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# Development of Doped Carbon Quantum Dot-Based Nanomaterials for Lubricant Additive Applications

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**Abstract:** The development of advanced lubricants is essential for the pursuit of energy efficiency and sustainable development. In order to improve the properties of lubricating fluids, high-performance lubricating additives are required. In recent research studies, carbon nanomaterials such as fullerenes, carbon nanotubes, and graphene have been examined as lubricating additives to water or oil. Lubricating oils are well known for the presence of additives, especially friction-reducers and anti-wear additives. As part of this work, we have studied the advancement in the research and development of carbon dot (CD)-based lubricant additives by presenting a number of several applications of CD-based additives. We have also highlighted the friction-reducing properties and anti-wear properties of CDs and their lubrication mechanism along with some challenges and future perspectives of CDs as an additive. CDs are carbon nanomaterials that are synthesized from single-atom-thick sheets containing a large number of oxygen-containing functional groups; they have gained increasing attention as friction-reducing and antiwear additives. CDs have gradually been revealed to have exceptional tribological properties, particularly acting as additives to lubricating base oils. In our final section, we discuss the main challenges, future research directions, and a number of suggestions for a complete functionalized or hybrid doped CD-based material.

**Keywords:** CDs; doped CDs; lubricants; lubricant additive; characterization; applications; mechanism

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## 1. Introduction

Tribology is the study of the friction, wear, and lubrication behavior of interacting surfaces during a relative motion [1,2]. This subject is highly interdisciplinary, involving multiple branches of physics, chemistry, material science, biology, and engineering [3]. Lubrication is a method/technique of using lubricants to decrease friction between two rubbing surfaces, and lubricants are an integral part of the lubrication process [4,5]. Since the development of modern science-based technology, in addition to the evolution of novel mechanical instruments, the lubricant has slowly moved from normal water to synthetic lubricating oils in the modern era [6]. In particular, the earliest recognized usage of lubricant can be dated back to prehistoric Egypt, where architects used water-lubricated wooden boards in order to move large stones to build the pyramids [7]. The water-based lubricants were slowly substituted by regular vegetable oils and animal fats, which then remained the primary lubricants until the advent of the petroleum industry [8]. As the petroleum-based industry boomed, different mineral oils started quickly displacing animal fats and vegetable oils as the main manufacturing lubricants [8]. Mineral oils brought about an innovative technological revolt in the field of manufacturing lubrication by virtue of their unique properties [9,10]. Modern mechanical equipment requires higher lubrication, which cannot be met by normal mineral oils due to their deprived oxidation resistance, thermal stability, and temperature dependency [11]. Nowadays, lubricant assists in reducing energy usage and exhaust emissions across the globe. There is no liquid lubricant present to prevent direct interaction between the rubbing surfaces layers [12,13]. Therefore, it is essential to add additional additives to advance the friction-reduction and wear-resistance of the lubricants, and this method is considered to be an effective way to improve the lubricating capacity of lubricants [14]. A lubricant additive may be classified according to its purpose, for example, as an antioxidant, corrosion inhibitor, friction-reducer, anti-wear additive, etc. In addition to this, friction-reducers and anti-wear additives play active roles in reducing friction and wear of rubbing surfaces by forming a physical adsorption/deposition film and/or a tribochemical reaction film [15–17].

With the development of nanoscience and nanotechnology, nanoscale-based lubricant additives have become a key research area in tribology. Frequently used nanoscale lubricant additives are metals, metal oxides, metal sulfides, metal borates, polymers, and carbon-based nanomaterials [18–20]. However, nanoscale carbon materials have become increasingly popular in the lubricant additive community due to their ecologically approachable nature, exceptional self-lubricating behavior, good chemical and high thermal stability and outstanding mechanical properties with respect to bulk carbon materials [21–23]. As shown in Figure 1, the most commonly used carbon-based lubricant additives are fullerene, graphene, nano-graphite, carbon nanotubes, and other bulk carbon materials. The development of nanosized materials is a developing area of scientific research that can have many possible applications in physical, biological, chemical, clinical, and medical research. One of the most common and abundant nanomaterials in research are carbon-based materials, such as carbon dots, carbon nanotubes (CNTs), graphene oxide, graphene, and graphene quantum dots (GQDs) [24–26]. In particular, CDs have inimitable physical properties that have drawn much attention for their application in a wide variety of industrial nanotechnology applications. Despite the promising friction reduction and anti-wear, anti-high-pressure, and anti-wear properties of the above carbon-based nanomaterials, CDs are a novel type of nanoscale carbon-based materials which offer many advantages as lubricant additives with respect to fullerenes, carbon nanotubes, and graphene [27,28].

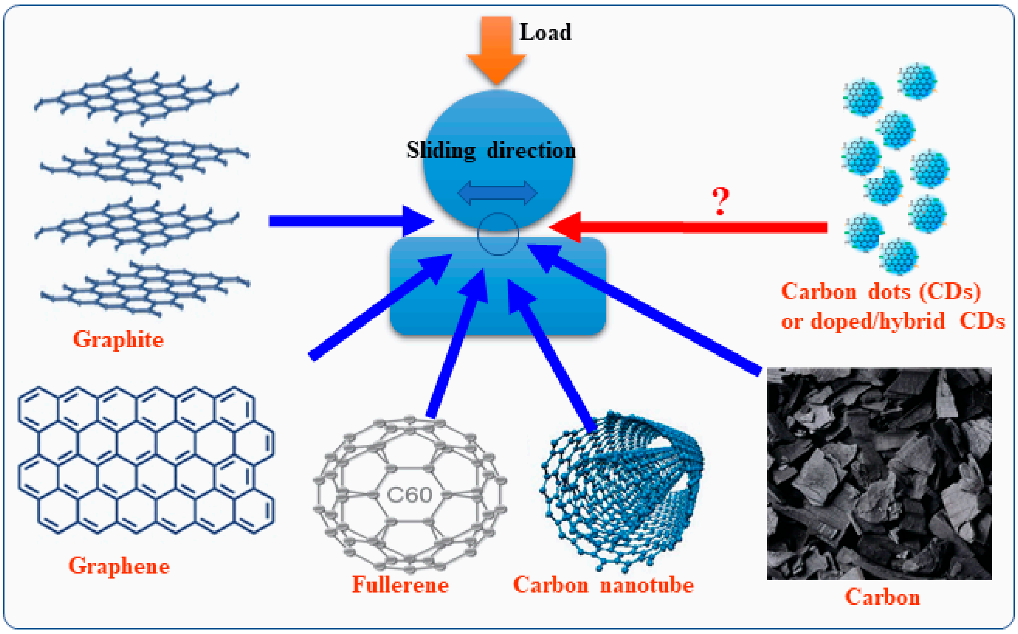


**Figure 1.** This scheme describes carbon-based nanomaterials that are commonly used in tribology.

CD materials can be described as quasi-zero-dimensional carbon nanomaterials that are less than 10 nm in size in all dimensions [29–31]. According to the increasing number of literature reports and citations each year, CD-based publications have become increasingly important [29–31]. CD refers to a wide variety of nanoscale carbon materials, including graphene quantum dots, polymer quantum dots, and carbon quantum dots. Generally, materials containing a significant proportion of carbon at the nanoscale are referred to as carbon dots [32]. Moreover, CDs shows uniform size distribution, favorable physicochemical properties, negligible toxicity, and eco-friendliness as well as convenient preparation and functionalization [32]. CDs are also recognized as CQDs (carbon quantum dots) and are very similar to graphene quantum dots (GQDs) [33]. As a zero-dimensional carbon-based nanomaterial, CDs appear to offer a promising solution to a number of challenging scientific and technological problems in the fields of biology, chemistry, and materials [32,34–36]. CDs were incidentally revealed in 2004, when Xu et al. were washing carbon nanotubes, because of their excellent photoluminescent properties; CDs were first reported using the laser ablation synthesis method [37]. The researchers recognized that CDs had the potential to compete with and replace conventional metallic semiconductor quantum dots. CDs are typically spherical carbon nanoparticles with diameters of less than 10 nm and contain a range of surface functional groups such as oxygen-containing groups, organic small molecules, polymers, and ionic liquids that are quite distinct from conventional metallic quantum dots [36–38]. In order to obtain desired properties for specific applications, one must control the CD’s physical properties during the synthesis and surface chemical modification via post-treatment procedures. The structure and main surface functional group of CDs contribute to their wide range of properties. Owing to abundance of surface states and quantum effects, CDs possess outstanding physical properties, including tunable photoluminescence. Due to their extraordinary properties, CDs are used for many applications, including bioimaging [39] and biosensing [40], drug delivery [41], solar cells [42], supercapacitors [43], photocatalysis [44], electrocatalysis [45], and photovoltaic devices [33] (Figure 2). To achieve this, CDs are doped with metal and non-metal elements, such as Ga and N, which have been verified as lubricants. [46], Moreover, the fluorescence quantum yield and the physical properties of the CD can be improved. Furthermore, several reports have shown that P-doped CDs, N-doped CDs, Ga- CDs, Sn-CDs, and Zn-CDs can be used to improve the tribological properties of CDs [47]. Currently, CDs and doped CDs are excellent nanomaterials in material technology and biomedical applications and are considered to be the most promising nanoscale carbon materials of the 21st century.

The tribological behavior of CDs and CD-based materials as lubricant additives has not yet been fully comprehended, despite a substantial number of experimental studies. Hence, this review will summarize the recent advancements in the area of lubricant additives based on functionalized CD materials over the past few years. In this paper, the emphasis is placed primarily on the chemical composition, the factors affecting the additive characteristics, and the lubrication regime instead of analyzing the entire array of experimental data. As per the major studies, adding CDs or functionalized CDs to lubricants can increase their addictive properties, which are largely determined by the composition of the lubricant. Furthermore, the improved tribological behaviors of bulk materials and lubricants with the addition of CD nanomaterials are discussed in Sections 3 and 4. In Section 5, we discuss the limitations and future prospects of CDs and CD-based materials for tribology. Finally, in Section 6, we provide conclusions and a summary of CDs and CD-based materials for the field of lubricant additives.

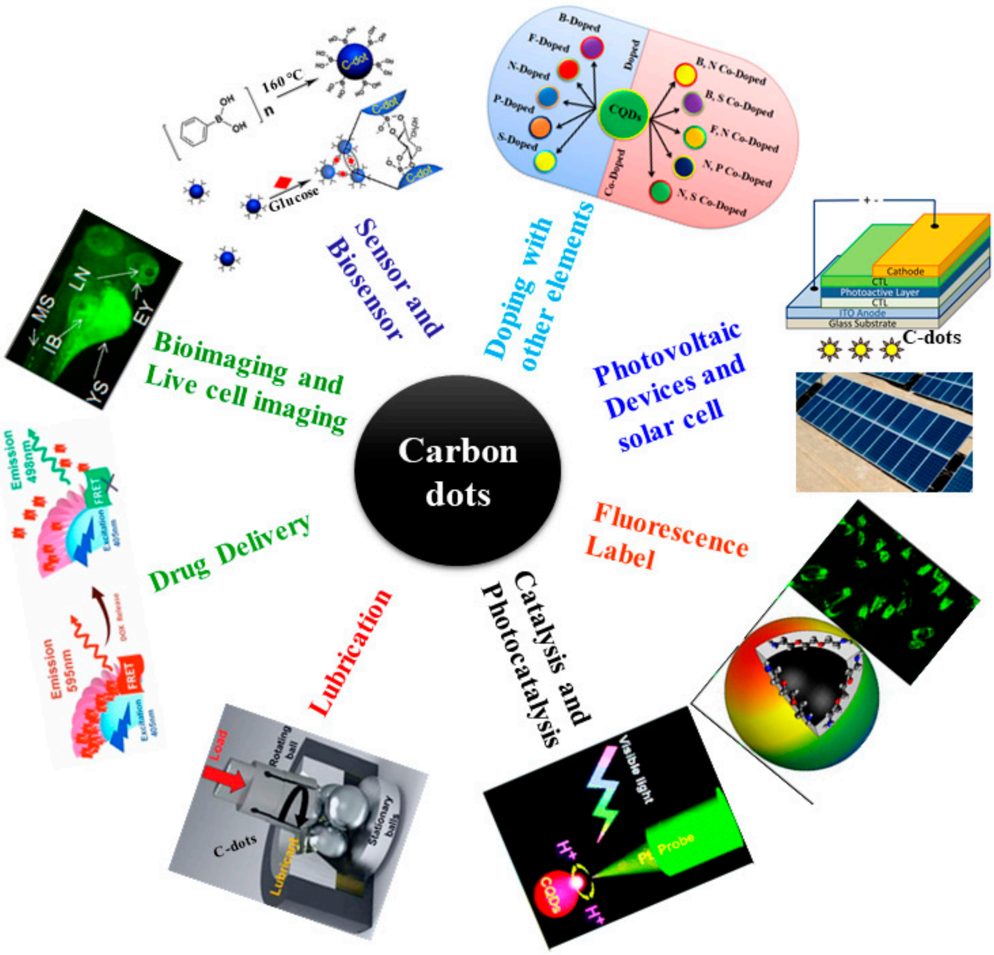


**Figure 2.** The possible applications of CDs in various fields.

## 2. Synthesis of CDs-Based Material for Tribology

CDs have inspired considerable research efforts to develop a novel type of nanoscale carbon-based material, because of their exceptional properties and potential applications. Currently, CDs and doped CDs are synthesized via two methods, namely the "top-down" and the "bottom-up" methods, as represented in Figure 3. Several synthesis techniques have been developed over the past 20 years, including arc-discharge, laser ablation, sonochemical, microwave, hydrothermal, and electrochemical methods as well as strong acid oxidation. First, small organic molecules were polymerized, followed by carbonization in order to create pristine CDs. A general classification of the synthetic methods for metal and non-metal-doped CDs are as follows: (i) top-down methods and (ii) bottom-up methods. The top-down methods involve the breakdown of larger carbon structures using chemical oxidation, discharge, laser ablation, electrochemical, or ultrasonic processes. The top-down approach has a number of advantages, including being simple to use and environmentally friendly as well as having the ability to generate many types of small fluorescent CD particles. It is also possible to generate noble CDs without ligands using the top-down approach. Despite its advantages, the top-down approach has some disadvantages, such as harsh reaction conditions, high material costs, and long reaction times. CDs and CD-based materials are difficult to obtain in the proper particle size and shape, which is a major disadvantage of this approach. In the bottom-up approach, carbon-based molecules are converted into compact discs of carbon materials of the desired size. A number of bottom-up methods have been developed, including sonochemical, microwave, hydrothermal thermal decomposition of organic molecules, pyrolysis of carbon-based materials, and solvothermal reaction synthesis [32]. Furthermore, CDs can be carefully developed and controlled with respect to their composition, structure, morphology, and particle size by choosing appropriate chemical precursors, functional molecules, and synthesis methods [48]. Given the progress made in the synthesis of CDs, researchers have begun to optimize and design the surface groups and/or carbon core structures of CDs in order to exploit their novel properties for targeted applications [49]. In order to achieve the aforementioned goals, two representative strategies have been utilized, namely surface functionalization and elemental doping. Due to the designability of CDs, they possess superior physicochemical, optical, and mechanical properties. At the same time, the range of applications for CDs is expanding based on a variety of surface functionalization techniques. In addition to their varied applications in sensors, designs for drug delivery, photovoltaic solar cells, different catalysis, and finally lubricant additives, CDs have recently drawn considerable attention as good lubricant performance additives owing to their many desirable properties, such as ultrafine small (~4–7 nm) and even particle size, high dispersion stability in different solvents, adaptable hydrophilicity, and molecular chemical inertness.

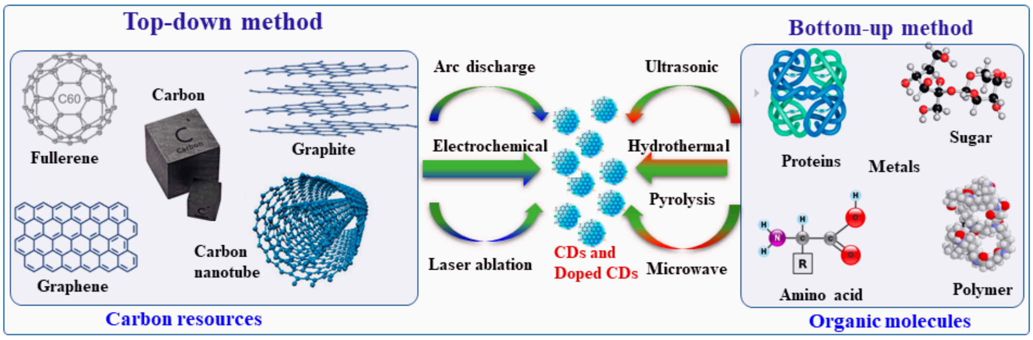


**Figure 3.** The commonly used method for preparation of CDs and doped CDs. Reprinted with permission from ref. [32].

Synthesis approaches for CDs are facile and fully mature; they do not require sophisticated equipment or any harsh synthesis conditions [28,50–53]. The tribological performance of CDs could be quickly modulated by engineering their carbon core structure and surface functionality by several organic molecules, which are based on a well-designed “bottom-up” approach [54]. In order to achieve the above purposes, it is necessary to select appropriate precursors, functional molecules, and CD synthesis methods. Besides the aforementioned merits, CDs are environmentally friendly [48,55], which is an important parameter to be considered when applying nanoscale carbon materials to lubricants. CDs are mainly composed of carbon, oxygen, nitrogen, and hydrogen as with other carbon-based nanomaterials; therefore, they do not pose a threat to the environment [48]. Thus, CDs have a number of advantages, such as the use of inexpensive and non-toxic raw materials, simple synthesis, bioimaging, biomedical applications, renewable resources, simple operations, and environmental friendliness.

## 3. Lubricant Properties and Applications of Doped CD-Based Materials

CDs nanomaterials can be used to modify the tribological properties of lubricants due to their homogeneous size distribution and other physical and chemical characteristics [56] Moreover, the size, shape, structure, surface functional groups, and concentration of materials play an important role in determining the tribological properties of CD material-based lubricants [57]. The application of CDs and doped CD materials as lubricant additives is still in its infancy, despite the fact that CDs and doped CD materials demonstrate a number of inimitable characteristics [58]. As lubricant additives, CDs and doped CD materials have enjoyed a relatively short history of about seven years since they were first used as a lubricant additive to base oils in the year 2015 [59]. Due to their outstanding properties, considerable attestation has been given to synthesized CDs, as well as doped CDs, as additives to lubricating base oils over the past few years. In this review article, we summarize the recent progress of the utilization of CDs and CD-based nanomaterials in lubricating base oils of various types such as mineral oils, water-based lubricants, and several synthetic oils [60]. Recently, it was found that CDs and doped CDs materials can be used as lubricant additives directly without any complicated and time-consuming post treatment or functionalization [60]. As depicted in Figure 3, the synthesis and functionalization of CDs and doped CD materials can be achieved by a facile, simple "bottom-up" approach, not requiring any sophisticated equipment or harsh synthesis conditions, and not even tedious pretreatments and post-treatments. Surface functionalization will improve the physicochemical, mechanical, and tribological properties of CDs and doped CD materials. Unquestionably, CDs and doped CD materials will benefit from the surface functional groups of CDs and doped CD materials to improve their compatibility and lubricity. There are several examples of CDs and doped CD nano-lubricants that have been described in the literature.

In the beginning, Huang et al. developed CuSx nanocomposites found to possess effective lubrication additives and metal-related wear restoration properties, which can be applied to CDs with multi-layered graphene structures and CuSx nanoparticles with high chemical activity [59]. HuaPing reported the synthesis of water-soluble CDs and their usage in lubricant additives with deionized water [54]. There was a decrease in the COF (coefficient of friction) in both types of tribological pairs after the addition of CDs. There were maximum reductions in COF of 30% and 14% for the $Si_3N_4$-steel and $Si_3N_4$-$Si_3N_4$ contacts, respectively [54]. Recent studies have investigated the tribological behavior of functionalized hybrid doped CDs, particularly metallic Ga-doped CDs (Ga@CDs) and nonmetallic nitrogen doped CDs (N@CDs) materials, and compared them with the properties of pristine CDs [47]. As part of this study, Tomala et al. described a simple method for synthesizing metallic and nonmetallic doped CDs, and they examined their tribological characteristics as a potential candidate for lubricant additives. The doping of CDs with different atoms/elements may be able to give them required properties for anti-wear and extreme-pressure performance (as shown in schematic Figure 4) [47]. Furthermore, Zhiqiang et al. also synthesized nickel-doped compact discs (NI-CDs) using citric acid and nickel acetate [61]. Based on observations, CD particles and Ni-CD nanoparticles could enhance the lubricant additive properties of PEG-200 molecules [61]. Ni-CDs particles, however, increase the lubrication properties more than CD nanoparticles alone. In tests with an applied load of 8 N and a correspondence speed of 25 mm/s over one hour, PEG-200-containing 2 wt.% Ni-CDs showed a reduced friction coefficient and wear rate of 35.5% and 36.4%, respectively, compared to PEG20-containing particles of pure CDs [61].

In recent years, Tang et al. has worked in the area of lubricant additives because of their unexpected tribological additive properties, especially in terms of friction reduction and found anti-wear properties of CDs and metal hybrid CDs [56]. Metal-doped/hybrid CDs are a novel type of CD, whose friction-reducing and anti-wear properties are more attractive for lubricant additives. Thus, sequences of CDs and hybrid/doped CDs with various metal ions have been synthesized via one-step pyrolysis [56] These metal-doped CDs have tribological properties in the following order: Zn-CDs > Cu-CDs >> Mg-CDs > Fe-CDs > U-CDs [56] The wear scar illustrated in Figure 5a of the ESM is extremely large and deep, with a width of 282 μm and a depth of 4.32 μm [56]. Figure 5b shows that when 1.0 wt.% U-CDs were added to the water-based lubricant, the width and penetration of the wear scar were reduced to 265 and 3.4 μm, respectively. There was still a significant wear scar on the U-CD dispersion, compared with the Fe-CDs, Cu-CDs, and Mg-CDs distributions (Figure 5c–f) [56]. Therefore, the dispersion of Zn-CDs demonstrated the best anti-wear properties among these studies.

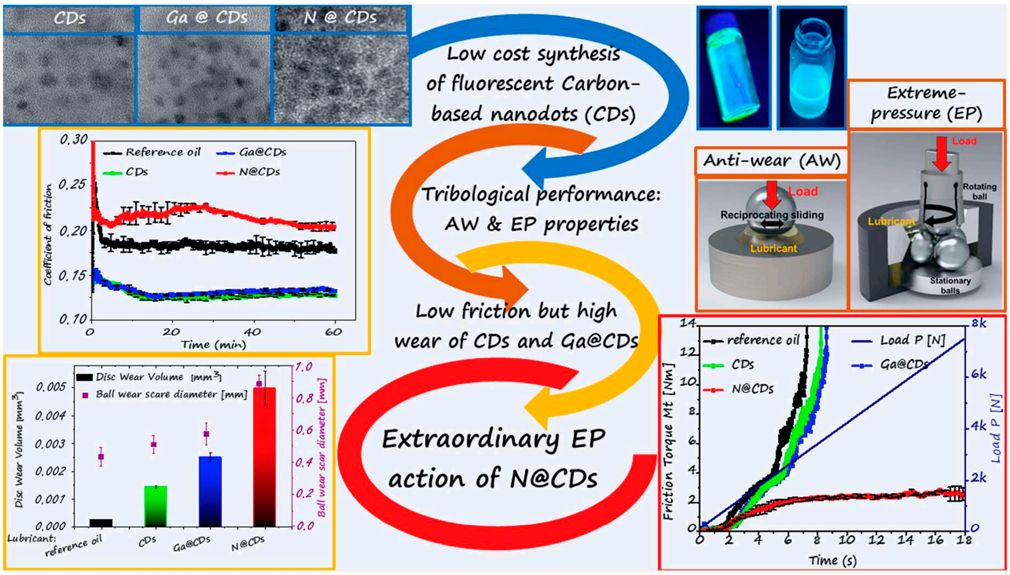


**Figure 4.** Schematic representation of tribological performance of multifunctional metal and nonmetal doped CDs. Reprint with permission from ref. [47].

A recent publication by Therinchet et al. reported the development of carbon dots for additives in lubricants by either using several ionic liquids as a carbon source or by using glutathione as a carbon source and then designing an approach to obtain carbon dots with large organic cations from the ionic liquid [62]. Researchers have observed that CDs originating directly from several organic ionic liquids, particularly methyl-tri-octylammonium chloride, are excellent candidates as additive lubricants in several different compositions of base oils (0.1%, *w/v*) and lubrication regimes, reducing COF by ~30% and wear scar by more than 60% [62]. Mou et al. designed and synthesized new functionalized CDs with polyelectrolyte (CDs-PEI-X) via the reversible phase transfer method (Figure 6a), and surface functionalization with polyethyleneimine (CDs-PEI) is shown in Figure 6b [49]. X is the symbol for the anionic surrounding of polyelectrolyte outer shells as well as the hexafluorophosphate ($PF_6$-) compound, the bis(trifluoromethane)sulfonimide ($NTf_2$-) molecules, the oleate (OL-) reagents, and the bis(salicylato) borate (BScB-) moiety (Figure 6c). Consequently, the hydrophobic CD-PEI-X showed outstanding dispersibility and long-lasting stability in PEG-200 liquid solvent (base oil) due to the favorable compatibility of these anions with PEG molecules. Additionally, functionalized CD-PEI-X has been used as a lubricant additive in PEG-200 due to their tribological behavior (Figure 6d) [49]. A critical parameter in determining the tribological behavior of nanoadditives is the concentration of additives. Figure 6e depicts the evolution tendency of curves of COF with the gradual adding of functionalized CDs-PEI-OL under a fixed applied load (50 N). Mou et al. found that dispersions of the CDs-PEI-OL containing 1.0 wt. % and 1.2 wt. % exhibited the lowest value of COF with almost no running-in period, indicating the optimal dosage of CD-PEI-OL dispersion. Additionally, Figure 6f confirms that the optimal dose of CD-PEI-OL is 1.2 wt.%, as demonstrated by the reduction of average COF by 45% and 83% in PEG-200 wear volumes, respectively [49].

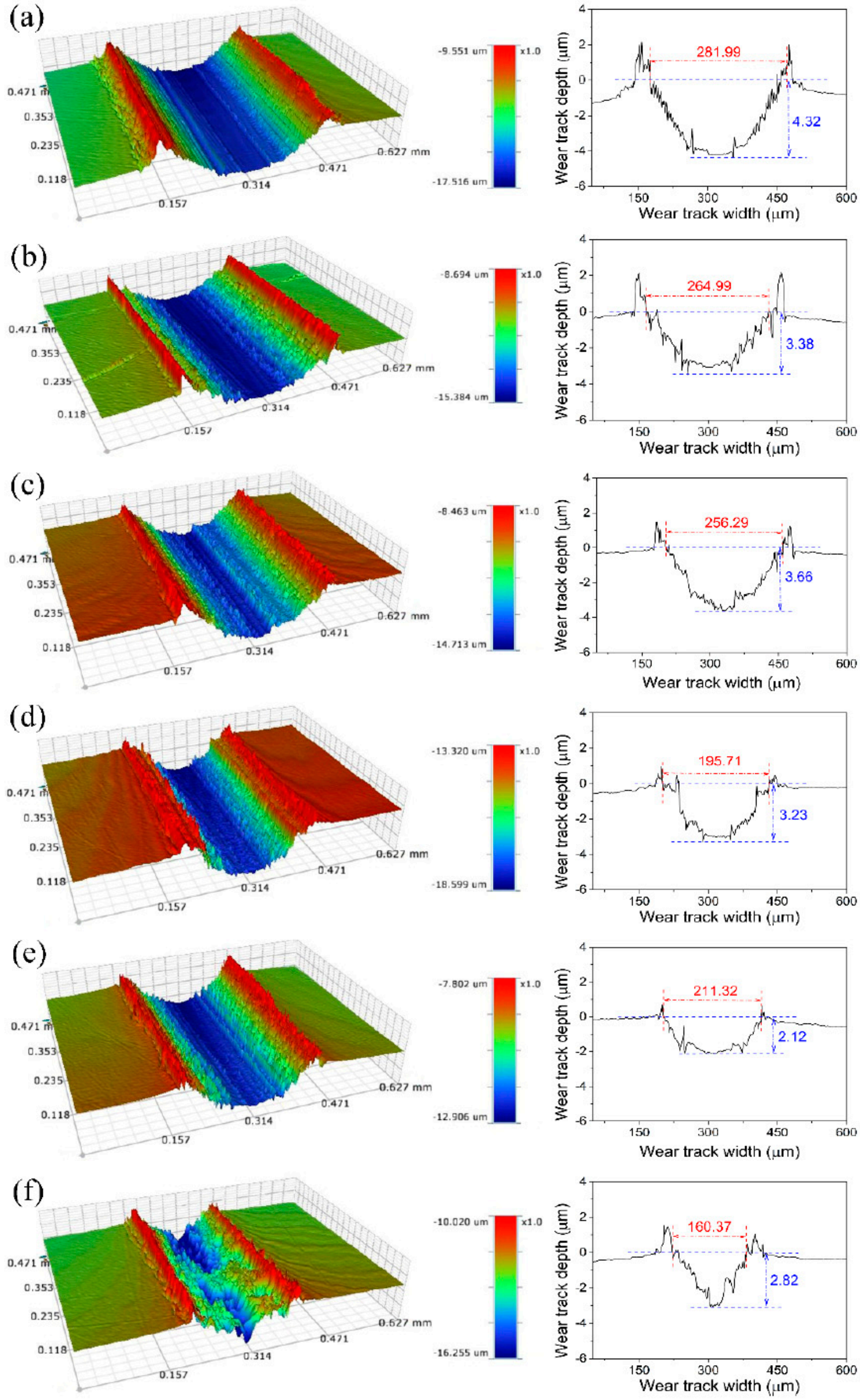


**Figure 5.** Three-dimensional morphologies and two-dimensional profiles of lower plates lubricated with (**a**) water, (**b**) U-CDs, (**c**) Fe-CDs, (**d**) Cu-CDs, (**e**) Mg-CDs, and (**f**) Zn-CD dispersions. Reprinted with permission from reference [56].

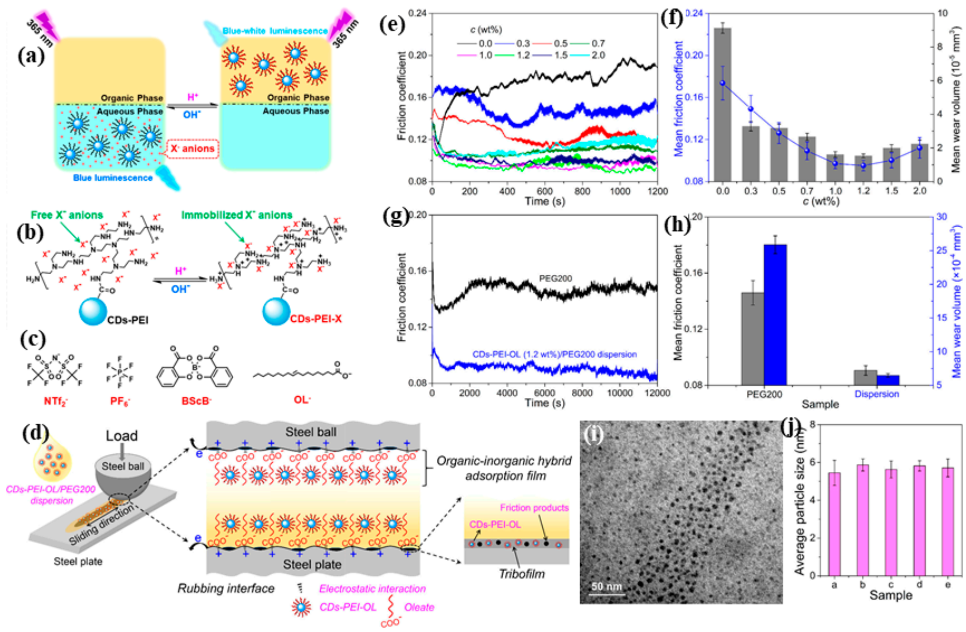


**Figure 6.** (**a**) A schematic representation of a reversible phase transfer synthesis approach for CD-functionalized materials. (**b**) The chemical representation of how CD-PEI is converted to CD-PEI-X and vice versa. (**c**) Description of the structures and abbreviations of the anion types used in the above procedure. (**d**) The lubricating chemical properties of functionalized CD-PEI-OL as a lubricant additive from PEG-200 base oil. (**e**) COF curve from functionalized CD-PEI-OL/PEG200 dispersions. (**f**) The mean COFs and wear volumes represented by functionalized CD-PEI-OL/PEG200 materials. (**g**) COF curve. (**h**) Mean COFs and wear volumes obtained by CD-PEI-OL and PEG200. (**i**) TEM images of CDs-PEI-OL. (**j**) The average size distribution of different CDs particles is represented by histogram (a = CDs-PEI NPs, b = CDs-PEI-NTf2 NPs, c = CDs-PEI-BScB NPs, d = CDs–PEI-$PF_6$ NPs, e = CDs-PEI-OL NPs). Reprinted with permission from ref. [49].

In comparison with PEG200, as shown in Figure 6g, functionalized CDs-PEL-OL/PEG200 dispersion was stable during the friction test but showed a slight fluctuation during the selected interval of the steady period (6000–6100 s). Similarly, Figure 6h illustrates that the average COF and the obtained wear volume by dispersion of the material are 37.9% and 75.0% lower than those of PEG200, respectively, showing that the CD-PEL-OL material does not exhibit major changes in tribological performance over the time. The morphological and size distribution features of different CDs were established by transmission electron microscopy (TEM) micrograph, as shown in Figure 6i,j [49] The results of this analysis demonstrate the feasibility and versatility of functionalizing surface molecules of CDs rapidly and effectively. The results also reveal the important role of the surface group as a shell and carbon as cores in the lubrication process, allowing for the development of functionalized CD-based lubricant additives [49]. Wolk et al. produced functionalized graphene oxide quantum dots (GQD, similar to CDs) by surface functionalization of a few upper layers of graphene oxide and measured them using SEM, AFM, and HRTEM [63]. In addition, the excellent solubility provides effective and rapid spray application of the surface-functionalized CDs to steel surfaces. Corrosion behavior of surface-functionalized CDs was studied with a steel specimen exposed to 20 spray cycles over 1 h in seawater (Figure 7a,b) [63]. The corrosion attack on the steel sample was relatively small after 20 spray cycles. An investigation of the potential of functionalized CDs as lubricants was conducted by spraying the suspension of dodecyl amine CDs on a fresh, new steel surface and measuring the lubricant properties with different levels of coverage (Figure 7c) [63]. The surface coverage was determined by the number of spray cycles, and as the number of spray cycles is increased, the COF value decreases. Thus, the macroscopic friction properties were examined with a novel Thwing-Albert FP-2250 friction test instrument. On steel, a developed CD-coated film of surface-functionalized graphene oxide quantum dots with dodecyl amine reduced the COF value from 0.17 to 0.11 and demonstrated significant corrosion inhibitory properties [63].

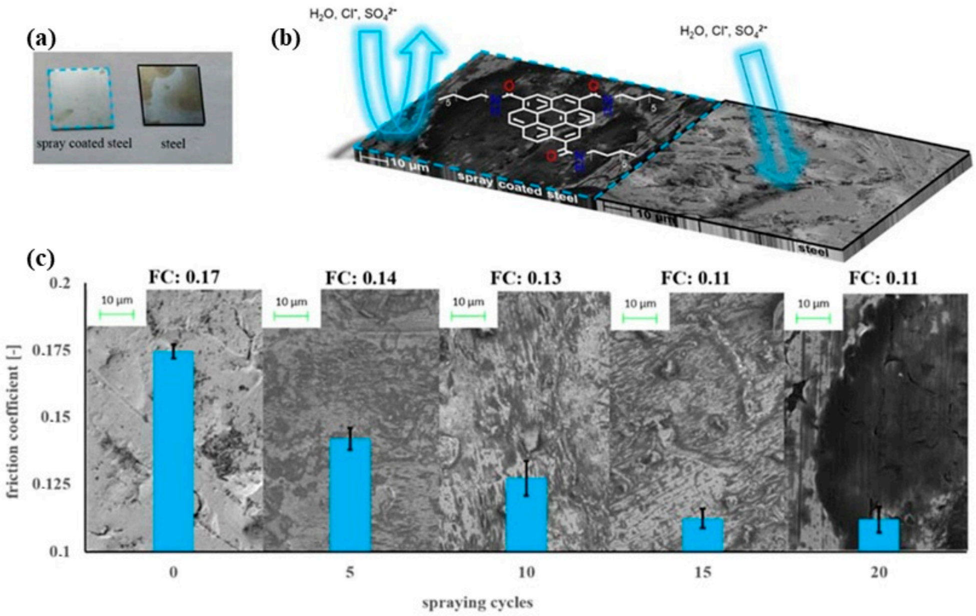


**Figure 7.** (**a**) Images of bare steel samples and after immersion in seawater for one hour. (**b**) The chemical mechanism of corrosion inhibition is illustrated by a SEM micrograph of bare steel and after 20 sprays of dodecyl amine-functionalized CDs. (**c**) The SEM micrograph shows a scatter plot of steel samples coated with dodecyl amine-functionalized CDs after various spray cycles as well as friction measurements. Reprinted with permission from ref. [63].

Furthermore, Shang et al. synthesized CDs by one-pot pyrolysis of citric acid (TDCA) [64]. Studies have been conducted on the relationship between microstructures, compositions, and tribological performance [64]. By increasing the load, more TDCA accumulated on the interface layer and the surface of carbon layer was disposed to degrade and form an orderly structure, which protected the interface layer from unwanted friction and wear [64]. Liu et al. has also modified CDs with PEG-400 by pyrolyzing a combination of gluconic acid and molecules of PEG-400 [65]. In particular, addition of 0.20 wt. % of PEG-200 functionalized CDs (CDs-PEG-200) to a base solvent resulted in the most significant reductions in COF value and wear volume: up to 84% and 91%, respectively, at a constant applied load (40N) [65].

## 4. The Friction and Possible Wear Mechanisms of the Doped CD-Based Lubricants

In the view of the present authors, the study of lubrication mechanism plays an important role in understanding the outstanding tribological characteristics of CDs and doped CD-based lubricants and in developing high-performance additives based on CDs and doped CDs. Currently, the exact mechanisms involving CD nanomaterials and doped CD-based nanomaterials lubricant additives are not understood, so the lubrication mechanisms of CDs and doped CD-based lubricant additives remain a subject of debate for numerous studies. Researchers have proposed reasonable mechanisms for CDs and doped CD-based lubricant additives, using a variety of surface analysis and simulation techniques. At present, CDs and the doped CDs-based lubricant additives are believed to have two main lubrication mechanisms: (i) The formation of lubricating film on the surface, including both physico-chemical and tribochemical films, and (ii) nanoscale lubricating effects, including mending, rolling, and rough or smooth polishing. It is important to note that there may be a close association between specific mechanisms and the morphology, particle size distribution, chemical functionalization, and composition of different crystal structures of

CDs. Recently, Zhiqiang et al. discussed the possible friction and wear mechanisms of CDs and metal-doped CDs (Ni-CDs) [61]. The reduction in friction and wear was attributed to friction causing the Ni-CDs to form a tribofilm, resulting in a low friction coefficient. In addition, the carbon content on the surfaces of Ni-CDs and the wear zones lubricated with PEG-200 containing 2 wt.% CDs and 2 wt.% Ni-CDs was considerably higher than on surfaces lubricated with pure PEG-200. On the basis of Figure 8, it is possible to validate the possible value of friction and wear mechanisms of CDs and Ni-CD particles [61]. Due to the exceptional tribological behavior of CDs and metal-doped CD-based lubricant additives, several metals or nonmetals can work together to alter the lubrication effects, rather than being caused by a single mechanism.

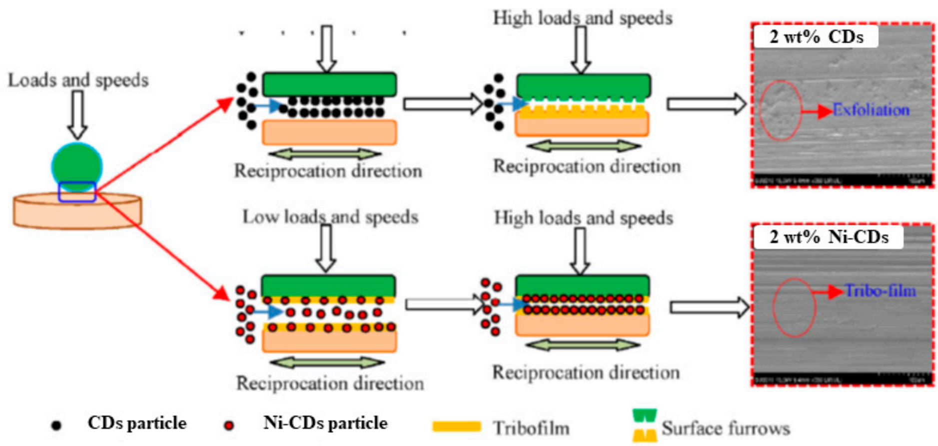


**Figure 8.** Friction and wear mechanisms of CDs and Ni-doped CD-based lubricants (Ni-CQD). Reprinted with permission from ref. [61].

Experimentation and theoretical studies demonstrate that doping carbon cores in CDs with other desired elements is another effective strategy for creating novel lubricant additive properties and mechanisms [56]. In order to accelerate the formation of the tribochemical film from doped CDs, different doping synthesis methods were utilized with elements such as B, P, Si, and N and metallic elements (Ni, Ga, U, Zn, Ag, Au, Mg, Cu, and Fe). However, the doped material is much more reactive and more inclined to stick to the rubbing surface than traditional materials. Similarly, doped CDs and functionalized CD lubricant additives can also be used to make extremely effective tribochemical films, which can reduce friction and wear between friction pairs or accelerate the transformation of the physical lubrication film into tribochemical film under extreme service conditions. Therefore, the heteroatom-doped CDs have typically displayed better film-forming abilities than conventional CDs, and subsequent research could open up a novel avenue for the commercialization of better-performance CDs and doped CD-based lubricant additives. In addition to providing surface protection, tribochemical films also reduce friction between the asperities of rubbing surfaces, thereby preventing crack propagation between friction pairs.

## 5. The Limits of CD-Based Lubricants and Their Future Prospects

Several additives have been demonstrated to have synergistic effects when combined in lubricants, as described in continuous publications by Pham et al. [66,67]. However, there are a number of additive combinations that exhibit competitive effects and decrease the effectiveness of the lubricant fluid [68–70]. Here, we have discussed the importance of CD additives in engine performance, as well as the relationship between CDs and wear as a result of formulated oils modified with CDs and doped CD materials. The exclusive and enviable physical and chemical characteristics of CDs and doped CD-based materials have led to their recognition as excellent fluorescence candidates for multifunctional applications in many scientific fields when compared to semiconductor quantum dots [32,45,58,71,72] In recent years, carbon nanomaterials such as CD, graphene quantum dots, nanodiamonds, and nanohorns have been investigated for their potential applications due to their shape effect and chemical inertness. In the tribological field, CDs and CD-derived materials with unique physical properties are capturing significant interest, particularly in lubricant nano-additives that benefit from their anti-wear properties. Higher lubrication behavior is attributed to the tribochemical reactions between CDs and their functional atoms doped with functionalities that result in the formation of lubrication thin films on steel contacting surfaces. As previously mentioned, CD yields are usually low and the corresponding production methods remain in the laboratory, limiting their application in tribology substantially. The mechanisms of lubrication underpinning the use of CD-based nanomaterials as novel lubricant additive materials are thoroughly explained in this present review. In spite of the fact that the precise mechanism of friction reduction and anti-wear of doped CD-based materials additives is as of yet unknown, extensive research efforts are being made by researchers to further investigate their lubrication mechanisms, using advanced analytical equipment and molecular dynamic simulation. A better understanding of lubrication mechanisms is essential for the advancement of novel doped CD-based materials additives that will improve lubrication performance. We hope that the study of CDs and CD-based materials will contribute to our understanding of tribochemical reactions between additives in engine oil and lead to a better design of engine oil components in the future.

## 6. Conclusions and Summary

The objective of this article was to review several applications in terms of CDs and CD-based materials as lubricant additives, particularly in tribological fields. This study provides an overview of recent developments in CD lubricant additives and functionalized CD-based lubricant additives for a variety of lubricating water-based lubricants, base oils, several mineral oils, and vegetable synthetic oils. Also, many results of CDs and doped CDs as well as functionalized CD surfaces showed positive lubricant additive behavior after doping and functionalization with metal and organic molecules, respectively. Furthermore, surface-functionalized CDs and doped CDs may be added to lubricating oils to enhance their lubricating properties. Comparatively to other types of lubricant additives (such as organomolybdenum materials, derivative of polymers, small organic molecules its derivative, different metal-organic salts, and nanomaterials), CDs were found to be superior in several aspects such as low toxicity, eco-friendliness, tunable size and shape, ease of preparation, low cost, and so on.

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