Achieving ultralow friction under high pressure through operando formation of PbS QDs/graphene heterojunction with 0D/1D nanostructure

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\textbf{A B S T R A C T}

It is a great challenge to utilize graphene for practical applications in moving parts, which meet high contact pressure and atmosphere environments. In this work, ultralow friction (0.054) of graphene was achieved under high contact pressure (1.03 GPa) and atmosphere environment via the operando formation of PbS quantum dots (QDs)/graphene heterojunction at the frictional interface. It is found that PbS QDs are trapped in graphene nanosheets via shear-induced rearrangement for obtaining the PbS QDs/graphene heterojunctions, which provide an excellent rolling effect to lower friction. It is also found that the heterogeneous PbS QDs/graphene tribofilms have a strong Pb-enriched function and heterojunction nanorod phase. Our objective is to uncover the physical and chemical mechanisms governing the friction of 0D/1D nanostructures within PbS QDs/graphene heterostructures through our studies. This research will enhance our comprehension of nanomaterials’ frictional behavior while offering valuable guidance and optimization strategies for their application in mechanical engineering and functional nanomaterials. Consequently, our efforts aim to foster the advancement of nanoscience and technology, leading to additional scientific and technological breakthroughs.

\section{1. Introduction}

Friction is responsible for approximately 30\% of the world’s primary energy consumption and around 80\% of component failure in moving mechanical devices [1-3]. Applying lubrication is one of the most efficient ways to address friction and wear issues. Solid lubricants, e.g., two-dimensional (2D) graphene, molybdenum disulfide (MoS\textsubscript{2}), and tungsten disulfide possess the ability to diminish friction by generating self-lubricating films via chemical reactions or physical adsorptions at the sliding interfaces where friction occurs [4-6]. There is a very low friction between MoS\textsubscript{2} layers due to its unique layered structure, and weak interlaminar interaction. But the low friction property will be reduced under moisture condition [7]. MoS\textsubscript{2} is a deliquescent material near oxygen and aqueous vapor. Graphene is prone to being failed because of friction-induced defects and oxidation [8]. Thus, the weak van der Waals thus can’t be achieved especially under macroscopic friction conditions [9,10]. Previous studies find that these 2D nanomaterials e.g., graphene, provide ultralow friction (friction coefficient named $\mu < 0.1$ [11]) and even superlubricity ($\mu < 0.01$ [12,13]) at the atomic or molecular scale, while at the macroscale, the typical friction coefficient of pristine graphene is always higher than 0.15 in the air [14-16]. Currently, the majority of machines and equipment operate in conventional environments like atmospheric environments. However, ultrahigh contact stresses (>1.0 GPa) and complex operating conditions increase macroscopic friction and rapid wear leading to surface failure and shorten lifespan of mechanic components [16-19]. In this context, 2D lubricating materials play a crucial role in maintaining and extending components’ surface lifespan. While, the macroscale ultralow friction of 2D nanomaterials can only be achieved under such a dry nitrogen atmosphere [20,21] and low Hertz contact pressures (<0.3 GPa) [21].

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Notably, previous studies have demonstrated that graphene can be easily destroyed by high contact pressure, i.e., GPa scale, resulting in various structure defects during the rubbing process \[20,22,23\]. Thus, it is a great challenge to utilize graphene in moving parts for practical applications, that meet high contact pressure and an atmosphere environment (see Schemes 1 and 2).

To improve the durability of graphene, additional zero-dimensional (0D) or 2D nanomaterials are often introduced in the frictional system to form heterojunctions (Sb/graphene \[24\], gold/graphene \[25,26\], hexagonal boron nitride/graphene \[27,28\], MoS\(_2\)/graphene \[29\]). These heterostructures exhibit good robustness, enhanced operational endurance, and exceptional efficiency for power usage and mechanical system durability \[30\--\[32\]. Heterostructures possess distinctive material characteristics, and the rubbing opposition at the point of contact can be diminished through the appropriate design of the configuration and appropriate material selection. For example, a MoS\(_2\)/a-C: H heterostructure with incommensurable stacked interlayer exhibits a significant reduction in contact point and has ultralow friction during the running-in period \[29\]. The ultralow friction of Ti\(_3\)C\(_2\)T\(_x\)/MoS\(_2\) heterostructure is also attributed to weakening contact points during the friction process \[30\]. Furthermore, both experiments and molecular dynamics (MD) simulations results have shown that in MoS\(_2\)/graphene heterojunctions, the pinned edges and interface steps play a crucial role in the sliding process \[7,26\]. These features are essential for achieving ultralow friction due to the significant lattice mismatch of interface, which is an order of magnitude lower than the single 2D materials. Besides, chemical bonds between layers are not easily formed in heterojunctions. In other words, it is not easy to produce tribo-chemistry between heterogeneous materials resulting in better mechanical stability. Moreover, the decrease in the lateral force constant between the

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Sch. 1. Schematic diagrams of the characterizations.

Sch. 2. Synthesis of Multilayer Graphene Film, PbS QDs, and PbS/graphene composite thin films (PGFs).
layers is in line with the findings from density functional theory (DFT) calculations indicates an extremely low potential energy corrugation during rubbing [28,32]. This reduction in potential energy corrugation can be attributed to the fluctuation in interfacial charge density induced by the sliding motion. Heterostructures can further decrease the resistive force produced by the touching interface by altering the form and texture of the substances [31-33]. To illustrate, the heterojunctions based on layered Metal-organic frameworks can diminish frictional strength by implementing design features like micro-protuberances [34]. Carbon nanotube arrays used as indentation and patterns effectively minimize friction at the sliding interface [35]. However, the involved nanomaterials are either pristine single-crystals or ones pre-synthesized on atomically flat single crystals, which brings a lot of problems including structural failure and weak adhesion [33,34]. In addition, the previously reported ultralow friction of graphene-based heterostructures can only be achieved at the microscale and low contact pressure. Recently, we have obtained the operando formation of transition-metal dichalcogenide (TMDC)/graphene heterostructures at the macroscale [13]. By trapping active amorphous carbon powder between TMDC flakes, the sandwich structures readily transform into TMDC/graphene heterostructures at the frictional interface during the running-in stage. The proposed heterostructures show an ultralow friction coefficient, but they could easily be disrupted if there exists some oxygen and water vapor, resulting in lubrication failure. Unlike those introduced nanomaterials originating from carbon, metal, TMDC, etc., PbS quantum dots (QDs) have high surface activity, available structure rearrangement [35,36]. For instance, PbS QDs are known for their ability to reduce the density of trap states by passivating defects, which is beneficial for commendable sliding durability [37–39]. This suggests efficient hole transfer at the interface between the layers to absorb photon energy and create electron-hole pairs for enhancing exceptional durability. By incorporating the exceptional sliding durability of PbS QDs into multilayer graphene layers, an air-stable heterostructure composed of graphene and PbS QDs can be fabricated, thereby ensuring excellent lubrication stability in the air. More interestingly, we have found that PbS QDs possess the desired long-term lubrication in the atmosphere environment compared with other QDs-based lubricants (Table S1). This state of affairs inspires us to explore a reasonable way to produce PbS QDs/graphene heterostructures enabling practical applications at high contact pressure and atmosphere environments.

In this work, a dual-aberration-corrected scanning transmission electron microscope (STEM) and electron energy-loss spectroscopy spectrometer (EELS) combined with elemental analysis were utilized to explore the impact of sliding interface on the tribological performances of a “sphere-layer” composite nanomaterials composed of PbS QDs and multilayered graphene, as shown in Sch. 1. The friction coefficient decreases with the increasing normal load reaching the lowest value of 0.054. Systematically studies and analyses indicated that the reduced friction coefficient should be attributed to the shear-induced rearrangement of PbS QDs nanoparticles and graphene nanosheets under high contact pressure of 1.03 GPa. To verify the conjecture, the same experiments were carried out on prolonged friction, which has a slightly different nanostructure in the tribo-film besides heterojunction nano- rods. The different variations in friction coefficient should be directly related to the heterojunction nanorods verified by interface structure and element composition. PbS QDs are trapped in graphene nanosheets to form the PbS QDs/graphene heterojunctions. The mechanisms of different friction stages were comprehensively evaluated via variation of the sliding interface.

2. Experimental

2.1. Materials and methods

Preparation of Multilayer Graphene Film: The large-area (20.0 × 20.0 mm² in size) multilayered graphene grown on a nickel foil (0.6 mm thick) was obtained from Six Carbon Technology Shenzhen Co., Ltd. Using chemical vapor deposition (CVD). The polished nickel foil was placed in a quartz tube furnace under a vacuum condition of 1 Pa at room temperature. Argon (50 sccm flow rate) and hydrogen gas (5 sccm flow rate) were continuously pumped into the furnace chamber, while the temperature was gradually increased to 1000 °C at a heating rate of 10 °C/min. The nickel foil was then kept in a hydrogen atmosphere at 1000 °C for 30 min to reduce surface oxides. Methane (20 sccm flow rate) was subsequently pumped for 30 min to grow the multilayered graphene. Finally, the methane was ceased, and the furnace was cooled down to room temperature, resulting in the formation of multi-layer graphene films on the surface of the nickel foil that could be used in the experiments. The synthetic process of multilayer graphene film is exhibited in Sch. 2.

Preparation of PbS QDs: PbS QDs were synthesized using the hot-injection method [37], with oleylamine serving as a ligand. In a three-neck flask (50 mL) at room temperature, PbCl₂ (278 mg, 1 mmol) and oleylamine (5 mL) were loaded and purged with nitrogen gas for approximately 1 h to remove oxygen. The mixture was then heated to 90 °C under magnetic stirring to form a homogenous PbCl₂/oleylamine suspension. Next, sulfur (2.5 mL, 0.33 mmol) in oleylamine stabilized at 90 °C was rapidly injected into the PbCl₂/oleylamine suspension under vigorous stirring, and the reaction was allowed to continue at the same temperature for 3 h. At various time intervals, aliquots of the reaction mixture were taken and quenched by cold hexane. Excess PbCl₂ precursors were precipitated by centrifugation at 4 °C, and further purification of PbS QDs was achieved with ethanol through repeated centrifugation and decantation to completely remove unreacted precursors. The synthetic process of PbS QDs is exhibited in Sch. 2.

Synthesis of PGFs: The graphene surface deposited with PbS QDs coating was prepared using the drop-casting method, which was previously utilized in our work on the PbS QDs-modified Silicon (Si) wafer surface [38]. A uniformly mixed solution (0.2 mL) of PbS QDs was slowly added to cover the entire surface of the multilayer graphene. The specimen was then stored at room temperature until the solution completely volatilized, resulting in the formation of PbS QDs deposited graphene composite thin films (referred to as PGFs), with the dry PbS QDs being adsorbed and deposited onto the graphene surface. The synthetic process of PGFs is exhibited in Sch. 2.

2.2. Characterisations

Structure of PbS QDs: To determine the chemical structure and composition of PbS QDs, Raman spectra (LabRAM HR8000, Horiba Jobin Yvon) were utilized with an Ar⁺ excitation laser of 514.5 nm in wave-length, and X-ray photoelectron spectrometer (XPS, Axis Ultra, Kratos) was used, respectively. The Shimadzu UV-3600 ultraviolet-visible (UV-vis) spectrophotometer and Omni-λ3007 spectrogrograph were used to verify the structure of PbS QDs. The PbS QDs solution was diluted and dried onto a copper grid with ultrathin carbon film for observation by a high-resolution transmission electron microscope (HRTEM, JEM-2101F, JEOL). The grain size was statistically observed by Gatan Digital Micrograph based on HRTEM images and atomic force microscope (AFM, Dimension Icon & FastScan Bio, Bruker). X-ray diffractometer (XRD, D/max-2200/PC, Rigaku) measurements were performed with a wavelength of 0.15418 nm.

Tribological Experiments: Tribological experiments were conducted using a Universal Macroscale Tribometer (UMT-5, Bruker) platform with a linear-reciprocating mode of ball-on-plate at room temperature under an atmosphere environment (temperature of 23 ± 2 °C and relative humidity of 15–30 %), which is displayed in Sch. 1. The upper tribo-ball was a SUJ2 bearing steel ball (6.0 mm in diameter), and the underlying tribo-plate was the PFG (10.0 × 10.0 × 0.09 mm³ in size) grown on the nickel foil. The nickel foil strongly adhered to the center of the Si wafer (15.0 × 15.0 × 1.0 mm² in size). The Si wafer was then fixed on the surface of the AISI-52100 steel disc (15.0 × 15.0 × 10.0 mm² in size),
and the steel disc was clamped on a reciprocating specimen platform. Pristine multilayered graphene specimens without PbS QDs were also tested under the same conditions for comparison. The applied normal loads were set to 1 N, 2 N, 4 N and 6 N, respectively, assuming Young’s moduli of bearing steel and nickel were 210 and 199.5 GPa, respectively, with their Poisson’s ratios of 0.3 and 0.312. Hence, the corresponding initial Hertz peak contact pressures were 0.65, 0.82, 1.03 and 1.18 GPa, respectively. The corresponding maximum Hertz peak contact pressures were 0.65, 0.82, 1.03 and 1.18 GPa, respectively. The reciprocating frequency and stroke length were set to 2 Hz and 3 mm, respectively.

Surface and Interface: We utilized the characterizations previously used in our works on GQDs-modified diamond-like carbon films [39] and PbS QDs-modified Si surfaces [38]. The wear surface morphology, including the wear track on the PGF and the wear scar on the steel ball, after tribological experiments were observed using a 3D white-light interference profilometer (NewView™ 8000, ZYGO) and an optical microscope (VHX-S650E, Keyence). Raman spectra were obtained using a laser confocal Raman spectrometer (LabRAM HR8000, Horiba Jobin Yvon) with an Ar+ excitation laser of 514.5 nm in wavelength. The chemical elements of the PGF were detected using XPS (PHI Quantera II, Ulvac-Phi) to reveal structural changes. The acquisitions were conducted using a monochromatic Al Kα X-ray source with 1486.6 eV photon energy. X-rays’ beam diameter and applied power were set to 100.0 nm and 23.56 W, respectively, and the incidence angle of X-rays was set to 45°. Lamellar specimens were prepared using a focused ion beam-scanning electron microscope dual-beam system (FIB-SEM, Quanta 3D FEG, FEI) with the function of low-kV Ga+ ion milling. Before milling, a layer of Cr was coated on the contact surfaces in the ion sputtering system, and then a thick supporting layer of Pt was deposited successively to protect the sliding contact interface from implantation artifacts and structural damage. The representative sections and elemental distributions of interfacial nanostructured tribo-films were observed using an HRTEM (JEM-2010F, JEOL) equipped with energy-dispersive spectroscopy (EDS, JEM-2010F, JEOL) operating at 200 kV. To confirm the nanostructured details of the as-formed tribo-films, the counterfacing tracks and scars were detected using a dual-aberration-corrected scanning transmission electron microscope (STEM, JEM-ARM200F, JEOL) and energy-dispersive spectroscopy (EDS, JEM-ARM200F, JEOL) equipped with an electron energy-loss spectroscopy spectrometer (EELS, JEM-ARM200F, JEOL). The acceleration voltage was set to 200 kV, yielding a bright field (BF) imaging resolution of 0.14 nm and a high angle annular dark field (HAADF) resolution of 0.08 nm. Details regarding the parameters and data acquisition, including the analysis methodology for plasmon energy, mass density, and bonding fraction calculations based on C–K core edges, can be found in our previous works [5,40].

3. Results and discussion

3.1. Structure analysis of PbS QDs

Fig. 1 displays the physicochemical information of PbS QDs and multilayer graphene film. It can be found that PbS QDs have uniform nanoparticle sizes on the ultra-thin copper mesh (Fig. 1a), and the average particle size of PbS QDs is around 7.95 nm (Fig. 1b and b2). The X-ray diffractometer (XRD) characteristic peaks, located at 22.0° and
26.8°, respectively, are (111) and (200) of PbS. The pristine PbS QDs powders also exhibit a PbO peak at 35.4°, as shown in Fig. 1c. Fig. 1d displays the Raman spectra of PbS QDs, which show related characteristic peaks ranging from 1209 to 2021 cm⁻¹. The Ultraviolet–visible (UV–vis) and photoluminescence (PL) spectra in Fig. 1e and 1e2 demonstrate that the PbS QDs solution emits near-infrared fluorescence at 1648 nm under 1049 nm excitation [36, 41]. Fig. 1f shows the X-ray photoelectron spectrometer (XPS) spectra, which display the characteristic peaks of Pb5d, Pb4f, S2p, C1s, Pb4d, O1s, and Pb4p, respectively. Besides, nanostructure of multilayer graphene film is clearly seen lamellar structure in Fig. 1g to i. The interlamellar spacing is approximately 0.3 nm.

### 3.2. Overview of tribological behaviors

Fig. 2a shows that after 10 min of rubbing (i.e., 2400 sliding cycles), the average μ under 1 N (0.65 GPa), 2 N (0.82 GPa), 4 N (1.03 GPa), and 6 N (1.18 GPa) is 0.062 ± 0.002, 0.054 ± 0.004, 0.052 ± 0.003, and 0.060 ± 0.010, respectively. Notably, the lowest μ (0.052 ± 0.003) under 4 N corresponds to a high Hertz peak pressure of 1.03 GPa, demonstrating the robust and stable lubrication of PGFs for engineering applications. After a long-duration tribological test under the 4 N load, the average μ is 0.063 ± 0.025 during the whole friction period (about 38 min, 9120 cycles). The stable μ remains below 0.065 (with an average μ of 0.054 ± 0.008) for a stable lubrication period (about 32 min, 7791 cycles) under ultrahigh contact pressure. However, the μ eventually rises...
to a maximum value of 0.15 (indicating that the PGFs have been worn out) after the stable lubrication period. With the increasing load to 6 N, the average \( \bar{\mu} \) arrives 0.060 \( \pm \) 0.01, which means a failure case of PGFs’ lubrication. For comparison, tribological experiments of pristine graphene films without PbS QDs are conducted under the same testing conditions with the results shown in Fig. 2b. After 10 min of rubbing (2400 cycles), the average \( \bar{\mu} \) of the comparative subjects is 0.164 \( \pm \) 0.020, 0.170 \( \pm \) 0.023, 0.170 \( \pm \) 0.024, and 0.181 \( \pm \) 0.026 under 1 N, 2 N, 4 N, and 6 N, respectively. These values are almost 2.65, 3.15, 3.27, and 3.02 times higher than that of the PGFs cases. In previous works, the typical macroscale \( \mu \) of pristine graphene sliding against steel under atmospheric conditions is usually between 0.15 and 0.2 [16], whether used as solid lubricants [42] or graphene-containing liquid lubricants [20]. This range is approximately 2.65–3.27 times higher than that of the PGFs cases. In previous works, the typical macroscale \( \mu \) of pristine graphene sliding against steel under atmospheric conditions is usually between 0.15 and 0.2 [16], whether used as solid lubricants [42] or graphene-containing liquid lubricants [20]. This range is approximately 2.65–3.27 times higher than that of the PGFs cases. In previous works, the typical macroscale \( \mu \) of pristine graphene sliding against steel under atmospheric conditions is usually between 0.15 and 0.2 [16], whether used as solid lubricants [42] or graphene-containing liquid lubricants [20]. This range is approximately 2.65–3.27 times higher than that of the PGFs cases.

3.3. Morphology of frictional counterfaces

To thoroughly understand the influences of PbS QDs, the contact surfaces tested under 4 N (1.03 GPa) are characterized using microscopes and spectrometers, as shown in Fig. 3. The variation trends of the Raman spectra of the 38-min testing specimens are quite similar to those of the 10-min testing specimens (Fig. 3a). The characteristic D-peaks (1343 cm\(^{-1}\)) and G-peaks (1581 cm\(^{-1}\)) of graphene can be observed in the Raman spectra of these two specimens. The intensity ratio of the D-peak to G-peak (I\(_D\)/I\(_G\)) of pristine PbS QDs can be found at around 2700 cm\(^{-1}\) and 2900 cm\(^{-1}\) in the Raman spectra of all tribological testing specimens. The Raman spectra of the ball scar tested for 38 min and 10 min show that the characteristic peaks of pristine PbS QDs at 2700 cm\(^{-1}\) and 2900 cm\(^{-1}\) are significantly stronger in the ball scar tested for 38 min than in the one tested for 10 min. Notably, these peaks are significantly stronger in the ball scar tested for 38 min than in the one tested for 10 min, similar to the Raman comparison of specimens at different durations in our previous study on PbS QDs lubricant coating [38]. These observations suggest that most PGFs have been transferred onto the surface of the steel ball from the nickel plate by friction force during the 38-min rubbing process. Furthermore, the optical morphologies of the counterparts indicate that some transferred films have formed on the surfaces of steel balls and nickel plates (Fig. 3b and c), implying that these transferred films are critical for achieving robust macroscale ultralow friction. These findings are similar to the friction performance comparison of specimens at different durations in our previous study on PbS QDs lubricant coating [38].
explore the microstructural variation on the sliding surface using HRTEM. The specimen with the lowest friction coefficient (via focused ion beam (FIB) milling to obtain lamellar specimens and 3.4. Interfacial nanostructure of tribo-counterfaces

To verify this friction-induced variation, the counterparts are sliced via focused ion beam (FIB) milling to obtain lamellar specimens and explore the microstructural variation on the sliding surface using HRTEM. The specimen with the lowest friction coefficient (μ = 0.052 ± 0.003) after the 10-min tribological test under a 4 N load was selected to observe the in-situ nanostructured transferred films (i.e., tribo-films) formed on the surfaces of the counterparts (PGFs and bearing steel ball), as shown in Fig. 4. There is a small number of nanoclusters at the bottom region of the tribo-films (Fig. 4b), a mass of synergistic rearranged nanostructures consisting of PbS QDs and graphene nanoflakes at the middle region of the tribo-films after the rubbing process (Fig. 4c), and two types of unique nanostructures on the top-most sublayer (Fig. 4d1 and 4d2, which represent one part of the direct contact surface in Fig. 4a) of the tribo-films. These resemble a merged 0D/1D heterojunction and an enriched multilayer [21], which comprises a core containing 0D PbS QDs nanoparticles and a coiled 1D-shell crafted with multi-walled exfoliated nanostructures originated from 2D graphene. This denotes a collaborative enrichment orientation (this refers to the formation of PbS QDs-enriched layers along the active surface of exfoliated graphene layers) and rearranged process (this refers to the friction-induced rearrangement of PbS QDs). Based on the statement, it is reasonable to infer that the unique and complex morphology of the tribological interface is the key to achieving the synergetic lubrication of graphene and PbS QDs. In other words, the friction-induced rearrangement of graphene and PbS QDs, as well as the newly formed 0D/1D heterojunction resembled nanorod, are significant factors in maintaining a robust macroscale ultralow friction of PGFs under ultrahigh contact pressure in an atmospheric environment.

3.5. Variation of interfacial elements

To systematically confirm the bonding structure of the tribo-film, their atomic structures and chemical components are characterized using an electron energy-loss spectroscopy spectrometer dual system (STEM-EELS). The bright field (BF), high angle annular dark field (HAADF), and color field (CF) images show the unique nanostructure of the tribo-film (Fig. 5a). The tribo-film is composed of 0D/1D heterojunction and PbS QDs-enriched layers near the sliding surface. The plasmon energy in the low-loss spectrum is identified at 23.1 eV, as shown in Fig. S7a. Meanwhile, EELS elemental maps of the tribo-film reveal that the wrap layer consists of plumbum (Pb–N map) and sulfur (S-L map) as depicted in Fig. S5. The major characteristic of the measured S-L edge is S-L2,3 (168.3 eV) in EELS core-loss spectra. Correspondingly, the Pb–N edge is mainly involved in the formation of Pb–N0 (143.9 eV) and Pb–N−1 (137.9 eV). Additionally, the O–K edge of the tribo-film has one peak at 531.6 eV. The HAADF- and BF-STEM results, along with the spectra-image mappings, quantitatively verify the interfacial shell-core nanostructures of the 0D/1D heterojunction: the shell of Pb and S atoms decomposed from PbS QDs and transfer to the sliding interface to form Pb-enriched multilayers near the core of PbS QDs nanoparticles, during which degraded graphene nanosheets are also involved in this process to form the ultralubric tribo-film. Finally, the tribo-film is composed of 0D/1D heterojunction and PbS QDs-enriched layers on the rubbing surface of the counterfacing ball.
Correspondingly, the BF-, HAADF-, and CF-STEM results also display the detailed nanostructure of the PGFs (Fig. 6a). The nanostructured film is composed of 0D/1D heterojunction, Pb-enriched multilayer structures, and graphene nanosheets. The EELS elemental maps of the multilayer graphene film demonstrate that this shear band has a similar composition concerning Pb–N, S-L, and O–K maps (Fig. S4b) with plasmon energies of 22.7 eV in low-loss spectra. Firstly, the S element is relatively volatile, and the multilayered graphene enables it to disturb the balance between P and S elements, even though some regions of the film contain lots of disaggregated Pb and S atoms. These results verify that the graphene layers provide oriented platforms to form Pb-enriched multilayer structures. Secondly, to comprehensively clarify the bonding structure of the film, the EELS core-loss spectra are shown in Fig. 6b. The measured Pb–N edge, S-L edge, and O–K edge are Pb–N (138.8 eV), Pb–N (144.7 eV), S-L (167.5 eV), and O–K (531.7 eV), respectively. The Pb signal is relatively intensive in the Pb-enriched multilayer structures. Additionally, PbS QDs nanoparticles and Pb-enriched multilayer structures are mainly involved in the formation of 0D/1D heterojunction-resembled nanorods, as revealed via the emerging peaks of Pb–N, Pb–N, and S-L. As such, the 0D/1D heterojunction possesses a nanostructure akin to a composite heterojunction comprising a one-dimensional PbS nanoparticle core and a multi-walled layered nanosheet shell formed through exfoliation of graphene nanosheets, enriched with Pb elements. First, the quantum dot–graphene interface in 0D/1D heterojunction is formed by friction drive [43]. There are few covalent or non-covalent bonds for graphene. The binding interface here is dominated by weak intermolecular forces and electrostatic attraction. The utilization of graphene's lubricity potential is maximized to achieve ultra-low friction. In contrast to the 10-min specimens, the HRTEM and EDS images of the 38-min tribo-couples are shown in Figs. S5 and S6.

Fig. 6. Interfacial nanostructures of the tribo-affected disc surface. (a) BF-STEM image and HAADF-STEM image, respectively, which is associated with Fig. 4g. The color field (CF) image is obtained from the mappings of white boxes. A rearranged nanostructure is displayed in Fig. S3b. (b) The Pb–N, S-L, and O–K core-loss spectra indicate the tribo-film structure. EELS elemental maps of the tribo-film are illuminated in Fig. S4. (A colour version of this figure can be viewed online.)

Fig. 7. Chemical elemental analysis of the as-formed nanostructure on the contact surface. (a) and (b) STEM-EDS images of the ball scar and disc track, respectively. The HAADF images are associated with Fig. 5a and 6a and. (c) XPS elemental analysis of PGFs and the contact surface contains Pb4f, S2p, C 1s, and O1s XPS spectra, respectively. The XPS full spectra of the contact surface are shown in Fig. S7. (A colour version of this figure can be viewed online.)
Pb and S elements embedded in graphene in the most direct contact sphere-layer nanoflakes and amorphous carbon. Subsequently, the 0D/1D heterojunction of the steel ball. Additionally, for the PGFs, the multilayer junction is generated by the rearrangement of the graphene and PbS -3.6. Tribo-physiochemistry mechanism

The X-ray energy dispersive spectroscopy (EDS) of Fig. 5a and b, it is evident that the sliding of the steel ball and slipping of the “sphere-layer” composite structure of the PGFs induce the enrichment of Pb and S elements embedded in graphene in the most direct contact region of the steel ball. Additionally, for the PGFs, the multilayer structures of graphene have been disrupted, forming some graphene nanoflakes and amorphous carbon. Subsequently, the 0D/1D heterojunction is generated by the rearrangement of the graphene and PbS QDs. Finally, the small-sized graphene nanosheets and PbS QDs are transferred to the most direct contact surface. The 0D/1D heterojunction mainly consists of PbS QDs nanoparticles and Pb-enriched multilayers like oriented shell-core nanostructure. In addition to the elemental composition of the 0D/1D heterojunction, the EDS elemental analysis of the most direct contact region in the tribo-films on the ball surface and the interfacial structures of the PGFs also presents the interfacial structural composition corresponding to HRTEM characterization (Fig. S2). The main constituent elements of the most direct contact region in the tribo-films on the ball surface and the PGFs are Pb, S, C, and O. From the XPS spectra in Fig. 7c, a new product FeS2 appears on both the wear scar of the steel ball and the wear track of PGFs, which is the result of the reaction between Fe and S. Additionally, the R-S organics in the blank PGF specimen also react during the rubbing process to generate FeS2 or volatilize directly. Overall, a variety of reaction products including PbO, PbS, Fe3O4. PbO was generated from oxidation between PbS QDs and oxygen during the friction process. It is worth noting that oxygen originates from the air, rather than graphene. From C 1s fine spectra in Fig. 7b, the intensities and locations of C-C and C=C signal peaks in the graphene nanosheets are almost the same with those from the friction areas. It means to some extent, the oxidation of graphene can be prevented and the lubricity stability of graphene is thus improved. In sharp contrast with 38-min specimens, there exists two structures on the most direct contact region: the enriched region of the Pb and S elements, and the wrinkled phases formed by the Pb atom and S atoms embedded in the graphene lamellae in Fig. S5d. The structure variation of tribo-film induced by slipping time gradually causes lubrication failure. The corresponding HRTEM, STEM-EELS, and Raman spectra indicate a low graphitization of 38-min samples without the formation of PbS QDs/graphene heterostructures Fig. 3. (Fig. S3 and S4). It should be noted that the steady frictional coefficient of PFGs is 0.054, and the disabled state is established only after 9000 sliding cycles. Raman spectra of the ball scar and the wear track with 9000 cycles show the rising I_D/I_G and the local enrichment of the amorphous phase, meaning the variation of the “sphere-layer” composite structures into 0D/1D heterojunctions occurs during the stable stage by trapping atomic state (the Pb atom and S atom) between graphene nanosheets, based on shear-induced rearrangement of PbS QDs and generated lead compound such as PbO. Then these 0D/1D heterojunctions are assembled into heterogeneous tribofilms to achieve robust macroscale ultralow friction at a

Fig. 8. A schematic tribo-model of the PGFs film showing the process for establishing a nanostructured and synergetic lubrication interface. (a) The 3D diagram of the initial loading state. (b) Interfacial structures of the ultralow-friction state. (c) Interfacial structures of the wear state (d) The 2D diagram of the rearrangement process for 0D/1D heterojunction, which is divided into four steps: i) Initial friction, ii) Half-finished 0D/1D heterojunction, iii) Full-finished 0D/1D heterojunction, and iv) Degraded 0D/1D heterojunction. (A colour version of this figure can be viewed online.)

3.6. Tribo-physiochemistry mechanism

Fig. 7 displays the interfacial element analysis of the tribo-couples (steel ball and PGFs) after the 10-min tribological test under a 4 N load. From the X-ray energy dispersive spectroscopy (EDS) of Fig. 5a and b, it is evident that the sliding of the steel ball and slipping of the “sphere-layer” composite structure of the PGFs induce the enrichment of Pb and S elements embedded in graphene in the most direct contact region of the steel ball. Additionally, for the PGFs, the multilayer structures of graphene have been disrupted, forming some graphene nanoflakes and amorphous carbon. Subsequently, the 0D/1D heterojunction is generated by the rearrangement of the graphene and PbS QDs. Finally, the small-sized graphene nanosheets and PbS QDs are transferred to the most direct contact surface. The 0D/1D heterojunction mainly consists of PbS QDs nanoparticles and Pb-enriched multilayers like oriented shell-core nanostructure. In addition to the elemental composition of the 0D/1D heterojunction, the EDS elemental analysis of the most direct contact region in the tribo-films on the ball surface and the interfacial structures of the PGFs also presents the interfacial structural composition corresponding to HRTEM characterization (Fig. S2). The main constituent elements of the most direct contact region in the tribo-films on the ball surface and the PGFs are Pb, S, C, and O. From the XPS spectra in Fig. 7c, a new product FeS2 appears on both the wear scar of the steel ball and the wear track of PGFs, which is the result of the reaction between Fe and S. Additionally, the R-S organics in the blank PGF specimen also react during the rubbing process to generate FeS2 or volatilize directly. Overall, a variety of reaction products including PbO, PbS, Fe3O4. PbO was generated from oxidation between PbS QDs and oxygen during the friction process. It is worth noting that oxygen originates from the air, rather than graphene. From C 1s fine spectra in Fig. 7b, the intensities and locations of C-C and C=C signal peaks in the graphene nanosheets are almost the same with those from the friction areas. It means to some extent, the oxidation of graphene can be prevented and the lubricity stability of graphene is thus improved. In addition, the PbO has low shear strength and a good self-lubrication property. And PbO is one kind of anti-friction materials [46,47]. It also finds that the friction coefficient decreases greatly due to the formed PbO-containing tribofilm on the friction area (Fig. 7b). Meanwhile, the Pb and S in the atomic state appear in the tribo-films at the sliding surface after the frictional slip, which corresponds to the EDS elemental distribution in Fig. S2a and Fig. S3b. Fig. 8 illustrates the process of the interface in situ tribo-physiochemistry for PGF, where (a)-(b) represent the initial loading stage, and after 10-min (2400 sliding cycles) and 38-min (9090 sliding cycles) rubbing, the ultralow-friction state (c) and the wear state (d) appear, respectively. Frictional inducement causes Pb and S atoms to form some Pb-enriched multilayer structures along the direction of graphene sheets. Under the heavy load, an important factor for the variation of PGFs is the introduction of PbS QDs into the interlayer space of graphene nanosheets at the sliding shear condition. 0D/1D heterostructures resemble nanorods, and the formation process is termed shear-induced rearrangement. The 2D graphene nanoflakes induce the laminating of PbS QDs, where the nanoflakes act as a pressure mold to provide uniform pressure for the rearrangement of inwrought PbS QDs, contributing to the formation of PbS QDs/graphene heterostructures with interfacial bonding (such as Pb-O bonds). This is verified by the obvious incorporation between PbS QDs and graphene (Fig. 4d and 7c), which clearly shows the formation of PbS QDs/graphene heterojunction. In sharp contrast with 38-min specimens, there exists two structures on the most direct contact region: the enriched region of the Pb and S elements, and the wrinkled phases formed by the Pb atom and S atoms embedded in the graphene lamellae in Fig. S5d. The structure variation of tribo-film induced by slipping time gradually causes lubrication failure. The corresponding HRTEM, STEM-EELS, and Raman spectra indicate a low graphitization of 38-min samples without the formation of PbS QDs/graphene heterostructures Fig. 3. (Fig. S3 and S4). It should be noted that the steady frictional coefficient of PFGs is 0.054, and the disabled state is established only after 9000 sliding cycles. Raman spectra of the ball scar and the wear track with 9000 cycles show the rising I_D/I_G and the local enrichment of the amorphous phase, meaning the variation of the “sphere-layer” composite structures into 0D/1D heterojunctions occurs during the stable stage by trapping atomic state (the Pb atom and S atom) between graphene nanosheets, based on shear-induced rearrangement of PbS QDs and generated lead compound such as PbO. Then these 0D/1D heterojunctions are assembled into heterogeneous tribofilms to achieve robust macroscale ultralow friction at a
steady stage by enhancing the rolling effect, stimulating strong Pb-enriched function, and eliminating wrinkled phase. Additionally, many graphene nanosheets, Pb, and S atoms are distributed near the Pb-enriched multilayer structures. During the continuous slip of the tribo-interface, these friction-induced Pb-enriched multilayer structures eventually form the shell of 0D/1D heterojunction, which wraps PbS QDs cores. As the rubbing continues, these 0D/1D heterojunctions are constantly being consumed, and numerous wrinkled layers and amorphous mixed phases appear at the tribo-interface, leading to the increase of the friction coefficient and wear. The 0D/1D heterojunction is the key to achieving robust macroscale ultralow friction of PGFs under ultrahigh contact pressure in the atmospheric environment.

The curve of $\mu$ against contact pressure for graphene and its composite materials under various working conditions is shown in Fig. 9, which lists the data from relevant literature [16,21,44–49]. Below 1.0 GPa, the stable $\mu$ cannot achieve less than 0.1 in the air. The reasons for the anti-heavy load capability of 0D/1D heterojunctions can be attributed to three factors. (1) The multi-walled shell composed of C, Pb, and S atoms exhibits strong van der Waals forces, enabling the withstanding of heavy loads and resist deformation [50]. (2) The PbS quantum dots (QDs) at the core of the heterojunction undergo continuous rearrangement, producing a thin tribo-film that acts as an antioxidant during sliding [51]. (3) The friction-induced formation of PbO and PbS results in hydrogen-bonding interactions with water from the air, which helps to mitigate oxidation and moisture between the graphene nanosheets [52]. These factors collectively contribute to the anti-heavy load properties of 0D/1D heterojunctions.

4. Conclusions

This study investigated the lubrication performance of PGFs and the in-suit tribo-physiochemistry mechanism of sliding surfaces in the atmosphere environment. A doping solid lubricating film with a “sphere-layer” composite structure was prepared using multilayer graphene films and PbS QDs. PGFs demonstrated robust macroscale ultralow friction ($\mu \approx 0.052$) under a high contact pressure of 1.03 GPa. Frictional forces induced Pb and S atoms to form Pb-enriched multilayers like shells along graphene nanosheets. Meanwhile, PbS QDs nanoparticles are dragged into Pb-enriched multilayers to form the core. Additionally, many graphene nanosheets, Pb, and S atoms were distributed near the Pb-enriched multilayer structures. Overall, the formed 0D/1D heterojunction that is the key for achieving robust macroscale ultralow friction of PGFs under ultrahigh contact pressure in the atmosphere environment.

CRediT authorship contribution statement

**Xuan Yin**: Conceptualization, Writing – original draft. **Haosheng Pang**: Conceptualization, Writing – original draft. **Huan Liu**: Writing – review & editing. **Jun Zhao**: Visualization, and, Supervision. **Bing Zhang**: Project administration. **Dameng Liu**: Visualization, Writing – review & editing. **Yijun Shi**: Visualization, Writing – review & editing.

Declaration of competing interest

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

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Appendix A. Supplementary data

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References
