## **Tribological Manufacturing of ZDDP Tribofilms Functionalised by Graphene Nanoplatelets**

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## Abstract

3D Tribo-Nanoprinting (3D TNP), which uses a highly controllable tribological contact to deposit tribofilms, has been proposed as a manufacturing method for nanoscale structures. Inspired by this, we show for the first time, as a proof of concept, the ability to electrically functionalise tribofilms for potential use in the manufacture of structures with nanoscale thickness. Zinc dialkyldithiophosphate (ZDDP) tribofilms have been generated to include varying concentrations of graphene nanoplatelets (GNPs) resulting in them becoming electrically conductive when tested using conductive atomic force microscopy (CAFM). In its highest GNP concentration, approximately 55% of the surface of the tribofilm was able to sustain current up to a threshold of 245 pA. The higher graphene content led to a suppression in film formation and decreased substrate coverage. Transmission electron microscopy (TEM) revealed a dual-layered tribofilm with a carbon-rich layer above a pure layer of ZDDP tribofilm. Within the carbon-rich layer, the GNPs formed into scrolls which created an internal network through which current could flow, being limited by the insulating pure ZDDP layer at the film-substrate interface, and the presence of surface graphene sheets. A modified lateral force microscopy (LFM) procedure supported the presence of surface graphene sheets. Despite limited deposition precision in terms of homogeneity and distribution of the tribofilms, this work provides a step towards the use of 3D TNP for the manufacture of electronic structures on the nanoscale by proving that tribofilms can be functionalised by the addition of particle additives.

## 1. Introduction

Current manufacturing techniques for high precision electronic devices can be complex, each with specific limitations [1], [2], [3]. The use of tribofilms for manufacturing has been little explored, but could provide a simple, single-step manufacturing process. However, research into tribofilms with beneficial non-tribological functions, such as electrical or magnetic properties, is limited and has only been reported as a side effect when testing tribofilms for their tribological properties [4], [5], [6]. Therefore, the ability to functionalise tribofilms must first be attained.

Small scale electronic devices such as nanosensors, which can detect a range of parameters from temperature to chemical changes, and are less than 100 nm in size, require specialised fabrication techniques to produce. These typically fall into one of two categories of manufacture: top-down, or subtractive, in which material is selectively removed from the bulk; and bottom-up, or additive, in which material is added to achieve the required form [7], [8].

For flat structures, such as electronic circuits, focussed beams of radiation, either in the form of light or electrons, can be utilised to etch a surface, as in electron beam lithography. However, due to the instrumentation required, electron beam lithography is intensive in both time and cost [9]. Alternatively, by utilising the beams to initiate chemical reactions such as polymerisation at the surface, structures can be built up [10]. This process is limited, therefore, to materials that can be solidified by polymerisation or a similar process. Electrodeposition can be used to create small features, but requires the components to be conductive [11].

Another set of techniques, which fall under the umbrella term of scanning probe lithography (SPL), utilise the controllability of a scanning probe, most often an atomic force microscope cantilever, to manipulate a surface to a desired effect. A benefit of SPL is that the process can be carried out whilst imaging with the same instrument. Among these are subtractive modes in which the probe mechanically removes material, such as nanoshaving, and additive modes, such as nanografting that produces self assembled monolayers (SAMs) on surfaces [12]. Dip-Pen Nanolithography also produces additive results, and has been used to manufacture magnetic structures for data storage [13]. However, the process is heavily dependent on ambient conditions, which can have a significant impact on deposition rates [14].

The fabrication of high precision devices such as integrated circuits is dominated by photolithography, which can be used at a high efficiency and throughput, but is inherently a multi-step process, and limited by the fabrication of masks, which require their own fabrication method [15]. Further, the technique requires high expertise and expensive equipment, along with high purity chemicals and ultra-clean environments [16].

On the larger microscale, various methods using inks have been shown to print conductive structures on surfaces; these inks are typically composed of a carrier fluid with additives, the conductive components of which are metallic nanoparticles, conductive organic polymers, or carbon-based particles [17], [18]. Effective metallic nanoparticles such as gold or silver can be expensive, and cheaper alternatives like copper are prone to oxidation, reducing their conductivity. Conductive polymers are similarly unsatisfactory in terms of electrical performance and dispersion in fluid environments.

Each of these techniques have their drawbacks, but an alternative could be found in 3D TNP. 3D TNP is a new manufacturing technique in the class of SPL which uses tribological contacts to initiate the generation of tribofilms via tribochemical reactions under an AFM contact [19], [20]. The AFM tip is immersed in a heated solvent, which contains a surface active chemical additive that under contact pressure and shear will form a 3D nanostructure called a tribofilm. That the reaction can happen only at the tip-surface contact leads to a highly controllable, precise film deposition method. Precisions in ZDDP tribofilm thicknesses, a typical chemical additive used in lubricants, on silicon substrates as high as < 10 nm have been achieved by Dorgham et al. [20] in zig-zag patterns, and Khare et al. [19] have shown that composite structures can be generated by sequentially layering films of zirconia and ZDDP. The single-step, bottom-up procedure of 3D TNP lends itself to scenarios in which simplicity is key, such as in an extra-terrestrial setting, where contamination must be also minimised.

ZDDP is traditionally used as an anti-wear additive in automotive lubricants and reliably forms pads of tribofilm on rubbing surfaces, making them ideal candidates to be functionalised. The films are composed of a bulk of pyro- or ortho-phosphate glass, an outer layer of zinc polyphosphates and a lower layer (at the surface) rich in sulphur [21]. These durable tribofilms

initially form in patches that subsequently grow to thicknesses of approximately 100-150 nm [22], [23].

Tribofilm formation in ZDDP is driven by shear stress, and follows a stress driven, thermal activation model, in which reactions are accelerated by applied stresses that reduce the thermal activation barrier [24]. High temperature conditions have been shown to increase tribofilm growth rate in both micro- and nano-scale tests [25]. The stresses can be applied via normal or shear forces, meaning that although films will readily form under boundary conditions, where the asperities of the interacting surfaces are in direct solid contact with each other, they can also form when a full film layer of lubricant is present, via the application of high shear forces [26]. Therefore, the tribofilms will only form under rubbing contact, and their positions and morphologies can be tuned by controlling the contact parameters [26].

Despite their advantageous mechanical properties, ZDDP tribofilms are electrically insulating and would have limited use for electronic applications. Therefore, it is proposed here that graphene nanoplatelets (GNPs) can be added to the tribofilms during generation, to impart their electrical properties to the ZDDP matrix. GNPs are composed of sheets of graphene a few layers thick with a given diameter, and are readily commercially available. GNPs have been shown to be highly effective when used in conductive inks by creating an interlinked network of conductive paths within hardened inks [27]. They disperse satisfactorily in base oil blends [28], with stability enough for the current application, making them an ideal candidate to functionalise ZDDP tribofilms.

In the tribological setting, 2D materials such as graphene and  $MoS_2$  are used widely to reduce friction and wear via a series of mechanisms. These include plane shearing, in which separate layers of 2D materials shear easily along their planes, reducing friction; and the introduction of rolling structures such as scrolls into the contact, which change the load-bearing capacity of the co-moving surfaces [29], [30]. Synergistic effects have been noted between ZDDP and graphene when used as a nanolubricant, where the addition of graphene increases wear resistance [31]. Graphene and ZDDP tribofilms have been shown to greatly reduce wear by producing a graphene tribofilm, which then integrates into the ZDDP tribofilm and creates a composite film [32]. It has also been shown that the addition of graphene increases the formation rate of ZDDP tribofilms due to the beneficial energy pathway through the graphene to the substrate [33]. Further, it has been demonstrated that the concentration of graphene affects the growth rate of ZDDP tribofilms, with a low concentration reinforcing the film, but a high concentration blocking its formation [28].

Alternate conductive nanoparticles, such as copper or gold, may also provide conductive effects, but these have their own drawbacks such as being predisposed to oxidation [18], reducing conductivity in the case of copper, or financial expense in the case of gold. The effective track record of GNPs in conductive inks, combined with their stability and cost make them strong candidates.

In this study a new method of tribofilm functionalisation is presented for the first time, by utilising a tribological contact to generate electrically conductive surface films on the microscale. To test the hypothesis that tribofilms could be functionalised, GNPs have been integrated into ZDDP tribofilms to produce electrically conductive structures which form only under a controllable rubbing contact, proving the utility of the concept of tribofilm deposition as a manufacturing technique. The electronic application is used as a proof of concept for a

wider functionalisation pathway. By selecting conductive nanoparticle additives, the current flows could be easily measured, thus demonstrating the functionalisation of the tribofilms.

The work opens up a range of possible applications from conductive functionalisation for generating simple electronic devices, such as sensors that employ wire structures, to magnetic and frictional functionalised materials for data storage and tribological performance, such as surface patterning. The technique is presented as an alternative to the other successful methods used in the manufacture of small scale devices.

## 2. Methods

#### 2.1) <u>Sample Preparation</u>

Tribofilms were generated using a Mini Traction Machine (MTM, PCS Instruments, London, UK). The MTM configuration is that of a ball on disc tribometer in which a ball is loaded against a disc whilst immersed in a lubricant blend (Figure 1). Both the disc and ball rotate independently to achieve a desired Slide to Roll Ratio (SRR); in this case the SRR was chosen to be close to pure sliding to best mimic the conditions within 3D Tribo-Nanoprinting, whilst avoiding excess wear [34], [35]. The test conditions are given in Table 1, and the properties of the steel disc and ball samples are shown in Table 2.



Figure 1: Schematic diagram of MTM showing how tribofilms are generated around the edge of steel sample discs. The disc is loaded against the ball and both rotate independently, creating the rubbing conditions necessary for tribofilm formation.

Five lubricant blends were produced with GNP contents varying between 1 - 15 wt.%. Firstly, a base solution of ZDDP/PAO4 was produced in a concentration of 1 wt.% ZDDP (primary) (Afton Chemical) in PAO4 base oil (Afton Chemical) by stirring for 20 minutes at a temperature of 60°C. The PAO synthetic hydrocarbon base oil used had a kinematic viscosity of 4 cSt at 100°C. This concentration of ZDDP was chosen as preliminary tests showed it to produce thick tribofilms, and matched the concentrations used in previous publications [36], [37].

To this blend were added varying amounts of GNPs such that GNP concentrations of 1, 3, 5, 10, 15 wt.% were achieved. This range was chosen to vary up to the maximum GNP content the oil could sustain whilst maintaining dispersion of the particles; above 15 wt.% the oil dried

out such that it was not usable in the MTM. Previous studies have shown that graphene can be dispersed in base oils without the use of chemical dispersants, albeit for a short time period, and in low enough concentrations [28], [32], [33]. GNPs are nanoparticles made up of short stacks of graphene sheets a few layers thick, with a platelet shape. The GNPs used here were commercially available in the form of a powder, with nominal particle diameters of  $< 2 \,\mu$ m, typical particle thicknesses of a few nm, and average surface areas of 750 m<sup>2</sup>g<sup>-1</sup> (Sigma-Aldrich, product number 900407, CAS number 7782-42-5). These GNPs have been shown experimentally to have approximately 20 layers [38].

The GNPs were magnetically stirred into the ZDDP/PAO4 solution for 20 minutes. Before testing, each blend was subject to a further 20 minutes in an ultrasonic bath to reduce sedimentation. The resulting blends of 1 wt.% ZDDP in PAO4 with varying GNP contents were then added to the MTM reservoir to cover the sample disc utilising a syringe, and were used to generate the tribofilms. One MTM disc sample was produced for each concentration, with each disc hosting multiple tribofilm analysis locations. The experimental conditions were based on reported tests, which all showed ZDDP tribofilm formation [39], [40], [41], [42].

Parameter	Value
Lubricant Temperature	80°C
Sliding Speed	100 mm s <sup>-1</sup>
Force	60 N
Slide-Roll Ratio	150%
Rubbing Time	90 minutes

Table 2: Properties of balls and discs used to generate tribofilms. The discs formed the substrates onto which the samples were deposited.

Parameter	Value
Disc	
Material	AISI 52100 steel
Roughness, Ra	$< 0.02 \ \mu m$
Hardness	720-780 Hv
<u>Ball</u>	
Material	AISI 52100 steel
Roughness, Ra	$< 0.02 \ \mu m$
Hardness	800-920 Hv

Once generation was complete in the MTM, the samples were cleaned with heptane in an ultrasonic bath to remove excess oil and debris (only the discs were used for further analysis). This was done in two stages; the first lasted 30 seconds and removed most of the oil; a further 150 seconds with fresh solvent was then used to remove any remaining oil from the surface. This method was found to remove as much debris as possible without damaging the films.

#### 2.2) Observing Formed Tribofilms

After generation, the films were observed using optical microscopy (Leica DM6000 M). Chemical analysis was provided by Energy Dispersive Xray Spectroscopy (EDX) (Carl Zeiss EVO MA15 SEM) at an accelerating voltage of 5 kV. These complementary methods were used to determine the effect of GNP content on the physical structure and composition of the tribofilms.

#### 2.3) <u>Conductive AFM</u>

Contact mode tunnelling AFM (TUNA) was employed with a PeakForce TUNA module on a Bruker Dimension Icon AFM for the CAFM, using SCM-PIC-V2 tips, to measure the electrical performance of the tribofilms. Using contact mode allowed a constant contact with the sample to be maintained, increasing signal stability, whilst allowing access to the high sensitivity amplifiers in the PeakForce TUNA module. CAFM functions by applying a voltage across the AFM cantilever and substrate, and the resulting current flow can be measured [43]. Scanning in a raster pattern over the samples builds images of the current distribution across the surface simultaneously with height images, allowing comparison of conductivity and topography. CAFM settings are shown in Table 3. A bias of 2V was selected to balance the ability to produce detectable currents whilst minimising damage to the samples.

The PeakForce TUNA module is capable of measuring currents from 100fA to  $10\mu$ A. The lateral resolution of the technique is dependent on the apex radius of the tip used but can be as good as 10 nm.

Table 3: Experimental settings used for CAFM measurements

Parameter	Value
Scan Size	3 µm x 3 µm
Applied Bias	2 V
Current Sensitivity	20 pA/V

#### 2.4) Lateral Force Microscopy

Lateral Force Microscopy (LFM) was used on a Bruker Dimension Icon AFM with Veeco ESP tips. In LFM the twist of the cantilever is measured as it is scanned across the sample surface, giving information on the lateral forces encountered by the cantilever as it rasters [44]. These lateral forces can be due to topography, or friction caused by materials changes. In this work LFM was employed using the trace minus retrace method in which the profile of the scan in one direction is subtracted from the scan in the opposite direction, thus suppressing the effects of topography and amplifying those due to frictional changes [45]. These analyses were conducted on Bruker's Nanoscope Analysis software.

#### 2.5) <u>Probing Internal Structure Using Focussed Ion Beam and Transmission Electron</u> <u>Microscopy</u>

To inspect the internal structure of the tribofilms, a Focussed Ion Beam (FIB) (FEI Helios G4 CX Dual beam) was used to remove a cross sectional slice of a tribofilm which was then observed using TEM and EDX (FEI Titan Cubed Themis 300 G2 FEG STEM). To do this, a

section of the sample was selected that contained a good coverage of tribofilm. This was then removed and placed into a copper TEM holder. TEM observations were performed using accelerating voltages of 300 kV, and EDX maps were simultaneously recorded. This data provided observations of the structures within the film, and elemental distribution, thus revealing how the GNPs were integrated into the tribofilms. The tribofilm selected for this analysis contained the highest concentration of GNPs, 15 wt.%, to have the best chance of showing GNP-derived features.

#### 2.6) <u>Calculation of Flash Temperature</u>

Maximum flash temperatures,  $\theta_{max}$ , were calculated using the method outlined by Reddyhoff et al. [46], building upon Greenwood [47], an overview is given below.

$$\theta_{max} = \frac{\dot{Q}_{in}}{bK} \left( \frac{0.5895}{\sqrt{J + 2.471}} \right) \tag{1}$$

where  $\dot{Q}_{in}$  is the rate of heat flowing into the contact, and is given by Equation (2), *b* is the half width of the contact, *K* is the thermal conductivity and *J* is a non-dimensional speed describing the relative motion of the surfaces and is given by Equation (3).

$$\dot{Q}_{in} = \mu W u_s \tag{2}$$

where  $\mu$  is the friction coefficient, W is the applied load and  $u_s$  is the sliding speed.

J

$$=\frac{u_s b}{\chi}$$
(3)

where  $\chi$  is the thermal diffusivity.

The half-width of the contact was the contact radius calculated using Hertzian contact mechanics [48]. The parameters used to calculate the flash temperature are given in Table 4.

Table 4: Parameters used in calculation of flash temperature.

Parameter	Value
Thermal Diffusivity, $\chi$	0.013
Sliding Speed, $u_s$	100 mms <sup>-1</sup>
Half Width of the Contact, b	0.157 mm
Thermal Conductivity, K	$46.6 \text{ x} 10^3 \text{ Wm}^{-1}\text{K}^{-1}$
Load, W	60 N
Friction Coefficient, $\mu$	0.069

#### 3. Results

#### 3.1) <u>Tribofilm Coverage and Chemical Composition</u>

Optical images of the tribofilms containing different GNP contents, from 1 wt.% to 15 wt.%, are shown in Figure 2. In general, the glassy tribofilms, appearing as blue, green, yellow and red highlights of colour to the naked eye, appear to have a less consistent distribution over the wear track as the concentrations increase, with the 15 wt.% case showing very little film material and more wear, as shown by the dark coloured scratches on the substrate. The case of 1 wt.% is close to what would be expected from a ZDDP tribofilm, with a characteristic patchy appearance [21]. As the concentration of GNPs increases these patches appear to transform into isolated, elongated strips of film that align with the rubbing direction.



Figure 2: Optical images of ZDDP tribofilms formed with concentrations of GNPs varying between 1-15 wt.%. The colourful regions (blues/reds) represent areas of light interference caused by the presence of ZDDP tribofilms, which occur more readily in the lower GNP concentrations. Yellow circles show accumulations of dark material, which may be formed of GNPs. Brown scalebars represent 100 µm



Figure 3: SEM-EDX scans collected at 500x magnification for zinc and copper for the ZDDP tribofilms containing GNPs in concentrations between 1-15 wt.%. Note that the images are not perfectly aligned with those in Figure 2 but do show similar locations on the wear scar. Purple scalebar represents 300 µm.

The distribution of carbon is difficult to discern in the optical data (Figure 2), the objective of this technique being to evenly distribute the GNPs throughout the film, but there are notable accumulations of dark material in each film. These may be composed of the GNPs and will be examined by EDX analysis. Large accumulations are seen in the 1 wt.%, 3 wt.% and 15 wt.% cases (circled in yellow). Although not shown in Figure 2, these were seen across the whole length of the wear track in various locations.

The EDX maps (Figure 3) showed that these accumulations were rich in carbon, suggesting the GNPs were aggregating. In four of the five cases it was seen in higher quantities within the wear region, such as in the 3 wt.% case, but in the 10 wt.% case the carbon was spread over the whole sample, with no discernible increase within the wear track region. Similar observations were made by Pham et al. [28] in which it was suggested that the patches could be aggregations of GNPs or amorphous carbon due to the breakdown of oil molecules during rubbing.

EDX was further used to identify the elemental chemical composition of the tribofilms. Shown in Figure 3 are EDX maps for carbon, zinc, phosphorous and sulphur over the 5 tribofilms with varying GNP concentrations. The zinc maps show high signals coming from the lower GNP concentration films, slowly decreasing as the concentration increases and suggesting that less ZDDP tribofilm is present. The 15 wt.% case shows almost no zinc signal. Viewed in conjunction with the optical data in Figure 2 it is likely that there is little ZDDP tribofilm material here, existing only in small, disparate strips. The phosphorous and sulphur maps show a similar trend, with an increased presence of the elements within the wear track in every case except the 15 wt.% case, in which it is difficult to discern any increase inside the rubbed region. Figure 4 shows EDX profiles taken across the wear track for the 5 wt.% case. Both phosphorous and sulphur show increases in concentration in the centre of the track, albeit much lower in magnitude than the signal due to zinc, strongly indicating the presence of ZDDP tribofilm. The carbon profile further shows the inhomogeneous distribution of carbon across the tribofilm.

To demonstrate the experimental repeatability of the tribofilm formation, two more formed ZDDP tribofilms are presented in Supplementary Material.



Figure **4**: SEM-EDX line scans for zinc, phosphorous, sulphur and carbon taken across the width of the wear scar shown in the 15 wt.% case in Figure 3. Note that a 10-point moving average was applied to smooth the data.

#### 3.2) <u>Conductivity of Tribofilms</u>

Due to the inhomogeneity of the tribofilms, sample locations for CAFM measurements were selected in patches with good film coverage.

AFM data taken from a pure ZDDP tribofilm is shown in Figure 5. Pure ZDDP tribofilms are electrically insulating [5], [49], demonstrated by Figure 5 in which current flows only in low height regions; in other words only where there is no film coverage and tip-steel substrate contact is maintained. This clearly shows insulating behaviour.



Figure 5: AFM topographic and current images for a section of pure ZDDP tribofilm showing insulating nature of ZDDP tribofilm. The light regions in Figure 5b are conductive, and align with bare substrate seen in Figure 5a, whereas the dark regions are insulating ZDDP tribofilm with high topography.

A typical example of a CAFM dataset from a tribofilm containing GNPs, which formed the basis of the following analysis, is shown in Figure 6. It shows a tribofilm sample created using the lubricant containing 15 wt.% GNPs, as this most clearly demonstrates how conductive patches are observed. The topography data shows that the film is composed of pads that form close to one another, with some areas having a smoother appearance than others (Figure 6a). When comparing the current data over this same area (Figure 6b), it can be seen that areas of low height tend to support higher current due to the AFM tip coming into contact with the conductive steel substrate (example marked by yellow arrows). However, there are a number of patches (Figure 6b) that sustain currents despite being covered in a thick film. Examples of these are circled in red.

The line profile (Figure 6c) indicates the variation of magnitudes along the dotted green line. Here a maximum value of 246 pA exists, with smaller non-zero values seen in several other locations. The blue circled region corresponds to one of these high current regions within an area covered by film.

The CAFM data has shown that the addition of the GNPs has induced conductivity inside the bulk of the tribofilm itself in small patches, quite different to the behaviour seen in the pure ZDDP tribofilm (Figure 5). Examples of CAFM scans taken for the other GNP concentrations can be found in the Supplementary Material.



Figure 6: AFM topographic image of section of ZDDP tribofilm (a) containing 15 wt.% GNPs, corresponding CAFM image (b) showing conductive patches throughout the film, and line profile of current magnitudes (c) relating to the green dotted lined in (a) and (b).

Next, the surface area of the films that had been made conductive was quantified. To calculate these values CAFM scans were performed on areas covered completely by films (precluding the chance of direct substrate-tip contact) and analysed using the procedure shown in Figure 7.

Measurements were taken at various locations across the films, and all effort was taken to exclude areas that may have included uncovered substrate. The mean of each concentration was calculated from 16 measurements taken in different locations on the films.

Examining the conductive proportion of the surface of the tribofilms against the GNP concentration shows an increase in the area that sustains current as the concentration increases, with 15 wt.% causing over half of the surface of the film to be conductive (Figure 8). In the lower concentrations the change in proportion was less significant, pointing to the need for high GNP concentrations to yield higher conductivity in the films. The error bars display the standard error in the data, and it is clear that there is overlap in the data at low concentrations, with significant increases in the conductive area being seen in the two highest concentrations.

The general trend in Figure 8 aligns with the observations from the optical data (Figure 2), which showed a greater presence of dark carbon-like material on the samples in the higher GNP concentrations. This aligns with the notion that the GNPs are integrating into the tribofilms and inducing conductive patches. Although tribofilm formation at higher GNP

concentrations was seen to be less in the optical data, the tribofilm material that has formed became more conductive.



Figure 7: Flowchart outlining analysis process for ascertaining conductive proportion of tribofilms.



Figure 8: Area of tribofilm that had become conductive for a range of GNP contents. Error bars display the standard error and circles represent the mean value.

The magnitudes of the currents varied up to the threshold that was possible to detect with the settings used (bias and sensitivity), at approximately 245 pA with only the 1 wt.% and 5 wt.% cases not exhibiting any currents above this detection threshold. Further investigations over larger scan areas at lower current sensitivities (allowing detection of higher magnitude currents up to approximately 25 nA) showed that all concentrations exhibited currents in the range of tens of nA in a small number of localised areas.

#### 3.3) <u>Visualisation of Surface Features</u>

After revealing the effects of the GNPs on the conductivity of the tribofilms it was deemed valuable to attempt to visualise the GNP sheets on the surface of the films. Topographic AFM images produced little of value, with the GNP flakes barely visible and difficult to differentiate from other rough features (Figure 9a,c), so an LFM trace-retrace method, described in the Methods section, was employed.

The processed LFM data was far superior in imaging the graphene sheets, as shown previously by Marsden et al. and Long et al. [50], [51]. Figure 9b is an LFM image, processed using the trace-retrace method, and shows a dark angular area in its centre with dimensions of approximately 215 x 95 nm, which is thought to be a sheet of graphene (circled in yellow). This feature exhibits very low lateral forces and jumps out as starkly different to the surrounding film in its morphology. Another example, generated using larger 25  $\mu$ m GNPs (Figure 9d), shows a large feature with dimensions of approximately 400 x 850 nm. Here, once more, is seen a very low friction region within the film, but this time it is possible to make out thin, bright striations on its surface, corresponding to higher lateral force regions (marked by yellow arrows). It is proposed that these are wrinkles in the graphene sheet, as previously noted [52], [53], [54].

The patches of current measured in the CAFM data (Figure 6) are typically of dimensions in the range 100-200 nm, suggesting that these surface graphene features, which in Figures 9a and b are 215 x 95 nm in extent, may be the cause of the local current patches. The significance of these surface features is elaborated on further in Section 4.4.

The features relate to objects that are well adhered to the surface, with 2 to 3 rescans producing the same data, giving confidence that these are real features rather than abnormal artefacts in the AFM data.



Figure 9: Topography AFM scans and corresponding LFM scans for tribofilms containing 15 wt.% of 2 um GNPs (top) and 3 wt.% of 25 um GNPs (bottom). The method allows for the detection of GNPs on the surface that are otherwise difficult to locate. GNP candidate circled (a, b), is only visible in the friction data. Examples of wrinkles are indicated by arrows (d). It should be noted that the mV values on the scale bars are modified values indicating the subtracted signal values from the detector, and therefore do not have a direct physical interpretation.

#### 3.4) Internal Structure of Tribofilms

Using TEM provided information on the overall cross-sectional appearance of a 15 wt.% GNP tribofilm (Figure 10). The thickness of the film varied significantly from hundreds of nanometres (Figure 10a) to a few nanometres in places. This, therefore evidently, included the edge region of the film. The main film material seen as the light layer (Figure 10a) contained numerous fibrous structures in a variety of configurations. The EDX map (Figure 10c) shows that this region is dominated by carbon. To the left of the EDX image is a zinc- and oxygenrich patch, likely a seam of pure ZDDP tribofilm that has not been infused with GNPs; further analysis of this patch showed a higher concentration of phosphorus and sulphur compared to the rest of the image, backing up the postulate that this is pure ZDDP tribofilm material.

Below the main film bulk a darker layer is seen on the TEM images. This layer is also rich in zinc, oxygen, phosphorous and sulphur and is likely a pure ZDDP layer formed during the early stages of rubbing. No carbon signals or fibrous structures are seen within. This layer is non-

uniform in height, with some areas having a thick covering and others having none at all (Figure 10b). The entire film is much thinner here, of the order 50 nm, with the darker pure ZDDP layer making up the whole height to the left of the image, and the lighter ZDDP/GNP material only inhabiting the volume to the right.

The darker layers to the top of the images are iridium and platinum layers used to protect the films while preparing samples.



Figure 10: TEM scans of different areas of the tribofilm, with EDX image. A thick section of film (a) with a large bulk contrasts with a thin section (b) which is dominated in thickness by the darker pure ZDDP layer. Example EDX spectrum (c) shows the domination of carbon within a separate area of the bulk of the film.

Close examination of the main bulk of the films reveals the tendril structures within (Figure 11) which resemble graphene scrolls[55], [56]. A clear example exists in Figure 11a. Here a large scroll is seen, with a lattice spacing of 0.36 nm, indicating graphene/graphite. Below this are many smaller scrolls, and close examination shows that these small wavy features appear all over the main ZDDP film, in almost all locations. Figure 11b displays more of these scrolls; some are seen to be vertically oriented, others horizontally, and numerous directions between. The sizes of these scrolls have a large variation, with some being very wide (such as in Figure 11a) and some smaller examples being almost single lines.



Figure 11: TEM images showing graphene scroll structures within the bulk of the tribofilm. A particularly large example (a) and examples of the varying orientations of the scrolls. Note that data is taken from different locations to those in Figure 10.

## 4. Discussion

### 4.1) <u>Conductivity of Tribofilms</u>

The CAFM data proved that current can be sustained through the depth of a ZDDP tribofilm once GNPs have been incorporated, with charge travelling from the upper surface of the film, through its thickness and into the substrate. Whilst CAFM can only access the surface of the sample, and hence only GNPs which are exposed at the surface will result in a CAFM signal, there must also be a current pathway through the film to the substrate in order for current to flow. This implies that any GNPs which are present at the surface, but which do not attach to such a current pathway, will show no CAFM signal, and hence the technique does not necessarily address the density of GNPs at the surface but rather the density of current pathways connected to the surface.

The magnitudes of the conductive patches are noteworthy. One may expect to see the current saturating in all conductive locations due to the high conductivities of the graphene and the steel substrate. However, a range of magnitudes are seen, suggesting that the current's path through the tribofilm may not always be direct from the top to the bottom surface. It is possible that the brighter, high current, patches represent a short and direct path through the film, whereas the darker, low current, patches require the current to flow in an indirect path, potentially tunnelling through thin regions of insulating material on its journey from the AFM tip to the substrate. Further, the small sizes of the GNPs limits their conductance, meaning that although the material is highly conductive, the amount of charge that can be transported through them is limited. These hypotheses led to the use of TEM to inspect a slice of the tribofilm further.

Due to the abundance of graphene seen within the film, it is possible that the graphene/ZDDP material may not be the dominant factor in determining whether an area of the film is conductive or not, and lead to the patches of current. A limiting factor may be the presence of graphene sheets on the surface, providing entry points into the bulk of the tribofilm. Any location on the surface of the film not sustaining graphene will be insulating, and current will not flow. Beneficially, this does not limit the possibility for the films to sustain current laterally, running along their length, parallel to the substrate. This is of relevance to the 3D TNP method of manufacturing, enabling conductive structures to be printed onto a flat surface and allowing current to flow, as in a wire. A limitation of the present method is its ability to solely measure current flowing through the thickness of the film, rather than along it.

The lower pure ZDDP layer is inhomogeneous, with gaps and varying thicknesses. This GNPfree layer limits the paths through which a current can flow to the substrate to those areas in which the layer hasn't formed. However, the effect of the insulating pure ZDDP layer at the substrate interface cannot be probed using the present setup. This is due to the ability of the charges to spread out once they enter the tribofilm bulk, meaning they can enter the substrate at any location; thus the CAFM setup registers only the location where the charge flowed into the film on the upper surface, not where they entered the substrate.

The increasing variability of conductive area grows as the concentration increases. This is likely due to the uncertainty in the concentration of GNPs in each mixture. As the GNP content gets higher, it becomes more difficult for the fluid to suspend the solids in the mix, and

sedimentation occurs. The lubricants used in the experiments were taken from the top of the blends, where less sedimentation occurred. Despite a good visual level of dispersion after extended sonication, it is likely that this accounted for a discrepancy in the true GNP concentration and introduced uncertainty.

For the application of electronics (via 3D TNP) the method appears feasible in some settings. Trigger currents for logic structures in integrated circuits can be as low as 10 pA [57], significantly below those measured here, meaning that there are viable applications for very high precision, low current carrying structures such as these. Ideally the current at which the conductive films are operating would be tuneable, allowing for the magnitude to be selected based on the application. Currents were observed up to approximately 250 pA, at which point the sensor saturated. This means higher currents may be sustained by the functionalised films, but the instrumentation was not able to measure these whilst also detecting the very small magnitude currents. Further tests were carried out with lower sensitivities, and currents up to the nA range were seen; again these saturated, suggesting the presence of higher-still currents.

The present work was limited by its inability to measure conductivities due to difficulties in accurately measuring the dimensions of the inhomogeneous tribofilms, making comparison to literature difficult. Therefore, only current values are presented. On the nanoscale these measurements would be heavily affected by the inconsistent contact area of the AFM tip on the differing gradients of the film material and inhomogeneous thicknesses, causing large variations in conductivity.

The process of adding the GNPs to the ZDDP/PAO blend proved challenging at higher concentrations due to the GNP powder drying out the oil and forming a paste. In this highly viscous form, the tribometer was unable to function. This introduced an upper limit to the concentration of GNPs that could be used with this setup; the limit was found to be around 15 wt.% GNPs. When generating functionalised tribofilms, the procedure should be to balance GNP content, achieving a large conductive area (such as in Figure 8), whilst keeping the concentration low enough that a low viscosity oil blend can be maintained. With the highest conductive area proportion of approximately 55% for 15 wt.% GNPs (Figure 8), this method may not be superior to other methods such as conductive inks for current flow through the film thickness, but it holds promise in the application of lateral current flow in nanoscale structures such as wires.

The CAFM images were taken from across the film-covered areas, meaning the data should be relatively representative of the entire film. This is however only the case for the areas where the film formed. As seen previously, the tribofilm is inhomogeneous, with a patchy appearance characteristic of ZDDP tribofilms, so the current work has only taken into account the proportion of the substrate that was covered by film.

#### 4.2) <u>Tribofilm Formation and Properties</u>

The suppression of the growth of the ZDDP tribofilms by the addition of higher concentrations of GNPs, resulting in lower film coverage, could have two origins. Either the addition of the GNPs lowered the shear force in the tribo-contact, removing the conditions necessary for tribofilm formation; or the volume of GNPs in the contact overwhelms the ZDDP molecules, keeping them from entering the contact and being transformed into tribofilm material.

Previous work by Kowalczyk et al. [33] investigated the tribological performance of lubricants containing graphene and ZDDP and showed that the graphene modified the tribofilm generation process, with the addition of graphene leading to a lower concentration of zinc material on the disc due to the graphene supplying extra energy to the ZDDP in the contact and causing it to decompose. Zhao et al. [32] also found that graphene and ZDDP affected each other's abilities to resist wear to the surface; this would likely be explained by the differences in the formed tribofilms. Both these studies used significantly lower concentrations of graphene than the present work.

Figure 6a highlighted the variations in the topography of the films, particularly evident in the smoothness of the surface. It is likely that the smooth area seen to the left of the image is an established area of ZDDP tribofilm (where the formation/wear processes have started to balance out), whereas the rough, more patchy material to the right has GNP material on the surface causing the change in its appearance. The material appears to be well adhered to the surface, proven by multiple AFM scans reproducing the features.

The inhomogeneous distribution and variability in topography of the ZDDP tribofilms limits the utility of the method for a precision manufacturing application, where a more reliable coverage would be necessary.

Under optical and electron microscopy, it was clear that the GNPs had accumulated into patches on the surface. The reason for this is likely due to the loose GNP material being compacted, effectively creating a localised sintered carbon tribofilm. The carbon signals seen outside the wear tracks in the EDX maps are likely due to either loose GNP-based material on the surface, or residual oil leftover from the tribofilm formation process. Inside the wear track this could also be the case, but it is more likely due to the compressed GNP material. It should be noted that the data presented in this work used the best case scenario (highest GNP concentration to initiate currents), but in reality this GNP content may be excessive and cause extra graphene to accumulate on the surface.

#### 4.3) <u>Tribofilm Functionalisation Mechanisms</u>

Despite the surface build-up of carbon material, the CAFM work confirmed that the GNPs had indeed been integrated effectively into the structure of the films to some extent. This was supported by the TEM cross-sectional images showing the scroll structures of the graphene within, revealing a semi-continuous network of conductive paths. For both of these datasets the tribofilm used was that of the 15 wt.% GNPs case. This sample was selected to give the best chance of observing graphene within the body of the film.

The TEM data revealed much about the internal structure of the films. Particularly noteworthy was the configuration of the scrolls of graphene within the bulk of the films. Considering that this was a 50 nm thick cross section, it is reasonable to conceive that the existence of conductive paths through the film thickness is feasible, travelling along the graphene scrolls. By considering these paths through the film, one can see how charge carriers could be reduced in number by interacting with small insulating gaps in the path. Some carriers could tunnel through the gap, while others couldn't. This would reduce the current measured in that area, thus creating variation in the currents measured over the whole film.

The wide range of widths and lengths of the scrolls is likely due to a couple of factors. Firstly, the angle at which the scroll has been sliced by the FIB will influence the width (sliced through its centre the scroll will appear wider than if it were sliced at its edge), and secondly, the size of the graphene sheet itself prior to being rolled. The sizes of the sheets are likely to vary, with a larger one rolling into a structure with more layers than that of a smaller sheet, as well as possessing a greater length. It should be noted that the TEM images are projections of a 3D volume onto a 2D surface, meaning that structures behind one another may overlap. During the analysis, care was taken to avoid any such features, focusing as best as possible on single features. Similarly, this projection effect can cause measurements to vary slightly due to viewing angle.

Atomic layer separations in the graphene were calculated using the scale bar on the TEM images, a histogram of these values is shown in Figure 12. Considering the calibration of the instrument, the discrepancy between the literature value of 0.33 nm and the value given here of 0.36 nm, along with the aforementioned difficulty in finding perfectly aligned examples, gives reasonable confidence that these are indeed scrolls of graphene.



Figure 12: Histogram showing the relative occurrences of lattice spacings.

Further, the nature of the tribofilm itself was of note, with a structure consisting of a carbonrich layer sitting atop a pure layer of ZDDP tribofilm. This carbon-rich layer did exhibit the elemental markers of ZDDP, but in far lower quantities than the lower ZDDP layer. This aligns with the observations of Pham et al. [28], who found that high concentrations of graphene suppressed the formation rate of ZDDP tribofilm material, and resulted in a dual-layer structure. With varying elemental makeup of the layers, it is likely that the conductivity of the tribofilm is dependent on the presence of the carbon-rich layer, with the base ZDDP layer blocking the paths of charges travelling through the tribofilm thickness. The inhomogeneity of the relative thicknesses of the layers also plays a role in the conductivity. It was seen that the relative thicknesses of the layers varied significantly (Figure 10), meaning that areas with a

thick ZDDP layer will be less susceptible to sustaining currents compared to thick regions of carbon-rich material.

When assessing the utility of this methodology for distributing GNPs within a ZDDP tribofilm for conductivity modification, the outcome was positive for the highest concentration case. The presence of the graphene scrolls ubiquitously throughout the bulk of the film suggests that current should be able to flow throughout it via the relatively even distribution of graphene.

#### 4.4) <u>Imaging of Surface Graphene</u>

While this experiment was not designed to characterise graphene wrinkles, meaning the tip geometry of the AFM lacked the very high precision needed to truly measure their topography, it was possible to carry out some rudimentary measurements of the width of these features using the LFM data. To the best of the authors knowledge, this is the first example of graphene wrinkles being detected on a ZDDP tribofilm via LFM when they were otherwise difficult to detect through topography data. The method is most useful for samples in which complex topography changes make detection via topographic AFM complicated, and simplifies the detection process.

Examples of line profiles from the LFM data can be seen in Figure 13. The values on the yaxes do not have a direct physical interpretation due to the fact that some impact of topography on LFM is difficult to avoid even using the trace-retrace method, but can loosely be interpreted as areas of higher friction. The distances on the x-axes however are physically meaningful, allowing the widths of these features to be quantified, with a maximum resolution imposed by the finite size of the AFM tip. The wrinkle features vary considerably in width, making them difficult to measure, with some being far larger than others. The very large features (such as those seen to the centre of the top of the low friction area) have been discounted and instead the high aspect ratio wrinkles have been considered. In other words, the more narrow features. It is possible that the larger accumulations are film material, but this cannot be confirmed by this dataset. By measuring 14 of the tendril-like structures at several locations, it was possible to quantify their base widths. Figure 14 plots the occurrences for each wrinkle thickness and shows that 76% of the wrinkles sit within the 15 - 25 nm category. This is in the range of those values seen in the literature. Wang et al. [52] reported wrinkle widths of around 11 nm and Hu et al. [53], when investigating the effect of strain on wrinkle suppression, found that samples under no strain supported wrinkles with widths of approximately 24 nm. Zhu et al. [54] found that wrinkles existed in a much wider range, with examples as low and high as ~16 nm and ~135 nm. Taking these values into account, the widths presented in this work sit in a similar area, towards the lower end. It could be that the wrinkles seen in this work were not subject to the extreme temperature changes brought on by the CVD process of those referenced previously, resulting in less material forming into the wrinkles. Further, this work solely considered the very thin wrinkles, but some of the larger features (that were difficult to identify here) may be relevant. It should be stated that the AFM tip radii were of a size comparable to

the lowest values detected, suggesting that smaller detected wrinkles would be more representative of the tip width than the true wrinkle width.



Figure 13: LFM data processed using the trace-retrace method (a), and plots showing the line profiles of wrinkles (b). Note that the units on the y axis are arbitrary, and do not represent height.



Figure 14: Histogram displaying the relative occurrences of different sized wrinkle features in Figure 9d.

The trace-retrace method has been shown to be effective in imaging graphene sheets on the surface of the tribofilms, working to enhance their visibility by highlighting very low friction regions on the surface while suppressing the effects of topography. This method could be utilised to image other atomically thin materials layered on substrates. Here the technique has revealed possible wrinkles in the graphene. Wrinkles have previously been observed often on graphene sheets formed via chemical vapour deposition (CVD) methods [52], [53], [58]. In the case of CVD, the wrinkles form due to the differential coefficients of expansion of the graphene

and substrates under cooling (the CVD process takes place at temperatures of the order 1000°C [53]. During cooling, the substrate shrinks while the graphene sheet expands, resulting in a bunching up of the graphene and wrinkles forming on its surface. This mechanism could be behind the wrinkles caused here, with the films being formed under elevated temperatures of 80°C, before cooling to room temperature for analysis. The flash temperatures involved, calculated using the method described in the Methods section, caused a rise of 21.2°C, meaning the temperatures are significantly below those found in CVD. Alternatively, the formation process under rubbing could be the cause. With shear forces being applied to the graphene, it is feasible that the sheet is deformed while the ZDDP material is forming around it, anchoring it in place. Wrinkles have been generated outside of the CVD method in graphene and graphene oxide by Liang et al. [59] and Deng et al. [60], but these were formed with specific apparatus designed to wrinkle the sheets by pre-stretching the substrates, rather than as a by-product of another process.

The size of these graphene features are much smaller than the nominal size of the GNPs. This may be due to the selective retention of smaller particles in the mixing process, whereby large GNP particles settle more quickly to the bottom of the lubricant blend, leaving the smaller, lighter particles available for use when filling the tribometer. It is also possible that the smaller particles are able to incorporate into the tribofilm, whereas the larger ones aggregate into the carbon patches seen in Figures 2 and 3; or that the sheets are damaged by the rubbing process, breaking into smaller particles in the process. An alternative suggestion is that the sheets are not adhered to the outer surface of the film, but embedded within the upper layers of the film, meaning the edges of the GNP sheets are submerged beneath the film surface. This suggestion holds with the supposition that the GNPs enable conductivity by creating a matrix through the depth of the tribofilms, allowing a conductive network to exist, carrying current from the upper to lower surface of the tribofilm.

#### Conclusion

This work has presented a method by which zinc dialkyldithiophosphate (ZDDP) tribofilms can be functionalised using graphene nanoplatelets (GNPs) to become electrically conductive; the amount of conductive area being dependent on the concentration of GNPs. Further, the higher the concentration of graphene, the less uniform the coverage of tribofilm due to suppression of the film growth. Transmission electron microscopy (TEM) analyses of tribofilms show that the graphene sheets roll into scroll structures and create a network through which the current can flow through the tribofilm thickness, which has a dual-layer structure, with the carbon rich layer sitting above a pure ZDDP layer. A method using lateral force microscopy (LFM) to detect surface graphene sheets that were not easily visible in topographic atomic force microscopy (AFM) scans has been demonstrated, as well as its ability to image features, such as wrinkles, in the graphene sheets, allowing for quantification of their widths. This work is the first experimental study that demonstrates the electronic functionalisation of tribofilms, and may one day find application as a single-process manufacturing technique for the fabrication of, for example, electronic structures such as wires, potentially in advanced environments such as zero gravity.

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