

Synergistic lubrication enhancement by load-driven edge self-passivation and structural heterogeneity in graphene/MoS₂ coatings

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Cite this article: Fan SY, Xiao S, Zhang H, et al. *Friction* 2026, **14**: 9441235. <https://doi.org/10.26599/FRICT.2026.9441235>

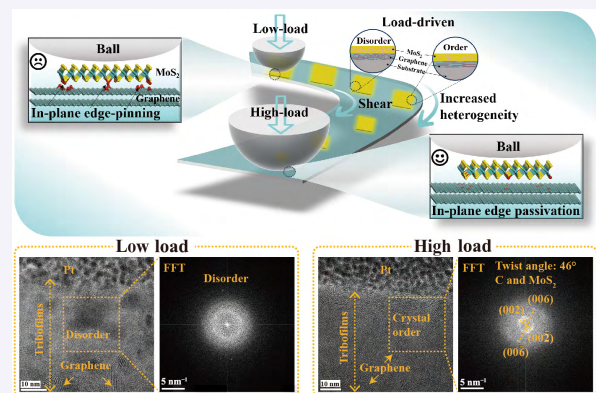
ABSTRACT: Graphene/molybdenum disulfide (MoS₂) heterostructure coatings are promising solid lubricants due to their intrinsic lattice mismatch and weak van der Waals (vdW) forces between chemically inert atomic layers. However, macroscale lubrication enhancement remains limited due to the competitive effect between in-plane edge interactions and incommensurability. Herein, graphene/MoS₂ heterostructure coatings with controlled heterogeneity are fabricated *in situ* by a magnetron sputtering method. The graphene/MoS₂ heterostructure coating outperforms its individual components in friction properties due to the synergistic integration of the chemical stability of graphene and the load-bearing capacity of MoS₂. Experiments and molecular dynamics (MD) simulations reveal that increased structural heterogeneity intensifies interfacial edge interactions, initially promoting structural disorder and frictional energy dissipation. Additionally, a load-driven self-passivation mechanism is uncovered to saturate dangling bonds and repair structural defects, consequently forming a robust passivated interface that facilitates smooth and well-ordered shear sliding. As a result of the synergistic interplay between load-driven edge self-passivation and structural heterogeneity, the highly heterogeneous graphene/MoS₂ coating exhibits a 3-fold friction reduction and 12-fold wear reduction under high-load conditions compared to low-load conditions. The results reveal a novel synergistic lubrication mechanism enabled by structural heterogeneity and load-driven interfacial engineering and offer insights into how to transform conventionally undesirable structural disorder into significant lubrication enhancements.

KEYWORDS: graphene/molybdenum disulfide (MoS₂); coatings; heterostructure; self-passivation; friction

1 Introduction

Friction and wear increase energy consumption and reduce the lifespan of mechanical components in precision instruments, aerospace, automotive, and industrial equipment systems [1, 2]. Solid lubricants provide better cost-effectiveness, environmental sustainability, mechanical robustness, and chemical stability than liquid lubricants, particularly in demanding load-bearing macroscale friction applications [3, 4]. Materials such as graphene [5], molybdenum disulfide (MoS₂) [6], hexagonal boron nitride

(h-BN) [7], tungsten disulfide (WS₂) [8], and MXenes [9], are effective solid lubricants due to their layered two-dimensional (2D) structures, where weak van der Waals (vdW) interactions between atomic planes enable low-resistance interlayer sliding under shear stress [10]. Integrating these 2D materials into van der Waals heterostructures, such as graphene/MoS₂ [11], graphene/h-BN [12], graphene/WS₂ [13], and MXene/MoS₂ [14, 15], has emerged as a promising strategy to enhance lubrication performance. In the graphene/MoS₂ heterostructure, the chemically inert graphene underlayer preserves the structural



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Received: August 18, 2025; Revised: January 12, 2026; Accepted: February 20, 2026

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stability of MoS₂, reducing environmental degradation, while the MoS₂ sandwich structure provides robust mechanical stability to alleviate the pressure sensitivity of graphene [16, 17]. This synergistic integration of complementary properties offers promising potential for robust tribological applications.

Graphene/MoS₂ heterostructures exhibit naturally low friction due to incommensurate contact interfaces, where lattice mismatch between chemically inert atomic layers weakens van der Waals interactions and cancels lateral forces [18, 19]. Although nanoscale graphene/MoS₂ flakes achieve superlubricity under ideal conditions [20, 21], scaling these properties to practical macroscale applications remains challenging. Macroscale lubrication involves fabricating large-area heterostructures, which introduce multiple contact interfaces and abundant edge sites that fundamentally alter tribological behavior [22, 23]. In controlled environments such as nitrogen (N₂) atmosphere or vacuum, weak interlayer coupling and reduced edge effects enable robust macroscale lubrication [24, 25]. However, in practical applications, graphene/MoS₂ heterostructures are inevitably exposed to ambient conditions, which poses a challenge due to environmental adsorbates accumulating at edges and disrupting interlayer weak coupling [26–28], resulting in complex macroscale friction behavior governed by the competing effects of weak interlayer interactions and edge interactions. To address these challenges, advances in interfacial engineering and structural design offer promising solutions for improving lubrication performance. One breakthrough involves fragmenting large sliding interfaces into distributed microscale contact regions, preserving intrinsic superlubricity while reducing strain accumulation and enabling uniform load distribution [25]. Additionally, interfacial modification strategies, including dopant-induced edge passivation, presliding treatment, and localized thermal activation, maintain structural incommensurability while suppressing edge effects, further enhancing tribological properties [29–31]. However, despite this progress, these systems require extended run-in periods, and the collective frictional interaction mechanisms of the incommensurate interface, edge density, and external conditions are not yet fully understood [32]. Developing efficient strategies and understanding the underlying mechanisms is essential for achieving robust macroscale lubrication in graphene/MoS₂ systems [33].

Two primary interfacial contact configurations govern the tribological response of the graphene/MoS₂ heterostructure: out-of-plane edge contacts, which naturally form between adjacent layers, and in-plane edge contacts, which arise from size-mismatched overlays [34]. Techniques such as edge oxygen incorporation, which weakens both contact types, show potential for achieving macroscale superlubricity [35]. However, the mechanisms and contributions of in-plane edge contacts to the overall friction behavior remain insufficiently explored. Recent studies highlight that friction mechanisms in layered heterogeneous interfaces are influenced by lattice mismatch [36]. In small-lattice-mismatch graphene/h-BN interfaces (~1.7%), friction is dominated by surface shear forces, while in graphene/MoS₂ heterostructures with large-lattice-mismatch interfaces (26.8%), edge-pinning effects prevail. Based on edge density, graphene/MoS₂ heterostructures can be categorized into highly heterogeneous and lowly heterogeneous interfaces, each with distinct frictional behaviors. Heterogeneous interfaces typically exhibit low friction through rotation-mediated incommensurate states [37]. A critical yet underexplored factor is the role of in-plane edge interactions in frictional properties of highly heterogeneous structures, where numerous edge contacts compete with incommensurability effects. While microscale studies suggest that strain-induced

friction modulation depends on the arrangement of overlaid 2D layers, scaling these findings to the macroscale introduces additional complexities [38]. Amplified in-plane edge effects under varying loads lead to intricate interfacial dynamics. Understanding how shear load, structural heterogeneity, and edge interactions collectively affect macroscale friction requires further experimental and theoretical investigation.

Herein, graphene/MoS₂ heterostructure coatings with tunable heterogeneity are fabricated *in situ* on industrial substrates to investigate the macroscale friction properties and mechanisms. The coatings are fabricated *in situ* by first depositing graphene using nickel-assisted hot-filament chemical vapor deposition (HFCVD), followed by depositing MoS₂ through time-controlled magnetron sputtering. These heterostructure coatings show superior friction-reducing properties beyond their individual components. The interplay between in-plane edge interactions and structural heterogeneity, along with their collective friction response mechanisms to different loads during shear sliding, is systematically analyzed. Molecular dynamics (MD) simulation is performed to investigate how varying structural heterogeneity affects interfacial edge interactions and frictional behavior during shear sliding. The results reveal that the synergistic friction mechanism of shear load-induced edge self-passivation and structural heterogeneity enables robust lubrication, offering a potential solution for advancing macroscale tribological systems.

2 Experimental

2.1 Sample preparation

The graphene coatings were deposited *in situ* on a polished WC-Co substrate ($\phi 18 \text{ mm} \times 4 \text{ mm}$, composed of 94 wt% WC and 6 wt% Co, with a roughness of 2.62 nm, supplied by Zhuzhou Cementer Carbide Cutting Tools Co., Ltd., China) with a Ni catalytic layer using HFCVD (Carbon Competence, Austria) [22, 39], and the MoS₂ coatings were deposited by pulsed direct current (DC) magnetron sputtering using high-purity MoS₂ targets (99.99%). Prior to the deposition of MoS₂ coatings, the chamber was evacuated to a base pressure of $1 \times 10^{-4} \text{ Pa}$. The graphene-coated substrate was subjected to Ar⁺ plasma etching at -300 V for 5 min to remove surface contaminants. The MoS₂ coatings were deposited at a substrate temperature of $300 \text{ }^{\circ}\text{C}$ and working pressure of 0.3 Pa using a target current of 1 A with pulsed DC parameters (40% duty cycle, 35 kHz) while maintaining a negative substrate bias of 1,000 V, which optimized for high crystallinity, density, and adhesion [40, 41]. The graphene/MoS₂ heterostructure coatings with different degrees of heterogeneity were synthesized by controlling the growth kinetics. The samples were designated GM-15, GM-30, GM-60, and GM-90, corresponding to MoS₂ deposition times of 15, 30, 60, and 90 min, respectively. The measured thickness range varied from 0.23, 0.5, 1.5, to $3.0 \text{ }\mu\text{m}$ for GM-15, GM-30, GM-60, and GM-90, respectively (Figs. S1 and S2 in the Electronic Supplementary Material (ESM)).

2.2 Friction experiments

The tribological properties were evaluated by a ball-on-disk rotational tribometer (MVT-2, Rtec, USA) under ambient conditions ($25 \pm 2 \text{ }^{\circ}\text{C}$, $55\% \pm 2\% \text{ RH}$). Al₂O₃ balls ($\phi 6 \text{ mm}$) served as counterparts against graphene/MoS₂ heterostructure coatings. The sliding speed was 0.2 m/s (corresponding to 382 r/min), and the wear track radius was 5 mm. The friction properties were determined under different shear loads between 1 and 5 N, corresponding to contact pressures of 590.5 and 1,009 MPa and

real contact areas of approximately 2,538 and 7,426 μm^2 , respectively. Each test was repeated three times to improve the statistics. Posttest analysis was conducted using 3D profilometer (Dektak XT, Bruker, USA) to characterize the wear volume and morphology. Volume loss (V) was obtained from three line-scan profiles across the wear track by computing cross-sectional areas in origin and integrating them. The specific wear rate was calculated by the equation $W = V/(F \times S)$, where V (mm^3) represents the volumetric material loss, F (N) denotes the applied normal load, and S (m) is the total sliding distance.

2.3 Sample characterization

The surface morphology, composition and topography of the coating were characterized by a field-emission scanning electron microscope (FE-SEM; SU8220, Hitachi, Japan), an energy-dispersive X-ray spectrometer (EDS; X-Max 80, Oxford Instruments, UK), and an atomic force microscope (AFM; Dimension Edge, Bruker, USA). AFM measurements were conducted in tapping mode with a scan area of $5 \mu\text{m} \times 5 \mu\text{m}$, and the surface roughness was quantified using the arithmetic average roughness (R_a). The interfacial structure and crystallinity of both the as-deposited and worn coatings were analyzed by a high-resolution transmission electron microscope (HR-TEM; Talos F200X G2, Thermo Fisher Scientific, USA). Electron-transparent slices with a thickness of 70 nm were prepared via a focused ion beam (FIB; Scios 2, FEI, USA) milling using an initial ion current of 7 nA for rough cutting and a final polishing current of 10 pA to ensure high-quality samples for TEM observation. The structural properties and chemical states were determined by an X-ray diffractometer (XRD; Smartlab, Rigaku Corporation, Japan) with Cu K α radiation (0.154 nm), a confocal Raman spectrometer (LabRAM HR) with a 532 nm laser at a power of 5 mW, and an X-ray photoelectron spectrometer (XPS; ESCALAB 250xi, Thermo Fisher Scientific, USA) with a monochromatic Al K α source. The surface wettability and adhesion strength were assessed using contact angle goniometer (OCA40, Dataphysics, Germany) and scratch tester (RST3, Anton Paar, Austria), respectively.

2.4 MD simulation settings

To investigate the effects of the structural heterogeneity of graphene/MoS₂ heterostructures on interfacial edge interactions and tribological mechanisms, MD simulations were performed with the large-scale atomic/molecular massively parallel simulator (LAMMPS) package [42]. The simulation models, constructed in Materials Studio, comprised a trilayer graphene substrate ($154.98 \text{ \AA} \times 153.39 \text{ \AA}$) with superimposed MoS₂ layers of two distinct sizes. The heterostructures incorporated a smaller layer ($31.66 \text{ \AA} \times 27.42 \text{ \AA}$) and a larger MoS₂ layer ($85.48 \text{ \AA} \times 93.22 \text{ \AA}$), both positioned at a height of 4.72 $\text{\AA}$ above the graphene surface to establish well-defined in-plane edge interfaces. Vacancy defects were introduced equally at both interfaces to simulate realistic conditions and their effects on interfacial interactions. Periodic boundary conditions were applied in the x and y directions, with the bottom graphene layer fixed, the middle layer acting as a thermostat, and all other atoms free to move [35]. Prior to the adhesion force and sliding simulations, the system underwent energy minimization followed by a 10 ps relaxation at 300 K using a Nosé-Hoover thermostat in an NVT ensemble [43, 44]. To characterize the interfacial adhesion, the MoS₂ layer was pulled away from the graphene substrate at a constant velocity of 0.01 $\text{\AA}/\text{ps}$ along the z -axis, while the adhesion force was recorded every 0.1 ps. The MoS₂ layers were first compressed along the z -axis (surface normal direction) at a constant velocity of 0.1 $\text{\AA}/\text{ps}$

until reaching potential energy thresholds of 200, 600, or 1,800 eV [45]. Subsequently, shear sliding was induced by displacing the top MoS₂ layer along the x -axis direction at a constant velocity of 0.1 $\text{\AA}/\text{ps}$ for 800 ps at 300 K, with all simulations employing a 1 fs timestep for lateral and normal force integration [46]. During the sliding process, both the lateral and normal forces were recorded to calculate the coefficients of friction (COF; $\mu = F_{\text{lateral}}/F_{\text{normal}}$, where F_{lateral} is the lateral force and F_{normal} is the applied normal load). The intralayer interactions were modeled using the adaptive intermolecular reactive empirical bond order (AIREBO) potential for graphene [47], the Stillinger-Weber potential for MoS₂ [48], and the Lennard-Jones potential (including dispersion terms) to capture interlayer physical interactions between 2D materials [35].

Considering the combined effects of interface sliding resistance and the edge-pinning effect on friction behavior, the in-plane edge effect between graphene and MoS₂ was quantified by calculating both shear strength (S) and edge-pinning strength (E). The definitions of S and E are provided in Eqs. (1) and (2) [38]:

$$S = \frac{F}{A} \quad (1)$$

$$E = \frac{F}{P} \quad (2)$$

where F is the friction force, A ($\text{\AA}^2$) is the area of the MoS₂ layer, and P ($\text{\AA}$) is the perimeter of the MoS₂ layer. S characterizes the interfacial bonding strength through the friction force per unit area, while E reflects the contribution of edge atoms to friction through the friction force per unit length.

3 Results and discussion

3.1 Microstructures of graphene/MoS₂ heterostructure coatings

Figure 1(a) illustrates the fabrication process and growth evolution of the graphene/MoS₂ heterostructure coatings. The growth of MoS₂ coatings on the graphene layers can be divided into the following steps [49]: (i) plasma-activated MoS₂ species diffuse across the graphene surface, forming primary nucleation sites via adsorption and reorganization; (ii) a continuous supply of precursor promotes the lateral expansion of initial nuclei, resulting in the formation of crystalline MoS₂ that interact with graphene through van der Waals forces; (iii) additional nucleation on existing MoS₂ layers initiates vertical growth while maintaining lateral expansion; (iv) multiple MoS₂ islands emerge on the multilayer base through Stranski-Krastanov growth mode, balancing interfacial and strain energies; and (v) progressive island growth and coalescence lead to continuous MoS₂ coatings with controlled thickness and crystallinity. The microstructure and spatial distribution of the GM-15 highly heterogeneous graphene/MoS₂ coatings were investigated by HR-TEM (Figs. 1(b)–1(j)). The transverse section TEM image (Fig. 1(b)) reveals discrete MoS₂ nanoparticles dispersed across the graphene surface to form island-like structures. The corresponding elemental mapping confirms the coexistence and heterogeneous distribution of C, Mo, and S throughout the coating (Figs. 1(c)–1(e)). The cross-sectional HR-TEM image (Fig. 1(f)) shows that MoS₂ nanodomains (marked by orange spherical dashed circles) are randomly distributed on the upper surface of the layered graphene structure (marked by orange dashed lines). The fast Fourier transform (FFT) pattern (inset of Fig. 1(f)) reveals distinct diffraction spots from both graphene and MoS₂, confirming the

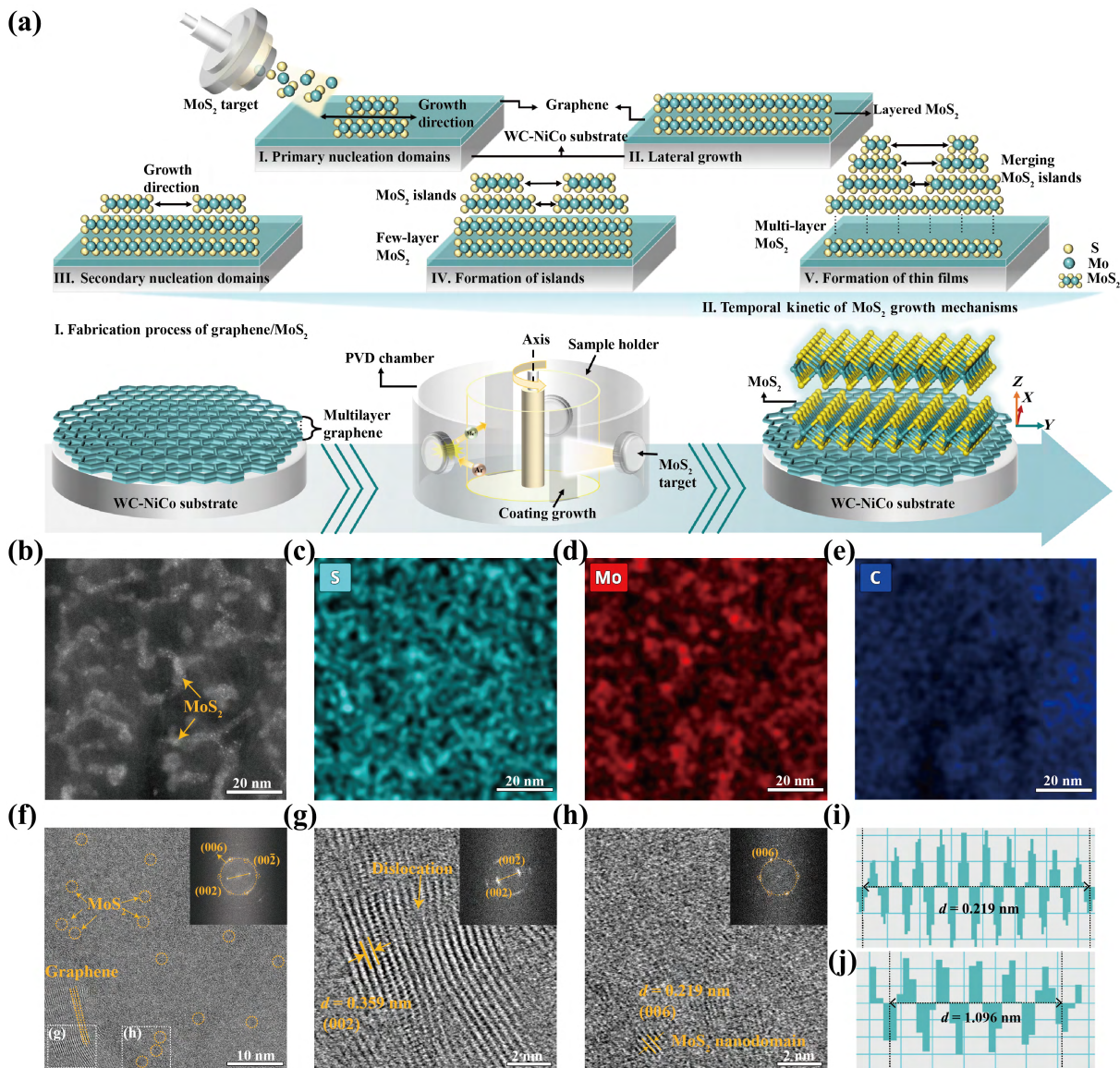


Fig. 1 Fabrication and microstructural characterization of GM-15 highly heterogeneous graphene/MoS₂ coatings. (a) Schematic illustration of fabrication and MoS₂ growth mechanism, depicting sequential stages of primary nucleation domains, lateral growth, secondary nucleation, island formation, and thin-film formation. (b) Transverse-sectional HR-TEM image showing the surface morphology. (c–e) EDS elemental maps of the same region revealing the spatial distributions of C, Mo, and S. (f) Cross-sectional HR-TEM image of graphene/MoS₂ interface (inset: FFT pattern). (g) Magnified HR-TEM view of region g marked in (f), showing graphene crystalline structure (inset: FFT pattern). (h) Magnified HR-TEM view of region h marked in (f), showing MoS₂ crystalline structure (inset: FFT pattern). (i) Measured interlayer spacing of graphene region marked in (g). (j) Measured interlayer spacing of MoS₂ region marked in (h).

successful formation of crystalline heterostructures. To observe the lattice of graphene and MoS₂, magnified views of white rectangles g and h are shown in Figs. 1(g) and 1(h), respectively. The graphene lattice exhibits distinct edge dislocations, while MoS₂ exists as discrete nanodomains. Higher magnification (Figs. 1(g)–1(j)) reveals d -spacings of 0.395 and 0.219 nm, corresponding to the graphene (002) and MoS₂ (006) crystal planes [50], respectively, in agreement with the XRD results. Specifically, graphene exhibits a multilayer structure with a thickness of approximately 6.4 nm (Fig. 1(g)), which is attributed to carbon segregation at Ni grain boundaries [51]. Moreover, these d -spacings deviate from the intrinsic lattice spacings of pristine graphene ($d_{002} = 0.34$ nm) and MoS₂ ($d_{006} = 0.21$ nm) [52, 53]. The lattice expansion primarily originates from the inherent lattice mismatch between graphene and MoS₂, while environmental water molecules intercalated during ambient exposure also contribute to the lattice expansion [54]. The mismatch creates an

incommensurate interface where the atomic registries of the two materials do not align periodically, leading to a reduced interfacial contact area and modified van der Waals interactions [55]. Additionally, the elongated and diffuse nature of the graphene (002) diffraction spots (inset of Fig. 1(g)) suggest structural edge disorder and lattice distortion at the heterogeneous interfaces due to a large lattice mismatch [56]. The interfacial structural evolution is fundamentally driven by the complex interplay of multiple factors. The discrete MoS₂ islands fragment the macroscale contact into numerous localized incommensurate interfaces, while the edge-terminated structures at MoS₂ island boundaries create active dangling bonds that can interact with adjacent graphene layers. These distinctive structural characteristics may generate competing tribological mechanisms during sliding. The incommensurate interfaces inherently reduce the effective contact area and weaken interfacial adhesion to promote easy shear between the layers. Nevertheless, the edge-

mediated interactions through dangling bonds at MoS₂ island boundaries can locally enhance interlayer coupling and increase the sliding resistance.

3.2 Surface and structure characteristics of graphene/MoS₂ heterostructure coatings

The evolution of the MoS₂ surface morphology on graphene progresses through four distinct growth stages (Figs. 2(a)–2(d)), with quantitative domain size and edge density analysis revealing heterogeneity variations (Fig. S3 in the ESM). The spherical morphology of MoS₂ particles results from interfacial energy minimization between MoS₂ and graphene, consistent with classical nucleation theory [57]. Initially, MoS₂ forms dispersed, discrete spherical particles with an average domain area of 0.472 μm^2 (Figs. S3(a) and S3(b) in the ESM). As deposition progresses, these particles coalesce into interconnected structures, then develop mixed-area domains, and ultimately form uniform large domains with an average area of 2.26 μm^2 (Figs. S3(g) and S3(h) in the ESM). Edge densities, which are used to quantify the relationship between domain area and edge structure, decrease from approximately 5.17 μm^{-1} for GM-15 to 2.36 μm^{-1} for GM-90, reflecting increasing surface coverage, reduced edge density, and decreased structural heterogeneity of the graphene/MoS₂ coating. This morphological evolution transitions from highly heterogeneous structures with discrete MoS₂ domains and abundant edge density to lowly heterogeneous structures with interconnected MoS₂ coverage, affecting tribological behavior through interfacial contact mechanics. EDS analysis confirms the presence and distribution of C, Mo, and S (Table S1 in the ESM), showing S/Mo atomic ratios of 2.362, 2.335, 2.252, and 2.427 in

GM-15, GM-30, GM-60, and GM-90, respectively. These ratios slightly exceed the ideal MoS₂ stoichiometry value of 2, indicating the presence of intrinsic structural defects and sulfur-rich edges. The progressive decrease in carbon content (from 14.50% to 5.83%) corresponds to increasing MoS₂ coverage, while rising Mo and S concentrations confirm the reduced heterogeneity of graphene/MoS₂ coatings.

AFM imaging shows that decreasing structural heterogeneity in graphene/MoS₂ coatings leads to progressively higher surface roughness (Figs. 2(e)–2(h)). The surface roughness increases from 111, 127, 137, to 175 nm for GM-15, GM-30, GM-60, and GM-90, respectively. This increase can be attributed to the initial formation of sharp MoS₂ domains, followed by vertical stacking and lateral coalescence, consistent with SEM analysis showing an increased domain area. Reduced surface roughness typically lowers friction by minimizing mechanical interlocking and plowing between asperities [25, 58]. External factors such as contact load, sliding velocity, and humidity may further influence these effects [59–62]. Surface wettability measurements show that decreasing structural heterogeneity in graphene/MoS₂ heterostructure coatings leads to increased contact angles from 78.0° to 89.9° (Figs. 2(i)–2(l)). This trend differs from conventional MoS₂ surfaces, which exhibit strong hydrophilicity due to sulfur-terminated basal planes facilitating water molecule interactions [63]. The wettability evolution is driven by structural heterogeneity-dependent surface chemistry and roughness [64, 65]. The highly heterogeneous structure, characterized by structural discontinuities and abundant edge defect density (supported by SEM and Raman analysis), creates energetically favorable sites for water adsorption, enhancing hydrophilicity. Additionally, the

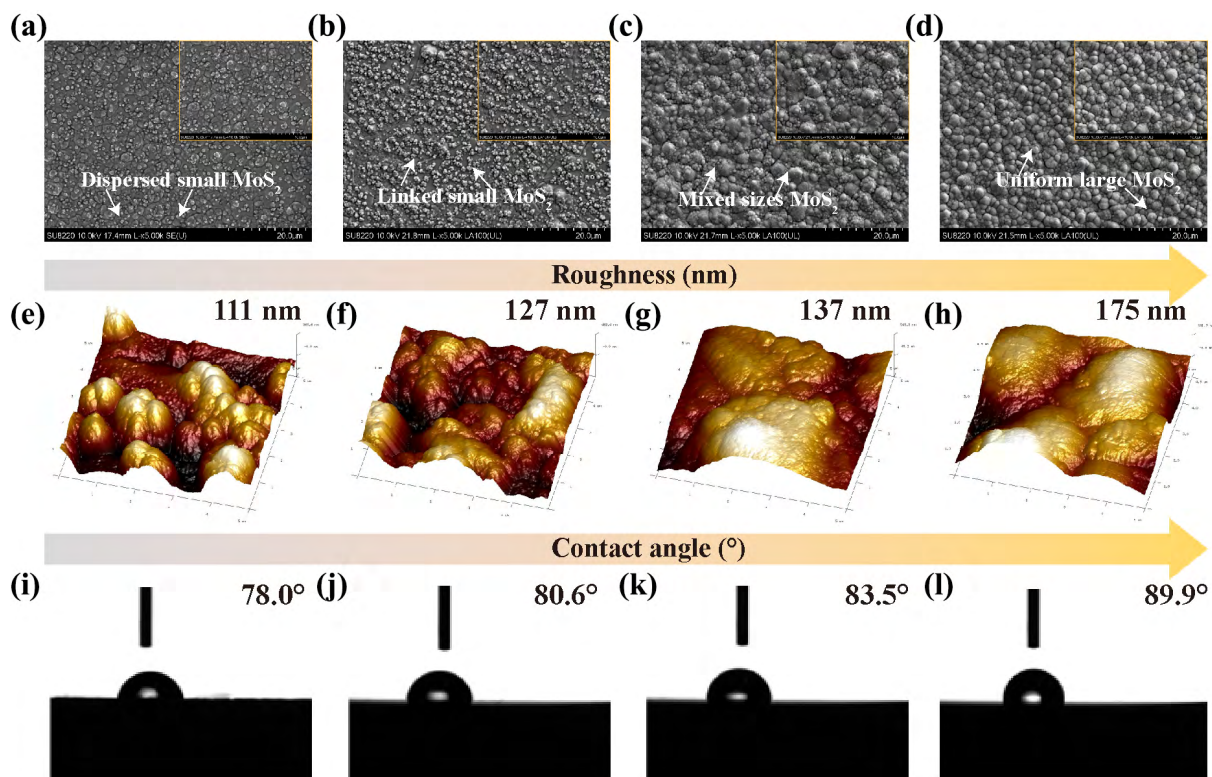


Fig. 2 Morphologies, topographies, and wettability of graphene/MoS₂ heterostructure coatings with varying degrees of heterogeneity. SEM images with higher magnification insets of (a) GM-15, (b) GM-30, (c) GM-60, and (d) GM-90 samples. Morphological evolution from dispersed small MoS₂ particles to uniform large MoS₂ structures is highlighted. AFM topographic images (5 $\mu\text{m} \times 5 \mu\text{m}$) of (e) GM-15, (f) GM-30, (g) GM-60, and (h) GM-90 samples, showing increasing surface roughness from 111 to 175 nm. Contact angle measurements for (i) GM-15, (j) GM-30, (k) GM-60, and (l) GM-90 samples, showing a gradual increase in contact angles ranging from 78.0° to 89.9°.

rough surface in a lowly heterogeneous structure forms air gaps, reducing the liquid contact area and further decreasing hydrophilicity [66]. This wettability transition reflects the evolution of the structural distribution and interfacial interactions, ultimately influencing tribological performance under ambient conditions. Statistically, the MoS₂ domain area, surface roughness, and contact angle all exhibit an increasing trend with decreased structural heterogeneity, driven by the progressive growth and coalescence of MoS₂ domains (Fig. S4 in the ESM).

XRD identifies diffraction peaks at 2θ values of 13.2°, 33.5°, 34.9°, 40.5°, 44.5°, 51.8°, 58.7°, 70.1°, 73.7°, and 76.2°, corresponding to crystalline MoS₂ (002), (004), (100), (103), (006), (105), and (110) planes, respectively, along with a peak at 26.6° arising from the (002) planes of graphene (Fig. 3(a)). With decreasing structural heterogeneity from GM-15 to GM-90, the intensified MoS₂(002) peak and weakened (006) reflection indicate a transition to well-aligned continuous layers with reduced stacking defects [67]. Meanwhile, the progressive decrease in the graphene (002) peak intensity reflects the transition from exposed graphene regions with scattered MoS₂ islands to extensively covered graphene surfaces with continuous MoS₂ films. Notably, the GM-15 sample exhibits the preferred orientations of the graphene (002) and MoS₂ (006) planes, as corroborated by HR-TEM and FFT. These orientations stem from the lattice mismatch between graphene and MoS₂, leading to incommensurate contact and enhanced dislocation, as evidenced by the TEM result.

Raman spectra show characteristic peaks of MoS₂ (E_{2g}^1 peak at 371 cm⁻¹ and A_{1g} peak at 410 cm⁻¹) [68] and graphene (D peak at 1,341 cm⁻¹ and G peak at 1,592 cm⁻¹) [69], confirming the coexistence of graphene and MoS₂ (Fig. 3(b)). The E_{2g}^1 peak corresponds to in-plane Mo–S atomic vibrations, while the A_{1g} peak relates to out-of-plane movements of S atoms along the c -

axis [70]. The D and G peaks indicate structural defects and in-plane tangential stretching of the sp² C–C bond, respectively [71]. In GM-15, a prominent 2D peak at 2,696 cm⁻¹ [72] arises from partial graphene exposure due to incomplete MoS₂ coverage, as confirmed by SEM. The D + D' peak at 2,934 cm⁻¹ attributed to intravalley resonance processes at defect sites reflects dangling carbon bonds at the highly heterogeneous interface [73]. The interfacial coupling strength, quantified by the frequency difference between E_{2g}^1 (sensitive to charge doping) and A_{1g} (sensitive to lattice distortions or strain) peaks ($\Delta = A_{1g} - E_{2g}^1$) [74]. The GM-15 sample shows the highest Δ of 37.53 cm⁻¹, followed by decreasing values of 34.61, 33.30, and 32.65 cm⁻¹ for the GM-30, GM-60, and GM-90 samples, respectively (Fig. 3(c)), indicating weaker interfacial interactions with reduced structural heterogeneity. This trend aligns with increasing I_D/I_G ratios (where I_D and I_G denote the intensities of the D band and G band in the Raman spectra, respectively; I_D/I_G represents the defect density) [75] of 0.66, 1.06, 1.55, and 1.73 for the GM-90, GM-60, GM-30, and GM-15 samples, respectively, reflecting higher defect density in highly heterogeneous structures. As structural heterogeneity decreases, more intense MoS₂ peaks and attenuated graphene signals indicate a transition from discrete domains to continuous layers, consistent with the XRD results.

The XPS spectra in Figs. 3(d)–3(f) show high-resolution peaks for Mo 3d, S 2p, C 1s, and inevitable O 1s (Fig. S5 in the ESM). As shown in Fig. 3(d), the Mo 3d peak is deconvoluted into six peaks with Mo⁴⁺ 3d_{5/2} at 229.6 eV and Mo⁴⁺ 3d_{3/2} at 232.7 eV corresponding to Mo–S bonds in MoS₂ [76]. Furthermore, Mo⁶⁺ 3d_{5/2} at 232.8 eV and Mo⁶⁺ 3d_{3/2} at 236.1 eV indicate Mo–O bonds from partial oxidation [77]. A small peak at 226.7 eV stems from the S 2s orbital [78]. The Mo⁶⁺ content decreases from 28.52% in GM-15 to 22.13% in GM-90, while the S 2s content increases with

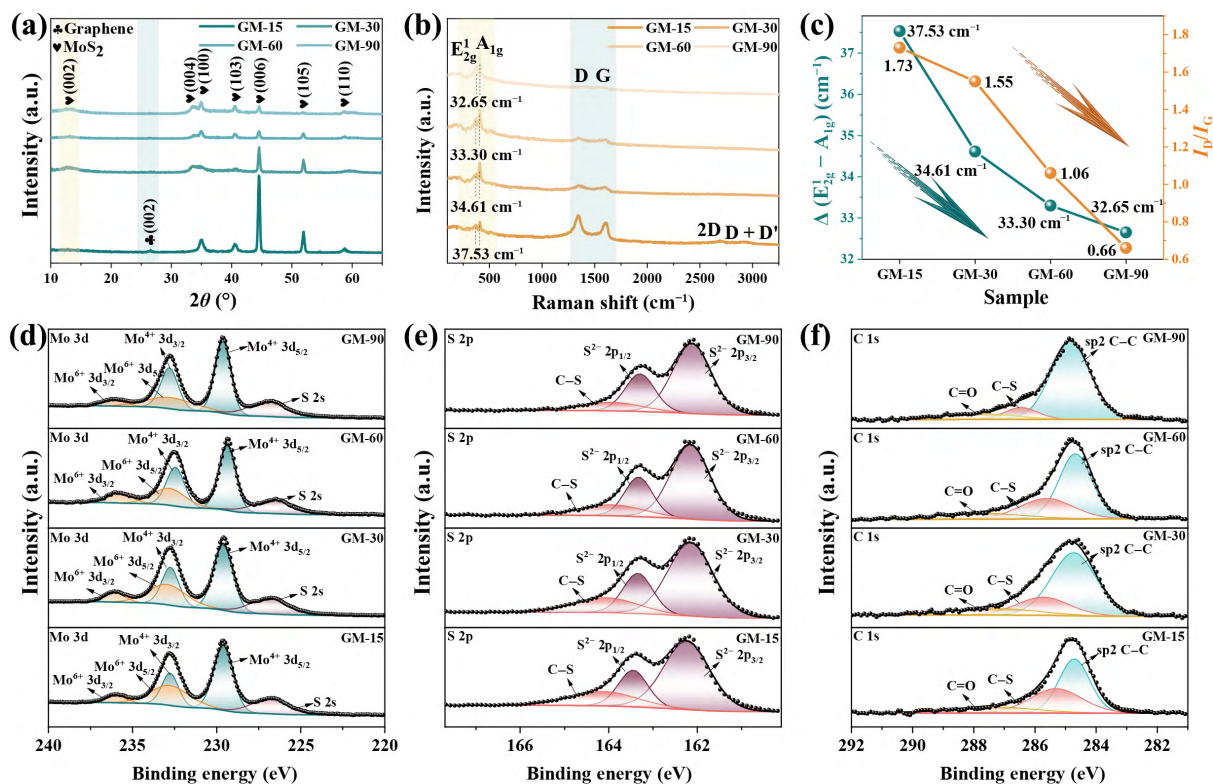


Fig. 3 Chemical structures of graphene/MoS₂ coatings with varying degrees of heterogeneity. (a) XRD patterns highlighting diffraction peaks of graphene and MoS₂. (b) Raman scattering spectra showing D and G bands of graphene and E_{2g}^1 and A_{1g} modes of MoS₂. (c) Quantitative analysis of defect ratio (I_D/I_G) and peak separation between E_{2g}^1 and A_{1g} modes. Deconvoluted XPS core-level spectra of (d) Mo 3d, (e) S 2p, and (f) C 1s.

decreasing heterogeneity, suggesting enhanced crystallinity and reduced oxidation (Table S2 in the ESM). As shown in Fig. 3(e), the S 2p peak displays three spin-orbit doublets at 162.2 eV for S²⁻ 3d_{3/2}, 163.5 eV for S²⁻ 3d_{1/2}, and 164.2 eV for the C-S bond [29], confirming direct interfacial interactions between MoS₂ and graphene edge dangling sites. The C 1s spectra in Fig. 3(f) shows peaks for sp² C-C at 284.7 eV, C-S at 285.6 eV, and C=O at 287.5 eV, while the O 1s spectrum shows peaks at 530.8 eV for Mo-O bands and 532.8 eV for C=O bonds [79, 80]. The C-S, Mo-O, and C=O bonds originate from dangling bonds at edge defects in the heterogeneous structure. Reduced structural heterogeneity decreases edge-terminated C and Mo atoms bonded to S and O atoms, consistent with previous characterization results. Highly heterogeneous structures create incommensurate interfaces that facilitate shear sliding, while edge defects enhance interfacial bonding through chemical interactions. This dual effect of interfacial heterogeneity significantly influences the mechanical and tribological properties.

3.3 Tribological properties and wear mechanisms of graphene/MoS₂ heterostructure coatings

Pure graphene and MoS₂ coatings demonstrate limitations under high loads, as shown in Fig. S6 in the ESM. Graphene with an ultrathin structure renders it susceptible to penetration, resulting in an elevated average COF of 0.132 under 1 N and 0.311 under 5 N, while MoS₂ is vulnerable to ambient humidity and oxidation, leading to tribological instability and eventual wear failure with a COF of 0.169 under 1 N and 0.236 under 5 N. Such a limited friction service lifetime of individual graphene under atmospheric conditions has been observed in previous studies [81–84]. Moreover, similar humidity-dependent friction failure has been previously observed in pure MoS₂ coatings [29, 85–87]. These inherent constraints underscore the necessity for engineered heterostructures with complementary properties. The tribological response of graphene/MoS₂ heterostructure coatings is investigated to understand the correlation between the structural heterogeneity and applied load during the shear sliding process (Fig. 4). As shown in Fig. 4(a), samples with reduced structural heterogeneity (GM-30, GM-60, and GM-90) deliver superior friction performance with average COFs below 0.2 under a 1 N load. Compared with pure MoS₂, the enhanced performance of graphene/MoS₂ is attributed to the graphene underlayer acting as an environmental barrier. This is supported by weaker Fourier transform infrared spectroscopy (FTIR) bands at 3,210, 1,656, and 806 cm⁻¹ assigned to O-H, C=O, and Mo=O related vibrations, respectively, indicating reduced adsorption of moisture- and oxygen-related species under ambient conditions (Fig. S7 in the ESM) [88]. Notably, the highly heterogeneous GM-15 sample with lower roughness and higher edge density initially exhibits a similarly low average COF but a sudden increase under 1 N, rising to a higher average COF of 0.280 with pronounced fluctuations. This behavior is attributed to the initial thin thickness, highest edge density, and discontinuous MoS₂ domains on the surface, leading to exposed edge sites and discrete particles, as observed in the SEM surface and transmission electron microscopy (TEM) cross-sectional morphology. These features are prone to intensifying abrasive wear and causing unstable friction and the eventual shift into a failure state [89], which is later evidenced by the wear track analysis. A remarkable load-dependent rather than thickness-dependent behavior emerges at 5 N, where all samples exhibit systematic friction reduction, namely, 0.092, 0.112, 0.104, and 0.128 for GM-15, GM-30, GM-60, and GM-90, respectively, outperforming other reported 2D heterostructure coatings under similar friction conditions [14, 15, 90]. The enhanced friction

properties under higher loads may result from load-induced structural changes at the interfaces [24, 91], which were later confirmed by TEM analysis of the frictional interfaces. This effect is expected to be particularly pronounced for the highly heterogeneous GM-15 sample, where abundant edge sites and discontinuous domains provide mechanochemically active regions that can be passivated into a more continuous tribofilm under higher loads. The three-dimensional profiles and line scans of the graphene/MoS₂ heterostructure coatings after sliding under various loads are shown in Figs. 4(d)–4(k). Samples display a distinct morphological evolution from V-shaped profiles under a 1 N load to U-shaped profiles under a 5 N load, demonstrating that an increased normal load broadens wear tracks while diminishing their depth. Under a 1 N load, wear track widths range from 197.4 to 289.2 μm with depths of 2.8–4.2 μm, while at 5 N, the widths increase to 399.1–447.0 μm and depths decrease to 2.1–3.0 μm (Figs. 4(d)–4(k)). Notably, the GM-15 coating with the highest heterogeneity exhibits the most pronounced Vtribofilm under higher edge sites and discontinuous deloads. The highly heterogeneous structure demonstrates a reversal in wear depth under increased load, suggesting a transition to a more stable surface through possible structural reorganization. As shown in Fig. 4(b), the wear rates of the GM-15, GM-30, GM-60, and GM-90 samples are 0.228×10⁻⁵, 0.471×10⁻⁵, 0.590×10⁻⁵, and 1.167×10⁻⁵ mm³/(N·m), respectively, under a 5 N load. These values are significantly lower than those observed under a 1 N shear load, followed by 2.864×10⁻⁵, 1.338×10⁻⁵, 1.820×10⁻⁵, and 2.039×10⁻⁵ mm³/(N·m), respectively. This relatively high wear rate indicates that the coating is not highly wear-resistant, which may be attributed to its limited thickness and incomplete interfacial strength, leading to easy material removal during sliding. Moreover, the load-dependent inversion is particularly remarkable for GM-15, which transitions from exhibiting the poorest wear resistance at 1 N to the best performance at 5 N. This shift can be attributed to its inherently lower surface roughness, higher contact area, and load-induced surface reconstruction. Furthermore, the wear tracks exhibit increased width but reduced depth with improved smoothness (Fig. S8 in the ESM), demonstrating that high contact pressure facilitates passivation layer formation in high structural heterogeneity to minimize asperity contact and friction [92]. Wear track element analysis observed in Fig. 4(c) shows minimal Mo and S with substoichiometric Mo/S ratios and significant oxygen enrichment, indicating the occurrence of MoS₂ decomposition and oxidative wear. From GM-15 to GM-90, increasing oxygen and decreasing carbon content highlight a trend of intensified oxidative wear under high loads. Notably, GM-15 exhibits less oxidation wear under high loads, demonstrating better structure stability.

The wear tracks (Fig. 5) reveal distinct load-dependent morphological evolution characterized by various wear features, including abrasive particles, cracks, furrows, wear debris, and delamination. At the 1 N load, abrasive wear dominates the tribological interface, manifesting as residual abrasive particles and wear debris (Figs. 5(a)–5(d)). These abrasive particles contribute to a higher friction coefficient and wear rate [93]. This wear mechanism is particularly evident in the highly heterogeneous GM-15 sample with a thin initial thickness and discontinuous surface, where discrete MoS₂ domains and high edge densities create mechanically vulnerable regions susceptible to debris generation, particle displacement, and surface breakdown. A mechanistic transition occurs under elevated load to compensate for the initial thinness and trigger edge self-passivation reconstruction. Specifically, the initially discrete MoS₂ domains and high edge densities become less distinct, accompanied by a

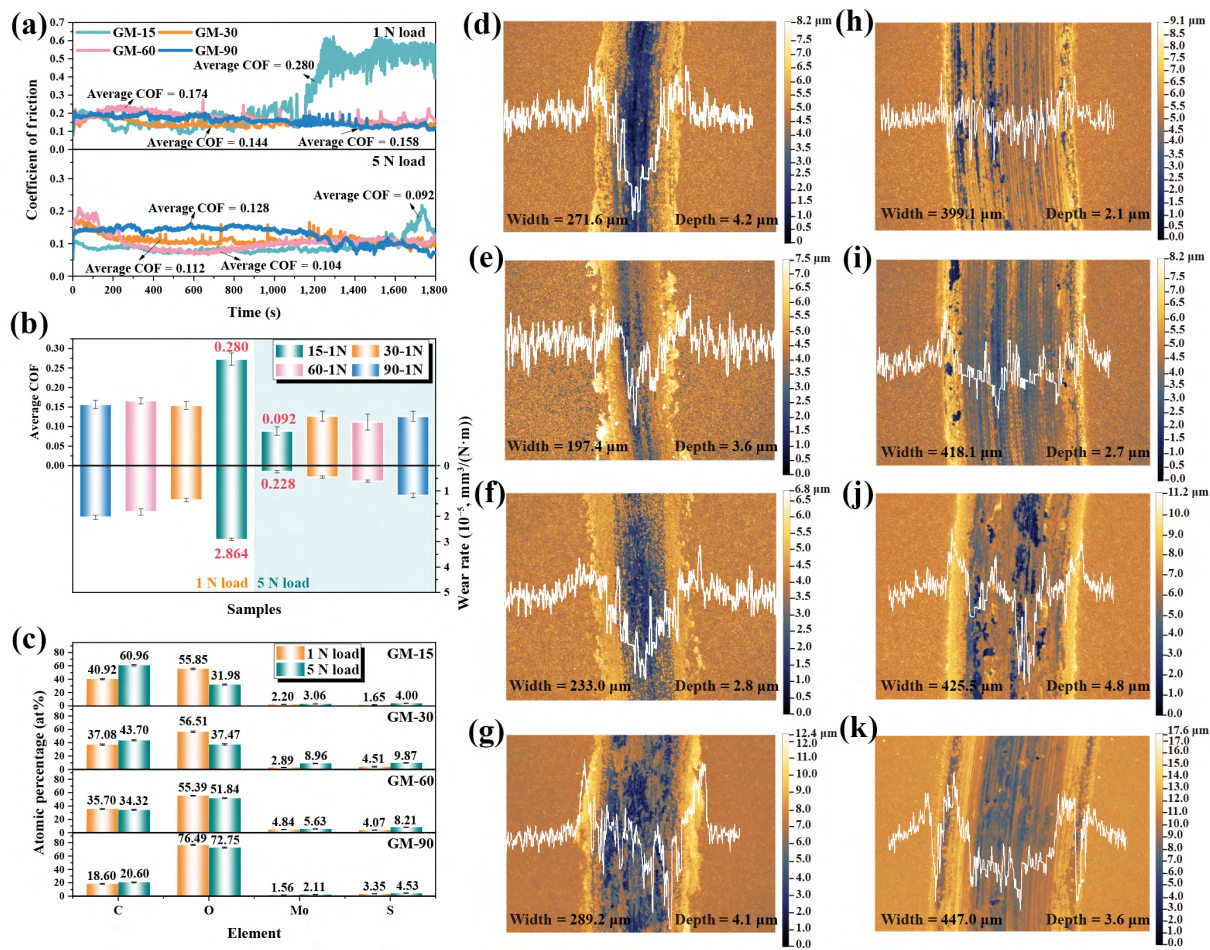


Fig. 4 Tribological properties of graphene/MoS₂ coatings with varying degrees of heterogeneity. (a) COF vs. sliding time for samples under 1 and 5 N loads. (b) Comparison of average COF and wear rate under different loads. (c) EDS chemical composition analysis of wear tracks under different loads. 3D morphologies and corresponding line-scan profiles (d–g) under 1 N load and (h–k) under 5 N load for GM-15, GM-30, GM-60, and GM-90 samples, highlighting wear width and depth.

smoother surface morphology, as shown in Fig. 5(i). This high-load-induced transformation facilitates edge self-passivation, effectively converting the highly heterogeneous structure with discrete MoS₂ domains and high edge densities into a uniform and smooth protective surface. This load-dependent structural evolution directly translates to the remarkable tribological enhancement of GM-15, which achieves a 3-fold reduction in friction and a 12-fold decrease in the wear rate under the 5 N load compared to 1 N load conditions. However, mildly heterogeneous structures with continuous domains and low edge densities are prone to cracking and delamination failure under increased contact pressure (Figs. 5(j)–5(l)). This underscores the importance of high structural heterogeneity in enhancing resistance to deformation by effectively introducing diverse stress pathways and preventing localized failure [94]. The dynamic interplay between structural heterogeneity and applied load thus emerges as a critical factor to optimize the tribological behavior of graphene/MoS₂ heterostructures, where high loads transform initial heterogeneity from a structural disadvantage into a tribological advantage through mechanically activated self-passivation processes. The Raman spectra show prominent E_{2g}¹ and A_{1g} modes of the MoS₂ crystal in addition to the D and G bands of graphene in both the center and edge of the wear track, indicating the formation of composite tribofilms at the friction interface (Figs. 5(e)–5(h) and 5(m)–5(p)). Postwear analysis shows larger $\Delta(E_{2g}^1 - A_{1g})$ and I_D/I_G ratios, as well as smaller 2D and D+D' peaks compared to pristine states (Table S3 in the ESM), suggesting a gradual loss of

crystallinity and higher structural disorder during shear sliding. Under a 1 N load, the broad peak at 925–940 cm⁻¹ corresponding to MoO_{3-x} indicates significant oxidation wear (Figs. 5(e)–5(h)), consistent with EDS. Under the 5 N load, the Raman spectra indicate load-induced structural reorganization at the sliding interface, evidenced by enhanced D and G peak intensities and diminished E_{2g}¹ and A_{1g} peaks (Figs. 5(m)–5(p)). Moreover, the 2D and D+D' peaks from both the center and edge of the wear tracks suggest the formation of ordered tribofilms with larger graphene concentrations, correlating with improved friction performance and reduced wear rates. Notably, the highly heterogeneous GM-15 sample exhibits distinct structural evolution under varying loads (Table S3 in the ESM). At 1 N, the absence of a 2D peak, a high I_D/I_G ratio, and severe MoS₂ lattice distortion ($\Delta(E_{2g}^1 - A_{1g}) = 50.03$ cm⁻¹) indicate a disordered graphene/MoS₂ structure and unstable frictional performance [95]. At 5 N, the emergence of the 2D peak across the wear track, a slight increase in I_D/I_G , and reduced MoS₂ distortion ($\Delta = 32.78$ cm⁻¹, 27.6% lower than at 1 N) suggest shear load-induced structural cooperative rearrangement and reduced interfacial interactions. The new appearance of D + D' peaks further confirms structural passivation, leading to improved friction performance [96]. The comparative analysis of wear track evolution reveals distinct tribo-chemical pathways. Under a 1 N load, the migration of MoS₂ and graphene signatures toward track edges suggests nonuniform tribofilm development impeded by debris accumulation. In contrast, the 5 N load promotes an

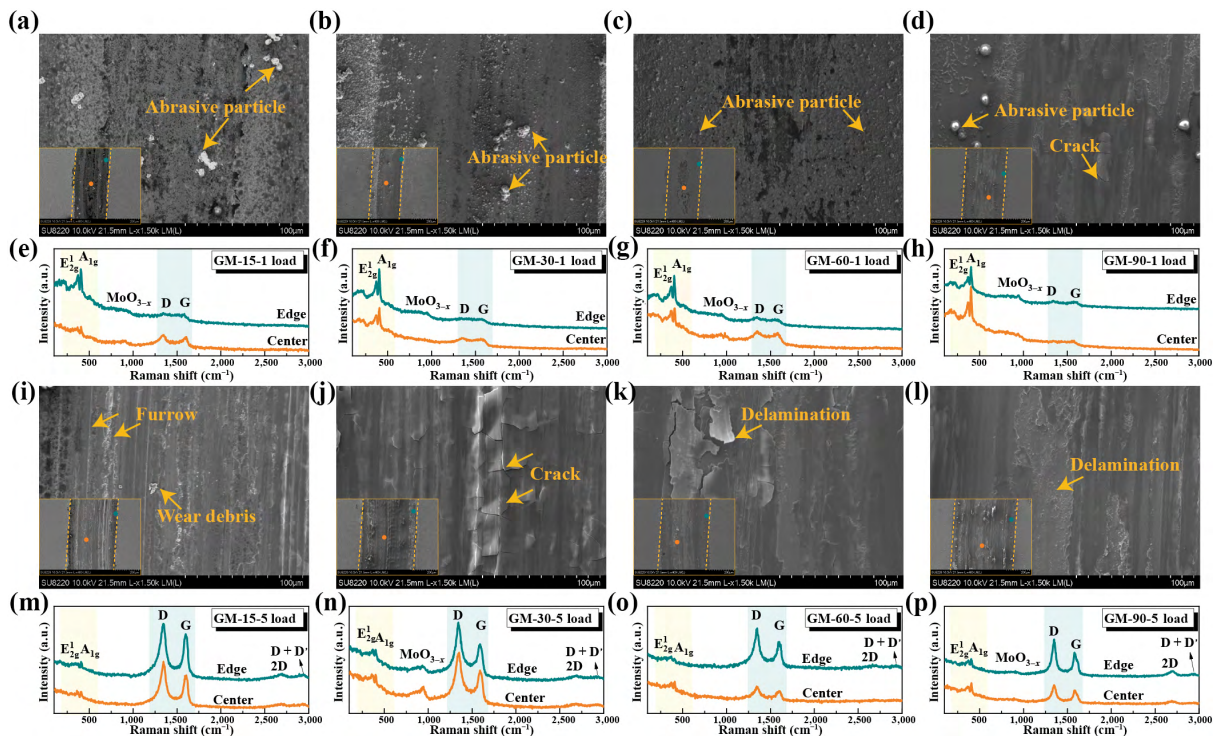


Fig. 5 Wear track characterization of graphene/MoS₂ coatings with varying degrees of heterogeneity. (a–d) SEM surface morphology of wear tracks under a 1 N load for GM-15, GM-30, GM-60, and GM-90 samples. Insets show global view of wear tracks with marked Raman test regions. (e–h) Raman spectra (edge and center regions in wear track) under a 1 N load for GM-15, GM-30, GM-60, and GM-90 samples. (i–l) SEM surface morphology of wear tracks under a 5 N load for GM-15, GM-30, GM-60, and GM-90 samples. Insets show global view of wear tracks with marked Raman test regions. (m–p) Raman spectra (edge and center regions in wear track) under 5 N loads for GM-15, GM-30, GM-60, and GM-90 samples.

ordered structure across the entire contact region to facilitate the formation of continuous and passivated tribofilms.

To analyze the tribo-chemical interaction of the highly heterogeneous graphene/MoS₂ coatings under different applied loads, the friction interfaces are characterized by XPS. XPS reveals the dynamic evolution of chemical states and bonding configurations during shear sliding under varying applied loads (Figs. 6(a)–6(d)). The high-resolution core level spectra of Mo 3d, S 2p, C 1s, and O 1s demonstrate load-dependent interfacial chemical state transformations. Compared to pristine surfaces, the variations in chemical states and relative contents indicate tribo-chemical reactions during shear sliding, which lead to the formation of chemically adsorbed tribo-films composed predominantly of Mo⁴⁺, S²⁻, and sp² C–C bonds. Under a 1 N load, significant oxidation occurs, as indicated by enhanced Mo–O and C=O components, particularly in highly heterogeneous structures. This is accompanied by increased C–S bond formation and oxidized species at reactive MoS₂ sites, suggesting intensive chemical interactions at layer interfaces (Figs. S9(a)–S9(d) in the ESM). In contrast, a 5 N shear load suppresses the chemical interactions through improved edge passivation and oxidation resistance to facilitate the formation of ordered sliding interfaces (Figs. S9(e)–S9(h) in the ESM). Detailed XPS analysis of highly heterogeneous GM-15 samples reveals significant chemical passivation transitions from pristine to worn states after shear sliding under different loads (Figs. 6(a)–6(d)). The Mo 3d spectra deconvolution indicates that the pristine surface comprises 53.51% Mo⁴⁺ and 28.52% Mo⁶⁺, with the remaining contributions from S 2s peaks. As shown in Fig. 6(a), the Mo⁴⁺ concentration decreases to 52.97%, while that of Mo⁶⁺ increases to 33.68%, reflecting enhanced oxidation and structural damage under a 1 N load. Conversely, the 5 N load reverses this trend, showing Mo⁴⁺

increasing to 58.72% and Mo⁶⁺ decreasing to 27.28%, demonstrating improved oxidation resistance through passivated tribofilm protection. The O 1s spectra (Fig. 6(d)) corroborate this behavior, showing reduced Mo–O and C=O components under the 5 N load. Similarly, the S 2p spectra show maintained S²⁻ bonds with decreasing C–S formation under the 5 N load, suggesting suppressed chemical interactions between MoS₂ and graphene layers (Fig. 6(b)). In addition, the C 1s spectra reveal fewer C–S and more sp² C–C bonds than the pristine ones and 1 N load conditions (Fig. 6(c)). The chemical evolution reveals that in graphene/MoS₂ coatings with pronounced structural heterogeneity, high loads promote interfacial self-passivation, leading to the formation of stable tribofilms that suppress chemical interactions and ensure structural stability. This phenomenon results from the synergistic interaction between shear load and environmental chemical reactions, where shear-induced shallow wear drives interfacial self-organization and facilitates the formation of a smooth and chemically inert protective layer that prevents deeper interfacial chemical interactions [97, 98]. Under high loads, C–S bonds rupture first, exposing reactive Mo and C dangling bonds. These sites then react with dissociated O₂ from the environment to form stable Mo–O and C=O bonds, reducing C–S interactions and overall chemical reactivity. In contrast, low loads fail to break sufficient C–S bonds, leaving reactive edge sites exposed. Instead of environmental passivation, these sites undergo further chemical reactions, increasing C–S bonds and defect densities, as corroborated by Raman and XPS spectra. Analysis of the Raman spectra of wear scars formed on Al₂O₃ balls further reveals critical load-dependent tribological mechanisms (Table S4 in the ESM). Under a 1 N load, all samples show weak D and G graphene peaks with MoS₂ peaks primarily at wear track edges rather than centers

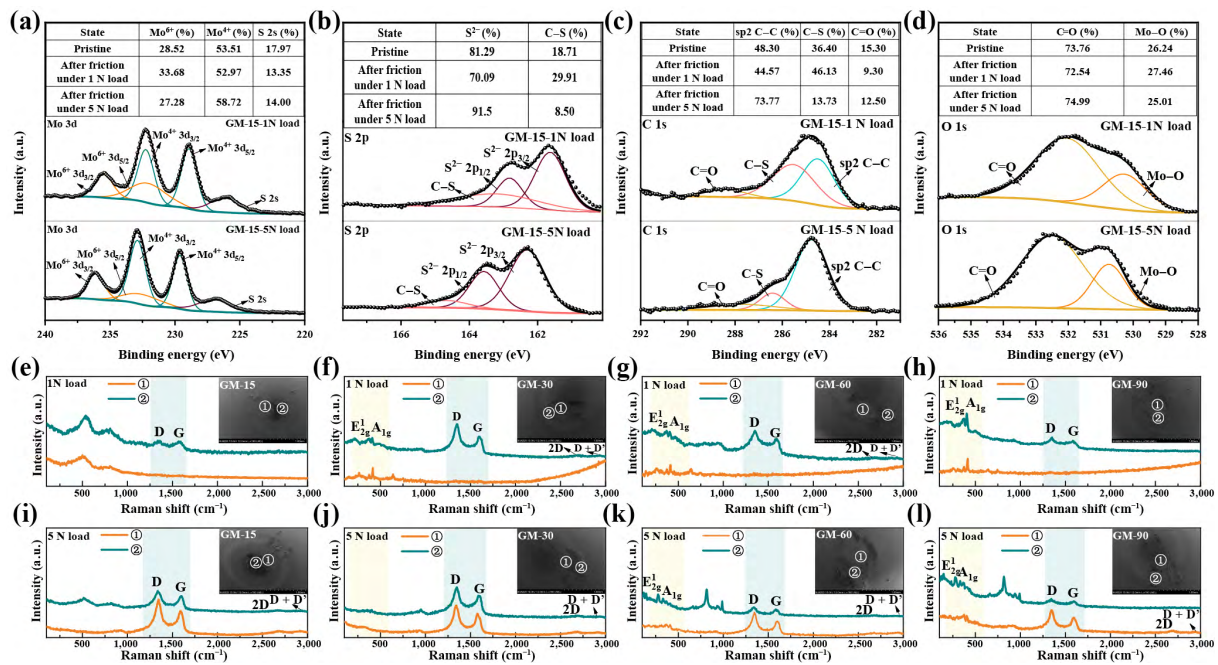


Fig. 6 Structural and chemical characterization of graphene/MoS₂ coatings. Deconvoluted XPS core-level spectra of (a) Mo 3d, (b) S 2p, (c) C 1s, and (d) O 1s orbitals of GM-15 sample, comparing pristine state and after friction tests of wear tracks under 1 and 5 N loads. Raman spectra showing D, G, E_{2g}, and A_{1g} bands collected from edge and center regions of wear scar formed on Al₂O₃ balls after sliding under a 1 N load for (e) GM-15, (f) GM-30, (g) GM-60, and (h) GM-90, respectively. Raman spectra showing D, G, E_{2g}, and A_{1g} bands collected from edge and center regions of wear scar formed on Al₂O₃ balls under 5 N load for (i) GM-15, (j) GM-30, (k) GM-60, and (l) GM-90, respectively. Corresponding SEM morphologies of wear scars formed on Al₂O₃ balls are shown as insets.

(Figs. 6(e)–6(h)). This indicates lubricant migration toward edges under low loads, creating nonuniform tribofilms. Under a 5 N load, we observe significantly enhanced and more uniform D and G peaks across all wear regions, with additional 2D and D+D' peaks appearing (Figs. 6(i)–6(l)). The applied load promotes the uniform distribution of tribofilms, which prevents direct contact at the sliding interface and ensures effective lubrication [99]. This confirms that heterogeneous structures possess superior load-activated self-passivation capabilities at friction interfaces, explaining why GM-15 transforms from having the poorest wear resistance at 1 N to the best at 5 N.

The effects of shear load-induced interfacial interactions on the tribological behavior of graphene/MoS₂ heterostructure coatings are investigated by microstructural characterization of the wear tracks and dynamic scratch tests (Fig. 7). HR-TEM and FFT analyses of highly heterogeneous GM-15 wear tracks reveal distinct crystal structural changes under varying applied loads (Figs. 7(a) and 7(b)). Under a 1 N load, the tribofilm beneath the Pt layer shows a disordered subsurface without clear lattice fringes. The corresponding FFT pattern exhibits diffuse rings, confirming amorphization and the loss of long-range order at the near-surface [100]. Such disorder, driven by intense interfacial interactions and oxidative processes during shear sliding, as revealed by XPS and Raman scattering, correlates with reduced tribological performance. In contrast, a high load promotes the formation of well-ordered layered structures with distinct lattice fringes extending to the graphene interface (Fig. 7(b)), as evidenced by distinct diffraction spots corresponding to crystalline graphene(002) and MoS₂(006) phases. The observed Moiré pattern with a 46° twist angle in the FFT pattern confirms the development of structurally robust incommensurate sliding interfaces, highlighting the critical role of load-induced structural reorganization in reducing the interlayer shear strength and enhancing the tribological performance [101]. Tribologically formed MoS₂ exhibits lower crystallinity observable in the FFT

than in the pristine state due to the high shear stress during sliding disrupting the long-range order of the MoS₂ layers, leading to amorphization or loss of periodicity [102]. A high shear load drives the transformation from initial interfacial disorder to ordered structures, as evidenced by the distinct diffraction patterns and Moiré interfaces. This high shear load-induced ordered interface, combined with incommensurate interlayer configurations, ultimately enhanced lubrication properties.

Progressive-load scratch tests (0.3–30 N) reveal distinct interfacial interactions in graphene/MoS₂ heterostructure coatings with varying degrees of heterogeneity. Analysis of the scratch track morphologies (Figs. 7(c)–7(f)) and variation curves (Fig. S10 in the ESM) shows that the highly heterogeneous GM-15 sample exhibits the highest critical failure load (L_c) of 23.3 N, compared to those of GM-30, GM-60, and GM-90 of 21.4, 19.7, and 17.6 N, respectively [103]. This variation suggests that the interfacial adhesion strength is influenced by the interlayer interaction modes in the graphene/MoS₂ heterostructure coatings [104]. The superior interfacial adhesion strength of GM-15 arises from two key mechanisms associated with its highly heterogeneous structure. First, Raman and XPS analyses reveal that the dispersed MoS₂ particles exhibit abundant edge dangling bonds, which act as anchoring sites by forming strong interactions at the graphene/MoS₂ interface. This edge-pinning effect enhances the interfacial stability and resistance to failure. Second, HR-TEM highlights the presence of robust incommensurate sliding interfaces unique to the heterogeneous structure. These interfaces exhibit structural flexibility, allowing them to adapt to interfacial stress and maintain the synergistic functionality of graphene and MoS₂. The exceptional interfacial adhesion strength of GM-15 directly contributes to its superior lubricating performance under high shear loads. Specifically, the shear load-induced structural adaptations include edge self-passivation, well-ordered layered structures, and incommensurate interfaces.

The lubrication performance of highly heterogeneous GM-15

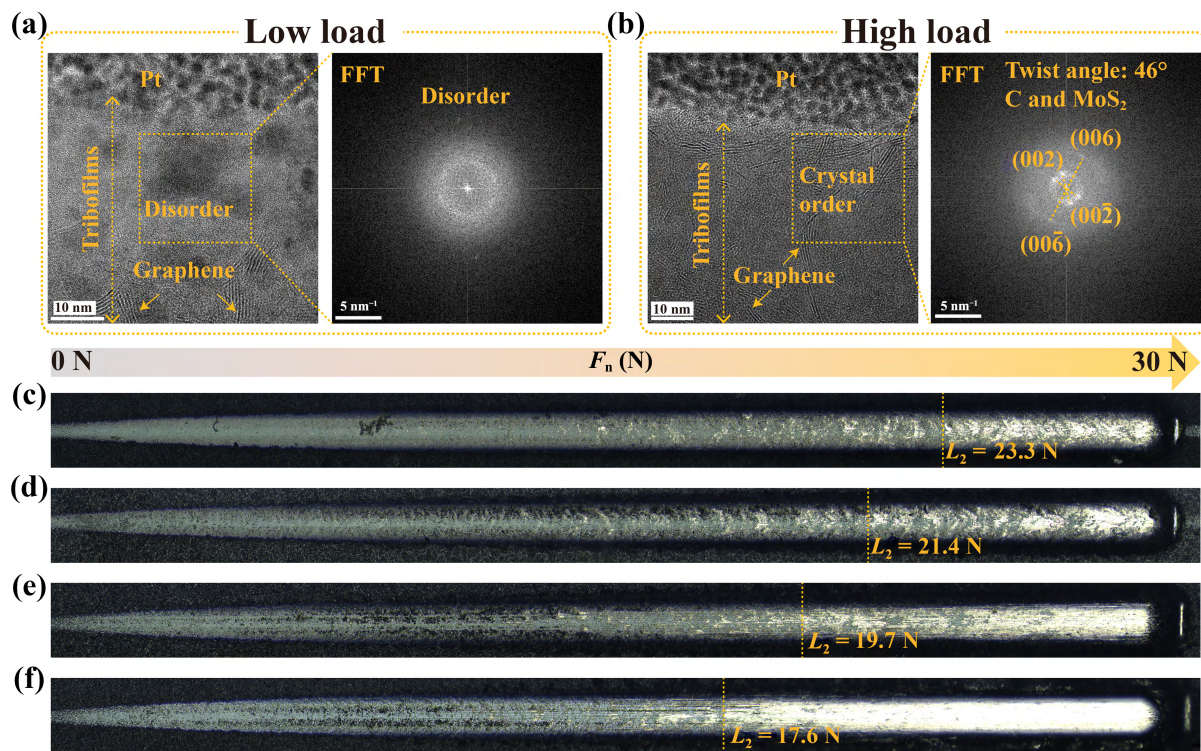


Fig. 7 Load-induced frictional interface and adhesion strength evolution of graphene/MoS₂ heterostructure coatings. Cross-sectional HR-TEM images (left) and corresponding FFT patterns (right) of tribofilms formed on GM-15 after sliding tests under (a) 1 and (b) 5 N loads, with dashed boxes marking the region of disordered and crystalline structures. Progressive-load scratch profiles (0.3–30 N, 3 mm track length) showing coating failure behavior, where L_2 are indicated in yellow for (c) GM-15, (d) GM-30, (e) GM-60, and (f) GM-90 samples.

arises from its structural diversity and load-driven edge self-passivation, a mechanism distinct from the idealized superlubricity observed in nanoscale systems (e.g., atomically flat graphene/MoS₂ heterostructures under ultralow load conditions) [19, 31] and macroscale systems under controlled atmosphere [25, 105]. In contrast, low-heterogeneity samples lack the structural adaptability needed for effective lubrication. This limitation often results in direct interfacial contact, poor stress distribution, and higher friction. For GM-15, its initial friction behavior benefits from edge dangling bonds, which strengthen interfacial interactions but also introduce some disordered interfaces at low loads. Unlike nanoscale systems where superlubricity is typically instantaneous and relies on pristine and perfect incommensurate interfaces with weak interfacial interactions [106], highly heterogeneous GM-15 enables dynamic adaptation under macroscale conditions. As the load increases, these active edges undergo self-passivation, transitioning into stable, low-friction interfaces. Simultaneously, shear forces drive the reorganization of graphene and MoS₂ layers, forming well-ordered tribofilms with parallel alignment. These self-passivating layers effectively prevent direct contact between surfaces and reduce friction. The formation of incommensurate sliding interfaces, characterized by Moiré patterns with a 46° twist angle, allows GM-15 to distribute stress efficiently and maintain low friction. This structural adaptability, coupled with preserved incommensurate interfaces, ensures robust tribological properties even in highly heterogeneous layered structures, offering a practical strategy for enhanced macroscale lubrication.

3.4 Theoretical friction properties and mechanisms of graphene/MoS₂ heterostructure coatings

To investigate the effects of structural heterogeneity on the tribological properties of graphene/MoS₂ heterostructure coatings,

MD simulations are conducted to model the interfacial physical interactions between graphene and small-sized MoS₂ vs. large-sized MoS₂ structures (Fig. 8). Figures 8(a) and 8(c) depict shear sliding along the x-axis direction of small-sized and large-sized MoS₂ flakes on a large-area defective graphene basal plane, representing a highly heterogeneous structure with discrete flakes and a lowly heterogeneous structure with continuous flakes, respectively. All systems contain an equal number of vacancy defects and edge dangling bonds on the graphene surface, with the initial interlayer spacing between graphene and MoS₂ layers set to 4.7 Å. The sliding behavior at the interface is monitored by analyzing the friction interface snapshots and evaluating both the lateral forces and COF. As the sliding distances increase from 0 to 80 Å (corresponding to a simulation time from 0 to 800 ps), significant interfacial interactions are observed from both graphene/MoS₂ interfaces, as shown by reduced interlayer spacings (Figs. 8(b) and 8(d)). Notably, the graphene/small-sized MoS₂ interface exhibits stronger interlayer interactions than the graphene/large-sized MoS₂ interface. This larger interaction strength is attributed to the localized stress concentrations in the smaller contact area, which drive the layers into closer proximity [107]. Due to the incommensurate contact induced by structural heterogeneity, both systems demonstrate superior frictional performance (Figs. 8(e) and 8(f)). This superior performance arises from the weak interlayer vdW interactions characteristic of heterostructures, which reduce the energy barrier for sliding [108]. The lateral force, defined as the resistance to sliding between the graphene and MoS₂ layers, is higher for the graphene/small-sized MoS₂ structure (average of 2.3224 nN) than the graphene/large-sized MoS₂ structure (average of 1.5710 nN), as shown in Fig. 8(e). Correspondingly, the calculated COF follows the same trend, with average values of 0.0023 and 0.0011 for the graphene/small-sized MoS₂ and graphene/large-sized MoS₂ structures, respectively.

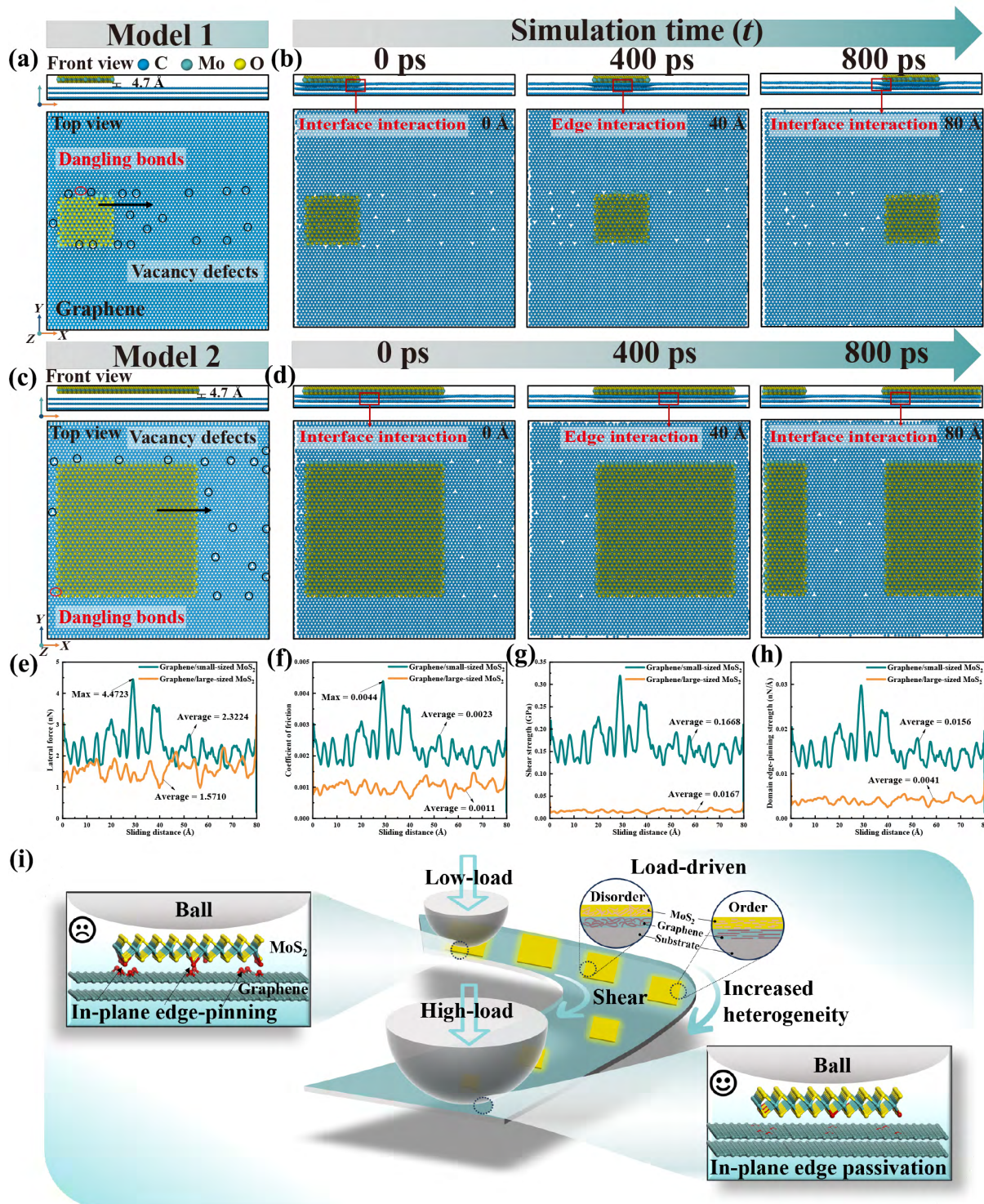


Fig. 8 MD simulation analysis of in-plane edge effects on tribological properties of graphene/MoS₂ heterostructures. (a) Initial model of small-sized MoS₂ on graphene surface (front and top views), showing dangling bonds and vacancy defects. (b) Evolution snapshots of small-sized MoS₂ sliding on graphene from 0 to 800 ps (front and top views), highlighting strong edge-pinning effects and interface interactions. (c) Initial model of large-sized MoS₂ on graphene surface (front and top views), showing same dangling bonds and vacancy defects. (d) Evolution snapshots of large-sized MoS₂ sliding on graphene from 0 to 800 ps (front and top views), showing weak edge-pinning effects. Comparison of (e) lateral force curves, (f) COF curves, (g) shear strength curves, and (h) domain edge-pinning strength curves for graphene/small-sized MoS₂ and graphene/large-sized MoS₂ models. (i) Schematic of shear load-induced tribological mechanism, where shear load facilitates in-plane edge passivation, driving structural disorder-to-order transition in graphene/MoS₂ heterostructure coatings.

(Fig. 8(f)). The similar performance of the graphene/complete-sized MoS₂ structure and graphene/large-sized MoS₂ structure confirms the validity of using finite small- and large-sized flakes for comparison (Fig. S11 in the ESM). Furthermore, energy-normalized simulations by adjusting the compression energy

proportionally further confirm that the graphene/small-sized MoS₂ structure consistently exhibits higher COF than the graphene/large-sized MoS₂ structure (Fig. S12 in the ESM). These results indicate that the graphene/small-sized MoS₂ structure has reduced lubricating properties due to larger sliding resistance,

consistent with macroscale experimental observations under low loads. Furthermore, when MoS₂ slides near the central region of graphene (approximately 30–40 Å), the lateral force and coefficient of friction for the graphene/small-sized MoS₂ structures increase to maximum values of 4.4723 nN and 0.0044, respectively. This increase is attributed to additional in-plane edge contact points, which induce edge-pinning effects in the central area, thereby enhancing frictional energy dissipation and local stress concentration [32]. To validate the performance robustness, sensitivity analyses were systematically conducted by varying the defect density (0–33 defects) and interlayer spacings (2.7–5.7 Å). The graphene/small-sized MoS₂ models consistently exhibited higher COF than the graphene/large-sized MoS₂ models across all tested parameters (Figs. S13 and S14 in the ESM), confirming the size-dependent friction trend in graphene/MoS₂ heterostructures. To elucidate the underlying mechanisms, the shear strength and domain edge-pinning strength are analyzed. A higher shear strength indicates enhanced interfacial interaction, while a larger domain edge-pinning strength signifies stronger edge-pinning effects. As shown in Figs. 8(g) and 8(h), reducing the size of MoS₂ on the defective graphene surface increases the shear strength from 0.0167 to 0.1668 GPa and the domain edge-pinning strength from 0.0041 to 0.0156 nN/Å. This suggests that the edge atoms of small-sized MoS₂ are more strongly pinned on the defective graphene surface, thus inhibiting interlayer shear sliding. Furthermore, weaker adhesion forces calculated for graphene/small-sized MoS₂ (Fig. S15 in the ESM) facilitate interlayer delamination, which exposes additional edge sites and is likely responsible for the enhanced edge-pinning strength. This is consistent with the experimental results, where the highly heterogeneous GM-15 is prone to delamination and exhibits an unstable COF along with severe abrasive wear. Raman scattering (indicating enhanced edge defect sites) and XPS (showing strengthened C–S bond interactions), in combination with dynamic scratch tests, corroborate the enhanced edge-pinning interaction of the graphene/MoS₂ coatings with highly heterogeneous configurations. Similar edge-dominated friction mechanisms and the improvement in frictional performance upon edge passivation have been explicitly demonstrated by Yang et al. [35] through MD simulation of oxygen-passivated multiflake MoS₂/graphene models. The friction force increases proportionally with the degree of structural heterogeneity, primarily due to the increased edge sites and their associated edge-pinning effects. Beyond the widely acknowledged low-friction mechanism of incommensurate contact, molecular dynamics simulations validate the experimental observations that the edge interactions arising from structural heterogeneity adversely affect the overall tribological performance of graphene/MoS₂ coatings. It should be noted that the MD simulations capture only the atomistic sliding response at the very early stage, corresponding to an idealized graphene/MoS₂ interface composed of few flakes, nanometer contact, and subnanosecond duration. Under these conditions, MD primarily explains the initial friction hierarchy among heterogeneous structures, which is governed by enhanced edge-pinning and interfacial shear strength. In contrast, the experimentally observed friction reversal at higher loads arises from a macroscale collective evolution, where repeated shear loading across many asperities facilitates tribofilm formation, structural reorientation, compaction, and load-driven passivation of reactive edge sites.

A systematic investigation reveals the synergistic effect between the structural heterogeneity and load-driven edge self-passivation behavior in graphene/MoS₂ coatings. The reduced MoS₂ domain

dimensions on the graphene surface increase the structural heterogeneity to produce more edge sites with distinctive shear load-dependent responses. As illustrated in Fig. 8(i), the highly heterogeneous system undergoes a mechanistic transition from edge-pinning to edge passivation dominated friction during shear sliding under varying load conditions. Under low loads, the interfacial friction behavior is dominated by in-plane edge-pinning effects, where unsaturated dangling bonds at MoS₂ edges preferentially form enhanced interactions with the underlying defective graphene surface, consistent with MD simulation. These edge-pinning effects induce enhanced interfacial interactions and elevated energy barriers for relative shear sliding, thereby leading to increased friction at structurally disordered sliding interfaces. Conversely, macroscale lubrication in highly heterogeneous graphene/MoS₂ coatings is achieved through a collective, high shear load-driven mechanism. The applied shear load induces edge self-passivation, weakening their contribution to interfacial resistance. At the same time, it facilitates the formation of well-ordered tribofilms while maintaining incommensurate interfacial contacts. This process ensures structural reorganization and stable lubrication performance under high shear load conditions.

4 Conclusions

Graphene/MoS₂ coatings with tailored structural heterogeneity achieve superior lubrication performance through the synergistic combination of structural heterogeneity and load-driven edge self-passivation. Experimental and molecular dynamics simulation results collectively demonstrate that increased structural heterogeneity enhances edge-driven interfacial interactions and raises the initial friction. The subsequent friction reduction in macroscale tests is governed by collective reorganization, resulting in a pronounced load-responsive behavior at multiple contact interfaces. Under low-load conditions, insufficient passivation of edge defects and dangling bonds leads to pronounced interfacial interactions, thereby elevating the shear strength and edge-pinning strength. Remarkably, upon increasing applied shear loads, an effective load-driven edge self-passivation process is triggered, converting detrimental edge-pinning sites into robust, passivated interfaces. The synergistic interplay between load-driven edge self-passivation and structural heterogeneity facilitates the formation of ordered tribofilms and stable incommensurate interfacial structures, enabling highly heterogeneous graphene/MoS₂ coatings to deliver remarkable friction and wear reductions (3-fold and 12-fold, respectively) under high-load conditions compared to low-load conditions. These findings reveal a powerful strategy for harnessing structural heterogeneity and load-induced interface passivation to turn structural disorder into a lubrication advantage, offering new pathways for designing robust lubricant coatings.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (No. 52375182), Natural Science Foundation of Guangdong Province (No. 2023A1515012308), Guangdong Province Science and Technology Plan Projects (No. 2023B1212060045 and No. 2023B121200008), Basic and Applied Basic Research Fund of Guangdong Province (No. 2024A1515010452), City University of Hong Kong Donation Research Grants (No. 9229021 and No. DON-RMG 9229021), and Ministry of Education (MOE), Singapore (MOE Tier 2 Project: MOE-T2EP50221-0003).

Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

Electronic Supplementary Material

Supplementary material is available in the online version of this article at <https://doi.org/10.26599/FRICT.2026.9441235>.

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