

Covalent organic framework/graphene oxide hybrids via in situ polymerization as high-performance lubricant additives

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Abstract

Covalent organic frameworks/graphene oxide (COFs/GO) hybrid nanocomposites were synthesized via an in-situ polymerization strategy and evaluated as lubricant

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additives in polyalphaolefin (PAO 10) under severe operating conditions. Two hybrids, TATP/GO and TADM/GO, were prepared and their tribological performance was systematically investigated. Structural characterization revealed that the in situ growth of TADM increased the interlayer spacing of GO and improved its dispersion behavior in PAO 10. At the optimal concentration of 0.05 wt.%, TADM/GO reduced the friction coefficient and wear volume by 30.43% and 95.58%, respectively, compared with neat PAO 10 in reciprocating sliding tests. Under four-ball conditions with an applied load of 392 N, TADM/GO maintained effective lubrication for 4 h, reducing the friction coefficient and wear volume by 35.71% and 69.37%, respectively. The wear volume after 4 h is only 47.54% higher than that measured in the independent 1 h test, demonstrating sustained anti-wear performance under prolonged severe contact conditions. The superior tribological performance of TADM/GO is attributed to the synergistic effects of surface filling, interlayer sliding, and tribochemical film formation. Raman analysis of the worn surface further revealed improved retention of the conjugated carbon structure in the TADM/GO-derived tribofilm under severe shear. These findings demonstrate the potential of molecularly engineered COF/GO hybrids as lubricant additives for severe contact conditions.

Keywords: Covalent organic frameworks; Lubricant additive; Friction reduction; Anti-wear performance; Tribochemical film

1. Introduction

Approximately one-third of global primary energy consumption is associated with friction-related losses ^[1-4]. The implementation of effective countermeasures can mitigate 30~60% of the losses induced by friction and wear. Polyalphaolefin (PAO) lubricants feature superior thermal/oxidative stability, broad temperature adaptability, high viscosity index, long service life and low volatility, making them the preferred high-performance synthetic lubricant for severe operating conditions in advanced mechanical systems ^[5,6]. Yet their intrinsic non-polar nature induces inherent deficiencies, including insufficient tribological performance with poor anti-wear and

extreme-pressure protection as well as weak polar adhesion to metal friction pair surfaces under severe operating conditions ^[7-9]. Therefore, functional lubricant additives are essential for enhancing the interfacial protection and tribological performance of PAO oils ^[10-12].

Two-dimensional materials, with atomic-scale sheet-like structures, have emerged as a breakthrough class of lubricant additives ^[13-15]. Their advantages span multi-dimensional improvements in performance, stability, and cost-effectiveness. In terms of friction reduction and anti-wear, materials such as graphene oxide (GO) nanosheets and molybdenum disulfide possess single-layer thicknesses of merely 0.1 to 10 nanometers, enabling them to generate a tribochemical protective film at the friction interface that converts direct metal-to-metal contact into indirect contact ^[16-18]. The weak van der Waals force between layers reduces sliding resistance, while their self-repairing capability further enhances durability ^[19]. When the friction pairs are damaged, dispersed particles migrate to and replenish the worn surface, restoring lubrication effectiveness ^[20]. Despite their promising tribological properties, the application of GO nanosheets as additives in nonpolar PAO oils remains limited by poor dispersion stability and insufficient interfacial affinity ^[21]. Its poor dispersion stability results in weak adsorption on metal surfaces and an inability to form stable boundary films under extreme conditions, such as low speed and high load, ultimately leading to lubrication failure ^[22,23].

Our previous work has demonstrated that methoxy-containing covalent organic frameworks exhibit remarkable lubrication benefits. This performance arises from their unique structural characteristics, which are engineered through $p-\pi$ resonance modulation to optimize tribological behavior ^[24]. Their skeletons are rich in polar nitrogenous functional groups, which form strong coordination and hydrogen bonds with metal surfaces, enabling robust interfacial anchoring and facilitating the formation of a dense and durable composite tribofilm. This $p-\pi$ resonance-regulated architecture reinforces the mechanical strength of the tribofilm, endowing it with excellent resistance to desorption and shear failure under high loads, thereby sustaining stable and effective lubrication ^[25].

Herein, an intercalation strategy is adopted to modulate the interlayer spacing of GO nanosheets via COFs precursor polymerization, and TADM/GO nanocomposites prepared by this approach exhibit excellent tribological performance. In reciprocating friction tests with lower maximum Hertz contact stress (0.77 GPa), TADM/GO-doped PAO 10 shows remarkable reductions in friction coefficient and wear volume relative to neat PAO 10. Even in four-ball tests under extreme maximum Hertz contact stress (3.45 GPa), the composite additive not only induces a remarkable decrease in friction coefficient and wear volume of the base oil but also endows it with durable anti-wear efficacy. The lubrication mechanism of TADM/GO was clarified by characterizing the worn surfaces using SEM, Raman spectroscopy and XPS. The results confirm that a compact tribofilm forms on the friction interface through micro-pit filling, interfacial adsorption and material deposition. This favorable tribofilm-forming behavior underpins the prominent anti-wear performance of the 2D COFs/GO hybrid nanocomposites, and this performance is responsible for the enhanced lubrication effects of the modified PAO 10.

2. Experimental section

2.1 Chemicals and materials

Graphene oxide aqueous dispersion (12.76 mg/g) was purchased from Gaoxiech Co., LTD. 1,3,5-Tris(4-aminophenyl)benzene (TAPB, >98%), terephthalaldehyde (TPA, >98%), 2,5-Dimethoxybenzene-1,4-dicarboxaldehyde (DMDD, >97%), and anhydrous ethanol (> 99.5%) were all obtained from Innochem Technology Co., LTD. N, N'-dimethylformamide (DMF, >99.5%), 1,4-dioxane, and 17.5 M acetic acid were supplied by Shanghai Aladdin Industry Co., LTD. PAO 10 lubricant base oil was purchased from Shanxi Luan Taihang Lubricating Oil Co., Ltd. All chemical reagents used in the experiments were of analytical grade and were utilized directly without additional purification.

2.2 Synthesis of COFs/GO composites (TATP/GO and TADM/GO)

TATP/GO and TADM/GO composites were fabricated via a one-pot method. For TADM/GO, TAPB (0.5 mmol) and DMDD (0.75 mmol) were dissolved in 20 mL 1,4-dioxane (mixture A), while 0.3 g of GO was dispersed in 15 mL 1,4-dioxane (mixture

B). After 20 min of sonication, mixture A was slowly poured into mixture B, followed by 2 mL of acetic acid. The mixture was heated at 120 °C for 12 h in a Teflon-lined autoclave, then washed with DMF and deionized water, and freeze-dried. TATP/GO was synthesized using TAPB, TPA and GO via the same procedure. The imine-linked COFs were formed between the GO layers via Schiff-base polymerization reaction. The preparation process is shown in Figure 1.



Figure 1 Schematic diagram of the fabrication process of TADM/GO and TATP/GO.

2.3 Preparation of COFs/GO-containing PAO 10 lubricant

The as-prepared TADM/GO and TATP/GO composites were dispersed into PAO 10 base oil at varying concentrations of 0.01, 0.03, 0.05, 0.08 and 0.1 wt.%, followed by 30 min of sonication to form homogeneous dispersions. The resultant additive-doped PAO 10 oils with different COF hybrid contents were designated as TADM/GO-1, TADM/GO-3, TADM/GO-5, TADM/GO-8, TADM/GO-10 and TATP/GO-1, TATP/GO-3, TATP/GO-5, TATP/GO-8, TATP/GO-10 in sequence.

2.4 Characterization

The microstructures of TADM/GO and TATP/GO composites were characterized using a field emission scanning electron microscope (FESEM, JSM-7800F, Japan) equipped with an X-ray energy-dispersive spectrometer (EDS). X-ray diffraction (XRD, Bruker D8 Advance, Germany) was performed at a scanning rate of 5° min⁻¹ to determine the chemical composition and crystallographic structures of TATP/GO and TADM/GO. X-ray photoelectron spectroscopy (XPS, Thermo Ecalab 250Xi, America) was utilized to analyze the elemental chemical states. Fourier transform infrared spectroscopy (FT-IR, Nicolet-6700, USA) was conducted over a spectral range of 400 ~ 4000 cm⁻¹ to identify the detailed functional group information. Confocal Raman

spectroscopy (Renishaw inVia Reflex, UK) with a 532 nm laser was employed to record the Raman spectra of the samples.

2.5 Tribological tests

The intrinsic friction-reducing and anti-wear performance of the as-prepared additives were determined using a UMT-3 ball-on-disk friction tester under the reciprocating sliding friction mode, and the test conditions were as follows: friction duration of 1 h, an applied load of 50 N, oscillation frequency of 2 Hz, and sliding amplitude of 2 mm. A 2 Hz low frequency was selected to maintain boundary lubrication, avoiding hydrodynamic interference and enabling accurate assessment of the intrinsic boundary performance of COFs/GO. A four-ball rotational tribotester was adopted to investigate the friction-reduction and anti-wear capabilities of oils under extreme-pressure conditions, with an applied load of 392 N and 1200 rpm rotational speed. At least three repeated tests were performed for each group to reduce experimental errors. The maximum Hertz contact stress for reciprocating friction is calculated by Eq. (1), and the maximum Hertz contact stress for rotational friction is calculated using Eq. (2).

$$\sigma_{\max}=0.388 \times \sqrt[3]{PE^2 \frac{1}{R^2}} \dots \dots \dots (1)$$

$$\sigma_{\max}=0.388 \times \sqrt[3]{PE^2 \left(\frac{R_1+R_2}{R_1R_2}\right)^2} \dots \dots \dots (2)$$

where $\sigma_{\max}$ is the maximum contact pressure (MPa), P is the normal load acting at each ball-ball contact (N), E is the elasticity modulus (MPa) of the GCr 15 steel ball and R is the radius (mm) of the steel ball. All tests were conducted in triplicate to ensure the reliability of experimental data. A white-light interferometer (WLI, Contour GT) was employed to quantify the 3D morphologies and wear volumes of wear tracks. Prior to wear volume calculation, the unworn regions surrounding the wear track were used to establish the reference level, and regions outside the effective wear track were masked to minimize the influence of surface inclination and local height variations on volume integration. A field emission scanning electron microscopy (FESEM) was utilized for analyzing their surface topographical features.

3. Results and discussion

3.1 Characterization of TATP/GO and TADM/GO composites

Figure 2 displays the morphology of GO, TATP/GO and TADM/GO. Figure 2b and 2c indicate that the growth of COFs does not significantly affect the morphology of GO, which remains lamellar before and after the solvothermal reaction. At low magnification, the surface of TATP/GO is relatively smooth, and TATP appears as microspheres on GO nanosheets. In contrast, the surface of TADM/GO is rough. Local magnification of the TADM/GO image reveals that the TADM nanosheets are vertically arranged on the GO surface. The elemental distribution was analyzed by EDS, and the elemental content of the composites is shown in Table 1. The atomic content of oxygen in TADM/GO reaches 15.13%, which is markedly higher than the 9.69% detected in TATP/GO. This disparity is ascribed to the oxygen-rich methoxy ($-\text{OCH}_3$) moieties present in the TADM phase. The fabrication of TADM's sheet-like microstructure has been elaborated in our prior research [24]. Overall, the lone-pair electrons of $-\text{OCH}_3$ groups enhance the p - π conjugation within TADM, thus improving its crystallinity and planarity [26]. Further, the steric hindrance from $-\text{OCH}_3$ groups restricts torsion between adjacent benzene rings, an effect that ultimately facilitates the formation of TADM's sheet-like morphology [27].

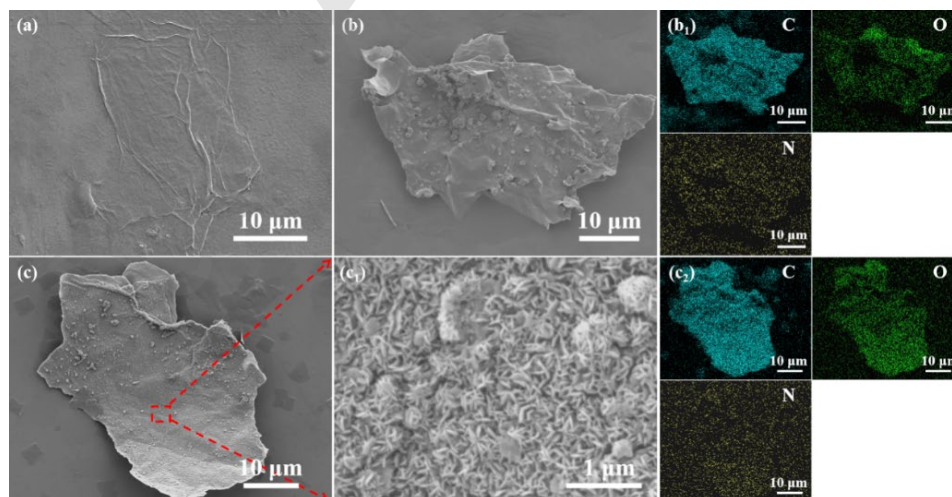


Figure 2 Morphologies and elemental distribution of (a) GO; (b) TATP/GO and (c) TADM/GO.

Table 1 Atomic percentage of elements in TATP/GO and TADM/GO

	C		N		O	
	wt. %	at. %	wt. %	at. %	wt. %	at. %
TATP/GO	84.72	87.81	2.81	2.50	12.47	9.69

TADM/GO	77.62	81.91	3.27	2.96	19.11	15.13
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FT-IR spectroscopy was employed to analyze the functional groups of the as-prepared samples over a wavenumber range of 400 ~ 4000 cm^{-1} . The chemical bonding features of TATP and TADM are displayed in Figure S1. A characteristic C=N stretching vibration at 1592 cm^{-1} confirms the successful Schiff-base reaction between -CHO and -NH₂ groups (Figure 3a) [28,29]. The characteristic peaks of GO (Figure 3b) appear at 3413 cm^{-1} , 1740 cm^{-1} and 1230 cm^{-1} , corresponding to the O-H stretching vibration, the C=O stretching vibration and the C-O-C stretching vibration, respectively [30]. In the TATP/GO and TADM/GO composites, the C=N structure is well preserved, while the C=O peak of GO disappears, confirming the successful incorporation of COFs onto GO. Additionally, a distinct Ar-O-C peak at 1037 cm^{-1} , originating from the methoxy groups (-OCH₃) of the DM structure, was observed in both TADM and TADM/GO.

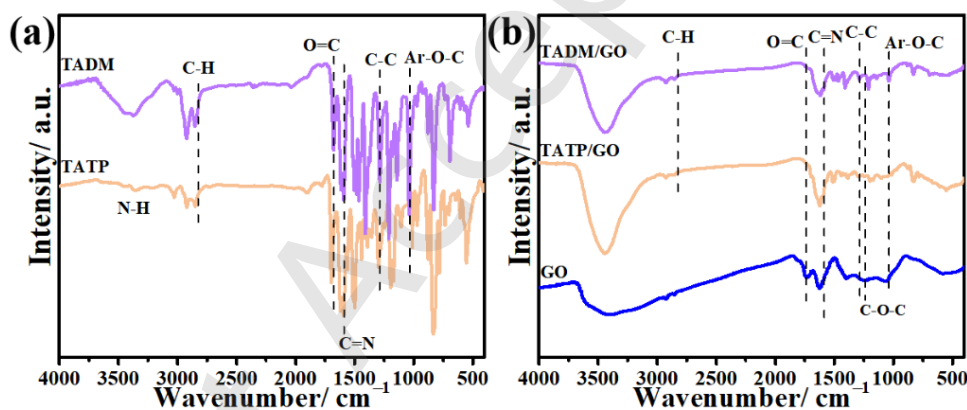


Figure 3 The FT-IR spectra of (a) TATP and TADM, (b) GO, TATP/GO and TADM/GO.

Figure 4a and 4b present the XRD patterns of pristine GO, pure COFs and COFs/GO composites. The interlayer *d*-spacing was calculated by the Bragg equation, showing an inverse relationship with 2θ [31]. Pristine GO exhibits a characteristic (001) diffraction peak at $2\theta = 10.46^\circ$, corresponding to an interlayer spacing of 8.44 Å. Following in situ COFs growth, the GO-related peak shifts to $2\theta = 9.89^\circ$ for TATP/GO and $2\theta = 9.67^\circ$ for TADM/GO, corresponding to interlayer spacings of 8.93 Å and 9.14 Å. These values represent increases of 5.81% and 8.29% relative to pristine GO. The expanded spacing is consistent with COFs incorporation between GO nanosheets, with TADM/GO exhibiting a 2.35% larger spacing than TATP/GO. Meanwhile, TADM/GO

retains a well-defined crystalline structure, with characteristic peaks at 5.52° and 7.43° , corresponding to the (020) and (120) crystal planes [32].

Figure 4c and d illustrate the Raman spectra. The relatively weak D bands of pure TATP and TADM are consistent with their comparatively ordered conjugated structures (Figure 4c) [33]. GO (Figure 4d) exhibits characteristic D and G bands at 1341 cm^{-1} and 1587 cm^{-1} , with an I_D/I_G ratio reflecting its defect density [34]. In the COFs/GO composites, the I_D/I_G ratio decreases markedly. This reduction is attributed to the interfacial interactions between the COFs frameworks and oxygen-containing groups of GO, which reintegrates defective carbon into the π -conjugated system [35]. Additionally, π - π stacking between the aromatic frameworks of COFs and the sp^2 domains of GO further contributes to structural ordering [36].

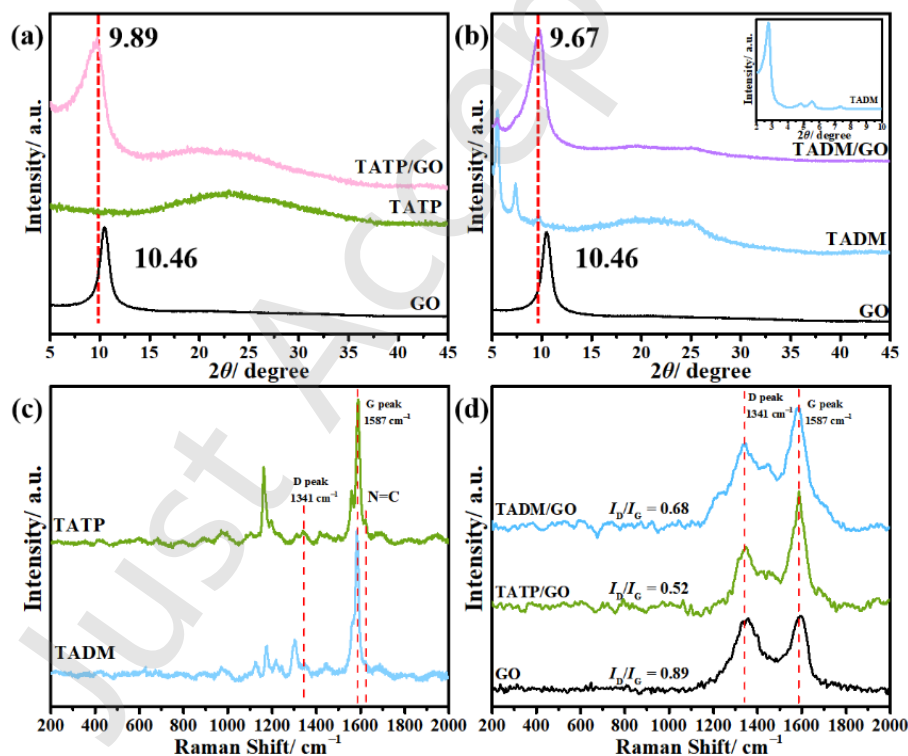


Figure 4 The XRD patterns of (a) TATP/GO and (b) TADM/GO. The Raman spectra of (c) pure COFs and (d) COFs/GO composites.

XPS analysis was conducted to determine the surface chemical compositions and bonding states of GO, TATP/GO, and TADM/GO (Figure 5). The survey spectra confirm the presence of C, N, and O in the COFs/GO composites, whereas GO contains only C and O. The high-resolution C 1s spectrum of GO (Figure 5b) is deconvoluted into four peaks at 283.8 eV (C=O), 284.8 eV (aromatic C), 286.9 eV (C–O), and 288.6

eV (O=C–O) [30,37]. In the COFs/GO composites, the intensity of the O=C–O peak decreases due to amidation reactions between the amino groups of COFs and the carboxyl groups of GO. New peak appear at 285.4 eV, corresponding to C=N bond formed via the Schiff-base reaction [38,39]. Additionally, TADM/GO exhibits a characteristic C–O–C peak at 287.6 eV originating from the DM structure [40]. The N 1s spectrum (Figure 5c) resolves into three peaks centered at 398.8 eV (C=N), 399.8 eV (C–N) and 401.6 eV (N–H), further confirming the successful formation of the COFs framework [41]. The O 1s spectrum (Figure 5d) displays three components at 531.1 eV (C=O), 532.4 eV (O–H), and 533.4 eV (C–O), with the disappearance of the O=C–O peak in the composites providing additional evidence for interfacial bonding between GO and the COFs.

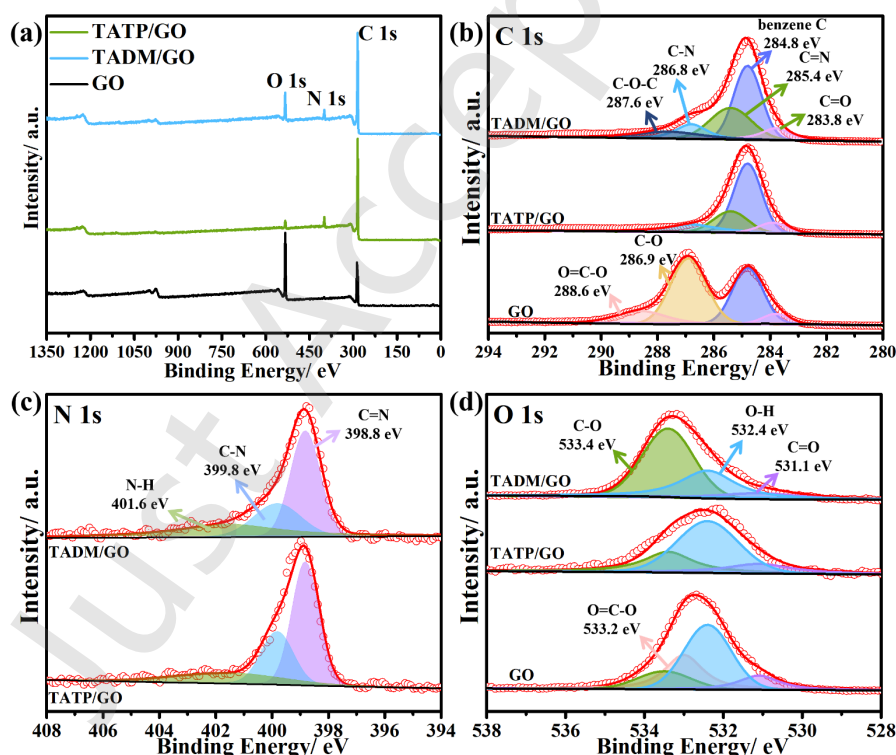


Figure 5 The (a) XPS survey spectra, (b) C 1s spectra, (c) N 1s spectra, and (d) O 1s spectra of COFs/GO.

The dispersion stability of GO, TATP/GO, and TADM/GO in PAO10 base oil was evaluated after 30 min of sonication followed by static storage for 7 and 14 days (Figure 6). After 7 days, the GO dispersion exhibited pronounced sedimentation, consistent with the limited compatibility between polar GO surfaces and the nonpolar PAO10

medium. TATP/GO showed partial settling and visible particle accumulation at the bottom of the bottle. In contrast, TADM/GO maintained a comparatively uniform appearance with less discernible sediment. This trend persisted after 14 days, indicating improved resistance to sedimentation for TADM/GO within the observation period. To complement these static observations, centrifugation tests were conducted at 3000 rpm for 10 min (Figure S2). The GO-containing oil exhibited pronounced separation into an upper liquid layer and a sediment-rich lower layer, whereas TATP/GO showed partial sediment accumulation at the bottom. Only a small amount of black material was observed at the bottom of the TADM/GO sample, indicating comparatively limited sedimentation under the same centrifugation conditions. These results are consistent with the static storage observations and further support the enhanced sedimentation resistance of TADM/GO. The difference may be associated with the molecular architecture and interfacial interactions of the COF components. The methoxy-functionalized aromatic framework of TADM may influence its association with GO and its interactions with the surrounding oil, while the attached COF structures may provide steric hindrance that limits GO restacking and aggregation. The more evident settling of TATP/GO suggests that its structure provides less effective stabilization under the same conditions. Overall, the static storage and centrifugation results qualitatively support the potential of COF structural design to improve the dispersion stability of GO-based lubricant additives.

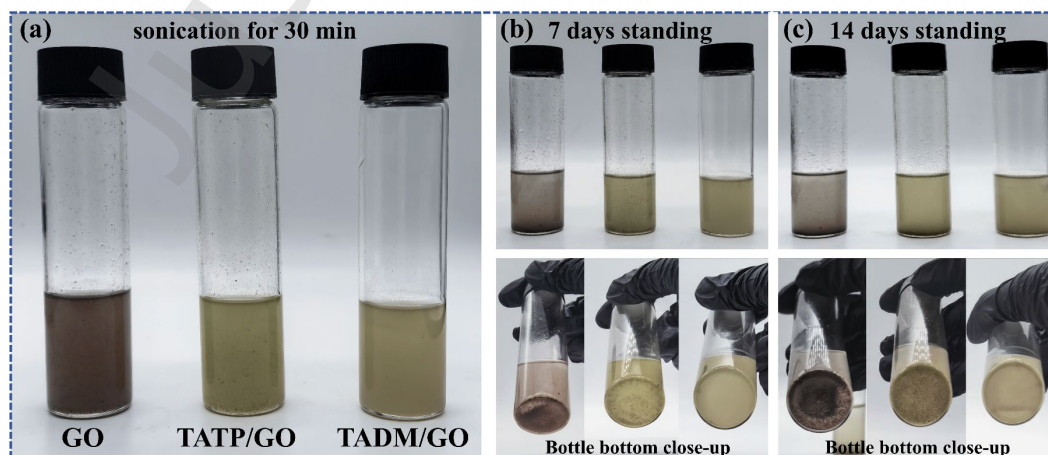


Figure 6 Optical images of PAO 10 containing 0.05 wt.% additives before and after standing for 14 days.

3.2 Tribological performance of TATP/GO and TADM/GO lubricant additives

3.2.1 Reciprocating friction test

Reciprocating friction tests were conducted under a point-to-plane contact model with an applied load of 50 N, corresponding to a maximum Hertz contact stress ($\sigma_{\max}$) of 0.77 GPa (calculated using Eq. 1). This reciprocating configuration simulates operating conditions involving periodic changes in sliding direction, start-stop motion, and moderate contact loads. The reproducibility of the tribological results was further evaluated based on three independent tests (Figure S3 and S4). Statistical analyses of the friction coefficient curves and the instantaneous values at selected time points show good consistency among the repeated measurements. As shown in Figure 7a, pure PAO 10 exhibits an initial friction coefficient below 0.09, which rapidly increases to 0.10 due to scuffing and eventually stabilizes at 0.115. In contrast, all PAO 10 blends containing TATP/GO at various concentrations display a running-in period before reaching stable friction. Among them, TATP/GO-5 (0.05 wt.%) achieves the lowest stable friction coefficient of 0.084. The 3D wear morphology analysis reveals a consistent trend: both wear width and wear volume decrease upon the addition of TATP/GO, reach minima at 0.05 wt.%, and subsequently increase at higher concentrations (Table 2). TATP/GO-5 exhibits the narrowest wear width (341.33 μm) and the smallest wear volume ($5.73 \times 10^4 \mu\text{m}^3$), corresponding to a 90.23% reduction in wear volume compared to neat PAO 10. These results confirm that the optimal incorporation of TATP/GO at 0.05 wt.% significantly enhances the anti-wear performance of PAO 10.

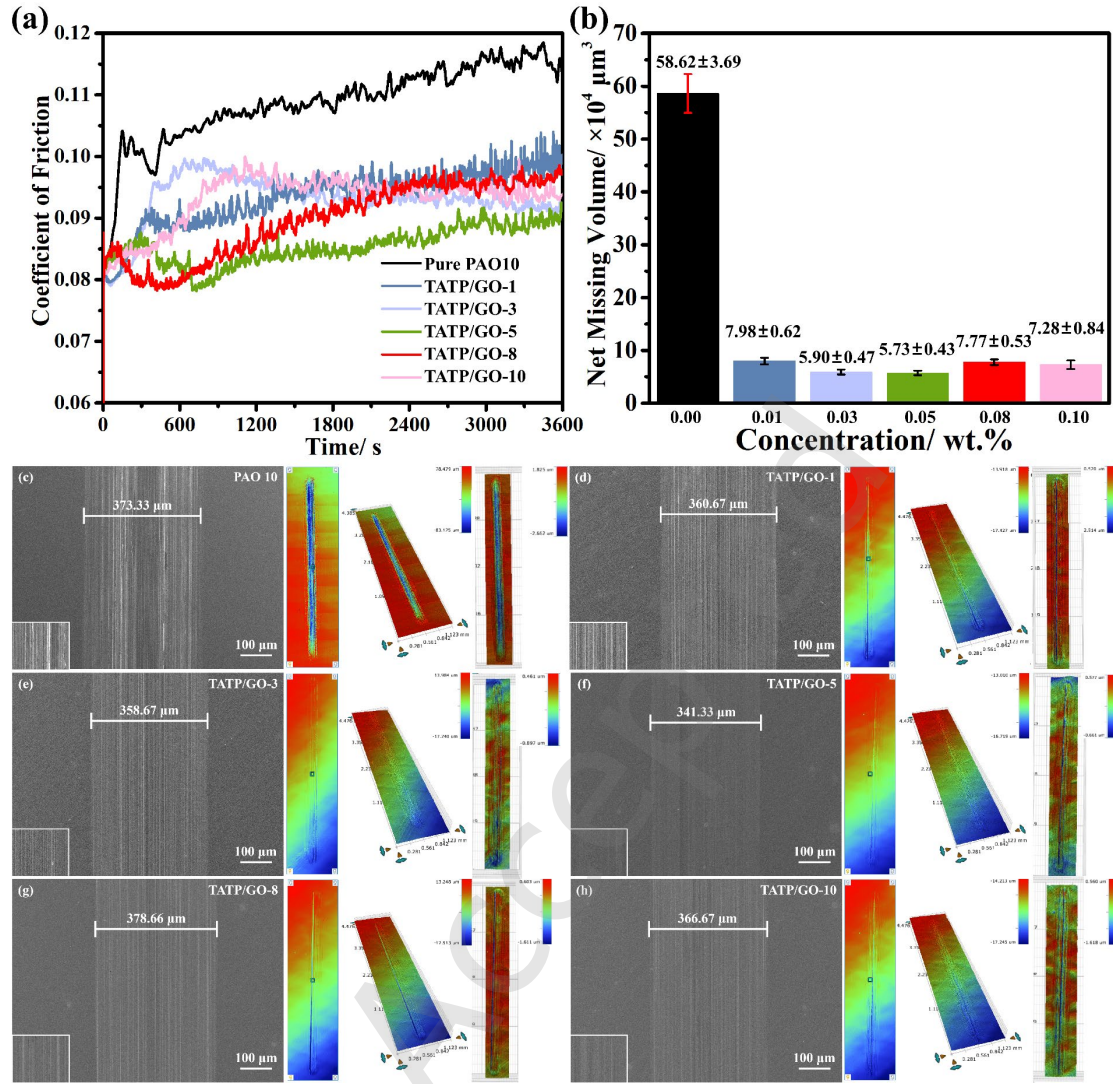


Figure 7 Friction-reduction and anti-wear behaviors of TATP/GO lubricant additive.

(a) Friction coefficient curves, (b) Wear volumes. (c-h) 2D micrographs and 3D contours of wear tracks for TATP/GO series lubricating oils.

At the optimal concentration of 0.05 wt.%, TADM/GO-5 reduces the friction coefficient of PAO 10 to 0.08, a 30.43% decrease compared to neat PAO 10 (Figure 8a). The corresponding wear volume is $2.59 \times 10^4 \mu\text{m}^3$, representing reductions of 95.58% relative to pure PAO 10 and 54.8% relative to TATP/GO-5 ($5.73 \times 10^4 \mu\text{m}^3$). Consistently, the wear width is also minimized with TADM/GO-5. Morphological examination of the wear tracks reveals distinct differences between the two additives. Surfaces lubricated with TATP/GO-containing oils exhibit prominent furrow-like marks, indicative of abrasive wear caused by hard particulate debris. In contrast, surfaces lubricated with TADM/GO display only shallow and sparse wear marks,

confirming its superior anti-wear performance.

Additional control tests using individual GO, TATP, and TADM additives at 0.05 wt.% were conducted to clarify the contribution of the hybrid structure (Figure S5). Compared with pure PAO 10, the wear-volume reductions achieved by GO, TATP, and TADM were 50.68%, 27.84%, and 78.68%, respectively, whereas TATP/GO and TADM/GO achieved substantially higher reductions of 90.23% and 95.58%. These results further support the synergistic lubrication effect between COFs and GO.

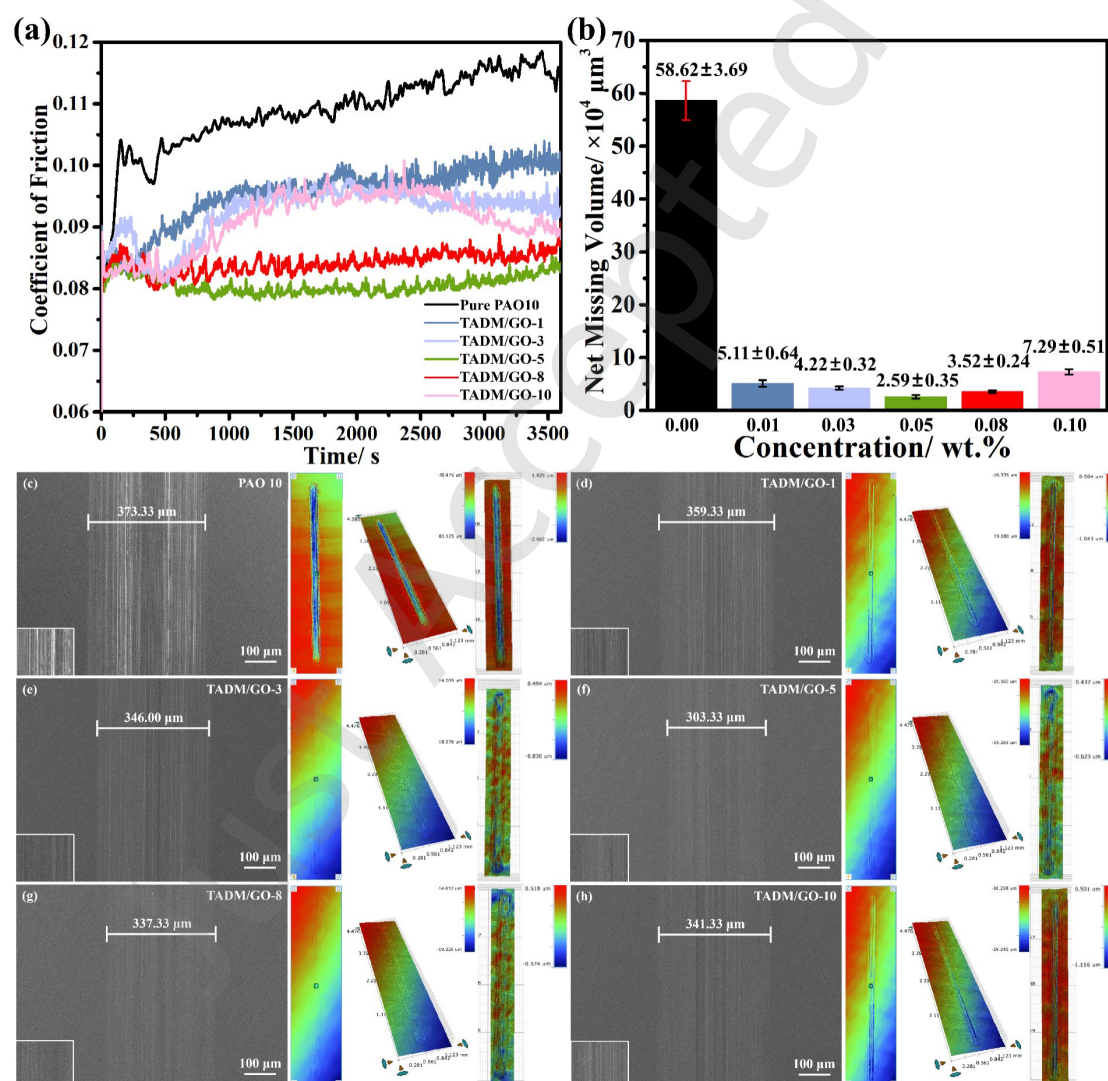


Figure 8 Friction-reduction and anti-wear behaviors of TADM/GO lubricant additive.

(a) Friction coefficient curves, (b) Wear track volumes. (c-h) 2D microscopic micrographs and 3D contours of wear tracks for TADM/GO series lubricating oils.

Table 2 The wear volume reduction of TADM/GO relative to TATP/GO

Concentration wt.%	TATP/GO		TADM/GO		Wear-volume reduction
	Wear Volume	Reduction %	Wear Volume	Reduction %	

	$\times 10^4 \mu\text{m}^3$		$\times 10^4 \mu\text{m}^3$		relative to TATP/GO %
0.00	58.62 ± 3.69	--	58.62 ± 3.69	--	--
0.01	7.98 ± 0.62	86.39	5.11 ± 0.64	91.28	35.96
0.03	5.90 ± 0.47	89.94	4.22 ± 0.32	92.80	28.47
0.05	5.73 ± 0.43	90.23	2.59 ± 0.35	95.58	54.80
0.08	7.77 ± 0.53	86.75	3.52 ± 0.24	94.00	54.69
0.10	7.28 ± 0.84	87.58	7.29 ± 0.51	87.56	--

3.2.2 Four-ball friction test

The anti-wear performance of the additives under extreme pressure was evaluated using a four-ball rotation test (Figure 9 and Figure S6a). Under an applied axial load of 392 N, the normal load at each ball-ball contact was calculated to be approximately 160 N based on the geometry of the four-ball configuration. Using a ball diameter of 12.7 mm, the maximum Hertz contact pressure was calculated to be approximately 3.45 GPa. Such a high local contact pressure represents a severe contact condition and may induce substantial subsurface stress, local elastic-plastic deformation, and accelerated surface damage. As shown in Figure 9a, the friction coefficient of neat PAO 10 remains below 0.07 during the initial stage but sharply increases to 0.078 at approximately 3000 s, likely due to abrasive particles entering the contact interface. Optical microscopy (Figure 9c) confirms severe wear, with distinct furrows and adhesive detachments. Adding 0.05 wt.% GO slightly reduces the friction coefficient to a stable 0.06, though furrow-like scratches and detachments persist.

Both COFs/GO hybrids markedly improve tribological performance. TATP/GO-5 and TADM/GO-5 reduce the friction coefficient to 0.053 and 0.042, corresponding to reductions of 32.1% and 46.2% relative to pure PAO 10, and decrease wear volume by 24.38% and 36.98%. Wear scar diameters are also reduced, with no deep furrows observed on the worn surfaces, particularly for TADM/GO-5, which exhibits superior anti-adhesive wear performance compared to TATP/GO-5 (Figure 9e₁ and f₁). This difference can be rationalized by the conjugated structure mechanism [24,42,43].

SEM-EDS elemental mapping and semi-quantitative analysis (Figure S7 and Table S1) provide compositional evidence supporting the formation of an additive-derived surface film. For PAO 10, the extremely low C and high O with a dominant Fe signal

confirm lubricating film failure, leading to severe adhesive and abrasive wear. In contrast, TADM/GO-5 exhibits the highest C and N contents on the wear track, demonstrating the formation of a composite tribofilm. This film isolates the metal substrates and inhibits adhesion, explaining its superior anti-adhesive wear performance. TATP/GO-5 shows lower N and higher O contents, indicating an unstable composite film. The comparatively higher O content is consistent with more extensive surface oxidation, which may be associated with less effective interfacial protection. These results further confirm the effectiveness of TADM/GO as a lubricant additive.

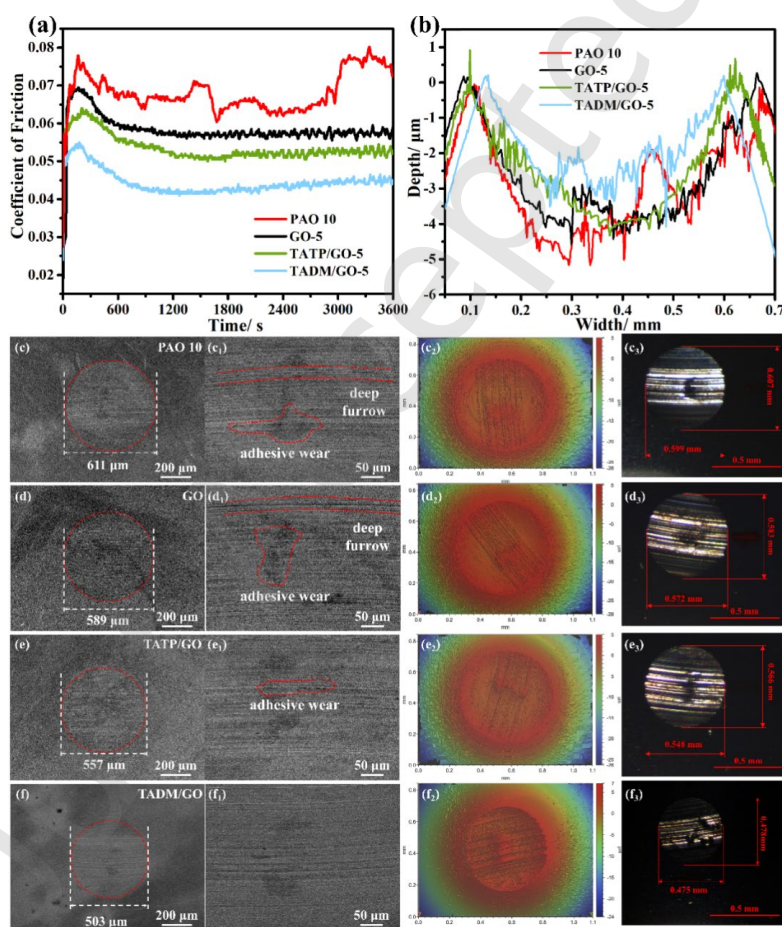


Figure 9 Extreme-pressure anti-wear performance of lubricating oils containing optimal concentrations of additives. (a) Friction coefficient curves, (b) Wear scar depths. (c-f) 2D micrographs and 3D surface contours of wear scars for lubricants formulated with optimal additive concentrations.

Table 3 The wear information obtained through WLI for 1 h four-ball rotation test

Sample	WSD/ mm	Wear Volume/ $\times 10^5 \mu\text{m}^3$	Wear Volume Reduction/ %
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PAO 10	0.61 ± 0.019	4.84 ± 0.24	--
GO-5	0.58 ± 0.013	4.38 ± 0.22	9.50
TATP/GO-5	0.56 ± 0.019	3.66 ± 0.18	24.38
TADM/GO-5	0.50 ± 0.024	3.05 ± 0.12	36.98

To further differentiate the anti-wear performance, independent 4 h four-ball tests were conducted using freshly prepared lubricant oils (Figure 10 and Figure S6b). For pure PAO 10, the wear depth increased from 5.1 μm in the independent 1 h test to 14.5 μm after 4 h (Figure 10b), accompanied by a substantial increase in wear volume. GO-5 exhibited moderate anti-wear performance, reducing the 4 h wear volume by 39.89% relative to PAO 10, which can be attributed to the interlayer sliding of GO that helps accommodate shear at the contact interface.

In contrast, both COFs/GO hybrids demonstrated superior and sustained anti-wear performance. After 4 h, the wear scar diameters of TATP/GO-5 and TADM/GO-5 were 0.76 and 0.73 mm (Figure 10c-f), with corresponding wear depths of 10.1 μm and 8.5 μm . Their wear volumes decreased from $14.69 \times 10^5 \mu\text{m}^3$ for PAO 10 to $5.67 \times 10^5 \mu\text{m}^3$ and $4.50 \times 10^5 \mu\text{m}^3$, corresponding to reductions of 61.40% and 69.37%, respectively (Table 4). Compared with the independent 1 h tests, the 4 h wear volumes of TATP/GO-5 and TADM/GO-5 were only 54.92% and 47.54% higher, respectively, indicating sustained wear protection during prolonged operation. TADM/GO-5 also reduced the friction coefficient by 35.71% relative to pure PAO 10, demonstrating its effective friction-reducing and anti-wear performance under prolonged severe contact conditions. A comparison with previously reported PAO-based additives is provided in Table S2.

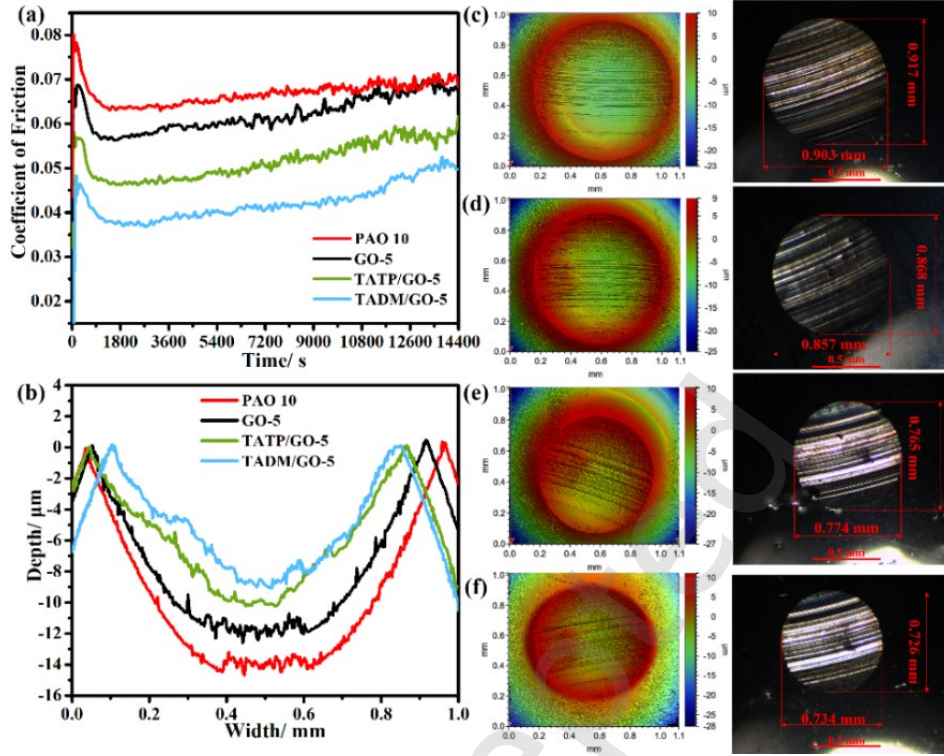


Figure 10 (a) Friction coefficient curves, (b) Wear scar depths. (c-f) 3D microscopic images and 3D contours of wear scars for 4 h four-ball rotation tests.

Table 4 The wear information obtained through WLI for a 4 h four-ball rotation test

Sample	WSD/ mm	Wear Volume/ $\times 10^5 \mu\text{m}^3$	Reduction/ %
PAO 10	0.91 ± 0.017	14.69 ± 0.46	--
GO-5	0.86 ± 0.022	8.83 ± 0.22	39.89
TATP/GO-5	0.76 ± 0.019	5.67 ± 0.14	61.40
TADM/GO-5	0.73 ± 0.016	4.50 ± 0.20	69.37

3.3 Characterization of tribochemical film

To clarify the tribofilm formation mechanism on worn lubricated surfaces with TADM/GO and TATP/GO additives, XPS analysis was conducted on the corresponding worn friction pairs. As shown in Figure 11, the C 1s spectrum obtained from the worn surface of the TADM/GO system shows characteristic peaks at binding energies of 284.8 eV, 285.2 eV, 286.3 eV and 288.3 eV, corresponding to benzene carbon, C=N bonds derived from the COFs framework, C–O/C–N bonds from the oxygen-containing groups of GO or the COFs framework, and carboxyl group-derived C=O bonds in COFs/GO, respectively. The Fe 2p spectrum displays peaks at 710.1 eV, 713.1 eV, 723.0 eV and 725.3 eV, corresponding to iron oxides such as Fe_2O_3 and FeO derived from

tribochemical reactions between the additive and metal substrate [44]. For the N 1s spectrum, the observed peaks at 398.8, 400.1 and 401.4 eV are assigned to C=N, C–N and N–H moieties, with these groups originating from TADM’s covalent framework [45,46]. Notably, the component at approximately 399.3 eV is attributed to Fe–N-associated species, suggesting possible Fe–N interfacial interactions during the tribological process [47–49]. These results confirm that a composite tribofilm consisting of carbon-based functional moieties, iron oxides and nitrogen-containing complexes is formed on the worn surface during sliding. Moreover, the Fe 2p spectra provide further insight into the interfacial interactions between the tribofilm and the Fe substrate. Compared with pure PAO 10 (Figure S8), the Fe 2p peaks of the worn surfaces lubricated with TATP/GO and TADM/GO (Figure 11b) shift toward lower binding energies, with a more pronounced shift observed for TADM/GO, suggesting stronger electronic interactions between the additive-derived tribofilm and the Fe substrate [50].

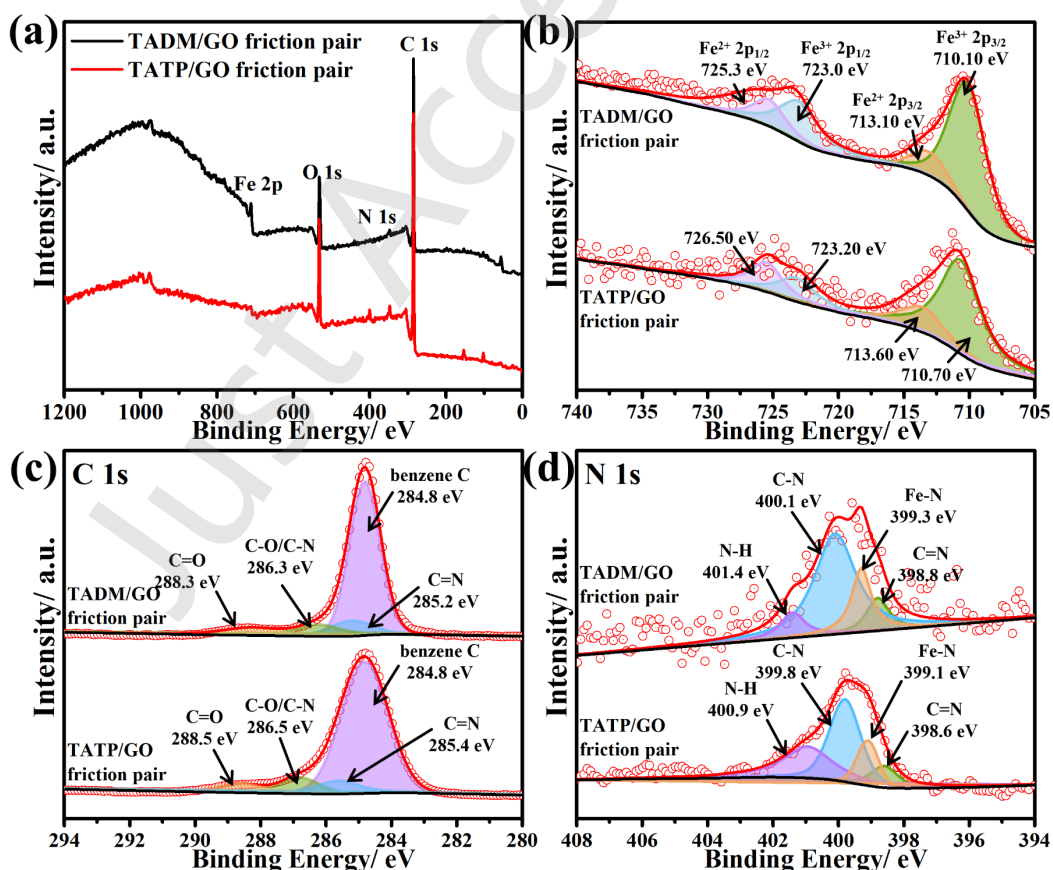


Figure 11 XPS spectra of wear scar lubricated with TATP/GO and TADM/GO (a) XPS survey spectra, (b) Fe 2p, (c) C 1s, (d) N 1s.

Raman spectroscopy was performed on wear scar surfaces to characterize the

transferred tribochemical films (Figure 12). The initial I_D/I_G ratios of GO, TATP/GO and TADM/GO nanocomposites were 0.89, 0.52 and 0.68, respectively. After friction, these ratios increased to 3.54, 2.61 and 0.75, indicating shear-induced sp^2 C=C cleavage and increased defect density ^[51]. This confirms stress-driven structural disordering rather than classical graphitization ^[52]. These newly formed defects act as active sites, promoting chelation between the oxygen-containing/nitrogen-containing functional groups of COFs/GO and Fe atoms from the steel substrate, which accelerates the formation of a robust tribofilm. However, excessive defects can cause structural collapse of carbon nanosheets, leading to the loss of lamellar sliding and the generation of hard carbonaceous debris that exacerbates wear (Figure 9) ^[53]. This highlights that proper retention of the two-dimensional layered structure is critical for wear resistance.

Notably, TADM/GO maintains a low I_D/I_G ratio of 0.75 post-friction, significantly lower than that of GO (3.54) and TATP/GO (2.61). This suggests that its tribofilm largely retains the conjugated sp^2 structure, correlating with its superior tribological performance. A characteristic C=N peak at 1627 cm^{-1} confirms the Schiff-base structure of TADM remains intact during friction, contributing to interfacial bonding. All carbon-containing samples exhibit a characteristic peak at $500\sim700\text{ cm}^{-1}$ assigned to Fe_3O_4 , confirming the formation of iron oxide composites tribochemical film via interfacial oxidation. In contrast, the neat PAO 10 shows no distinct D or G peaks, indicating an inability to form a protective carbon-based film.

Raman analysis of the recovered products further reveals the structural evolution of the additives during prolonged sliding (Figure S9). The I_D/I_G ratio of TATP/GO increased from 0.52 to 0.79 and 1.17 after 1 and 4 h, respectively, whereas that of TADM/GO increased from 0.68 to only 0.81 and 1.09. The smaller variation in I_D/I_G for TADM/GO indicates less friction-induced structural disorder and better structural retention during prolonged sliding, consistent with its sustained anti-wear performance.

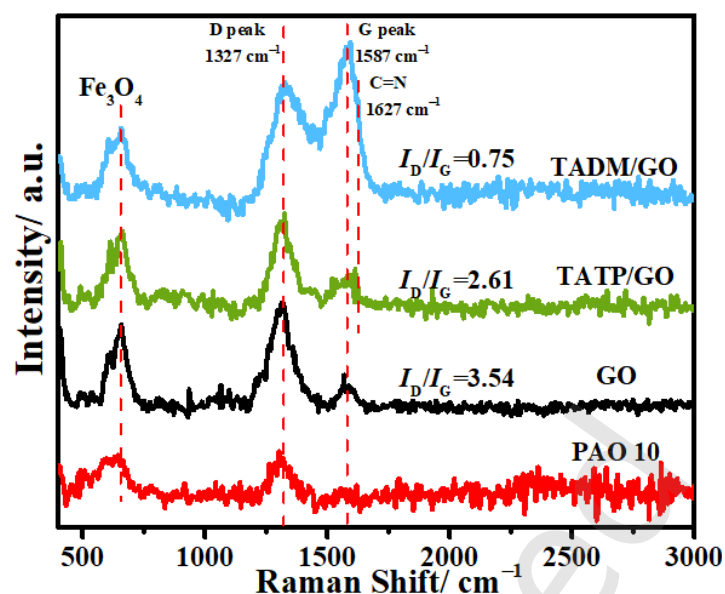


Figure 12 Raman spectra of wear scars after the friction process

3.4 Lubrication mechanism

Based on the above analyses, Figure 13 presents the proposed lubrication mechanism of TADM/GO, involving surface filling, interlayer sliding, and composite tribofilm formation. In situ growth of TADM expands the GO interlayer spacing from 8.44 to 9.14 Å, while the resulting hybrid exhibits improved sedimentation resistance in PAO 10. These characteristics may facilitate nanosheet availability at the contact interface and interlayer shear during sliding. Upon entering the contact zone, the nanosheets can accommodate surface irregularities and fill asperity valleys, limiting direct contact between opposing steel surfaces. Their layered structure may further facilitate sliding and reduce interfacial shear resistance. Shear-induced fragmentation could also contribute to gap filling and expose additional sites for interfacial interactions. Meanwhile, Raman results support comparatively improved structural retention of TADM/GO during rubbing, suggesting that the additive retains features favorable for lubrication under prolonged contact. XPS analyses provide evidence for a composite tribofilm containing additive-derived species and iron-containing compounds, consistent with additive deposition and tribochemical interactions with the steel surface. Rather than implying a strictly sequential transition, these physical and chemical processes likely operate together to reduce friction and protect the substrate. The combined mechanism is consistent with the sustained lubrication performance

observed in the 4 h four-ball tests at an initial maximum Hertzian contact pressure of 3.45 GPa.

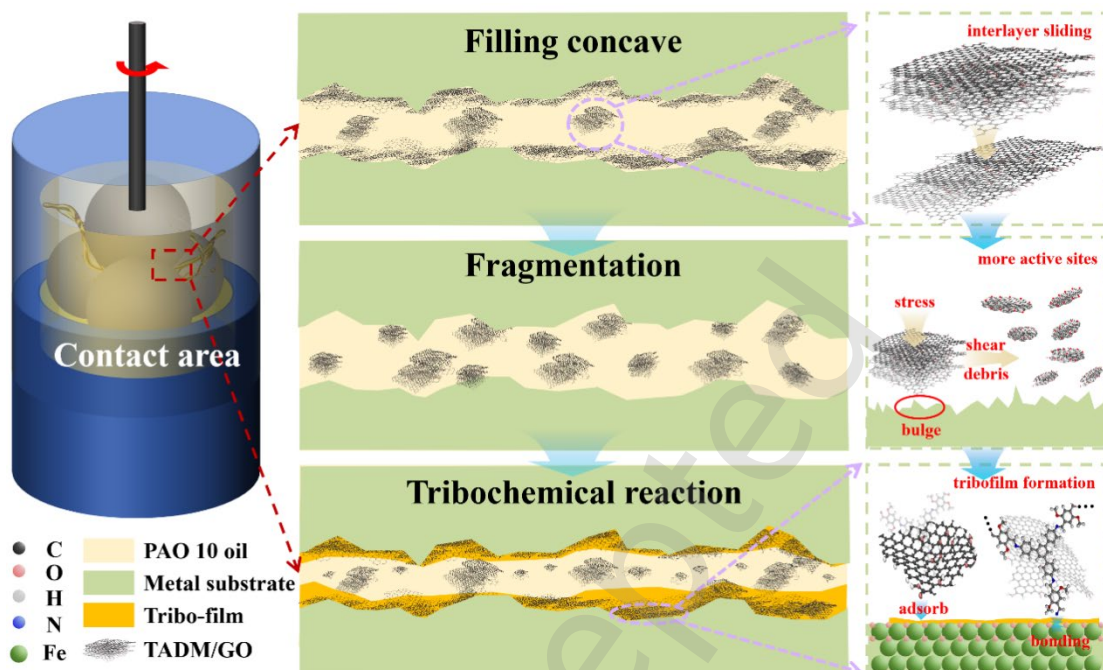


Figure 13 The lubrication mechanism of COFs/GO as lubricant additives.

4. Conclusion

This study investigates the tribological performance and proposed lubrication mechanism of TADM/GO as an additive in PAO 10 under reciprocating and severe four-ball contact conditions. The main conclusions are as follows:

(1) The proposed lubrication mechanism combines surface filling, interlayer sliding, and composite tribofilm formation. TADM/GO nanosheets may accommodate surface irregularities and facilitate interfacial shear, limiting direct metal contact. Raman and XPS analyses support comparatively improved structural retention and the formation of a composite tribofilm containing additive-derived species and iron-containing compounds. These complementary physical and chemical effects contribute to sustained friction reduction and wear protection.

(2) In situ polymerization of TADM expands the GO interlayer spacing from 8.44 Å to 9.14 Å. Static storage for 14 days and centrifugation at 3000 rpm for 10 min provide qualitative evidence of improved sedimentation resistance in PAO 10. The TADM/GO-derived wear scar film exhibits an I_D/I_G ratio of 0.75, compared with 2.61

for TATP/GO, consistent with comparatively better preservation of carbon structural order under the tested conditions.

(3) Tribological tests demonstrate that 0.05 wt.% TADM/GO reduces the friction coefficient and wear volume by 30.43% and 95.58%, respectively, under reciprocating conditions (0.77 GPa), and by 35.71% and 69.37% in 4 h four-ball tests (3.45 GPa). Notably, the 4 h wear volume is only 47.54% higher than that in the independent 1 h test, indicating sustained anti-wear performance under prolonged severe contact.

These findings highlight the potential of COF/GO hybrid design to improve sedimentation resistance and lubrication performance under severe contact conditions.

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Declaration of competing interest

The authors declare no competing financial interest.

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