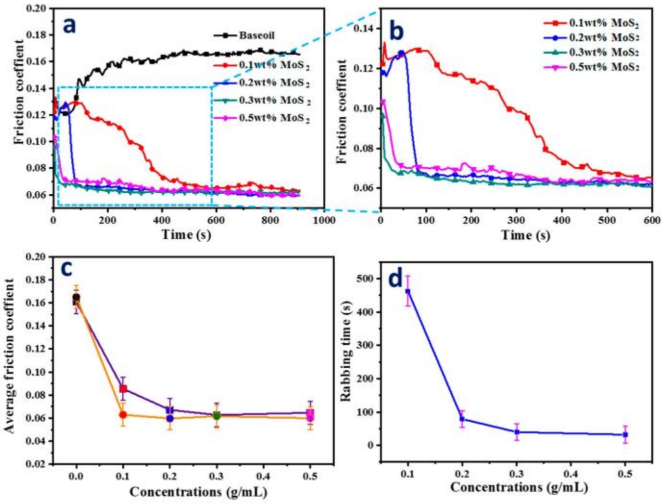

Fig. 8. (a) Tribological test results of paraffin oil with different amounts of molybdenum disulphide quantum dots added; (b) coefficient of friction (COF) of MoS2 quantum dots with different additions; (c) average and steady-state COF after friction; and (d) variation of friction time at different concentrations [34]

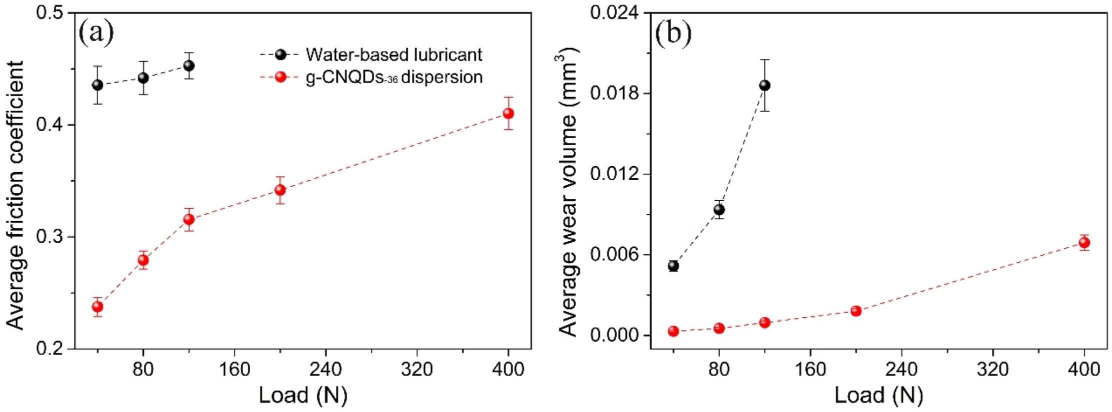

Fig. 9. (a) Average friction coefficient and (b) average wear volume of the water-based lubricant and 1.0 wt% of g-CNQDs-36 dispersion as a function of load. (Test conditions: 5 Hz, 20 min, and room temperature) [39]

According to the tribological evaluation results, the friction reduction and antiwear functions of g-CNQDs-based lubricant additives were ranked as follows: g-CNQDs-36 ＞g-CNQDs-24＞g-CNQDs-48＞g-CNQDs-12＞g-C3N4 powders＞ water-based lubricant. The average friction coefficients and average wear diameters of the water-based lubricants were reduced by 8.8% to 45.5% and 48.3% to 94.0%, respectively, when the g-CNQDs were added at a level of 1.0 wt%, with the best friction-reducing and anti-wear function of g-CNQDs-36. These results not only reflect the good tribological properties of g-CNQDs nano-additives, but also confirm that their tribological properties may be closely related to their particle size and physical size. The addition of gCNQDs-36 to the water-based lubricant increased the load carrying capacity from 120 N to more than 400 N, which was greater than 233%. In addition, the lubrication performance of g-CNQDs-36 dispersion (1.0 wt%) was not significantly attenuated when the friction test time and load were increased by 6 and 3 times, respectively, indicating that g-CNQDs-36 as an additive still possesses good tribological performance under severe working conditions. According to the results of wear track surface analysis, under severe friction conditions, the g-CNQDs dispersion undergoes a complex friction chemical reaction with the metal friction surface, which rapidly forms a strong and thick friction film. In addition, the gCNQDs embedded in the friction film and the exfoliated nanosheets derived from g-CNQDs will provide patching, polishing, rolling, and interlayer sliding effects to further reduce the frictional wear of the friction pair. the film-forming effect and multiple nanolubrication effects of the g-CNQDs are the main reasons for the good tribological performance of the lubrication system.

6. FRICTION MECHANISM OF QUANTUM DOTS AS LUBRICANT ADDITIVES

Exploring the lubrication mechanism of cqds is of special significance for understanding the excellent tribological properties of cqds and developing high performance lubricant additives. Currently, the exact mechanism of action of quantum dots additives is unknown, and determining the lubrication mechanism of quantum dots additives is still the subject of many research debates. In recent years, researchers have used various surface analysis and simulation techniques to propose plausible mechanisms for quantum dot-based lubricant additives. Currently, the lubrication mechanisms of cqds-based additives can be categorised into two dominant theories: (1) friction film formation, including physical and friction chemical films; and (2) nano-lubrication effects, including rolling, sliding, patching and polishing effects. It is worth pointing out that the specific mechanisms are related to the morphology, particle size distribution, chemical composition and crystal structure of the quantum dots.

6.1 Lubricating Film

It is well known that during friction, the surface of a metallic friction sub-surface becomes positively charged due to the emission of low-energy electrons from the point of contact. Many quantum dots commonly used in tribology are covalently modified by various ionic liquids and their derivatives, leading to the fact that the outermost layer of these quantum dots is usually covered by negatively charged anions; quantum dots in lubricants can be readily adsorbed on the friction surface through electrostatic interactions to form stable adsorption films [40,41]. Other types of quantum dots modified by non-ionic liquid groups and oxygen-containing groups can also form adsorption films on friction surfaces through van der Waals forces. At the same time, quantum dots also tend to deposit into the friction surface to form a deposition film, which acts as an adsorption film [42]. Usually, the adsorption film and the deposition film always coexist in the friction process, and work together to alleviate the friction and wear of the friction partner. In summary, the excellent film-forming ability of quantum dots can be attributed to the electrostatic and van der Waals interactions between the functional groups on the surface of quantum dots and the metal friction surface.

In addition, during friction, quantum dots may react with oxygen and nitrogen in the air as well as with the surface substrate to produce a friction-responsive film, which is effective in reducing friction and lowering wear. For example, in Tang et al.'s study [29], TEM cross-sectional images showed that a continuous, uniform, and dense friction film with a thickness of about 90 nm could be formed between the Pt protective layer and the steel substrate on the wear track lubricated by the BPQDs, as shown in Fig. 10 (a). In Fig. 10 (b) and Fig. 10 (c), it can be seen that the formed friction film is almost amorphous and embedded with many nanocrystals. In Fig. 10 (d), the EDS elemental maps of selected regions show that the friction film has high content of C, O, N, and P, and low content of Fe. This proves that the BPQDs form a friction-responsive film on the friction surfaces to reduce the friction and lower the wear.

6.2 Rolling and Sliding Friction Effects

Spherical nanoparticles can roll between the concave and convex surfaces of the friction surface and can enter the contact region of the friction surface, acting as tiny ball bearings and converting sliding friction into rolling friction at the microzone interface, thus significantly reducing friction and wear in the contact region [43]. Carbon quantum dots are essentially spherical or quasi-spherical and have a uniform size distribution. Meanwhile, carbon quantum dots have good embedding stability due to their abundant surface groups, which are not extruded out of the friction surface during friction [44]. The excellent embedding stability distinguishes it from conventional nanoparticles. However, under low load conditions, the shape and stiffness of the carbon quantum dots can be maintained, but the carbon quantum dots will be irreversibly deformed, thus losing their 'rolling bearing' role.

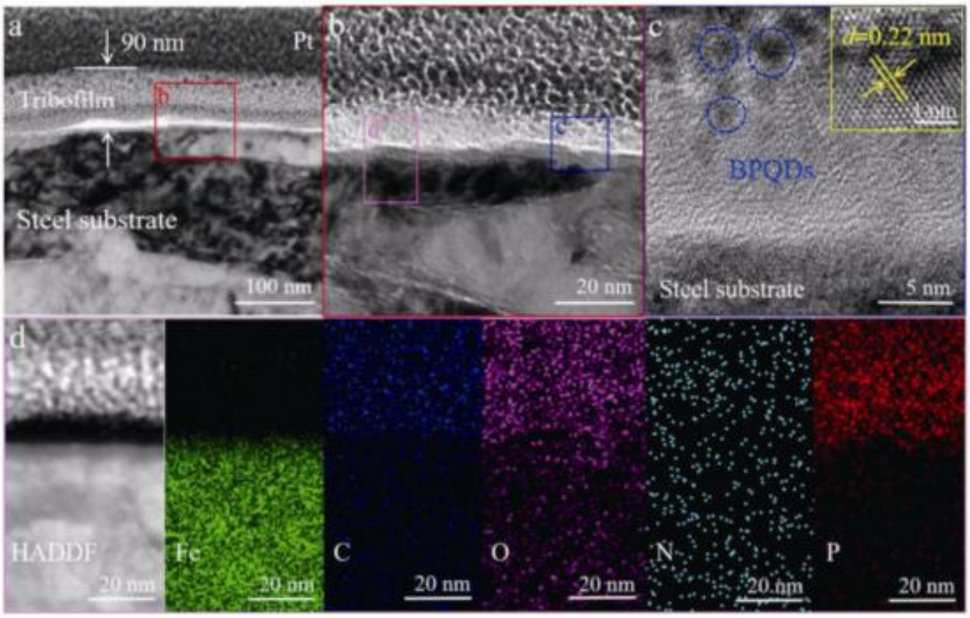

Fig. 10. (a-c) Bright-field transmission electron microscopy (TEM) cross sections and (d) EDS elemental maps of plate wear marks under lubrication of BPQDs dispersion (0.005 wt%). (Test conditions: 5hz, 20min, 40n, room temperature) [29]

Table 1. Types of quantum dot lubrication additives and lubrication mechanisms

Quantum Dot Lubrication Additives	Lubricants	Lubrication mechanisms	Referrence
Carbon quantum dots (CQDs)	deionized water, triethanolamine aqueous solution, PEG,	Lubricating film, Rolling friction effects, Repair effect	[14,15,16,17,18,19]
Graphene quantum dots (GQDs)	water, aqueous ethylene glycol solution	Lubricating film, Rolling friction effects, Repair effect	[20,21]
Black phosphorus quantum dots (BPQDs)	deionized water, ultrapure water	Lubricating film, Sliding friction effects, Repair effect	[29,30]
MoS2 quantum dots	paraffin oil	Lubricating film, Sliding friction effects, Repair effect	[33,34]
Graphitic carbon nitride quantum dots (g-CNQDs)	deionized water	Lubricating film, Sliding friction effects, Repair effect	[39]

Many of the quantum dots predecessors are a layered material that can be prepared by exfoliation in the form of single or fewer layers, and their quantum dots have similar two-dimensional properties. Examples include black phosphorus quantum dots, graphene quantum dots, and carbon nitride quantum dots. When two contact surfaces rub against each other under normal force, the 2D nanomaterials inside the contact surfaces are also subjected to normal pressure. The relative motion of the contact surfaces produces shear stresses on these materials. The easy shear and frictional contact between layers forms a sliding system [22,45].

6.3 Repair Effect

Nanoparticles can repair friction-induced surface defects and improve tribological performance. Through the effect of surface repair, the friction surface roughness is significantly reduced and the friction wear performance is significantly improved. The repair effect can effectively extend the service life of mechanical equipment, reduce material loss and energy consumption, and improve energy efficiency. The cqds-based lubricant additive (PEG) prepared by Wang et al. [17] can not only form a protective film on the friction surface, but also play a repairing role by filling deep scratches, which is a direct reason for the significant friction reduction and anti-wear performance under high loads.

7. CONCLUSIONS

In conclusion, the study of quantum dots as lubrication additives is still in the exploratory stage, but preliminary experimental results and theoretical analyses suggest that quantum dots may have a potential positive impact on lubrication performance. This review summarises the types and lubrication mechanisms of quantum dots as lubrication additives, as shown in Table 1. The size effect and quantum properties of quantum dots may enable them to exhibit unique behaviour in terms of lubrication performance, being able to form thin films on metal surfaces, thereby reducing direct contact between metal surfaces, lowering the coefficient of friction and reducing wear. Quantum dots can enhance the stability of the lubrication system, improve performance under extreme conditions such as high temperatures and high loads, and can increase oxidation resistance for longer service life.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc.) and text-to-image generators have been used during the writing or editing of this manuscript.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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