Tribological behaviors of Ni-modified citric acid carbon quantum dot particles as a green additive in polyethylene glycol

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Abstract: A novel green lubricating oil additive (carbon quantum dot (CQD) particle-doped nickel (Ni-CQD)) was synthesized from citric acid and nickel acetate. The effects of CQD and Ni-CQD nanoparticles on the tribological behaviors of polyethylene glycol (PEG200) were investigated under different loads and reciprocation speeds. The results indicate that CQD and Ni-CQD particles can both enhance the lubrication properties of PEG200. However, the Ni-CQD nanoparticles enhanced the lubrication properties more than the plain CQD particles did. The average friction coefficient and wear rate of PEG200 containing 2 wt% Ni-CQDs were reduced by 35.5% and 36.4%, respectively, compared to PEG200 containing pure CQDs under a load of 8 N and reciprocation speed of 25 mm/s over 60 min. The friction and wear mechanisms are attributed to the fact that friction induces the Ni-CQDs to participate in the formation of a tribofilm, resulting in a low friction coefficient and wear rate.

Keywords: friction; dynamics; joint clearance; numerical models; impact; durability

1 Introduction

The fuel energy consumed in combat friction and wear in modern industries amounts to approximately 30%–40%. Thus, numerous scientists have developed lubrication additives and low-friction materials [1–3]. Commercially available lubricant additives such as zinc dialkyl dithiophosphates (ZDDP) and molybdenum dialkyl dithiophosphates, which contain P, Mo, and S, are used as multifunctional additives. These additives have anti-wear, extreme pressure resistant, and anti-oxidant properties [4–6]. However, traditional lubricant additives are unfit for real-time applications owing to the strict environmental protection regulations [7]. Over the past decade, inorganic nanoparticles such as carbon materials, niobium particles, molybdenum disulfide, and tungsten disulfide have been extensively applied as lubricants to improve tribological performance of equipment, save fuel energy, and protect equipment [8–10]. Carbon materials, such as fullerene, carbon nanotubes, graphene, and their hybrids and derivatives, have been widely used as solid lubricants or oil additives owing to their unique self-lubricating effects [7, 11–20]. However, the dispersibility of these materials in base oils is poor, thereby limiting their industrial application. Therefore, stable dispersion additives must be fabricated [21, 22] to enhance tribological performance of equipment and to enable their real-time application in industries.

Carbon quantum dots (CQDs, <10 nm), as a novel type of carbon material, have been extensively investigated based on their outstanding optical properties, robust chemical inertness, and good biocompatibility [14, 23–26]. CQDs have small particle size,
high specific surface area, and controllable functional surfaces [12]. The dispersibility and storage stability of CQDs in lubricants are substantially improved compared to conventional carbon materials. Limited number of CQD materials have been developed for tribological applications through surface functionalization. Shang et al. [23] investigated the tribological behaviors of carbon hybrids containing CQDs and graphene oxide (GO). The excellent tribological performance of the hybrids was attributed to the synergistic effect of the sphere-like CQDs and GO adsorbed on the sliding surfaces such as the surface of steel. Zhang et al. [27] synthesized a novel N/B-codoped nanomaterial (carbon dots/ionic liquid, CD/IL), and found that the anti-wear and friction-reducing properties of polyethylene glycol (PEG) were improved with the addition of CD/IL particles. Ma et al. [28] fabricated novel CQD and IL nanoparticles and discovered that the tribological behavior of these nanoparticles affects the lubrication of PEG, similar to the results found by Zhang [27]. Wang et al. [29] used a one-pot pyrolysis method to synthesize IL (1-aminopropyl-3-methylimidazolium bromide)-capped carbon dot particles. They indicated that the friction and wear mechanisms of composite particles involve the rolling, mending, and polishing of composite particles under friction, resulting in outstanding tribological behaviors in PEG. Ma [26] reported that the tribological properties of CQD/CuS nanoparticles, when used as additives, can enhance lubrication and metal-wear surface-repair capabilities. Yu and Jiang et al. [30–33] fabricated graphene-nickel composites in situ by using powder metallurgy, and then investigated their tribological behaviors and mechanisms. They found that the resulting tribofilms are responsible for the self-lubricating properties of the composites.

As implied by the studies above, research on the preparation of CQD-doped Ni and its tribological behaviors is limited.

In this study, novel Ni-CQD nanoparticles were prepared from citric acid using a facile hydrothermal method. Modern analysis technologies and tribological tests were implemented to investigate the morphology, structure, composition, and tribological properties of the Ni-CQDs. This study aims to develop new lubricants and lubricant additives to prolong the service life and reduce the cost of machinery.

2 Experiments

2.1 Materials and sample preparation

Four grams of commercially available hydrated citric acid (C6H8O7·H2O) were purchased from Jiangsu Qiangsheng Functional Materials Co., Ltd. Commercially available ethylenediamine (C2H8N2) was purchased from Tianjin Baishi Chemistry Co., Ltd. Commercially available nickel acetate was purchased from Tianjin Damao Chemical Co., Ltd. CQD and Ni-CQD particles were prepared from citric acid using a facile hydrothermal method [34].

The citric acid (4.0 g) and ethylenediamine (1.43 mL) were mixed and stirred using a glass rod for 30 min to form a transparent solution. The solution was then transferred to a hydrothermal reaction kettle (HT-50H-316L, Anhui Kemi Co., Ltd.) to react for 5 h at 160 °C. A rotary evaporation device (RE-201D, Gongyi Yuhua Co., Ltd.) was used to remove the reagents and a dialysis bag (retained molecule weight of 1000 Da) was used to remove the ions. The remaining solution was then placed in a freeze dryer (SCIENTZ-12N, Ningbo Scientz Biotechnology Co., Ltd.) for 24 h to obtain high-quality CQDs. Using the same process, 4.0 g of citric acid, 1.43 mL of ethylenediamine, and 0.3 g of nickel acetate were combined to create high-quality Ni-CQDs. Oil samples of 1 wt%, 2 wt%, and 3 wt% CQDs and Ni-CQDs were prepared via simple mechanical mixing and were then treated ultrasonically for 10 min.

2.2 Analysis methods

High-resolution transmission electron microscopy (HRTEM, JEOL model 2010) was used to investigate the morphologies of the CQDs and Ni-CQDs [35]. Fourier transform infrared spectroscopy (FTIR, Nicolet model 6700) was applied to investigate the chemical compositions and surface functional groups of the two nanomaterials [36]. Friction and wear tests were conducted by using a multifunctional reciprocating tribometer (model CFT-1, Zhongke Kaihua Technology Co., Ltd.) with different loads (8 N, 20 N, and 100 N) and reciprocation speeds (200 rpm, 300 rpm, and 400 rpm, amplitude of 5 mm) for 60 min at room temperature (Approximate 25 C). Commercially available steel balls (GCr15, 10 grade, Chinese standard) with
diameters of 6 mm were used as the stationary upper counterparts for the friction tests. The hardness of the steel balls was in the range of 60 HRC–63 HRC. The lower specimens were steel disks (GCr15) each with a diameter of 28 mm, thickness of 2 mm, and surface roughness of 0.03 μm. The hardness of the steel disks was in the range of 50 HRC–60 HRC. A detailed schematic diagram of the tribometer is shown in Fig. 1. Prior to the friction tests, the friction pairs were washed with acetone in an ultrasonic cleaner for 10 min. All friction tests were conducted three times under the same conditions to ensure repeatability and reliability. Next, 3D laser scanning microscopy (mode VK-X100K) was utilized to investigate the wear profiles of the steel balls and disks. A multi-file analyzer was used to calculate the wear scar diameter, wear width, and wear area. The wear rate of the disks was evaluated using the following formula [37]:

\[ K_o = \frac{S_a \times A}{L \times N} \]

where \( K_o \) is the wear rate (mm\(^3\)/Nm), \( S_a \) is the wear area (μm\(^2\)), \( A \) is the amplitude (mm), \( L \) is the sliding distance (m), and \( N \) is the load (N). The morphologies and element contents of the wear zones on the surfaces of the disks were analyzed using scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS, model JSM-6700F). The element valence states of the wear zones were investigated using X-ray photoelectron spectroscopy (XPS, ESCALAB250, Thermo). XPS analysis was performed with a monochromatized Al Ka source (1486.6 eV) with a pass energy of 40 eV and tilt angle of 90 °C. The operating voltage was 12.5 kV and the filament current was 16 mA. Internal calibration used the C–C or C-H components of the C1s spectra at a binding energy of 284.6 eV as references [38]. After subtracting the nonlinear background (straight line), the spectra were deconvoluted using a peak fitting software with a Gaussian fitting method. Raman spectroscopy (LabRAM-HR, resolution of 0.6 cm\(^{-1}\) and scanning repeatability of ± 0.2 cm\(^{-1}\)) was used to investigate the chemical compositions of the wear zones on the disks and to identify the friction and wear mechanisms.

3 Results and discussion

3.1 Characterization of particles

Figure 2 illustrates the HRTEM images of the CQDs and Ni-CQDs. The CQD particles were agglomerated, as shown in Fig. 2(a). The average particle size (APS) of the Ni-CQD particles was approximately 5 nm–10 nm. The dispersion capacities of the two types of nanomaterials were also investigated, as shown in Fig. 2(c). Both types of particles can be uniformly dispersed in PEG. Figure 2(d) shows the results of FTIR analysis. The wavenumber at 3,435 cm\(^{-1}\) is attributed to –OH stretching vibrations. The peaks at 2,912 cm\(^{-1}\) and 2,848 cm\(^{-1}\) are attributed to –CH\(_3\) and –C\(_2\)H\(_2\)- groups,
respectively. The peaks in the range of 1,702 cm$^{-1}$–1,786 cm$^{-1}$ are attributed to C=O groups. The peaks in the range of 1,565 cm$^{-1}$–1,643 cm$^{-1}$ are attributed to $\text{-C}_6\text{H}_5$ groups. The peak at 1,079 cm$^{-1}$ is attributed to $\text{-OH}$ bending vibrations. Figure 2(e) presents the Ni2p spectrum analysis of the Ni-CQDs. The peaks at 855.2 eV and 871.6 eV indicate that NiO nanoparticles exist on the surfaces of the CQD particles.

3.2 Friction reduction

Figure 3 presents the variation in the average friction coefficients of PEG200 and the different Ni-CQD particles at different loads with a reciprocation speed of 25 mm/s over 60 min. Figure 3(a) reveals that the Ni-CQD and CQD particles enhanced the lubrication ability of PEG200 under a load of 8 N with a
reciprocation speed of 25 mm/s over 60 min. The average friction coefficient decreased by 35.5% when compared to pure PEG200, when 2 wt% Ni-CQD particles were added to the PEG200. The Ni-CQD particles provided better anti-friction properties to the PEG200 when compared to the plain CQD particles. The results for both types of particles under a 20-N load are presented in Fig. 3(b). The average friction coefficient of the PEG200 with 2 wt% Ni-CQDs was 10.5% smaller than that of the PEG200 with 2 wt% CQDs. The results for both types of particles under 100 N load are presented in Fig. 3(c). Under such a heavy load, the CQD particles could not modify the anti-friction properties of the PEG. However, adding 2 wt% and 3 wt% Ni-CQD particles did modify the anti-friction properties of the PEG. The average friction coefficients for these particle additions decreased by 22% and 27%, respectively. Figure 4 presents the variation in the average friction coefficients with different oil samples under a load of 100 N with different reciprocation speeds over 60 min. The average friction coefficients of the PEG200 with different CQD and Ni-CQD particle contents decreased at the testing conditions of 17 mm/s and 33 mm/s, respectively, when compared to pure PEG200.

In summary, Ni-CQD particles can enhance the anti-friction properties of PEG200 and their efficacy is greater than that of pure CQDs. A typical tendency chart for friction coefficients with different oil samples was used to verify these results, as shown in Figs. 5 and 6.

### 3.3 Wear resistance

Figure 7 illustrates the variation in the wear rates of the disks under different loads with a reciprocation speed of 25 mm/s over 60 min. Figure 7(a) illustrates the variation in the wear rates of disks lubricated with different oils at a load of 8 N. The wear rate with the PEG200 containing 1 wt% CQDs decreased by 45.7% when compared to that with the pure PEG200. The wear rate of the disk lubricated with PEG200 containing 1 wt% Ni-CQDs decreased by 88.9%. The wear rates of the disks lubricated with PEG200 containing 2 wt% and 3 wt% CQDs increased due to the aggregation of CQD particles. However, the wear rates of the disks lubricated with PEG200 containing 2 wt% and 3 wt% Ni-CQDs decreased by 36.4% and 23.7%, respectively. These results indicate that the Ni-CQD particles provided better anti-wear properties than the CQD particles. Figure 7(b) illustrates the variation in the wear rates of disks lubricated with different oil samples under a load of 20 N. The wear rates of the disks with PEG200 containing 1 wt% CQDs and 1 wt% Ni-CQDs decreased by 40.8% and 11.1%, respectively, compared to those of the disks with pure PEG200. The wear rates with PEG200 containing 2 wt% and 3 wt% Ni-CQDs decreased by 24.6% and 60.7%, respectively. Figure 7(c) illustrates the variation in the wear rates of the disks lubricated with different oil samples under a load of 100 N. The wear rates of the disks lubricated with PEG200 containing 2 wt% and 3 wt% Ni-CQD particles decreased by 46% and 74.8%, respectively, compared to those of the disks lubricated with pure PEG200. Figure 8 illustrates the variation in wear rates for different oil samples under a load of 100 N with different reciprocation speeds over 60 min. The wear rates with PEG200 containing different amounts of CQD and Ni-CQD particles decreased when

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**Fig. 4** Variation of average friction coefficient for different oil samples including the 1 wt%, 2 wt% and 3 wt% CQD or Ni-CQD particles at the load of 100 N for 60 min at room temperature conditions under different reciprocation speeds: (a) 17 mm/s; (b) 33 mm/s.
compared to those with pure PEG200. Therefore, we can conclude that the CQD and Ni-CQD particles play important roles in the wear resistance properties of PEG200.

3.4 Surface analysis

Table 1 shows optical images of the wear zones on the steel balls and disks lubricated with different oil samples under a load of 100 N with a reciprocation speed of 25 mm/s over 60 min. The CQD particles did not enhance the lubrication properties of PEG200 under a load of 100 N. However, the wear scar diameters on the steel balls lubricated with PEG200 containing 1 wt%, 2 wt%, and 3 wt% Ni-CQDs were smaller than those on the balls lubricated with pure PEG200. The wear widths on the disks lubricated with PEG200 containing different amounts of Ni-CQD particles were also smaller than those on the disks lubricated with

Fig. 5  Variation of friction coefficient as a function of the friction time at 25 mm/s for 60 min under the different loads: (a) 8 N; (b) 20 N; (c) 100 N.

Fig. 6  Variation of friction coefficient as a function of the friction time under 100 N for 60 min at the different reciprocation speeds: (a) 17 mm/s; (b) 33 mm/s.
PEG200 containing different amounts of CQD particles. The average wear width on the disks lubricated with PEG200 containing 3 wt% Ni-CQD decreased by 12.36% compared to that on the disks lubricated with pure PEG200. Overall, the Ni-CQD particles enhanced the wear resistance properties of PEG200 more than the CQD particles did.

Figure 9 shows SEM/EDS images of the wear zones on the disks lubricated with different oil samples. Exfoliation zones, furrows, and plastic deformation were observed on the surfaces of the steel balls lubricated with PEG200. These defects can be attributed to fatigue wear [37]. Significant wear occurred on the surfaces of the disks lubricated with PEG200 containing different amounts of CQD particles and the number of furrows increased. The surfaces of the disks lubricated with PEG200 containing different amounts of Ni-CQD particles were also investigated. The furrows and exfoliation zones decreased slightly, which resulted in a smoother surface, when 2 wt% and 3 wt% Ni-CQD particles were added to the PEG200. Compared to the plain CQD particles, the Ni-CQD particles had a much greater effect on the lubrication properties of the PEG200. The EDS results revealed that Ni was present on the surfaces of the wear zones lubricated with PEG200 containing different amounts of Ni. The
Table 1  Optical images of wear zones lubricated with different oil samples at 100 N and 25 mm/s for 60 min.

| Items       | Steel ball | Disk | Change rate in wear width (%) |
|-------------|------------|------|--------------------------------|
| PEG         | ![Image](image1.png) | ![Image](image2.png) | –                              |
| 1 wt% CQD   | ![Image](image3.png) | ![Image](image4.png) | –42.9                          |
| 1 wt% Ni-CQD| ![Image](image5.png) | ![Image](image6.png) | –2.8                           |
| 2 wt% CQD   | ![Image](image7.png) | ![Image](image8.png) | –15.5                          |
| 2 wt% Ni-CQD| ![Image](image9.png) | ![Image](image10.png) | 8.4                            |
| 3 wt% CQD   | ![Image](image11.png) | ![Image](image12.png) | –28.26                         |
| 3 wt% Ni-CQD| ![Image](image13.png) | ![Image](image14.png) | 12.36                          |
Fig. 9  SEM/EDS analysis of wear zones lubricated with different oil samples at 100 N and 25 mm/s for 60 min.
weight percentages of Ni were 0.79 (1 wt% Ni-CQD), 0.05 (2 wt% Ni-CQD), and 3.22 (3 wt% Ni-CQD). Additionally, tribofilms formed on the surfaces when 2 wt% and 3 wt% Ni-CQD particles were added to the PEG200.

To determine if Ni-CQD particles can be used as a green lubricating additive in PEG200, the wear areas were also analyzed using a 3D software package, as shown in Fig. 10. The wear area was 2371.06 μm² for pure PEG200. The wear areas of the disks increased by 307.2%, 4.34%, and 195% when lubricated with PEG200 containing 1 wt%, 2 wt%, and 3 wt% CQD particles, respectively, compared to that of the pure PEG200. For the Ni-CQD particles, the wear areas of the disks decreased by –7.1%, 46%, and 74.8% when 1 wt%, 2 wt%, and 3 wt% Ni-CQD particles were added, respectively. These results prove that Ni-CQD particles enhance the lubrication properties.

Fig. 9 (Continued)

Fig. 10 Crossing areas of wear traces of disks lubricated with different oil samples at 100 N and 25 mm/s for 60 min. (a) PEG; (b) 1 wt% CQD; (c) 1 wt% Ni-CQD; (d) 2 wt% CQD; (e) 2 wt% Ni-CQD; (f) 3 wt% CQD; (g) 3 wt% Ni-CQD.
of PEG200 more than CQD particles do.

3.5 Friction and wear mechanism analysis

The CQD particles were able to modify the lubrication properties of the PEG200 at low loads and reciprocation speeds due to the large oil film thickness [40]. The small CQD particles entered the friction surface, resulting in a low average friction coefficient and wear rate during friction testing. The diameter of the Ni-CQD particles was smaller than that of the CQD particles after friction testing, as shown in Fig. 11 and Table 2. For high loads and reciprocation speeds, the number of CQD particles entering into the friction surfaces of disks decreased due to the formation of a thin oil film and large shear force during friction testing [41]. Numerous furrows, pits, and exfoliation zones were created on the surfaces of the disks, resulting in abrasive wear during friction, as shown in Fig. 9.

The small Ni-CQD particles entered into the friction surface to participate in the formation of a tribofilm owing to the induced friction, which resulted in a smooth surface, as shown in Fig. 9. Characterization of the tribofilm was performed using XPS and Raman spectroscopy, which indicated that the Ni-CQD particles participated in the formation of lubrication films, which resulted in low friction coefficients and wear rates [35, 41]. XPS and Raman spectroscopy were used to verify the friction and wear mechanisms of CQD and Ni-CQD particles in PEG200. Figure 12 illustrates the variation in element chemical valence on the surfaces of wear zones lubricated with different oil samples. Figures 12(a), 12(b), and 12(c) illustrates the variation in chemical valence of the carbon element on the surfaces of the wear zones on the steel balls lubricated with different oil samples. The peaks at 284.6 eV, 286 eV, and 288.0 eV are attributed to C–C (or C–H), −C−O−, and −COOH groups, respectively [38]. The −C−O− and −COOH contents of the wear surfaces on the steel balls lubricated with PEG200 containing 2 wt% CQD, and PEG200 containing 2 wt% Ni-CQD, increased compared to those when using pure PEG200 for lubrication. These results are attributed to the CQD and Ni-CQD particles that took part in the formation of boundary lubrication films. Figures 12(d), 12(e), and 12(f) illustrates the variation in chemical valence of the O element on the wear surfaces of the steel balls lubricated with different oil samples. The peaks at 529.4 eV, 530.8 eV, and 532 eV are attributed to iron oxides, −OH, and FeOOH groups, respectively [38]. The −OH and FeOOH groups played an important role in forming the boundary lubrication films because the CQD and Ni-CQD particles participated in the formation of tribofilms and dehydrogenation of long-chain hydrocarbon molecules in the lubricating oils [42]. The FeOOH contents of the wear zones on the steel balls lubricated with PEG200 containing 2 wt% CQDs and Ni-CQDs were higher than those when using pure PEG200 for lubrication. Figure 12(g) illustrates the variation in the Fe element on the surfaces of the steel balls lubricated with different oil samples. The peak at 707 eV is attributed to Fe atoms. The peaks at 710.1 eV and 724.4 eV are attributed to Fe_{1/2} and Fe_{2/3}, respectively. The peaks in the range of 709 eV–711 eV are attributed to iron oxides, such as FeO, Fe_{2}O_{3}, and Fe_{3}O_{4}. A peak at 707 eV (Fe atom) was detected on the surfaces of the wear zones lubricated with PEG200 containing 2 wt% CQDs and Ni-CQDs. These results indicate that a tribofilm can protect the base material, resulting in excited Fe atoms, low friction coefficients, and low wear rates. The results of Raman analysis also revealed differences between the tribofilms on the surfaces of the steel disks lubricated with different oil samples, as shown in Fig. 13. The

![Figure 11](image-url) Diameter distribution images of two kinds of Particles in PEG after friction. (a) CQD; (b) Ni-CQD.

| Particle interval distribution (μm) | Quantity percentage (%) | CQD | Ni-CQD |
|-----------------------------------|--------------------------|-----|--------|
| 0–5                               | 82.3                     | 87.8|        |
| 5–15                              | 17.2                     | 12.1|        |
| ≥15                               | 0.45                     | 0.029|       |

Maximum particle area (μm²) 520.74 185.35
Fig. 12  C1s, O1s, Fe2p and Ni2p spectra of wear zones lubricated with different oil samples.
Fig. 13  Raman spectroscopy of wear zones lubricated with pure PEG200, PEG200+2 wt% CQD, and PEG200 + 2 wt% Ni-CQD particles.

peaks at 255 cm$^{-1}$ and 672 cm$^{-1}$ are attributed to iron oxides. The peaks at 1,350 cm$^{-1}$ and 1,580 cm$^{-1}$ correspond to the D and G peaks of carbon, respectively. Furthermore, the carbon contents on the surfaces of the wear zones lubricated with PEG200 containing 2 wt% CQD and 2 wt% Ni-CQD were higher than those on the surfaces lubricated with pure PEG200. The friction and wear mechanisms of CQD and Ni-CQD particles can be verified by referring to Fig. 14.

4 Conclusions

Ni-CQD particles were successfully prepared using a facile hydrothermal method. The effects of these particles on the lubrication properties of PEG200 were investigated using a reciprocating tribometer with different loads and speeds. The results were compared to those of pure CQD particles. The following conclusions were obtained.

1) The APS values of the two nanomaterials were in the range of 5 nm–10 nm and they showed good dispersibility in PEG200.
2) Compared to the plain CQD particles, the Ni-CQD particles had a greater effect on the lubrication properties of PEG200.
3) Compared to PEG200 containing 2 wt% CQDs, the average friction coefficient and wear rate of PEG200 containing 2 wt% Ni-CQDs decreased by 35.5% and 36.4%, respectively, under a load of 8 N with a reciprocation speed of 25 mm/s.
4) Compared to PEG200 containing 3 wt% CQDs, the friction coefficient and wear rate of PEG200 containing 3 wt% Ni-CQDs decreased by 22% and 27%, respectively, under a load of 100 N with a reciprocation speed of 25 mm/s.
5) The friction and wear mechanisms of the Ni-CQDs were attributed to the fact that friction induced the Ni-CQDs to participate in the formation of a tribofilm, resulting in a low friction coefficient and wear rate.

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