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Review

Structural engineering design of carbon dots for lubrication

Chuang He[a], Shuang E[b,*], Honghao Yan[a], Xiaojie Li[a]

[a] State Key Laboratory of Structural Analysis for Industrial Equipment, Dalian University of Technology, Dalian 116024, China
[b] Research Center for Analytical Sciences, Northeastern University, Shenyang 110819, China

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ABSTRACT

Carbon dots (CDs) have opened up a new field of carbon nanomaterials and successively attracted increasing attention since their discovery in 2004. Owing to their ultrasmall size, tunable surface functional groups, excellent dispersibility, attractive stability, low toxicity, environmental friendliness, facile synthesis and low-cost precursors, CDs have been developed as green and promising friction-reducing and anti-wear materials in lubrication science, applied to energy conservation and extension of mechanical service life in recent years. However, there are few reviews focusing on the application of CDs in the important field of lubrication. In this review, we comprehensively summarize the development of CDs in lubrication for the first time. Firstly, three strategies for structural engineering design of CDs to improve their tribological characteristics are fully analyzed, in terms of size and shape control, surface modification and heteroatom doping. Secondly, the advance in lubrication application of CDs, including CDs as additives for lubricants, greases, gel and magnetorheological fluids as well as CDs as lubricating coatings, is systematically highlighted. Thirdly, the lubricating mechanisms of CDs as additives are introduced in detail. Furthermore, the remaining major challenges and opportunities for CDs in lubrication field are discussed and outlined.

1. Introduction

Energy conservation and environmental protection is one of the most concerned topics for human development, but still remains a considerable challenge. For example, the friction and wear in modern industries accounts for more than 30% of fuel energy consumption used worldwide [1], causing enormous loss of energy and generating a large amount of greenhouse gas, thus dramatically exacerbating the issues of energy shortage, environmental pollution and global warming [2–4]. Besides, mechanical wear has shortened service life of equipment and increased in the cost of production [5,6]. Therefore, a great deal of research has been focused on the development of lubrication approaches to control friction and wear [7–12]. So far, using lubricants is the most popular and efficient way [13–15]. The additives in lubricants are the most important and indispensable components. Among them, friction-reducing and anti-wear agents are regarded as a significant role to improve the lubricating properties [8,16–18]. As a result, the efficient lubricant additives with excellent tribological properties have attracted extensive research.

Conventional lubricant additives including phosphorus, sulfur or chlorine elements, such as zinc dialkyl dithiophosphates (ZDDP), demonstrate favorable antifriction and anti-wear behaviors [19–22], but cannot meet the requirement of environmental protection because of the known environmental and biological hazards [23]. Over the last decades, nanomaterials considered as the most feasible and effective alternative have attracted more and more attention on account of their small size, high corrosion resistance as well as morphology and thermal stability [24–28]. Among them, carbon-based nanomaterials (Fig. 1), such as onion-like carbon (OLC) [29–31], fullerene [32,33], carbon nanotube (CNT) [34–36], nanodiamond [37,38], graphene [39–42], carbon sphere (CS) [43,44], mesoporous carbon nanoparticle (MCN) [45,46] and their derivatives [47–49], not only provide impressive results in tribological investigation, but also are green and environment-friendly compared to sulfur-containing molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2) nanomaterials [50,51], opening up a new way for the development of green and efficient additives. However, in practice, the application of these carbon-based nanomaterials in lubrication suffers from multitudes of unavoidable drawbacks: a) poor dispersibility and stability. The dispersion and stability are vital for tribological performance of lubricant additives [52,53]. Owing to their chemical inertness, the above carbon nanoparticles possess poor dispersibility and

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* Corresponding author.
E-mail address: llleshuang@126.com (S. E).

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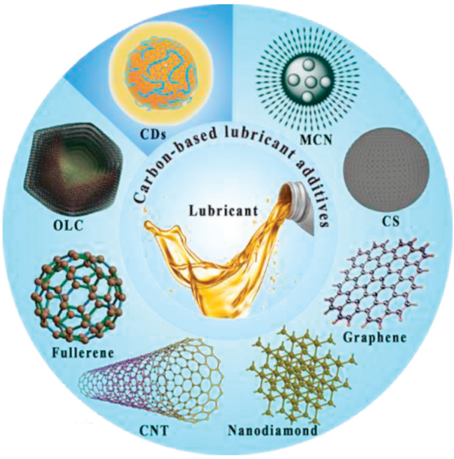


Fig. 1. Types of carbon-based nanomaterials as additives.

stability in lubricants, especially in water-based lubricants [39,40]. Although the dispersibility of the above carbon nanomaterials can be improved by adding surfactant or surface modification [34,36,42,48], these methods are high-cost and low-efficiency, restricting their widespread use; b) nonuniform size. The particle sizes of above carbon nanoparticles, such as carbon nanotube and graphene, are generally nonuniform [35,49], giving rise to the poor embedded stability between the micro-bulges of friction interfaces; c) unfavorable synthesis methods. The synthesis approaches of the above carbon nanoparticles are usually costly, low-yield, time-consuming and ecologically unfriendly. More importantly, complicated post-processing is inevitable, leading to the result that it is difficult to realize large-scale and high-purify synthesis for the above carbon nanoparticles [38,45]. Therefore, it is still urgently essential to make more efforts to further exploit green, efficient and low-cost lubricant additives.

Fortunately, carbon dots (CDs), incidentally discovered during purifying single-walled carbon nanotubes derived from arc-discharge soot in 2004 [54], have served as anti-wear and friction-reducing additives to improved tribological properties of lubricants and offered great potential for the development of green and efficient additives (Fig. 1) [55–57]. CDs generally are defined as spherical-like carbon nanoparticles with sizes below 10 nm and fluorescence as their instinct properties [58,59]. In sharp contrast to other reported carbon-based nanomaterials, CDs acting as a new class of lubricant additives have demonstrated a broad set of distinguished merits: a) excellent dispersibility and stability. Superior dispersibility and stability are the fundamental prerequisites for the practical applications of CDs in lubrication [52,53]. The abundant oxygen/nitrogen-containing surface functional groups endow CDs with dispersibility and stability in water [60–62]. More importantly, it is effortless and low-cost to accurately manipulate hydrophilicity and hydrophobicity of CDs by using different surface passivation agents or applying suitable precursors [63–65], making CDs available as the additives for water-based and oil-based lubricants [63,64]; b) low toxicity and environmental friendliness. Compared with semiconductor quantum dots, CDs have been proven to be low-toxicity and eco-friendly due to the absence of heavy metal elements, bringing about the widespread use in biosensing and bioimaging [60,65–67]. It is desirable for CDs to act as green lubricant additives; c) facile synthesis and low-cost precursors. By development of more than ten years, CDs have been economically and easily synthesized on a large scale by a wide variety of methods, such as microwave treatments, solvothermal method and thermal decomposition [65,67–70]. More recently, some sustainable and green preparation methods including base catalysis, self-exothermic synthesis and reduction methods are exploited in succession [71–73]. Meanwhile, a majority of carbonaceous materials, such as graphite, coal, leaves, grass, domestic waste, paper pieces, tire soot and plastic waste, are suitable for the use as low-cost precursors, further reducing the preparation cost of CDs [72,74]; d) high specific surface areas and uniform nanostructures. CDs with sizes below 10 nm are endowed with high specific surface areas. At the same time, CDs possess uniform nanostructures, normally containing he structures of sp^2/sp^3 carbon and oxygen/nitrogen-based groups or polymeric aggregations, making CDs easily participate in reactions at frictional interfaces to improve lubricating performance [1,52,57]. Therefore, on account of the above unique and outstanding advantages, CDs are viewed as promising lubricant additives. It should be noted that apart from as lubricant additives, CDs also serve as lubricating coatings [75,76], as well as the additive for greases [77], gel [78–80] and magnetorheological fluids [81].

By virtue of the variety of precursors and synthetic strategies, CDs with different morphology possess numerous names, such as carbon nanoparticles [61], carbon quantum dots (CQDs) [73], carbon nanodots (CNDs) [59]. Taking into consideration their nature, crystalline structure and quantum confinement, a rational and systematic classification of CDs have been performed by Yang's group [82]. CDs are divided into three categories: graphene quantum dots (GQDs), CNDs and polymer dots (PDs). GQDs with quantum confinement and crystalline structures are anisotropic with lateral dimensions larger than their height, possessing single or several layers of graphene structure in their carbon cores. The spherical morphology is the typical characteristic of CNDs, indicating that lateral dimensions of CNDs approximately equal to their height. According to the difference of photoluminescence (PL) center, CNDs are further divided into carbon nanoparticles (CNPs) and CQDs. The CNPs do not have a crystal lattice, while CQDs have an obvious crystal lattice. PDs without quantum confinement effect are aggregated or cross-linked polymers prepared from small molecule precursors or polymer precursors. At present, owing to their outstanding optical properties, diverse structure, excellent biocompatibility, attractive catalytic performance, low toxicity and environmental friendliness, CDs, as a new member of carbon nanomaterials, have been extensively applied in bioimaging [65–67,83,84], sensing [72,85–87], catalysis [62,88–91], optoelectronic devices [74,92–97], plant systems [98–101] and functional materials [102,103]. So far, various reviews of CDs have focused on synthesis methods, formation mechanism, fluorescence behaviors and origin, electrochemical performance and the applications in energy conversion and storage, catalysis, sensing, bioimaging and plant systems [59,72,82,99,101,104–108]. However, the application of CDs in the important field of lubrication has not been reviewed yet. The pioneering work on CDs for lubrication has been reported by Kang's group in 2015 [1]. After that, a great deal of research has been done to improve tribological characteristics of CDs and impressive progress has been made [52,55,57,76]. Therefore, a review about the development of CDs in lubrication would aid research in this area.

In this review, the different strategies for structural engineering design to modulate tribological properties of CDs are specifically highlighted, and the lubricating applications and corresponding mechanisms of CDs are comprehensively summarized with illustrative examples (Fig. 2). We hope it will raise awareness about the amazing tribological properties of CDs and stimulate the development in green and efficient lubricating materials of research.

2. Structural engineering design of CDs

In general, the synthetic approaches of CDs fall into top-down and bottom-up categories [59,82,107]. The top-down methods

Fig. 2. Structural engineering design, lubricating applications and corresponding mechanisms of CDs.

involve exfoliating bulk graphene materials into CDs *via* arc discharge, laser ablation, electrochemical approach, acid oxidation and thermal decomposition, while bottom-up ways are achieved by polymerization and carbonization of suitable molecular or polymer precursors, consisting of microwave treatment, pyrolysis, hydrothermal/solvothermal reactions and ultrasonic route [59,70,74,82,104–108]. The varieties of the preparation procedures and raw materials give rise to great differences in the intrinsic properties of the obtained CDs products, *i.e.*, size, shape, surface groups and degree of crystallinity, eventually resulting in the diversities of PL, polarity, charge and stability [59,72,82,99,101,104–108]. In comparison with that of CDs applied in energy conversion and storage, sensing as well as bioimaging, the structural engineering design of CDs used in lubrication pays more attention to the performances of polarity, charge and stability instead of PL properties (excitation/emission wavelength and quantum yield) [1,52,55,57,76]. A great deal of research has indicated that microstructural features of nanoparticles are of great importance for the friction/wear properties [44,109–111]. Up to now, three strategies for structural engineering design of CDs including size and shape control, surface modification as well as heteroatom doping to improve the tribological performance are summarized in detail below.

2.1. Size and shape control

It is well-known that the size and shape of nanoparticles significantly affect the lubricating performance [8,52,111,112]. The smaller nanoparticles could more easily enter into the frictional interfaces, consequently improving tribological performance. Meantime, spherical morphology is favorable for rolling mechanism to reduce friction coefficient, and multilayered graphene structure in nanoparticle cores is beneficial to lubrication because of easy-sliding interlayer structure [1,52,111]. It has been demonstrated the size and shape of CDs can be accurately manipulated by synthetic routes and the corresponding process conditions, helpful to the application of CDs in lubrication [52,111,113].

In 2011, Pang's group reported that the sizes of CDs synthesized by electrochemical ablation could be controlled by only adjusting the applied potentials without further separations or surface passivation [114]. Until 2015, Kang's group firstly employed CQDs fabricated through electrochemical ablation of graphite for lubrication. The water-soluble CQDs with a diameter of approximately 5 nm and multilayer structure (Fig. 3a) were obtained applying a static potential of 30 V for 120 h, which could efficiently reduce the size of the CQDs/CuS_x composites, making them uniform and monodisperse with a relatively narrow size distribution (5–20 nm) (Fig. 3b), consequently enabling them a highly efficient additive for liquid paraffin [1]. Although the pathway of electrochemical ablation can prepare the CDs with small size and multilayer structure used as lubricant additives, it suffers from time-consuming process. In 2016, Liu's group proposed a facile microwave method to synthesize uniformly spherical CQDs with an average diameter of 3 nm for lubrication, yielding multigram-scale powders in 6 min with citric acid and urea as precursors, overcoming the drawbacks of electrochemical ablation. More importantly, the CQDs as exfoliation agents and stabilizers decorated 2D nanosheets, helpful to improve the lubricity of aqueous lubricants (Fig. 3c) [55].

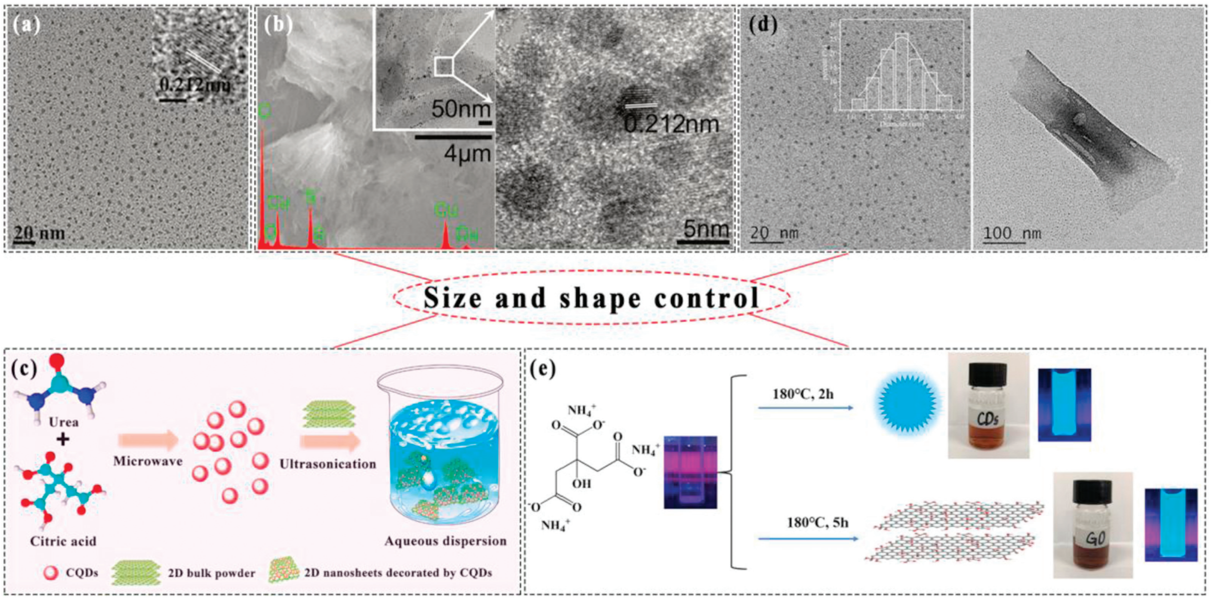


Fig. 3. (a) TEM image of CQDs and (b) SEM and HRTEM images of CQDs/CuS_x nanocomposites. Copied with permission [1]. Copyright 2015, Royal Society of Chemistry. (c) Schematic of the generation of 2D nanosheets decorated by CQDs. Copied with permission [55]. Copyright 2016, American Chemical Society. (d) TEM images of CQDs and CQDs/GO hybrid. Copied with permission [118]. Copyright 2017, Elsevier. (e) Schematic of the preparation process for CDs and GO. Copied with permission [56]. Copyright 2019, Elsevier.

Pyrolysis route not only controls the size and crystallinity of CDs, but also affects the proportion of CDs and by-products by changing the pyrolysis temperature and time [87,115–117]. As a result, in 2017, Cai's group synthesized four kinds of CQDs/graphene oxide (GO) hybrid nanomaterials as lubricant additives for polyethylene glycol (PEG) through tuning pyrolysis time of citric acid at 210 °C from 0.5 h to 4 h. When the pyrolysis time was 0.5 h, the obtained CQDs are spherical, exhibiting uniform and well dispersed with an average diameter of approximately 2.5 nm. With pyrolysis duration prolonging, more GO was generated because a part of the small CQDs converted into GO (Fig. 3d). Ultimately, the synergistic effect of sphere-like CQDs and GO endows the lubricant with the excellent tribological performance [118]. In 2019, Zhao's group tuned size and shape of the products by the pyrolysis time as well. The water-soluble CDs with a diameter of approximately 3–4 nm were formed by one-pot pyrolysis of ammonium citrate at 200 °C for 2 h. When the pyrolysis time was prolonged to 5 h, the structure of the product transformed from CDs to larger-sized GO (Fig. 3e). The CDs as lubricant additives for deionized (DI) water showed superior lubricating properties than GO [56].

The acid oxidation treatment for the preparation of CDs has prominent advantages of using a common carbon source, low cost, high yield, and one-step facile process [119,120]. In 2017, Fan and coworkers used acid oxidation approach to cut the micrometer-sized carbon fibers into GQDs with an average size of 3 nm and a high degree of crystallinity employed as additive for multialkylated cyclopentanes (MACs) to enhance the tribological ability [111]. The acid oxidation route can successfully fabricate the GQDs with preferable tribological performance, but the use of acid harms environment. In 2018, our group developed a one-pot gaseous detonation method to fabricate GQDs within 3–5 ms [121]. Soon afterwards, our group used the gaseous detonation method to prepare four kinds of GQDs with different average sizes (6.3, 28.3, 5.6 and 2.0 nm) by altering the molar ratio of precursors and explosive sources. The GQDs possessed multilayered structures and a good degree of crystallinity, serving as excellent friction-reducing and anti-wear additives for mineral oil [113]. In 2019, Wang's group synthesized water-soluble GQDs with a mean diameter of 2 nm as lubricant additives for ultrapure water *via* the hydrothermal route at 200 °C for 12 h. Compared with GO, GQDs were more effective to enhance the tribological performances of water [122]. The same year, Mehran's group also carried out the hydrothermal method to form the CDs as additives for lithium lubricating greases [77].

Normally, the sizes of CDs are less than 10 nm, and it is fairly easy to prepare CDs with small sizes [59,72,82,99,101,104–108]. Up to now, there are plenty of environmental and economical methods to synthesize CDs with controllable size and shape, but

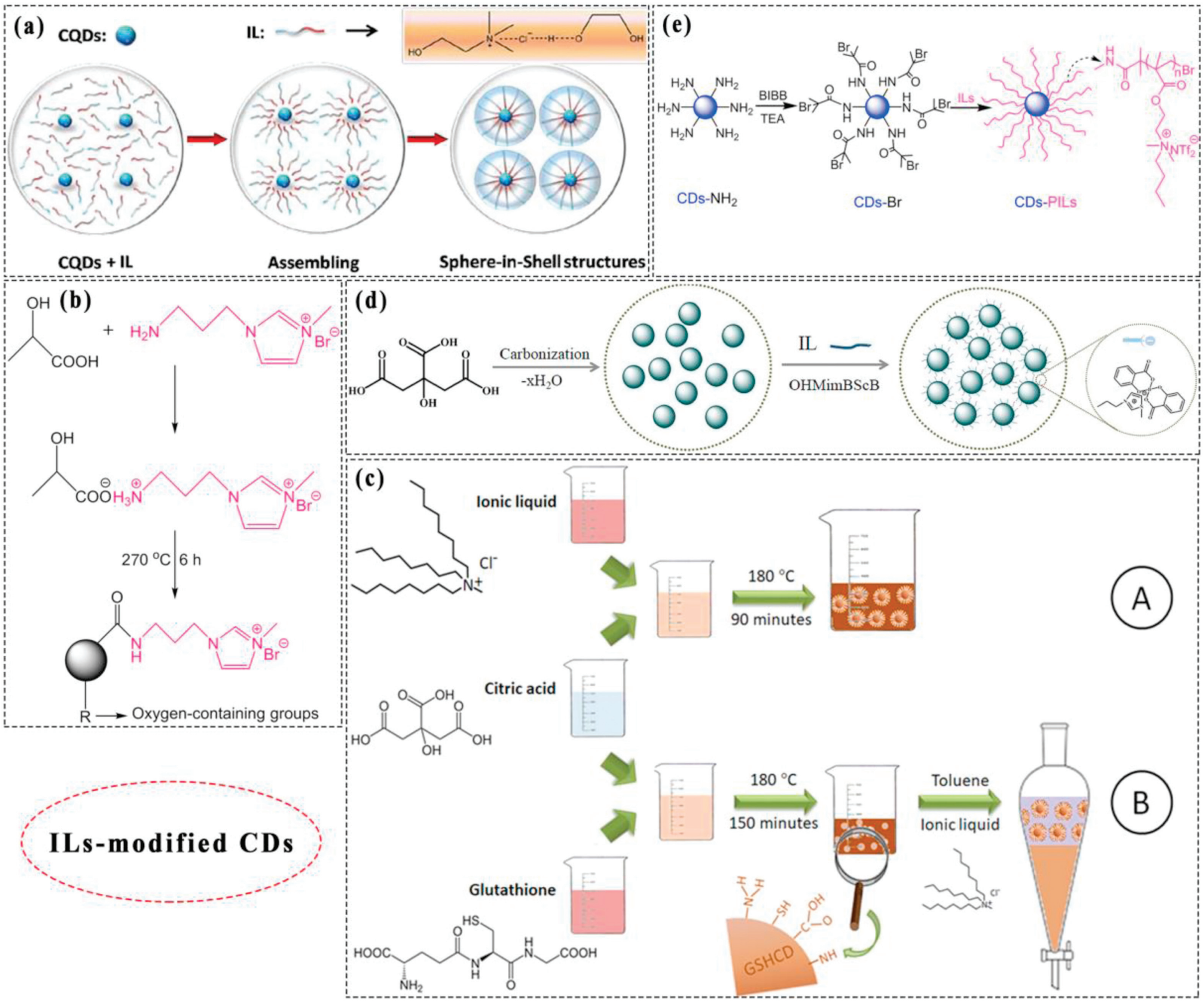


Fig. 4. (a) Schematic of the assembling process of IL-modified CQDs. Copied with permission [76]. Copyright 2017, Elsevier. (b) One-step pyrolysis method for fabrication of ILs-capped CDs. Copied with permission [130]. Copyright 2018, Springer. (c) Synthesis procedures: one-step hydrothermal treatment and two-step ion-pair route. Copied with permission [131]. Copyright 2020, Elsevier. (d) Schematic of the formed process of CQDs–OHMimBScB. Copied with permission [134]. Copyright 2018, Elsevier. (e) Schematic of the preparation process for CDs-PILs. Copied with permission [133]. Copyright 2019, Elsevier.

the research on tribological properties of the obtained CDs is still inadequate.

2.2. Surface modification

Surface modification is a widely used strategy for manipulating the tribological properties of nanoparticles [34–36,39,42,48,123–126]. The surface functional groups not only increase carbon nano-additives stability, but also make nanoparticles easily adsorb a rubbing surface and then form a protective film, minimizing the contact between friction interfaces. At the same time, the synergistic effect of the surface functional groups and particle cores of nanoparticles play an important role in reducing friction and improving wear-resistance for lubricants. Therefore, surface-modification process is indispensable for nanoparticles as lubricant additives. Fortunately, a multitude of one-step approaches for the formation of CDs allow the direct incorporation of specific surface functional groups during their generation without the requirement for later modification steps, simplifying the preparation process and reducing the cost [12,84,127]. More importantly, due to their large surface areas with multiple active sites, CDs are prone to be decorated with other specific molecules, making their polarity and stability adjustable [58,63–65], thus imparting them with a substantial competitive advantage in lubrication [63,64].

2.2.1. Ionic liquids (ILs)-modified CDs

In recent years, on account of their high thermal and chemical stability, promising tribological properties and controlled miscibility, ionic liquids (ILs) applied in lubrication have attracted more and more attention [7,16,124,128,129]. And many efforts have been made to construct the nanoparticle-based hybrids with unique core-shell structure using ILs as the shell to improve their dispersion stability and tribological properties. The ILs-coated nanoparticles such as CuO nanorods [128], graphene [129] and silica nanoparticles [124], combining the advantages of ILs and nanoparticles, have been employed as the efficient lubricant additives. Recently, impressive progress has been made in synthesis strategies of ILs-modified CDs, and the ILs/CDs hybrid has become a kind of high-performance lubricant additive [52,76,130–134]. In 2016, for the first time, Wang and coworkers reported a kind of ILs-capped CDs (CDs_{-NTf2}) as a high-performance friction-reducing and anti-wear additive for PEG by two-step synthesis. Firstly, ILs-capped CDs (CDs_{-Br}) were formed by pyrolysis for 6 h using citric acid monohydrate and 1-aminopropyl-3-methyl-imidazolium bromide as raw materials. Secondly, The CDs_{-NTf2} with wonderful dispersion stability in PEG were obtained taking advantage of an anion exchange reaction between CDs_{-Br} and $LiNTf_2$ [52]. In 2017, Zhang's group also used two-step route to prepare ILs-modified CQDs with an average diameter of 5.6 nm as lubricant material for silicon chips. The CQDs firstly were synthesized by the acid assisted ultrasonic treatment from glucose and HCl. Then the ILs-modified CQDs were attained by grinding the CQDs and ILs. During the process, the ILs were randomly distributed on the surface of CQDs. Subsequently, owing to interaction of the CQDs with ILs, the ILs became orderly distributed. Finally, the sphere in-shell structures were formed due to the charge effect and the shape of the CQDs (as the core) and IL (as the shell), displaying excellent tribological performance (Fig. 4a) [76]. Soon afterwards, Wang's group developed a simpler one-step pyrolysis method to fabricate ILs-capped CDs as water-based lubricant additives, shortening complicated and long processing (Fig. 4b). Through pyrolyzing the gel (made of lactic acid and ILs) [130] or mixture (made of citric acid monohydrate and ILs) [132], the ILs-capped CDs with a high yield were successfully synthesized [130,132]. All the ILs-modified CDs mentioned above are hydrophilic, and consequently fail to serve as additives for water-based lubricants. To make ILs-modified CDs soluble in organic media, more recently, R. Badía Laíño and coworkers developed two approaches (one-step hydrothermal treatment and two-step ion-pair route) to achieve the CDs surface functionalization using ILs with long alkyl chains, providing CDs with a hydrophobic character. Specifically, the hydrothermal method was performed by heating the solution of citric acid and ILs at 180 °C for 90 min. By changing the ILs species, the IL-modified CDs with different long alkyl chains and sizes could be attained. The ion-pair route firstly fabricated CDs using citric acid and glutathione as raw materials by hydrothermal process, then took advantage of the surface functional groups of obtained CDs to

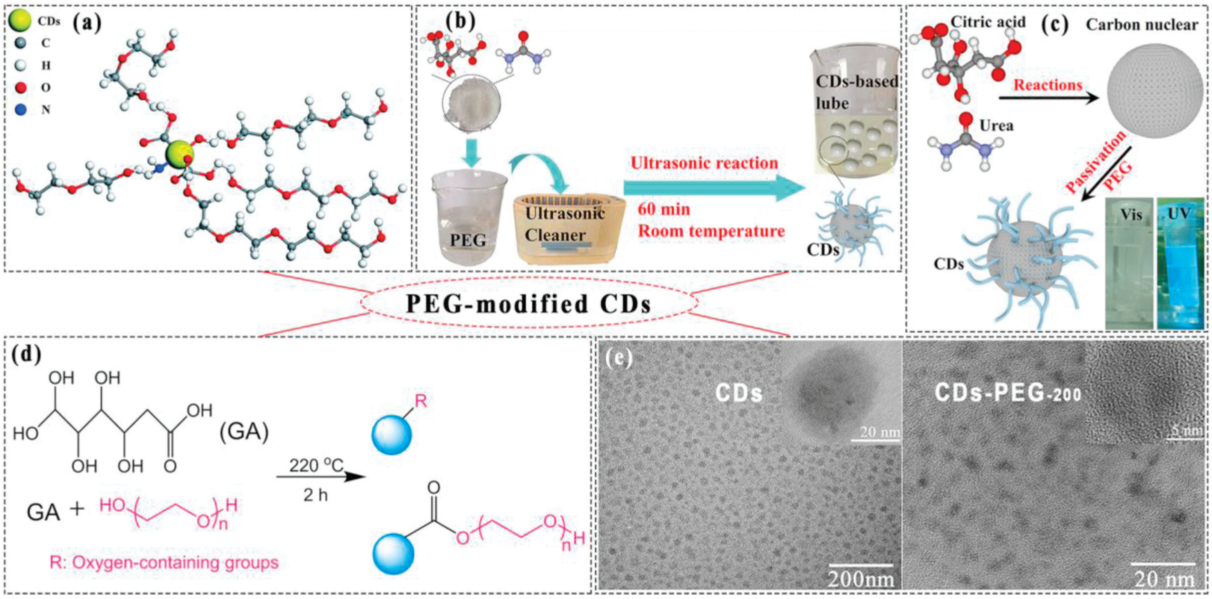


Fig. 5. (a) Schematic of the particular structure of PEG-modified CDs. Copied with permission [78]. Copyright 2017, Royal Society of Chemistry. (b) Schematic of the green and *in situ* synthesis and (c) the preparation process of CDs-based lubes. Copied with permission [57]. Copyright 2019, Royal Society of Chemistry. (d) Schematic of the synthesis procedures of CDs-PEG-200 and (e) TEM images of CDs and CDs-PEG-200. Reproduced with permission [138]. Copyright 2019, Taylor & Francis Group.

form extractable ion-pairs with ILs. The ILs-modified CDs with alkyl groups remained long-term stability in organic media and served as one of the best candidates as additives in oil-based lubricants (Fig. 4c) [131]. In addition, to enhance the friction-reducing performance of ILs-modified CDs under high load, in 2018, Cai's group synthesized ILs/CDs hybrid nanomaterials through covalent grafting of 3-(hydroxypropyl)-3-methyl imidazolium bis(salicylato)borate onto the surfaces of CDs (synthesized by heating citric acid in an oil bath at 210 °C for over 1 h) (Fig. 4d). Due to the presence of boron element, the product was able to act as high-performance additives for PEG under high load [134]. More recently, Wang's group used poly(ionic liquid)s (PILs) as a substitute for ILs and synthesized the PILs brush-grafted CDs by surface-initiated atom transfer radical polymerization (Fig. 4e). Although the process containing three steps was complicated, the product could be better lubricant additives for PEG [133]. All the previous investigation has demonstrated that the ILs groups on the surfaces of CDs can significantly improve the tribological properties of CDs as additives by promoting their absorption and embedding stability on frictional interfaces. However, the high cost and pollution problems of ILs are the main obstacles for their application as modifiers of CDs. Thus, much more efforts should be made to exploit CDs modified by new low-cost and eco-friendly ILs as efficient lubricant additives.

2.2.2. PEG-modified CDs

In comparison with ILs, PEG is evidently low-cost, eco-friendly and degradable, commonly used in high performance lubricants and the biomedical field to reduce friction and wear [52,125,135]. Moreover, grafting PEG onto the surfaces of nanomaterials such as graphene and carbon black is one of the efficient ways to dramatically improve their dispersion stability the lubricating properties [125,126]. More importantly, PEG is fairly easy to graft on the surfaces of CDs. In previous work, PEG has been used to complete the surface passivation of CDs and then promote the PL performance [58,136,137]. Until 2017, Dong's group reported the good lubrication effect of PEG-grafted CDs fabricated by two-step method for the first time. Firstly, the CDs with amidogen (–NH_2), hydroxyl (—OH) and carboxyl (—COOH) groups were synthesized using DL-alanine as the carbon source by microwave irradiation. Then the obtained CDs and PEG and chitosan were mixed and stirred to prepare the CDs/PEG/chitosan composite gel. In the gel, PEG was grafted on the surfaces of the CDs *via* hydrogen bond, forming the lubricant and leading to excellent lubrication effect (Fig. 5a) [78]. Soon afterwards, using the similar method, they prepared different kinds of hydrogels containing PEG-grafted CDs to achieve slow-release lubricity [79,80]. In 2019, our group firstly designed a one-step and simple ultrasonic treatment to form PEG-grafted CDs for lubrication. The low-cost precursors including PEG, citric acid and urea were easily treated by ultrasound for 1 h (Fig. 5b). During the process, citric acid and urea underwent dehydration and carbonization to form N-doped CDs. Meantime, PEG not only acted as the base liquid, but also served as passivating agent to attach to the surfaces of N-doped CDs (Fig. 5c). The product exhibited the highly efficient lubricating properties [57]. The same year, Chen's group applied one-pot pyrolysis of the mixture of gluconic acid and PEG at 220 °C for 2 h to prepare PEG-modified CDs which showed far superior tribological properties than CDs without modification (Fig. 5d) [138].

2.2.3. Other polymers-modified CDs

Surface-grafted brush-like polymers can significantly enhance the lubricating properties of nanomaterials [125,126,133,139]. In addition to PEG, there are other polymers used to modify CDs. In 2017, to develop new oil-based additives for polyalphaolefin (PAO) widely adopted base oils, Wang's group designed a facile one-pot pyrolysis method to synthesize the oleylamine (OA)-modified CDs with particle sizes of 25–35 nm. The precursors only including OA and citric acid were easily pyrolyzed by oil bath at 300 °C for 3 h. During the process, citric acid went through dehydration, polymerization, and carbonization to form the carbon core. Meanwhile, the OA was covalently attached onto the carbon cores by amidation to gain OA-modified CDs. The target product as the lubricating additives significantly improve the lubrication performance of PAO (Fig. 6a) [140]. Subsequently, Cai's group also prepared OA-capped CDs through chemical grafting route, in which hydrophilic CDs and OA were pyrolyzed for 6 h and finally the OA as the surface passivation agent was grafted on the surfaces

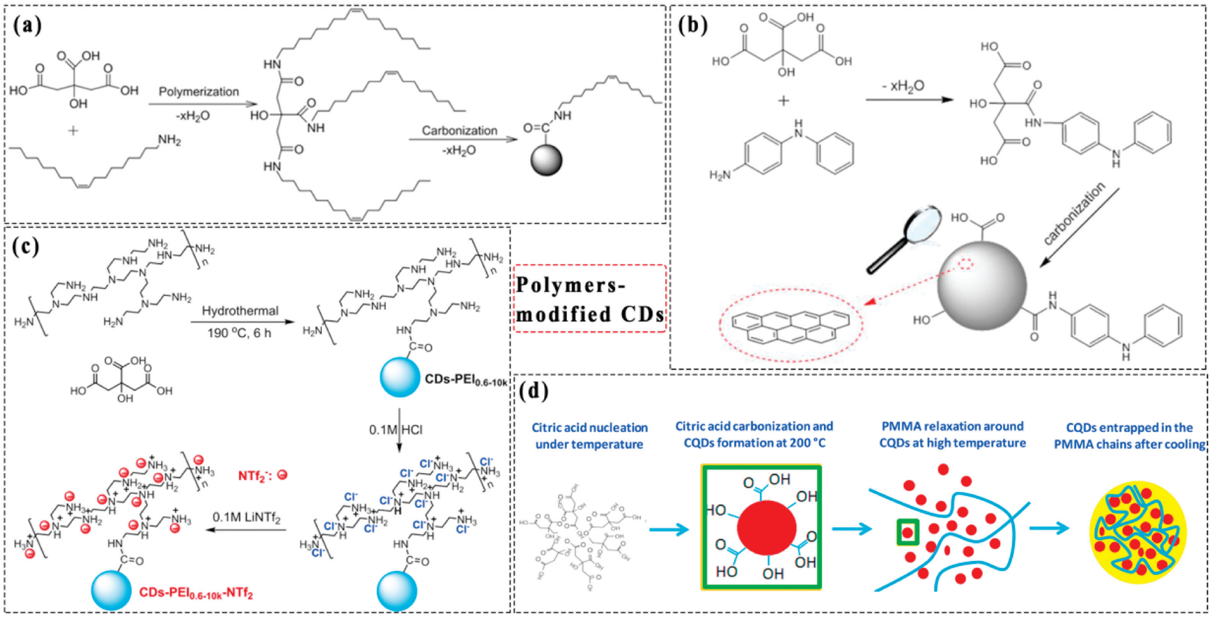


Fig. 6. (a) One-pot pyrolysis method to form OA-modified CDs. Copied with permission [140]. Copyright 2017, Springer. (b) Schematic formation of DPA-modified CDs by pyrolysis. Copied with permission [141]. Copyright 2018, Elsevier. (c) Synthesis procedures of CDs-PEI and CDs-PEI-NTf_2. Copied with permission [139]. Copyright 2019, Elsevier. (d) Schematic of formation of PMMA-modified CDs. Reproduced with permission [147]. Copyright 2020, Elsevier.

of CDs to form OA-capped CDs with hydrophobicity. The product as lubricating additives was endowed with enhanced anti-wear performance, anti-oxidant performance and superb thermal stability [63,64]. Owing to its simple operation, the pyrolysis method was extensively adopted to surface functionalized CDs in one step [141,142]. In 2018, Cai and coworkers successfully prepared diphenylamine (DPA)-modified CDs by pyrolyzing the mixture of 4-aminodiphenylamine and citric acid monohydrate at 300 °C for 3 h. The DPA-modified CDs with a narrow size distribution ranging from 1.5 nm to 2.7 nm as a multifunctional additive for PEG exhibited not only antioxidant but also anti-wear and friction-reducing performances (Fig. 6b) [141]. The same year, René Wilhelm and coworkers synthesized dodecyl amine functionalized GQDs *via* multiple steps way including the preparation and covalent functionalization of GQDs. The modified GQDs showed excellent solubility in various organic solvents and great lubricating performance as coatings [75]. Since 2012, various polyethyleneimine (PEI)-grafted CDs have been fabricated *via* one-pot thermal treatments or two-step methods, widely used in fluorescent sensing, cell imaging, gene delivery and photocatalysis, but not in lubrication [143–145]. Until 2019, Wang's group firstly studied the tribological property of PEI-grafted CDs synthesized by the one-step hydrothermal treatment of citric acid and PEI for 6 h. The obtained PEI-modified CDs with excellent dispersion stability in water were used as the additives to promote the lubricating effect of water [146]. Moreover, by magnetic stirring the precursors of PEI-modified CDs and $LiNTf_2$, the polyelectrolyte was grafted on the surfaces of PEI-modified CDs to form with the aid of protonation and anion exchange processes (Fig. 6c). The product as additives for PEG exhibited superb friction-reducing and anti-wear performances [139]. Poly(methyl methacrylate) (PMMA) as viscosity modifier reduces the lubricant oil viscosity dependence on temperature variations [147]. Meantime, the preparation of PMMA/CDs composites has been reported, but the synthesis route consists of a two-stage process and there is no research on the lubrication effect of PMMA/CDs composites [148,149]. More

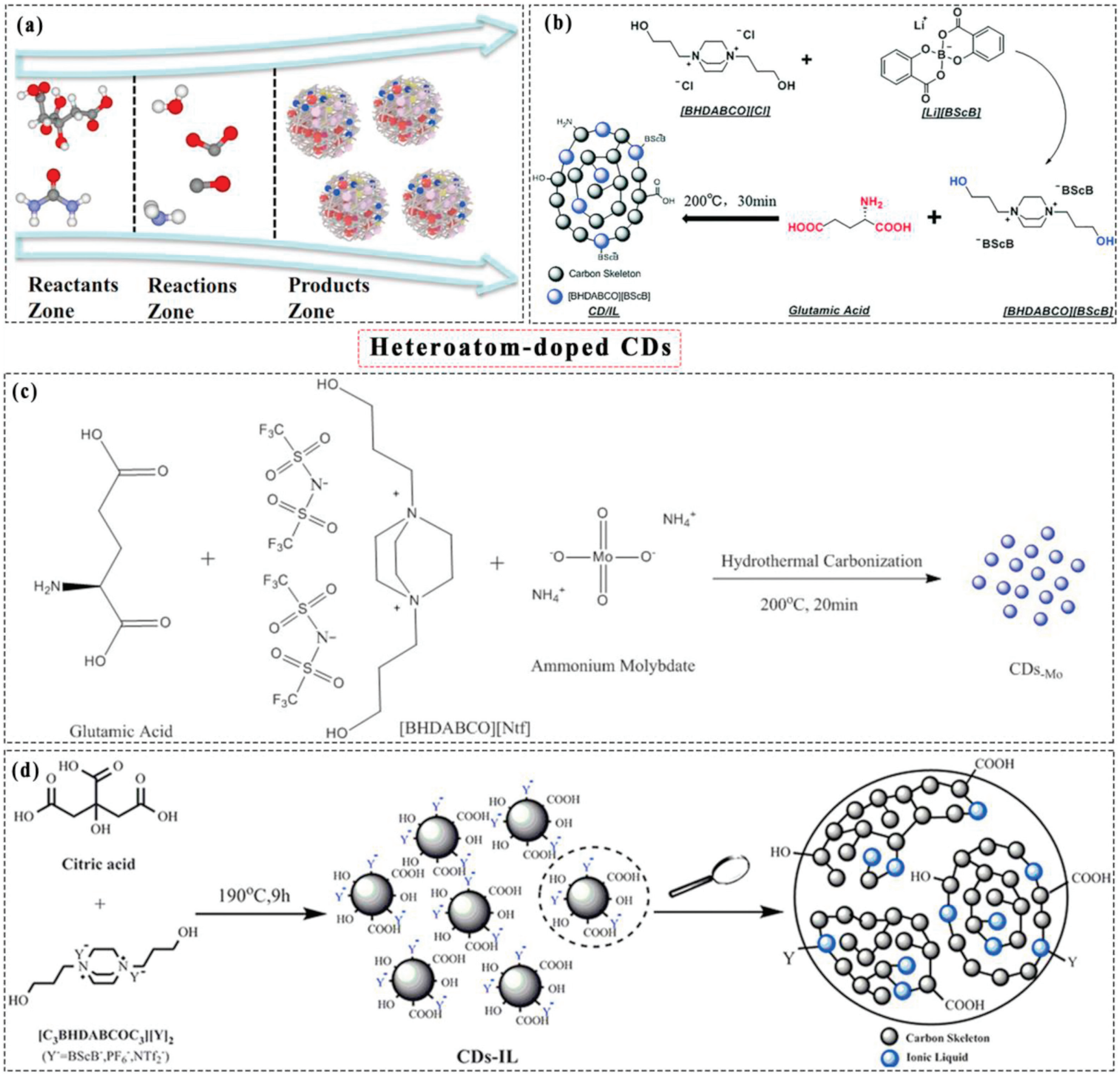


Fig. 7. (a) Schematic of the formation of N-doped CDs by gaseous detonation. Copied with permission [156]. Copyright 2018, Elsevier. (b) Possible synthesis procedures of B, N-codoped CDs by pyrolysis. Reproduced with permission [151]. Copyright 2016, Royal Society of Chemistry. (c) Illustration of the preparation procedure of Mo-doped CDs *via* a pyrolysis way. Copied with permission [157]. Copyright 2019, Elsevier. (d) Synthesis route of F-doped CDs by hydrothermal method. Copied with permission [152]. Copyright 2019, Elsevier.

recently, Maria Sarno's group optimized the preparation approach and confirmed the great lubricating property of PMMA-coated CDs. The one-step pyrolysis was applied to form the product, in which the mixture of citric acid, oleic acid and PMMA was heated up to 200 °C for 2 h under magnetic stirring (Fig. 6d). The resulting product with an average diameter of 3 nm as additives for mineral oil displayed remarkable lubricating performance [147].

The above research has demonstrated that the surface modification of CDs confers them with the unique core-shell structure, not only changing their polarity, but also strikingly enhances the tribological properties and thermal stability in comparison to the original CDs. More importantly, due to their facile surface functionalization nature, there are multiple simple and low-cost ways, such as pyrolysis, microwave method and hydrothermal treatment, to achieve surface modification of CDs.

2.3. Heteroatom doping

Similar to surface modification, heteroatom doping is a normally adopted strategy for manipulating the tribological properties of nanoparticles [39,43,47,150]. As for CDs, a large number of studies have indicated that the invasion of intrinsic structure of CDs arising from heteroatom doping inevitably leads to structural and electronic distortions, providing a new path to modulate electronic properties, elemental composition and surface chemistry, and thus eventually affecting the PL and lubrication properties of CDs significantly [64–66,69,151–157]. Up to now, various heteroatoms consisting of nitrogen, boron, sulfur, fluorine and mental elements have been incorporated into the CDs framework, and the obtained heteroatom-doped CDs generally display favorable lubricating performance [64,151–157].

2.3.1. Doping with nitrogen

Nitrogen is a typical dopant by virtue of its comparable atomic size to carbon and its available valence electrons for forming strong valence bonds with carbon atoms [158]. N-doped CDs are endowed with favorable water solubility and strong electron-withdrawing ability, and thus their stability and fluorescence quantum yield are significantly enhanced. Since 2012, substantial effort has been made to probe the optical properties of N-doped CDs [65,159,160]. Until 2018, the special researches on lubrication performance of N-doped CDs were done by Cai's group. Using citric acid and urea as carbon and nitrogen sources respectively, the N-doped CDs were prepared by the one-pot pyrolysis at 180 °C for 30 min. Owing to multiple nitrogen- and oxygen-containing groups, the N-doped CDs with strong hydrophilicity exhibited a long-term homogeneous phase without any noticeable precipitation in polar solvents, and obviously reduced both friction and wear as highly efficient water-based additives for PEG [64]. In 2019, our group also applied citric acid and urea as precursors to directly synthesize solid-state N-doped PDs with an average diameter of 5.7 nm by a one-pot gaseous detonation method. The product without any purification displayed excellent friction-reducing and anti-wear performance as the additives for PEG (Fig. 7a) [156]. More recently, Agnieszka's group used bovine serum albumin as carbon and nitrogen sources to prepare the N-doped CDs *via* the hydrothermal method at 180 °C for 6 h, and demonstrated that compared to the reference base oil, the as-synthesized N-doped CDs with extraordinary extreme pressure ability [155].

2.3.2. Doping with boron

The incorporation of boron into the CDs structures renders fascinating optical properties and new applications [66]. Meantime, owing to their anti-oxidation friction modifier, wear resistance and low toxicity, boron-containing nanoparticles have attracted intense attention [161,162]. Thereby, it is necessary to determine the influence of boron doping on the tribological properties of CDs. In 2017, Cai's group synthesized B,N-codoped CDs as an efficient lubrication additive by pyrolyzing the mixture of L-glutamic acid and bis(salicylato)borate ILs at 200 °C for 30 min. Different from ILs-modified CDs, the ILs containing B element were inserted in the carbon skeleton of CDs, causing high-performance lubricating performance (Fig. 7b) [151]. Afterwards, this group used citric acid and bis(salicylato)borate ILs as precursors to form B,N-codoped CDs by hydrothermal method at 190 °C for 9 h. The product with mean diameter of 1.1 nm also played an important role in enhancement of tribological performance of base oil [152].

2.3.3. Doping with metal elements

Apart from the common dopants of nitrogen and boron, metal elements have also been used to further improve the lubricating performance of CDs [154,155,157]. In 2019, Cai's group firstly prepared Mo-doped CDs using ammonium molybdate, glutamic acid and ILs as raw materials *via* pyrolysis way at 200 °C for 20 min. By means of their strong interaction with Fe(III) of rubbing surfaces, Mo-doped CDs as additives for PEG could been easily captured on the interfaces, thereby showing good tribological behaviors (Fig. 7c) [157]. In 2020, Agnieszka's group fabricated Ga-doped CDs through ultrasonication method using gallium and PEG as reactants. The anti-friction capability of Ga-doped CDs was clearly better than reference PAO oil, but not superior to the Ga-free CDs formed in a similar manner without gallium [155]. More recently, Wang's group synthesized Ni-doped CDs as a lubricating oil additive applying citric acid, ethylenediamine and nickel acetate as raw materials by a facile hydrothermal method at 160 °C for 5 h. Due to much easier access to the friction surfaces, the Ni-doped CDs possessed significantly better lubrication properties than the Ni-free CDs [154]. In comparison with nonmetallic elements doping CDs, the CDs doped by metal elements suffer from main drawbacks including higher preparation costs and greater risk to environmental pollution.

2.3.4. Doping with other heteroatoms

Besides doping with the above atoms, sulfur and fluorine can also be doped into CDs to get excellent tribological properties [152,153,163]. In 2018, Wang's group applied rice husk powder to fabricate S, N-codoped CDs as additives for PEG through a hydrothermal reaction for 24 h, providing a reference for the utilization of rice husk resources [153]. In 2019, Xiao and coworkers prepared the water-soluble S-doped CDs as additives for DI water by hydrothermal treatment using sodium thiosulfate as the sulfur source [163]. Although the S-doped CDs improve the tribological performance of PEG or water, the presence of sulfur in CDs failed to meet environmental requirements. In 2019, Cai's group fabricated F-doped CDs by hydrothermal method at 190 °C for 9 h using citric acid and hexafluorophosphate functionalized ILs as precursors (Fig. 7d). The product even displayed better anti-wear and friction-reducing properties than B,N-codoped CDs, providing a more suitable candidate as the lubricant additive [152].

Abundant evidence mentioned above indicates that three strategies for structural engineering design of CDs achieve the improvements of tribological performance, making them as promising friction-reducing and anti-wear additives for water-bail or oil-based lubricants. Particularly, more and more researches suggest that surface modification tends to confer CDs with higher lubricating performance [57,133,139,141], shown in section 3.1 in detail. However, the low-yield and time-consuming purification process of CDs have largely limited their practical application in lubrication. The several days of dialysis is necessary during the preparation processes of CDs using electrochemical approach, acid oxidation, microwave treatment, pyrolysis, hydrothermal way and ultrasonic route [52,55,118,130,133,134,139,141,151,153]. Rapid, large-scale and low-cost synthesis of CDs is a prerequisite for their application in lubrication. Recently, Dai's group developed a green and effective one-pot hydrothermal method for the synthesis of CDs without time-consuming dialysis purification process [67]. Chen's and coworkers proposed a magnetic hyperthermia method to synthesize CDs on a large scale with a high efficiency of 85 g/h and a high yield of 60% using low-cost citrate and carbamide as precursors [164]. Our group reported an *in situ* and high-yield preparation of CDs-based lubricants without any post-treatment *via* facile ultrasonic processing [57]. The latest research overcomes shortcomings of existing preparation methods of CDs, extremely advantageous for CDs in lubrication. Therefore, compared with other lubricating materials, CDs have demonstrated unique advantages in preparation and purification.

3. Applications of CDs in lubrication

Besides the excellent dispersibility and stability, the unique features such as small sizes, tunable surface groups, low toxicity and environmental friendliness render CDs a promising lubricating material [52,57]. The progress in lubrication application of CDs is systematically introduced below.

3.1. CDs as additives for lubricants

By virtue of the merits of high friction reduction and wear resistance, good fluidity, excellent cooling and cleaning, the lubricant is one of the most popular and effective lubricating means [13–15,64]. Therefore, for their lubrication application, CDs mainly act as lubricant additives.

3.1.1. Preparation of CDs-based lubricants

The CDs-based lubricants can be obtained *via* either two-step or one-step approaches. The commonly used two-step method tends to prepare CDs firstly and then adds them to base oils/liquids [1,52,111,118,132,134]. Because of their abundant surface groups, it is comparatively easy for CDs to disperse in base oils/liquids. Kang's group [1] and Cai's group [118,134] prepared the CDs-based lubricant by a simple natural-dissolving way, in which the CDs-based nanocomposites or pure CDs dissolved in the base oil/liquid (liquid paraffin or PEG) without any dispersants, ultrasound or shocks (Fig. 8a). To accelerated dissolution and obtain homogeneous CDs-based lubricants, Wang [52,132,133,154], Cai [141], R. Badía-Laíño [131], Xiao [163], Fan [111], Chen [138], Yan [113,156] used magnetic stirring (Fig. 8b) or ultrasonic treatment (Fig. 8c) during the processing. As a result, for the two-step way, the large-scale, high-yield, low-cost and green preparation of CDs-based lubricants depends on the preparation methods of CDs.

The two-step method inevitably brings the drawback of time-consuming processing. Consequently, our group elaborately designed a one-step, green, facile and economical synthesis approach of CDs-based lubricants, in which citric acid and urea were added to PEG at room temperature under ultrasonic treatment for 1 h (Fig. 5b). The CDs-based lubricant without any post-treatment could be prepared at the rate of 1 kg/h on a large scale [57]. Thus, one-step route provides a new thought to develop CDs-based lubricants.

3.1.2. Physicochemical properties of CDs as additives

The physicochemical properties of CDs, consisting of dispersity, thermal stability, viscosity and antioxidation, play an important role for the tribological performance of CDs-based lubricants.

(1) Dispersion stability. To be effective lubricant additives, the long-term dispersion stability in base oils/liquids is required for nanoparticles [52,53]. It has been verified that CDs show the outstanding dispersion stability in water- or oil-based lubricants by visual inspection [63,131,139,141,146], UV-light irradiation [52,118,156], UV intensity as a function of time [63] and zeta potential [55].

R. Badía Laíño's group found no perceptible aggregation or sedimentation in CDs/PAO suspensions using the naked eye after 15 days rest, suggesting that the obtained ILs-modified CDs with long alkyl chains possessed good dispersion stability in PAO base oil [131]. Cai's group extended the standing time of CDs/PEG dispersions to more than 5 months, and found no sedimentation, indicating that the DPA-modified CDs had long-term dispersion stability in PEG [63,141]. Wang's group demonstrated that even under harsh conditions (standing for one month at −20 °C and 150 °C and centrifuging for 20 min at 10,000 rpm), PEI-grafted CDs could remain the excellent stability in PEG (Fig. 9a) [139,146]. Even after tribo-test, the CDs-based lubricants kept transparent without any precipitations (Fig. 9b) [152]. Apart from visual inspection, UV-light irradiation is an effective means to evaluate dispersion stability of CDs. It has been validated that the highly dispersed CDs in solvents can emit visible fluorescence under UV-light irradiation, while the PL of CDs will weaken even vanish if they are agglomerated because of aggregation-induced quenching. Based on the fact that the CDs/PEG suspensions with different contents emitted bright fluorescence under UV-light irradiation after standing for 3 months, even 6 months, Wang's group [52], our group [156] and Cai's group [118] demonstrated the favorable dispersion stability of ILs-modified CDs, N-doped PDs and CDs/GO hybrids in PEG (Fig. 9c), respectively. Recently, Cai's group employed UV intensity as a function of time to evaluate the dispersity stability of CDs-based lubricants. The relative absorbance of the dispersion decreased slowly after standing more than 90 days, indicating that DPA-modified CDs ($CQDs_{-N}$) and OA-capped CDs ($O\text{-}CQDs_{-N}$) in base oils exhibited excellent dispersion

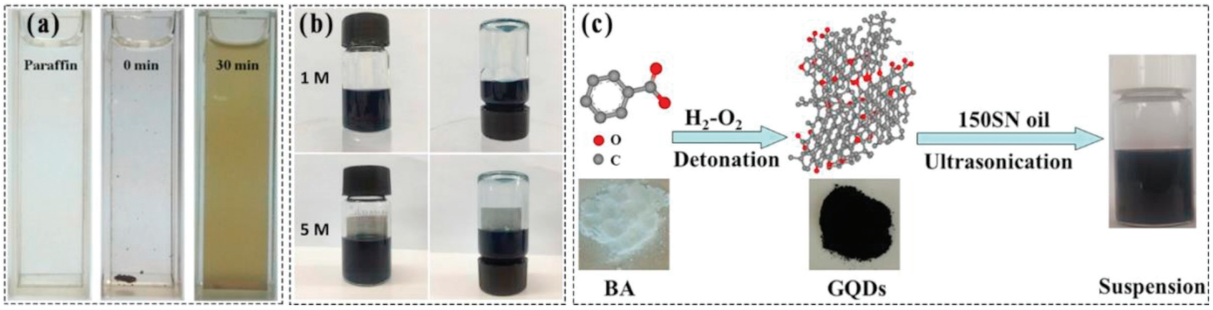


Fig. 8. (a) Photographs of CQDs/CuS_x soaked in liquid paraffin at different time periods by a natural-dissolving way. Copied with permission [1]. Copyright 2015, The Royal Society of Chemistry. (b) Photographs of CDs/PEG dispersions prepared by magnetic stirring (M: mol/L). Reproduced with permission [141]. Copyright 2018, Elsevier. (c) Schematic for the preparation of GQDs/mineral oil suspension by two-step method. Copied with permission [113]. Copyright 2018, Elsevier.

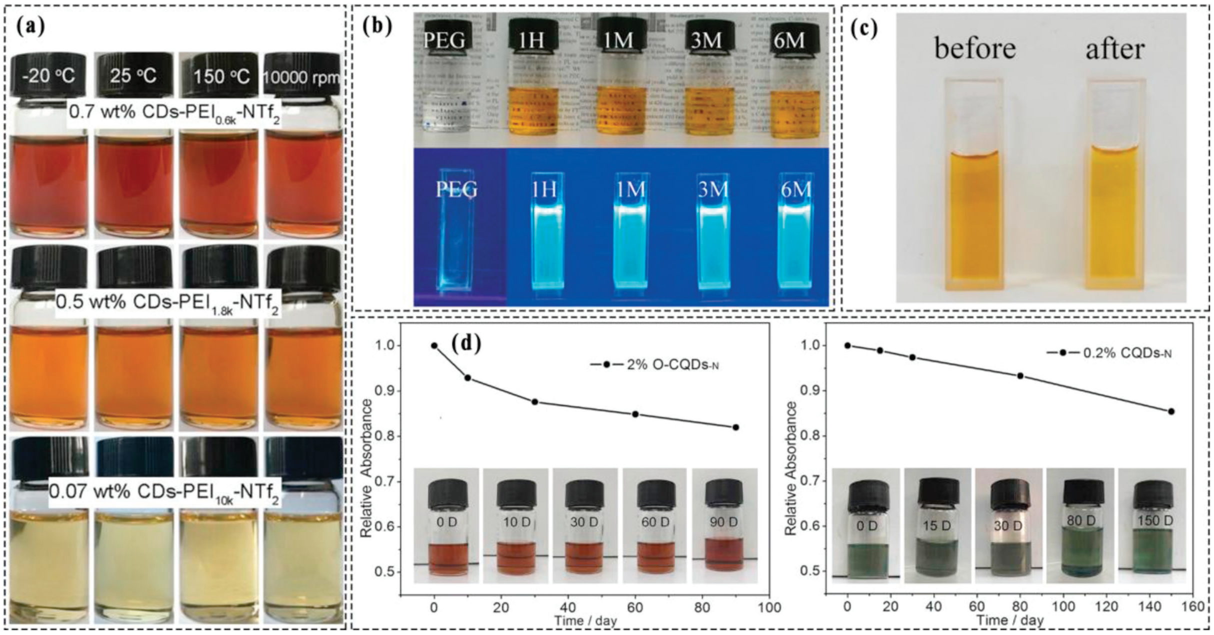


Fig. 9. (a) Photographs of various PEI-grafted CDs/PEG dispersions after standing for one month under harsh conditions (Reproduced with permission [139]. Copyright 2019, Elsevier); (b) solubility of PEG with 1 wt% CDs before and after friction (Copied with permission [152]. Copyright 2019, Elsevier); (c) digital images of dispersion of CDs/GO hybrids in PEG (Copied with permission [118]. Copyright 2018, Elsevier); (d) digital images and dispersion stability of PAO with 2 wt% O-CQDs$_{\text{-N}}$ and castor oil with 0.2 wt% CQDs$_{\text{-N}}$ as a function of time. Copied with permission [63]. Copyright 2019, Elsevier.

stabilities (Fig. 9d) [63]. Moreover, the zeta-potential value of a nanoparticle dispersion system is an important indicator of its stability. A nanoparticle dispersion is generally stable if its zeta potential is higher than 25 mV or smaller than −25 mV [126]. Liu's group revealed that CDs-decorated 2D nanosheets aqueous dispersions exhibited zeta-potential values near −40 mV, confirming their good dispersion stability [55].

The excellent dispersion stability of CDs is attributed to a large number of groups on their surfaces. Tuning the surface groups of CDs makes them good dispersibility and long-term stability in polar and apolar mediums [63–65], and grafting polymer to the surfaces of CDs conduces to the improvement of dispersibility [53,133,139].

(2) Thermal stability. The thermal stability of the lubricant is one of most important factors for its service life [52]. As a consequence, CDs as lubricant additives are expected to have high thermal stability. Wang's group firstly applied thermogravimetric (TGA) and differential scanning calorimetry (DSC) to reveal the effect of ILs-modified CDs on the thermal stability of PEG base liquid under air atmosphere. Compared to those of PEG, the sharp

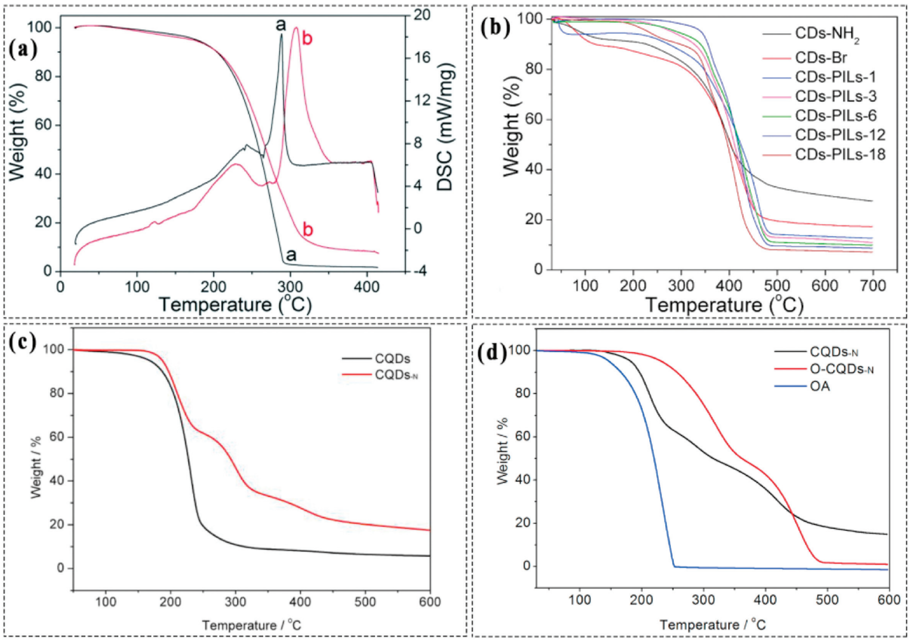


Fig. 10. (a) The TGA and DSC curves of PEG and 0.5 wt% CDs-NTf$_2$/PEG suspension. Copied with permission [52]. Copyright 2016, Royal Society of Chemistry. (b) TGA curves of various PILs brush-grafted CDs. Copied with permission [133]. Copyright 2019, Elsevier. (c) TGA curves of CQDs and DPA-modified CDs (CQDs$_{\text{-N}}$). Copied with permission [141]. Copyright 2018, Elsevier. (d) TGA curves of OA-capped CDs (O-CQDs$_{\text{-N}}$) and CQDs$_{\text{-N}}$. Copied with permission [63]. Copyright 2019, Elsevier.

weight loss temperature and thermo-oxidative decomposition temperature of CDs/PEG suspension shifted to a higher value, demonstrating that ILs-modified CDs with the thermal decomposition temperature higher than 400 °C possessed particularly high thermal stability (Fig. 10a) [52]. Afterwards, Wang [133,139,146], Cai [63,141], René [75], Xiao [163] employed TGA to further verified that surface modified CDs and heteroatom-doped CDs containing branched polyelectrolyte grafted CDs, PILs brush-grafted CDs (Fig. 10b), DPA-modified CDs, dodecyl amine functionalized GQDs and S-doped CDs exhibited a prominent thermal stability higher than pure CDs (Fig. 10c) [141] or the corresponding surface groups (Fig. 10d) [63,75]. CDs as the additives can meet the demand of thermal stability, and grafting polymer to the surfaces of CDs is beneficial to the improvement of thermal stability [141].

(3) Viscosity. Lubricant viscosity is one of key parameters to control the friction and wear. The low viscosity is disadvantageous to form effective tribo-film between the rubbing surfaces, leading to poor lubrication performance [38], while high viscosity may bring big friction coefficient, causing a very large energy waste in the powertrain [53]. For some base oils/liquids with low viscosity, such as water, the desirable additives should not only improve their antifriction and anti-wear functions, but also increase their viscosity. Fortunately, Liu’s group reported that the aqueous dispersion of obtained CQDs possessed higher shear viscosity than that of water, helpful to the improvement of lubrication performance of water [55]. Our group demonstrated that with the increase of GQDs content, the viscosity of GQDs/150SN mineral oil suspension increased [113]. For some base oils with high viscosity, such as PEG, the favorable additives should not increase their viscosity and not interfere with their rheological properties, contributing to the delicate balance of the final industrial formulations of lubricants [147]. Cai’s group [141] and our group [57] proved that for PEG base liquid, due to its higher viscosity and CDs good dispersity, CDs without or with surfaces grafting polymer had little influence on the viscosity of PEG. Maria Sarno’s group confirmed that the presence of PMMA/CDs composite did not significantly modify viscosity of commercial VG 220 oil at both 100 °C and 40 °C [147].

(4) Other properties. Nowadays, the development trend of lubricants requires them to possess not only wear- and friction-reducing performance, but also the better antioxidation and corrosion inhibition properties, indicating that the preferable lubricant additives are supposed to have a variety of functions and high performance. Thus, the development of multifunctional additives is of significance. Fortunately, besides the distinguished dispersity stability and thermal stability, a growing body of evidence suggests that CDs with suitable surface groups possess outstanding antioxidant behavior [63,141] and corrosion resistance properties [56,165,166]. For example, Cai’s group used the pressure differential scanning calorimetry test to measure the oxidative stability of CDs with DPA surface groups [63,141]. DPA groups as the radical scavenger could provide active hydrogen atom to alkoxy or alkyl peroxy radical groups produced during the chain oxidation process of the base oil to interrupt the chain reaction, making DPA-capped CDs as additives remarkably delay the oxidation process of base oils/liquids (Fig. 11a) [141]. Corrosion resistance is an important property for water-based lubricants in practical applications. Zhao’s group carried out weight loss tests to determine the corrosion resistance properties of the CDs as additives of water-based lubricant (Fig. 11b). Probably due to the formation of a carbon-based protective film, the CDs could suppress corrosion of carbon steel, rendering them a promising additive for water-based lubricants [56].

3.1.3. Lubrication effects of CDs-based lubricants

Owing to their outstanding physicochemical properties, it comes as no surprise that CDs-based lubricants possess excellent lubrication effects. More importantly, by varying their surface groups, CDs are capable to serve as additives for both oil- and water-base lubricants [1,52,57,63,64]. Generally speaking, anti-friction and wear-resistance properties, reflected by coefficient of friction (COF) and wear scar diameter/volume (WSD/WSV) respectively using the four-ball or ball-on-disk model (Fig. 12a), are the main indicators to evaluate the lubrication effects of lubricants [5,6,16,17].

(1) Lubrication effects of CDs-based nanocomposites as additives. Kang's group firstly revealed the great potential of CDs-based nanocomposites in lubrication in 2015. The tribological properties of CQDs/CuS_x composites as additives for liquid paraffin were investigated using a four-ball model. Under different friction time and loads, COF and WSV of CQDs/CuS_x composites suspension with the concentration (c) of 5 wt% reduced significantly compared with the values of pure liquid paraffin, deducing that CQDs/CuS_x composites effectively improved the friction-reducing and anti-wear abilities of base oil (Fig. 12b). And the efficient repair effect of CQDs/CuS_x nanocomposites for metal worn surface enhanced the precision of machine tools and repaired the worn engine efficiently [1]. Apart from as additives for oil-based lubricants, CDs-based composites could serve as excellent additives for water-based lubricants demonstrated by Liu’s group. The CQDs-decorated 2D nanosheets (MoS_2, WS_2, graphene, *etc.*) aqueous dispersions realized a friction coefficient as low as 0.02 and even achieved a super-lubricity on a ball-on-disk apparatus under a load of 5 N, dramatically improving the lubrication of water [55]. Afterwards,

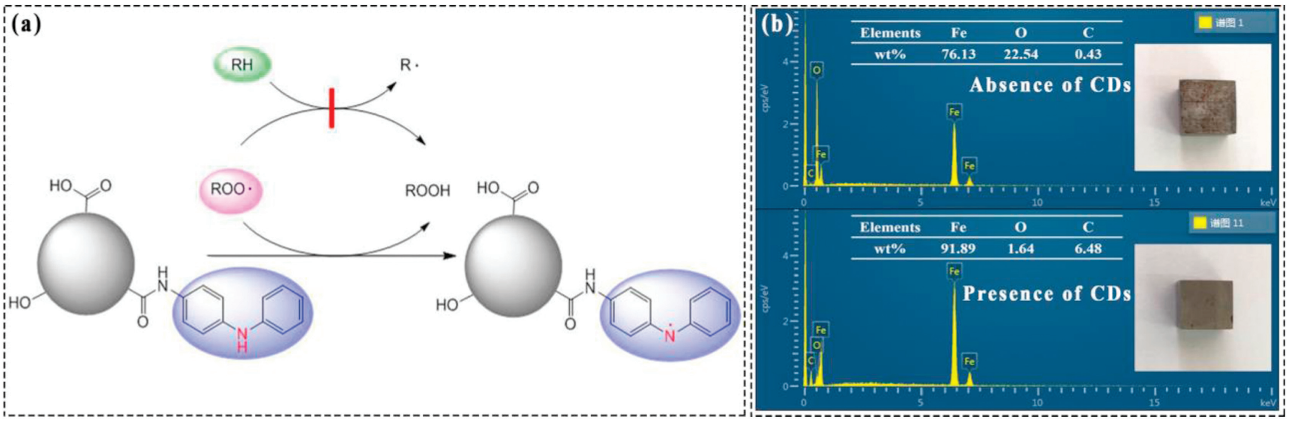


Fig. 11. (a) Possible antioxidant mechanism of CQDs-N in PEG. Copied with permission [141]. Copyright 2018, Elsevier. (b) EDS spectra and elemental composition of carbon steel surface immersed for 46 h in the absence and presence of CDs. Reproduced with permission [56]. Copyright 2019, Elsevier.

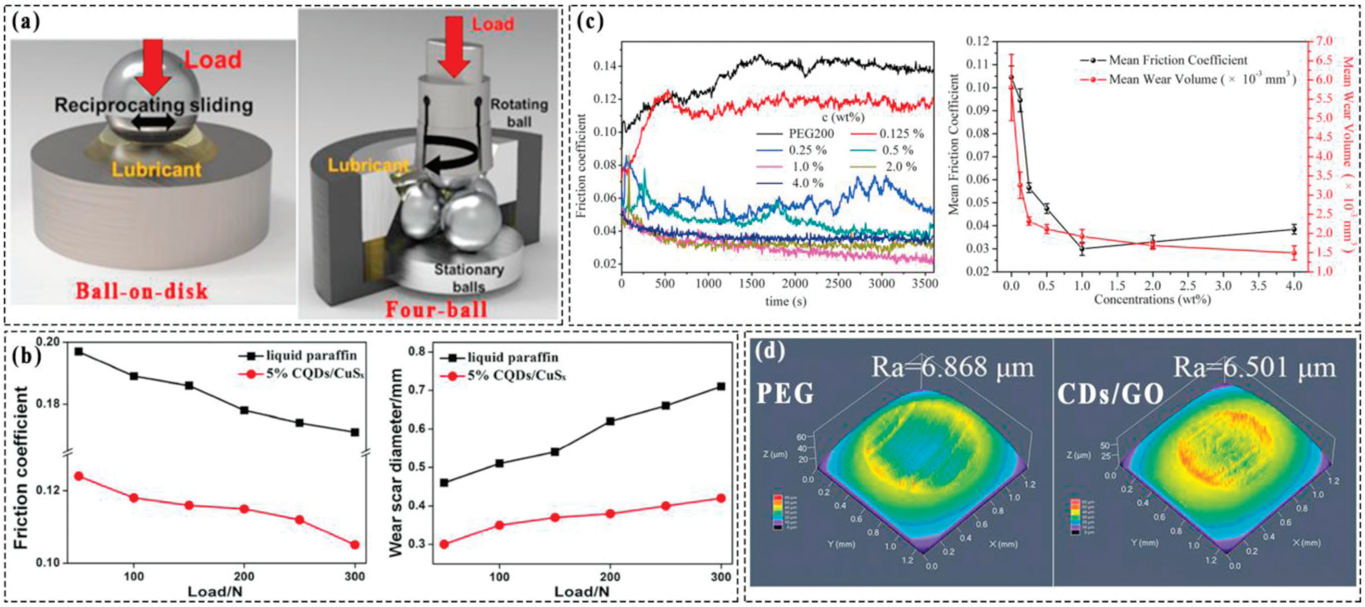


Fig. 12. (a) Schematic of four-ball and ball-on-disk model. Reproduced with permission [132]. Copyright 2019, MDIP. (b) The variation of COF and WSD with load using 5 wt% CQDs/CuS_x composites and liquid paraffin. Copied with permission [1]. Copyright 2016, Royal Society of Chemistry. (c) COF curves and mean COF and WSV lubricated by CDs/GO in PEG with various *c*, and (d) 3D images of PEG and CDs/GO in PEG (load: 392 N; speed: 1200 rpm; duration: 60 min). Copied with permission [118]. Copyright 2018, Elsevier.

He's group proved the extraordinary tribological behavior of GQDs/graphene/sulfurized isobutene (SIB) composites as additives for water on a four-ball machine. GQDs/graphene/SIB aqueous dispersions possessed smaller COF and WSD than DI water [27]. And Cai's group reported that using a four-ball model under 392 N, CDs/GO hybrids as additives in PEG with *c* of 1 wt% fulfilled 71.4% and 66.9% improvement of COF and WSV respectively than pure PEG (Figs. 12c and d). Importantly, the anti-wear and friction-reduction performance even enhanced with increased loads [118].

(2) Lubrication effects of pure CDs as additives. It has been verified that pure CDs designed by three strategies as additives can improve the lubrication effects of base oils/liquids [52,56,57,111,113,122,134]. Fan's group investigated tribological properties of nanoparticles including MoS_2, GQDs, *etc.* as additives for MACs by a ball-on-disk mode. Due to their small size and spherical shape, GQDs displayed the smallest and the most stable COF as well as the lowest WSV than other additives under high loads (Fig. 13a), indicating that GQDs provided the best tribological behaviors [111]. Our group probed tribological properties of four kinds of GQDs as additives for 150SN mineral oil by a four-ball tester under 392 N. Among them, the GQDs with small size, multiple layers and massive groups alleviated COF and WSD by 65% and 43%, respectively, at optimal additive concentration of 0.8 wt%, exhibiting the best tribological performance [113]. Zhao's group showed the water-soluble CDs as additives for DI water not only exhibited lower friction coefficient, more outstanding wear-resistance than GO prepared by the same way and raw materials, but also excellent corrosion inhibition effects [56]. Wang's group also compared the lubrication effects of GQDs and GO, and studied the tribological properties of water with the addition of various *c* of GQDs *via* a disk-on-disk type tribometer. Compared with GO, GQDs was more effective to enhance the tribological performances of water at the relatively low concentration (Fig. 13b), offering promising potential to be employed as high-performance additive. In particular, GQDs aqueous dispersion with *c* of 4% showed the excellent tribological performances with a 42.5% reduction of friction coefficient and a 58.5% decrease of wear rate compared with those of the water [122].

More and more researches have indicated that polymer-grafting CDs possess higher lubricating performance [57,133,139,141]. ILs are extensively used as a surface modifier for the synthesis of a variety of ILs-modified CDs to improve tribological properties of CDs [52,130,131,133,134]. In 2017, Wang's firstly investigated the lubrication effects of ILs-modified CDs (CDs_{-NTf2}) as the lubricant additive for PEG in detail using a four-ball model. When the *c* of CDs_{-NTf2} with NTf_2^- anion was introduced, the COF and WSD lubricated by PEG were correspondingly reduced by 70% and 33% under 392 N (Fig. 13c). Moreover, CDs_{-NTf2} exhibited superior anti-wear properties with the load increasing, and remained stable friction-reducing and anti-wear capabilities after working for more than 5 h [52]. Afterwards, this group further demonstrated that ILs-modified CDs prepared by different ILs and carbon sources could increase load-carrying capacity of base liquid besides showing remarkable friction-reducing and anti-wear properties far superior to the CDs and ILs [130,132]. In addition, this group also showed that PILs brush-grafted CDs (CDs-PILs) as additives for PEG fulfilling the good tribological properties against friction and wear [133]. Cai's group also proved that ILs-grafting CDs (CDs-OHMimBScB) with a sphere-in-shell structure exhibited more remarkable friction-reducing and anti-wear properties as additive for PEG than CDs and ILs alone as well as their blend [134]. More recently, to make ILs-modified CDs serve as additives for oil-based lubricants, R. Badía Laíño and coworkers prepared series of IL-modified CDs with different long alkyl chains and evaluated their tribological properties. Among them, IL-modified CDs using methyltrioctylammonium chloride as ILs sources was the best candidate as additives for PAO base oil, remarkably enhancing the lubrication effects of base oil in the most extreme of the tested conditions [131]. To enhance the lubricating effects of CDs, PEG is also used to achieve the functionalization of CDs due to its good qualities including low cost and promising tribological properties [57,138]. In 2019, our group firstly investigated the lubrication effects of PEG-grafting CDs as the lubricant additive for PEG in detail using a four-ball model. The PEG-grafting CDs with 0.8 wt% in PEG exhibited optimal tribological performance with a super-low

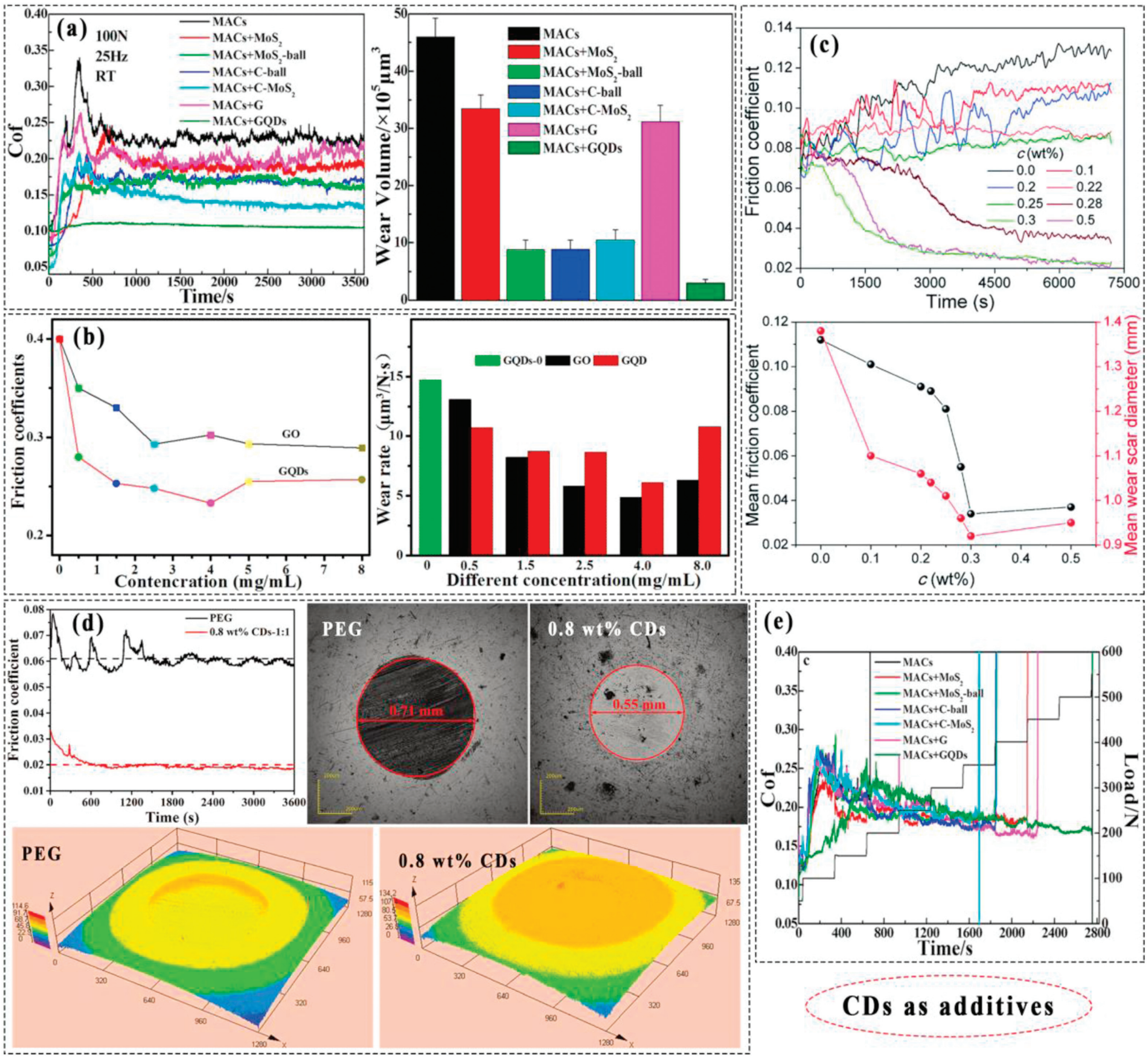


Fig. 13. (a) Friction curves and WSV lubricated by MACs and MACs with solid nanoparticles. Copied with permission [111]. Copyright 2017, American Chemical Society. (b) COF and wear rate of GQDs and GO aqueous dispersions. Copied with permission [122]. Copyright 2019, Springer. (c) COF curves and WSD of CDs-$_{NTf2}$/PEG suspensions with various *c*. Copied with permission [52]. Copyright 2016, The Royal Society of Chemistry. (d) COF curves and WSD images of CDs and PEG. Copied with permission [57]. Copyright 2019, Royal Society of Chemistry. (e) Extreme pressure properties of MACs with solid nanoparticles. Copied with permission [111]. Copyright 2017, American Chemical Society.

mean friction coefficient of 0.02 and a WSD of 0.55 mm under 600 N (Fig. 13d) [57]. Chen's group further studies the influence of PEG with different average molecular weight from 200 to 4000 on lubrication effects of PEG-modified CDs as the water-based lubricant additives. Among them, probably because the lower molecular weight resulted in high intensity of CDs, PEG$_{-200}$-modified CDs possessed superior tribological properties, giving rise to the largest COF and WSV reduction up to 83.5% and 90.9%, and dramatically increasing load carrying capacity of base liquid [138]. In addition, OA, DPA, PEI and PMMA are also used as functional groups to modify CDs, and then improve lubrication effects of CDs [63,64,139–141,147]. For instance, both Wang's group and Cai's group revealed that in comparison with pure PAO, OA-capped CDs/PAO suspension showed better friction-reducing, anti-wear and load-carrying capacities under low or high loads [63,64,140]. Importantly, OA-capped CDs not only exhibited excellent anti-oxidant performance [63], but also could work for 8 h without weakening the lubrication capability [140], and even raised the tribological properties of commercial 5W-30 engine oil [64]. Cai's group reported there was an effective improvement of anti-wear, load-carrying and anti-oxidant capacities of castor oil when DPA-modified CDs were added, suggesting that DPA-modified CDs could act as multifunctional additives for castor oil [63]. And for PEG base liquid, DPA-modified CDs also enhanced its friction-reducing property, showing the great potential as a more outstanding multifunctional additive for PEG [141]. Wang's group evaluated the tribological properties of branched PEI-grafted CDs as the water-based additives by the four-ball mode [146]. Compared to base liquid, PEI-grafted CDs with *c* of 0.15 wt% made the COF and WSV reduced by 53.4% and 94.9% respectively, greatly improving the lubrication ability of water. Afterwards, this group further demonstrated the excellent friction-reducing and anti-wear performances of different types of branched polyelectrolyte grafted CDs (CDs-PEI$_{0.6-10k}$-NTf$_2$) as additives for PEG. Specially, CDs-PEI$_{0.6-10k}$-NTf$_2$ with low *c* of 0.07 wt% made the COF and WSV of PEG reduce by 53.8% and 79.9%, respectively [139]. Maria Sarno and coworkers proved that PMMA-covered CDs as additive in commercial mineral oil showed remarkable lubrication performance at different *c*, temperature and loads [147].

Apart from the surface modified CDs, the lubrication effects of heteroatom-doped CDs have been investigated as well [64,151,152,156]. Owing to the existence of nitrogen-containing groups on their surfaces, N-doped CDs share a favorable dispersion in PEG. In light of the advantage, both Cai's group [64] and our group [156] studied the lubrication effects of N-CDs as additives for

Table 1
Tribological properties of CDs as lubricant additives.[a]

Additive	Optimum *c*	Base stock	Operating conditions	Mating surfaces	COF; Reduction rate	Wear; Reduction rate	Ref.
CQDs/CuS$_x$ composites	5 wt%	liquid paraffin	four-ball, 1450 rpm, 100 N, 15 min	Steel-steel	0.12; 36%	WSV 1.08×10^{-4} mm^3; –	[1]
MoS$_2$/CQDs composites	–	Ultrapure water	ball-on-disk, 0.183 m/s, 5 N	Steel-steel	less than 0.01; –	–	[55]
CDs/GO hybrids	1 wt%	PEG$_{-200}$	four-ball, 1200 rpm, 392 N, 60 min	Steel-steel	0.03; 71.4%	WSV 1.92×10^{-3} mm^3; 66.9%	[118]
GQDs/graphene/SIB composites	–	DI water	four-ball, 1450 rpm, 196 N, 60 min	YG8 hard alloy	less than 0.07; 50%	WSD 0.224 mm; 64%	[109]
GQDs	2 wt%	MACs	ball-on-disk, 25 Hz, 100 N, 60 min	Steel-steel	0.1; 58%	WSV 3.0×10^{-4} mm^3; 93%	[111]
GQDs	0.8 wt%	150SN mineral oil	four-ball, 1200 rpm, 392 N, 60 min	Steel-steel	0.031; 65%	WSD 0.559 mm; 43%	[113]
CDs	0.1 mg/mL	DI water	ball-on-disk, 5 Hz, 10 N, 60 min	Al$_2$O$_3$-steel	0.26; 32%	Wear rate 1.5×10^{-6} mm^3 N^{-1} m^{-1}; 38%	[56]
GQDs	4 mg/mL	Ultrapure water	ball-on-disk, 20 Hz, 100 N, 60 min	Steel-steel	0.23; 42.5%	Wear rate 6.11 μm^3 N^{-1} s^{-1}; 58.5%	[122]
CDs$_{\text{-NTf2}}$	0.3 wt%	PEG$_{-200}$	four-ball, 1200 rpm, 392 N, 120 min	Steel-steel	0.034; 70%	WSD 0.92 mm; 33%	[52]
CDs-ILs	0.5 wt%	2 wt% triethanolamine aqueous solution	four-ball, 600 rpm, 50 N, 60 min	Steel-steel	0.094; 65%	WSD 0.62 mm; 21%	[132]
CDs-ILs	0.015 wt%	2 wt% triethanolamine aqueous solution	four-ball, 600 rpm, 40 N, 60 min	Steel-steel	0.14; 57.5%	WSV 1.1×10^{-3} mm^3; 64%	[130]
CDs-PILs	1.5 wt%	PEG$_{-200}$	ball-on-disk, 10 mm/s, 40 N, 20 min	Steel-steel	0.08; 61.9%	WSV 1.3×10^{-4} mm^3; 82.5%	[133]
ILs-modified CDs	0.1% (w/v)	PAO	ball-on-disk, 15 Hz, 120 N, 20 min	Steel-steel	–; 21%	WSV –; 63%	[131]
CDs-OHMimBScB	1 wt%	PEG$_{-200}$	four-ball, 1200 rpm, 392 N, 60 min	Steel-steel	0.029; 73.15%	WSV 1.2×10^{-3} mm^3; 75.55%	[134]
PEG-grafting CDs	0.8 wt%	PEG$_{-400}$	four-ball, 1200 rpm, 600 N, 60 min	Steel-steel	0.02; 67.2%	WSD 0.55 mm; 29.1%	[57]
CDs-PEG	0.2 wt%	2 wt% triethanolamine aqueous solution	four-ball, 600 rpm, 40 N, 60 min	Steel-steel	0.05; 83.5%	WSV 4×10^{-4} mm^3; 90.9%	[138]
OA-modified CDs	1.0 wt%	PAO	four-ball, 1200 rpm, 392 N, 240 min	Steel-steel	0.055; 47%	WSD 0.7 mm; 30%	[140]
OA-capped CDs	0.5 wt%	PAO	four-ball, 1200 rpm, 392 N, 60 min	Steel-steel	0.09; –	WSD 0.621 mm; 28.5%	[63]
OA-modified CDs	1.0 wt%	PAO	four-ball, 1200 rpm, 392 N, 60 min	Steel-steel	0.06; 47.1%	WSV 7.5×10^{-4} mm^3; 90.5%	[64]
DPA-modified CDs	0.2 wt%	castor oil	four-ball, 1200 rpm, 392 N, 60 min	Steel-steel	0.06; –	WSD 0.335 mm; 44.7%	[63]
DPA-modified CDs	1 wt%	PEG$_{-200}$	four-ball, 1200 rpm, 392 N, 60 min	Steel-steel	0.03; 75%	WSD 0.61 mm; 34.8%	[141]
PEI-grafted CDs	0.15 wt%	2 wt% triethanolamine aqueous solution	four-ball, 600 rpm, 40 N, 60 min	Steel-steel	0.13; 53.4%	WSD 0.55 mm; 52.6%	[146]
CDs-PEI$_{10k}$-NTf2	0.07 wt%	PEG$_{-200}$	ball-on-disk, 10 mm/s, 40 N, 20 min	Steel-steel	0.12; 53.8%	WSV 2×10^{-5} mm^3; 79.9%	[139]
PMMA-covered CDs	0.3 wt%	VG 220 mineral oil	ball-on-disk, 10 Hz, 19 N, 60 min, 25 °C	Steel-steel	0.11; 20.2%	WSD 0.24 mm; 41.6%	[147]
N-doped CDs	1 wt%	PEG$_{-200}$	four-ball, 1200 rpm, 392 N, 60 min	Steel-steel	0.0295; 75.9%	WSV 9.66×10^{-4} mm^3; 82.8%	[64]
N-doped PDs	0.8 wt%	PEG$_{-400}$	four-ball, 1200 rpm, 600 N, 60 min	Steel-steel	0.024; 6.7%	WSD 0.57 mm; 19.7%	[156]
B, N-codoped CDs	1 wt%	PEG$_{-200}$	four-ball, 1200 rpm, 588 N, 60 min	Steel-steel	0.045; 62.18%	WSD 0.745 mm; 42.82%	[151]
CDs-PF$_6$	1 wt%	PEG$_{-200}$	four-ball, 1200 rpm, 588 N, 60 min	Steel-steel	0.03; 72.7%	WSV 1.99×10^{-4} mm^3; 96.5%	[152]
S-doped CDs	5 wt%	DI water	ball-on-disk, 150 cycles/min, 2 N, 12 min	Si$_3$N$_4$-steel	0.5; 36%	–	[163]
S, N-codoped CDs	0.1 wt%	PEG$_{-200}$	ball-on-disk, 25 mm/s, 40 N, 30 min	Steel-steel	0.106; 16.6%	Wear rate 2.7×10^{-7} mm^3 N^{-1} m^{-1}; 75.9%	[153]
Mo-doped CDs	1 wt%	PEG$_{-200}$	our-ball, 1200 rpm, 392 N, 60 min	Steel-steel	0.046; 62.90%	WSD 0.745 mm; 33.29%	[157]
Ni-doped CDs	2 wt%	PEG$_{-200}$	ball-on-disk, 25 mm/s, 8 N, 60 min	Steel-steel	0.17; 35.5%	Wear rate 1.8×10^{-7} mm^3 N^{-1} m^{-1}; 36.4%	[154]
Ga-doped CDs	–	–	ball-on-disk, 50 Hz, 100 N, 60 min	Steel-steel	0.132; 27.9%	WSD 0.58 mm; –	[155]

[a] The reduction rates of COF and wear are calculated based on the corresponding values of the base oils/liquids or reference oil.

PEG by a four-ball tester. Typically, there were more than 50% improvement of COF and WSV after adding N-CDs into PEG [64,156], even under higher load [156]. Furthermore, due to the incorporation of boron into the CDs framework besides nitrogen, B, N-codoped CDs were verified to be a more high-performance lubricant additive by Cai's group [151,152], improving significantly the anti-wear and friction-reducing properties of PEG under the high load [151]. Afterwards, F-doped CDs (CDs-PF_6) were proved to be a more excellent additive for PEG than B, N-codoped CDs (CDs-BScB), achieving the maximum reduction by 72.7% and 96.5% of COF and WSV of PEG respectively [152]. Besides, Xiao's group reported that the water-soluble S-doped CDs as water-based additives were able to effectively reduce COF and wear track size for both Si_3N_4-steel and Si_3N_4-Si_3N_4 contacts [163]. Wang's group further showed the excellent anti-wear and friction-reducing properties of S, N-codoped CDs as additives for PEG [153]. Metal elements-doped CDs have been applied to improve the lubricating performance of base oils. For example, the Mo-doped CDs were explored as additives in PEG, reducing the COF of 62.90% and WSV of 80.21% simultaneously, reported by Cai's group [157]. Wang's group revealed that the Ni-doped CDs as additives achieved more enhancement of the lubrication properties of PEG than the plain CDs under most loads and reciprocation speeds [154]. More recently, Agnieszka's group demonstrated that compared with reference PAO oil, Ga-doped CDs had better anti-friction capability, but unsatisfactory anti-wear property [155].

In addition, in comparison with liquid lubricants, grease lubricants contribute to sealing, force transfer purposes and

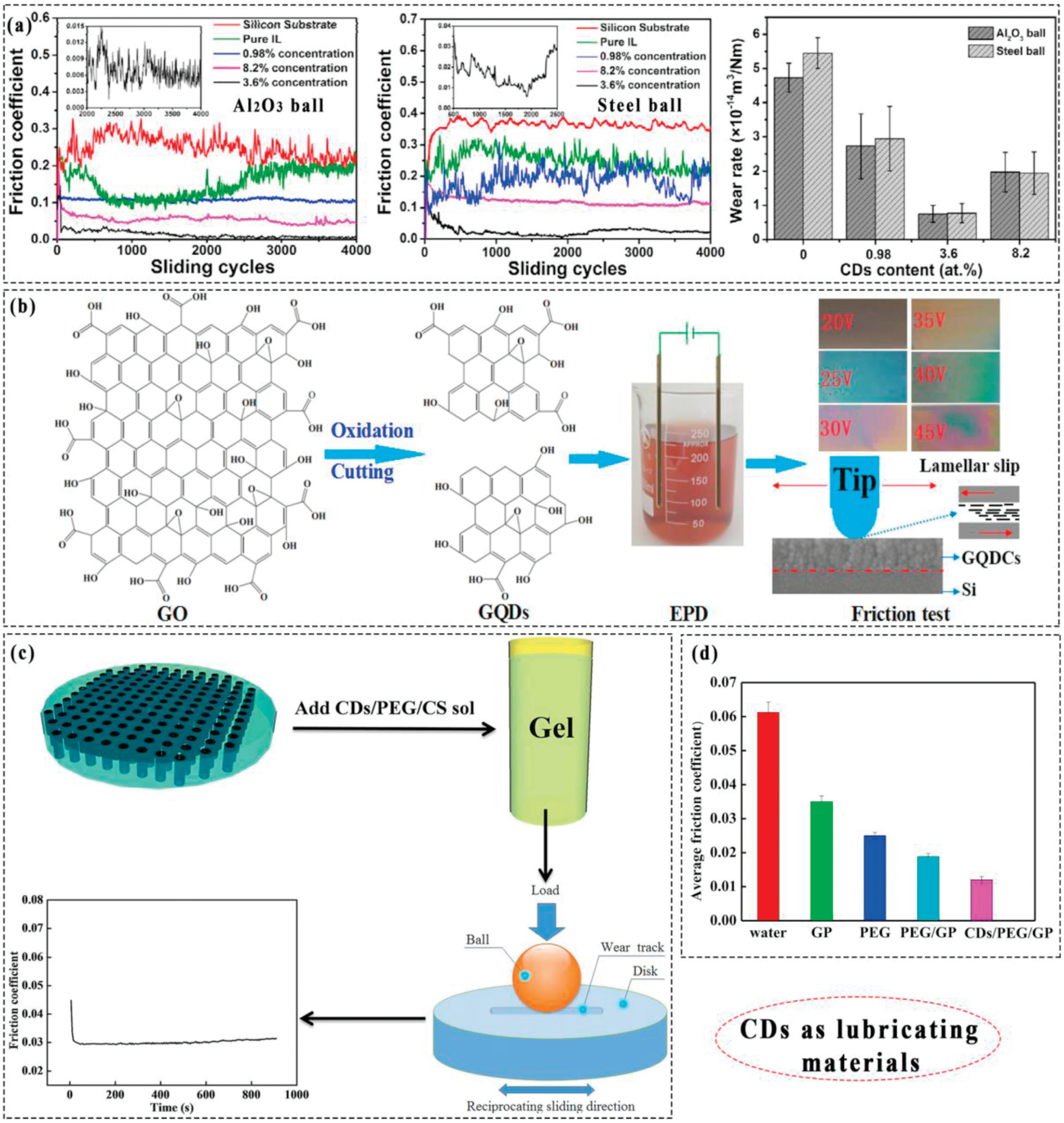


Fig. 14. (a) COF curves and wear rate of IL-modified CDs as a function of the CDs content. Reproduced with permission [76]. Copyright 2017, Elsevier. (b) Schematic of preparing GQDs coating and the corresponding friction test. Copied with permission [167]. Copyright 2020, Elsevier. (c) Schematic of CDs/PEG/chitosan gel stored in textured surfaces and the corresponding friction test. Copied with permission [78]. Copyright 2017, The Royal Society of Chemistry. (d) COF of different solutions. Copied with permission [79]. Copyright 2018, Elsevier.

anticorrosion besides controlling the friction, applicable in transportation industrial valves and bearings. Mehran's group confirmed that CDs could act as additives for lithium lubricating greases to achieve the enhancement of lubricating, sealant and anticorrosion properties [77]. However, up to now, there is no other literature focusing on the research about CDs as additives for grease lubricants.

More data from studies on tribological properties of CDs lubricant additives as are summarized in Table 1. It must be taken into account that besides the types of additives, the lubricating performance of lubricants has a strong correlation with the *c* of additives, material compositions of the contact surfaces and rubbing conditions. Therefore, there is little comparability of COF and WSV between different researches.

It should be noticed that in addition to anti-friction and wear-resistance capabilities, CDs as additives also possess extreme pressure property, and even render the COF decline with increasing load [1]. Fan's group demonstrated that GQDs endowed base oil higher load-carrying capacity than other nanoparticles (Fig. 13e) [111]. And Agnieszka's group reported that N-doped CDs with extraordinary extreme pressure ability improved the scuffing resistance more than 15 times than PAO reference oil [155]. In a word, all the evidence manifests that CDs are one of most hopeful and competitive candidates to serve as effective multifunctional oil or water-based lubricant additives.

3.2. CDs as lubricating materials in other fields

Besides as additives for lubricants, several recent studies have manifested that CDs are also able to serve as lubricating coating, gel and magnetorheological fluids additives [75,76,78–81]. Lubricating coatings as a means of important lubrication have attracted a recent surge of interest owing to great application prospect in micro/nano-electrical-mechanical systems [167–169]. To date, a number of nanoparticles, such as diamond-like carbon [168,169], MoS_2 [170], graphene [171], GO [172] and CDs [75,76,167] have been used as lubricant coatings to enhance lubricating effects of the substrates. Among, CDs coatings are considered to be the most promising and effective lubricant coatings due to their excellent tribological properties and corrosion inhibition effect. In 2017, Zhang's group firstly demonstrated excellent tribological performance of ILs-modified CDs coatings on the surfaces of silicon (111) chips using the rotating ball-on-disc tester. The prepared CDs coatings obtained a super-low COF of 0.006 and wear rate of $7 \times 10^{-6}\,mm^3\,N^{-1}\,m^{-1}$ (Fig. 14a) [76]. In 2018, based on the fact that the excellent solubility of dodecyl amine functionalized GQDs in toluene solution offered the possibility of efficiently and rapidly forming the coatings to steel surfaces by spray deposition way, René's group created GQDs coatings on steel surfaces. The thin GQDs coatings lowered the COF of steel and revealed a significant corrosion inhibition effect [75]. In 2020, Taking into consideration that the GQDs possessed good water solubility and a mass of negative charges, Yang's group obtained smooth and high dense GQDs coatings on the surfaces of silicon (100) wafers in GQDs aqueous dispersions thought a simple electrophoretic deposition way (Fig. 14b). Importantly, the thickness and roughness values of the GQDs coatings could be tuned *via* altering the deposition voltages. The optimum GQDs coating realized effective reduction in COF of 85% and WSV of 97% relative to those of the bare substrate, improving the lubricating performance and extending the wear life of silicon-based devices remarkably [167]. All the reports above suggest that CDs as outstanding lubricant coatings have a broad prospect in micro/nano-electrical-mechanical systems application field.

As a new lubricating material, CDs not only manifest tremendous application potential in the field of industrial lubrication and friction, but also in the area of bio-tribology by virtue of biocompatibility and biodegradability properties [78–80]. Dong's group investigated the bio-tribological performance of CDs-based gels on textured surfaces of Cr–Co–Mo alloy by a ball-on-disc tribometer for the first time, providing a new and green approach to enhance the lubricating performance of artificial joints. In which, the fabricated CDs/PEG/chitosan gel stored in textured surfaces, avoiding dilution of body fluid and absorption of the human body, slowly released the CDs/PEG lubricant with excellent lubrication effects, thus causing good and long-lasting lubrication effect (Fig. 14c) [78]. On this basis, this group further prepared other types of CDs-based gel with better lubrication abilities (Fig. 14d), and verified that CDs could make the gel have better intermolecular interactions, thus intensifying the rheological and mechanical properties of the gel [79,80]. These new findings are conducive to promote the development of CDs in bio-tribology fields.

In addition, CDs were also used as additives for magneto-rheological fluids to improve their shear stress and sedimentation rate, enabling them used in mechanical systems requiring the active control of vibrations or the transmission of torque [81].

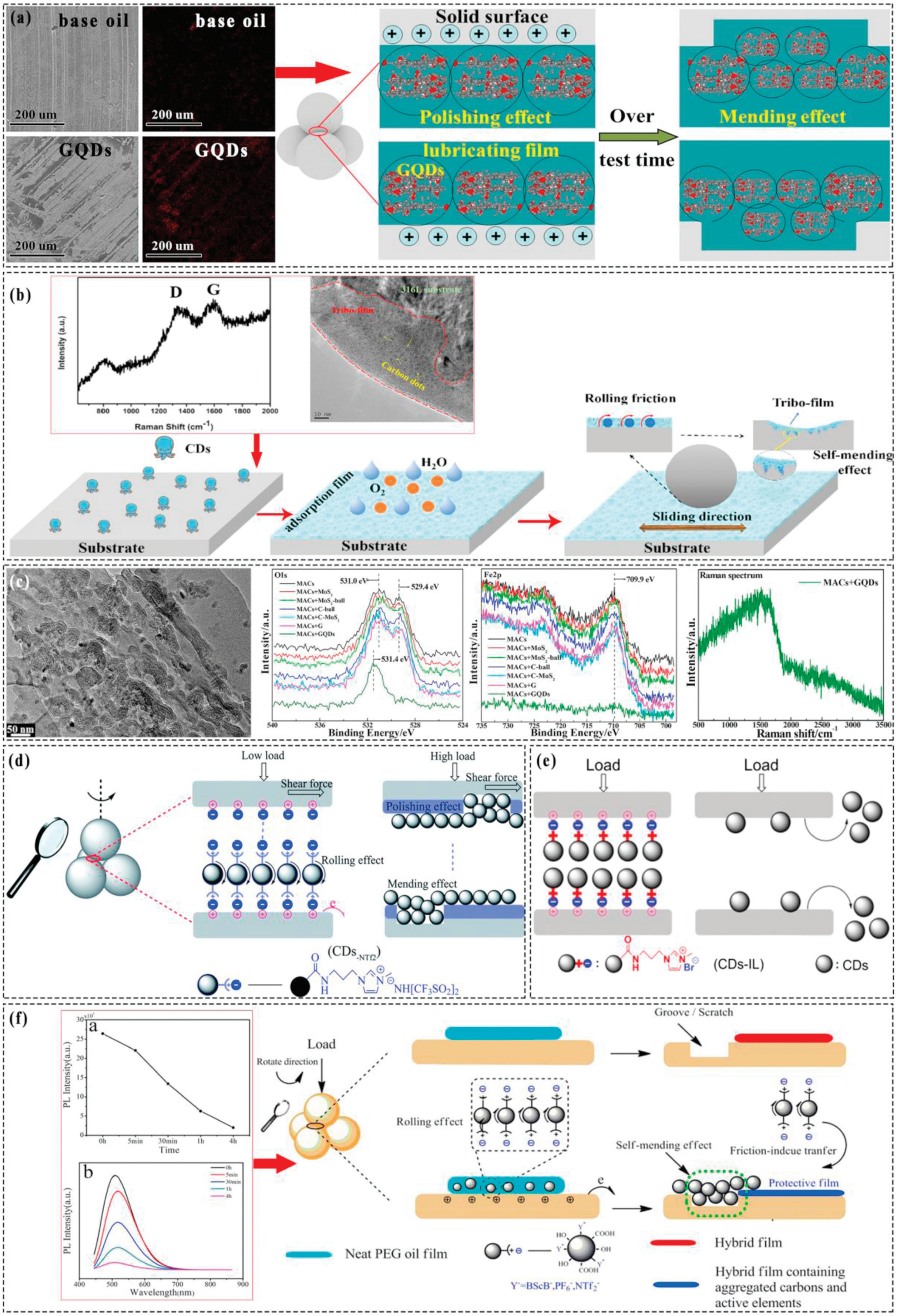
As mentioned above, owing to their outstanding friction reducing and anti-wear performance, favorable biocompatibility and environmental friendliness, CDs have been widely employed for lubrication fields, especially as additives for liquid lubrications. However, compared with the application of CDs in sensing, bioimaging catalytic, *etc*., the research on lubrication application of CDs is still not sufficient.

4. Lubrication mechanism

It is of great significance to explore the role of nanoparticles in lubricants and explain the friction mechanisms. On the basis of a large number of experimental characterization and analysis, the lubrication mechanisms have been proposed to explain the improvement of the lubrication effects of lubricants using nanoparticles as additives, roughly classified into four types [111,173,174]: (a) the protective film, as spacers or third body materials to prevent the friction pairs from straight asperity contact; (b) the rolling effect, playing a role of ball bearing between the friction interfaces; (c) the mending effect, depositing on the worn surface and compensating for the worn loss; (d) the polishing effect, reducing the roughness of the friction surfaces through nanoparticle abrasion. The protective film and rolling effect mainly act on COF reduction, while the mending and polishing effects principally lead to the enhancement of surface quality. According to the Stribeck curve a famous tool to define the lubrication regimes, the lubrication regimes of CDs whose tribological tests are conducted on four-ball or ball-on-disk testers generally belong to boundary lubrication [109]. Based on existing lubrication mechanisms and characteristics of CDs, some researchers have discussed the lubrication mechanisms of CDs.

4.1. The lubrication mechanisms of pure CDs

It is well known that during friction process, contact convex points of friction pairs become positively charged by means of emission of the low-energy electrons [141,175]. Thus, CDs with negatively charged anions tend to absorb onto the frictional surfaces by electrostatic interactions. Moreover, if CDs contain higher electronegativity atoms such as N and O, the nonbonding electrons of N and O will form coordinate covalent bonds with electron-deficient orbitals in metals of friction pairs, helpful to facilitate CDs absorbing onto the worn surfaces by covalent interaction [56]. The absorption of CDs on the worn surfaces opens up possibilities to the formation of a lubricating layer and conduces


(a)
base oil
base oil
200 um
GQDs
GQDs
200 um
Solid surface
Polishing effect
lubricating film
GQDs
Over
test time
Mending effect
(b)
D
G
Intensity (a.u.)
Raman Shift (cm^{-1})
316L substrate
Tribo-film
Carbon dots
10 nm
CDs
Substrate
adsorption film
H_2O
O_2
Substrate
Rolling friction
Tribo-film
Self-mending effect
Sliding direction
Substrate
(c)
50 nm
O1s
531.0 eV
529.4 eV
531.4 eV
MACs
MACs+MoS_2
MACs+MoS_2-ball
MACs+C-ball
MACs+C-MoS_2
MACs+G
MACs+GQDs
Intensity/a.u.
Binding Energy/eV
Fe2p
709.9 eV
Raman spectrum
MACs+GQDs
Raman shift/cm^{-1}
(d)
Low load
Shear force
Rolling effect
High load
Shear force
Polishing effect
Mending effect
(CDs_{-NTf2})
$NH[CF_3SO_2]_2$
(e)
Load
Load
(CDs-IL)
: CDs
(f)
a
PL Intensity(a.u.)
Time
0h
5min
30min
1h
4h
b
PL Intensity(a.u.)
Wavelength(nm)
Load
Rotate direction
Groove / Scratch
Rolling effect
Self-mending effect
Friction-indcue tranfer
Protective film
Neat PEG oil film
Hybrid film
Hybrid film containing aggregated carbons and active elements
Y^-=$BScB^-$,PF_6^-,NTf_2^-

to playing the role of rolling and mending, leading to high friction-reducing and anti-wear properties [52,133,134,141]. Therefore, to reasonably speculate lubrication mechanisms of CDs, it is essential to analyze the worn surfaces using SEM, EDS, Raman, XPS and TEM.

Our group carried out SEM and EDS to investigate morphology and carbon element distribution of worn surfaces, and found that the wear scar lubricated by GQDs-based lube possessed more dark color active areas and higher carbon content than that of base oil, meaning attachment and embedment of plenty of GQDs on the worn surfaces. Thus, the lubricating mechanism was attributed to the lubricating film, polishing and mending effect. To be specific, GQDs with oxygen-containing groups could easily absorb on the frictional surfaces to form a lubricating film. The multilayered and small GQDs were in favor of the polishing effect. With prolongation of test time, some rupture occurred in the lubricating film, and GQDs played a mending role by filling the deep scratches (Fig. 15a) [113]. To clarify the lubricating mechanism of CDs as additives for water-based lubricants, Zhao's group performed Raman spectra on the wear scars and observed the cross section of the wear scars by TEM. The Raman spectra contained the D peak and G peak, meaning that the carbon element on the wear scars existed in the form of graphene structure. It could be clearly seen in TEM images that a protective lubricant film containing CDs was formed on the surface of the wear scar. Thereby, the lubricating mechanism was that CDs not only could absorb on the surfaces to form a protective film, but also play a vital role in converting the sliding friction into rolling friction and fill into the wear scars. Specially, CDs with high electronegativity could adsorb on the wear surfaces to form an adsorption film. During the sliding tests, the adsorption film was embedded into the wear scars and converted into stable tribo-film. The presence of CDs played a ball-bearing effect, transforming the sliding friction into rolling friction. And the CDs with small diameter could be filled into the micro-pits and furrows of wear scars, providing a "self-mending" effect (Fig. 15b) [56].

The research on the microstructure of CDs after tribological tests is beneficial to explore the role of GQDs in the process of friction testing [109]. Inspired by this, Fan's group further applied TEM to observe the structural changes of GQDs debris from the worn surfaces under the high applied load apart from the analyses of worn surfaces by XPS and Raman. TEM images showed the "ganoderma lucidum cloud"-like morphology of GQDs debris, illustrating that a large number of GQDs participated in the friction process. Besides, the fact that there were weak O 1s peak and no Fe 2p peak in XPS, and Raman showed a wide and strong peak at 1516 cm^{-1}, indicated that GQDs could readily absorb on the sliding surfaces to form a high-density and easily shearing protective layer, and under harsh conditions GQDs as third body prevented the mating surfaces from straight asperity contact, thereby improving the tribological performance (Fig. 15c). Thus, the lubrication mechanism of GQDs were contributed from the synergistic effect of a densely protective film on the sliding surfaces and the graphene-like debris in the contact area [111].

To revealed lubrication mechanisms of surface modified CDs under different loads, Wang's group [52,130–132,139,140,146,153,154] and Cai's group [64,134,152,157] employed more detection means, such as XPS, SEM, EDS, Raman and TEM analyses study the worn surfaces. The reason why surface modified CDs possessed higher lubricating performance was attributed to the synergistic lubricating effect, including film lubrication of surface groups and nano-lubrication of carbon cores such as rolling, mending and polishing effects. The surface groups made CDs easily adsorb onto the positively charged sites of the worn surfaces by electrostatic attraction. Subsequently, a lubricating film composed of the layers of CDs and PEG molecules formed around these initial adsorbates. Under low load, the lubricating film formed by physical absorption alleviated friction and wear by preventing the direct contact of rubbing surfaces and the rolling effect of CDs. Under high load, the surface groups of CDs reacted with the substrate to form tribo-chemical reaction films. And carbon cores of CDs not only formed a protective film on the shear surfaces but also exhibited a mending effect by filling the deep scratches and rolling and polishing effects by acting as "ball-bearings" (Fig. 15d) [52]. With increasing test duration, the ordered carbon materials were gradually forming, inhibiting the undesirable wear. However, if the CDs without grafting groups were prone to be squeezed out of the rubbing surfaces during the boundary shear friction process under high load, causing a poor lubrication effect (Fig. 15e), also demonstrated by Chen's group [138]. In addition, Xiao's group demonstrated that the lubricating mechanism of S-doped CDs as water-based additives was rolling effect [163].

In comparation with other nanoparticles, CDs possess unique PL characteristic, offering an effective pathway to trace their final location, thus explaining their role in lubrication. Inspired by this, Cai's group [151,152,157] and our group [57] compared the PL intensity before and after tribo-tests besides analyzing wear scars to probe the lubrication mechanism of CDs. Cai's group found that the PL intensity clearly decreased with increasing applied pressure and test duration, meaning that CDs transferred from lubricants to frictional interfaces and formed a lubricating protective layer, thus making the fluorescence decrease, even quench (Fig. 15f) [151,152]. While our group observed that the PL intensity of CDs-based lube was nearly constant after a one-hour tribotest, illustrating that few CDs shifted from the lubricant to interfaces, thereby CDs served as rolling effect [57].

As mentioned above, through the analyses of worn surfaces, debris and lubricants using SEM, EDS, Raman, XPS, TEM and PL, the lubricating mechanisms are mainly attributed to the protective film, rolling effect, polishing effect and mending effect, and may vary with CDs preparation methods and precursors.

4.2. The lubrication mechanisms of CDs-based nanocomposites

The CDs-based nanocomposites as additives aim to make full use of advantages of CDs and other nanoparticles to further intensify lubrication effects, thus, their lubrication mechanisms are attributed to the synergetic effects of CDs and other nanoparticles [1,55,109,118]. For instance, the lubrication mechanism of CQDs/CuS_x nanocomposites was attributed to the combination of the multi-layer graphite structure of CQDs and the high chemical activity of CuSx nanoparticles by XPS, SEM and EDS analyses of worn surfaces. In detail, the CQDs with tiny size and graphitic fragment structure rendered size distribution of CQDs/CuS_x composites uniform and narrow, conducing to homogeneous attachment of the composites on rubbing surfaces; while CuS_x with high chemical activity easily formed $CuFe_yS_{x-y}$ alloy with steel substrate, forming a surface protective film to resist wear, thus improving the lubrication performance [1]. On basis of

Fig. 15. (a) SEM images and Carbon element of wear scars lubricated by 150SN mineral oil and GQDs, and schematic of the lubricating mechanism of GQDs-based additives. Reproduced with permission [113]. Copyright 2018, Elsevier. (b) Raman spectra and TEM of wear scars lubricated by DI water with addition of CDs, and schematic of the corresponding lubricating mechanism. Copied with permission [56]. Copyright 2019, Elsevier. (c) TEM of wear debris derived from solid nanoparticles after friction, and XPS and Raman of worn surfaces. Copied with permission [111]. Copyright 2017, American Chemical Society. (d) Schematic of lubricating mechanism of ILs-modified CDs under different loads. Copied with permission [52]. Copyright 2016, Royal Society of Chemistry. (e) Schematic of the lubrication mechanism of CDs with and without surface modification. Copied with permission [130]. Copyright 2019, Springer. (f) PL intensity and emission spectra of CDs/PEG after various test time, and the schematic of the relevant lubricating mechanism. Reproduced with permission [152]. Copyright 2019, Elsevier.

lots of tribological tests, Liu's group proposed that the synergistic effect of CQDs/2D nanosheets composites led to excellent lubrication properties. As illustrated in Fig. 16a, the CQDs tended to attach on the rubbing surfaces to form a lubricating film under low load, but their lubricating property was significantly weakened under high load owing to extrusion of the contact area. While CQDs/2D nanosheets composites assembled on the rubbing surfaces were difficult to be fully squeezed out as they contained 2D nanosheets with relatively large surface area, at the same time, CQDs in the composites acted as a wheel to help the easy sliding under high load, resulting in synergetic lubricating performances [55]. Cai's group employed SEM, EDS and Raman spectra to analyze worn surfaces lubricated by CDs/GO hybrid-based lubricants, and ascribed the excellent tribological performance to the synergistic effect of CDs and GO including the tribo-chemical reaction film and self-mending effect (Fig. 16b) [118].

The microstructure transfer of interfacial nanoparticles under high load and fast speed has a close relation with tribological properties, providing a practical method to understand their lubrication mechanism. Based on this, He's group used TEM technique to probe the microstructure of GQDs in the transfer film and the lubricant fluid after tribological tests, and attributed the lubrication mechanism of GQDs/graphene and GQDs/graphene/SIB composites to the boundary and solid lubrication effect of transfer film and nanocrystals. Specifically, under the sliding-induced effect, the GQDs were transformed into fullerene quantum dots (fullerene QDs) in the transfer film, making the grain refinement. The transfer film including fullerene QDs as well as sliding-induced WO_2 and anti-wear WO_3 nanocrystals was beneficial to enhance the boundary lubrication. The WO_2 nanocrystals were inset into fullerene-like structure of fullerene QDs, well improving the solid lubrication. And SIB as an extreme pressure additive could further reduce friction and wear during sliding (Fig. 16c) [109]. On the grounds of the reported lubrication mechanisms, it is greatly hopeful to fabricate CDs-based nanocomposites with better lubricating effects.

It can be seen that significant efforts have been made to explore the lubrication mechanisms of CDs as additives for lubricants and impressive progress has been made. However, because of the difficulties in tracking and characterizing the complicated

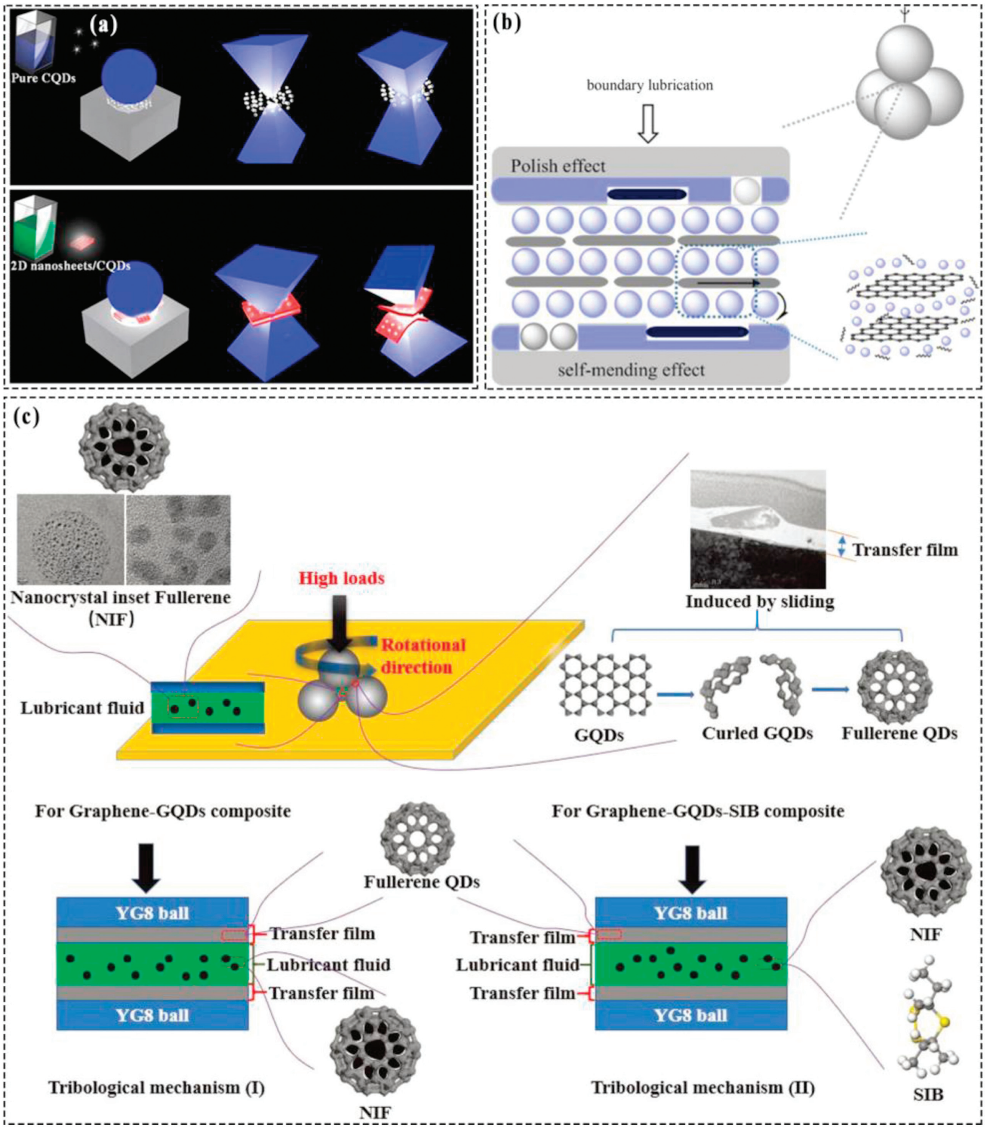


Fig. 16. (a) Proposed lubrication model for CQDs and CQDs-decorated 2D nanosheets. Copied with permission [55]. Copyright 2016, American Chemical Society. (b) Schematic of the lubrication mechanism of CDs/GO hybrids as additives. Reproduced with permission [118]. Copyright 2018, Elsevier. (c) Schematic of the tribological mechanisms of GQDs/graphene/SIB composites. Copied with permission [109]. Copyright 2018, Wiley.

reactions and intermediates at the contact zone during friction process, the lubrication mechanisms of nanoparticles rely on the analyses of worn surfaces after tribotest, thereby still remain not fully understood. The detailed lubricating mechanism of CDs as additives awaits further understanding.

5. Conclusions and perspectives

In summary, this review comprehensively highlights new insights into the various strategies, including size and shape control, surface modification and heteroatom doping, for improving tribological features of CDs, and their employment as a powerful friction-reducing and anti-wear material for lubrication. These exciting research results reveal that owing to their ultrasmall size, tunable surface functional groups, natural excellent dispersion stability, favorable biocompatibility, low toxicity, environmental friendliness and facile synthetic routes, CDs have been developed as green anti-wear and friction-reducing materials for lubrication applications, especially in the industrial lubrication field, and their lubrication mechanisms are dominantly ascribed to the protective film, rolling effect, polishing effect and mending effect.

Despite the tremendous progress, CDs as new emerging carbon-based nanoparticles have been much less studied and evaluated for lubrication application in comparison with their other applications such as bioimaging, sensing, catalysis and optoelectronic devices. The research on lubrication application of CDs has recently emerged in the literature in 2015. Currently, only less than fifty records on lubrication application of CDs can be searched from Web of Science, far fewer than that of other applications. Therefore, it is still in an infancy stage to employ CDs for lubrication, and there are still a few issues requiring to be addressed: a) lack of a rapid, low-cost, facile, high-yield and large-scale fabrication approach for preparing high-quality CDs. Although various low-cost raw materials and multiple methods can be applied to form CDs, the time-consuming post-processing commonly containing several days of dialysis greatly restricts their full use in lubrication. A few preparation methods have avoided time-consuming dialysis purification process, but it is still a shortage of research on the tribological performance of as-obtained CDs. More recently, one-step way for fabricating CDs-based lubricants offers a new idea to overcome the shortcomings of complicated reprocessing, whereas it is unachievable to fabricate customized CDs. As a consequence, increasing efforts are urgently required to develop better synthetic routes of CDs; b) inadequate systematic studies on comprehensive properties evaluation of CDs-based additives. There is a great deal of research focusing on dispersion stability, thermal stability, antifriction and wear-resistance properties of CDs-based additives, but it is inadequate to evaluate their viscosity-temperature, antioxidation, corrosion inhibition and extreme pressure properties, making them far from practical applications. More importantly, few studies have referred to the correlation between the structure (size, crystallinity, surface groups) and friction-related properties of CDs, giving rise to a lack of systematic understanding on the tribological performance of CDs. As a result, more efforts should be made to perfect the related research; c) unclear lubricating mechanisms of CDs as additives. It is difficult to clearly elaborate the lubricating mechanism of CDs as additives under boundary lubrication. At present, the studies of their lubrication mechanisms primarily depend on the analyses of worn surfaces, CDs debris and PL intensity. The rapid development of computers makes computer simulations including the molecular dynamics simulation, the first-principles computation, and multiscale analysis a popular tool in nanotribology, employed to study the friction process and reveal frictional mechanisms of onion-like carbon, fullerene, carbon nanotube, nanodiamond and graphene. Until now, there is no relevant research on CDs. Therefore, it is of great importance to develop computer simulations to investigate the CDs lubricating mechanism. In addition, Limited to existing separation methods, impurities such amorphous carbon, oligomers and other carbon nanoparticles inevitably exist in CDs samples. Thus, the contribution of impurities involved in the CDs to lubrication effects cannot be excluded. To better understand the lubrication mechanisms of pure CDs, the relevant control experiments should be properly added or high-purity CDs are obtained using new separation ways.

In spite of remaining some issues and far from being fully exploited, CDs have already demonstrated their significant potential for lubrication applications, particularly as additives for lubricants, regarded as good candidates as green and high-performance additives. A very small number of CDs as additives can remarkably enhanced reducing-friction and anti-wear properties of oil- or water-based lubricants. It can be envisioned that further optimization of efficient synthetic methods and a better understanding on lubricating mechanisms of CDs will greatly promote the CDs development in lubrication science. We hope that the introduced successful lubrication applications of CDs provide the consideration and possibility of CDs or next generation nanoparticles with better friction-reducing and anti-wear behaviors, stimulating further impactful discovery and significant development of nanomaterials and nanotechnologies for energy conservation and environmental protection.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Biographies of authors

Chuang He received his Ph.D. in engineering mechanics from Dalian University of Technology (China) in 2020. His current research interests include the development of functional nanomaterials for lubrication.

Shuang E received her BSc in Analytical Chemistry from Liaoning University (China) in 2015. She is currently a Ph.D. candidate at the Research Centre for Analytical Sciences at Northeastern University. Her research is devoted to the functionalization of carbon dots and their applications in biosensing analysis and bioimaging.

Honghao Yan is a professor at the Faculty of Vehicle Engineering and Mechanics at Dalian University of Technology (China). Prof. Yan was awarded a Ph.D. in engineering mechanics by Dalian University of Technology (China) in 2003. His current research interests focus on the development of new techniques and materials for lubrication, photoelectric device and photocatalysis.

Xiaojie Li is currently a professor at the Faculty of Vehicle Engineering and Mechanics at Dalian University of Technology (China). He obtained his Ph.D. in solid mechanics from University of Science and Technology of China in 1998. His current research interests focus on explosive working and detonation synthesis of nanomaterials.