Composite Nanosheets of Graphene and Boron Nitride for Lubrication Application

by

Yuchen Liu
(B. Eng.)

Submitted in fulfilment of the requirements for the degree of

Master of Engineering

Deakin University

November, 2017
I am the author of the thesis entitled

**Composite Nanosheets of Graphene and Boron Nitride for Lubrication Application**

submitted for the degree of **Master of Engineering**

This thesis may be made available for consultation, loan and limited copying in accordance with the Copyright Act 1968.

'I certify that I am the student named below and that the information provided in the form is correct'

Full Name: ...........................................Yuchen Liu.................................................................

Signed: ..............................................................................................................................................

Date: .................................................. 9/11/2017..................................................................
I certify the following about the thesis entitled (10 word maximum)

**Composite Nanosheets of Graphene and Boron Nitride for Lubrication Application**

submitted for the degree of **Master of Engineering**

a. I am the creator of all or part of the whole work(s) (including content and layout) and that where reference is made to the work of others, due acknowledgment is given.

b. The work(s) are not in any way a violation or infringement of any copyright, trademark, patent, or other rights whatsoever of any person.

c. That if the work(s) have been commissioned, sponsored or supported by any organisation, I have fulfilled all of the obligations required by such contract or agreement.

d. That any material in the thesis which has been accepted for a degree or diploma by any university or institution is identified in the text.

e. All research integrity requirements have been complied with.

'I certify that I am the student named below and that the information provided in the form is correct'

**Full Name:** Yuchen Liu

**Signature Redacted by Library**

**Signed:**

**Date:** 09/11/2017
Acknowledgement

I express my heartfelt thanks to Prof. Ying (Ian) Chen, my associate supervisor Dr. Dan Liu and Dr. Luhua Li. All my supervisor team gave me an excellent guidance, encouragement and supervision. Every valuable suggestion guides me on the right track of my research. I would like to thank Dr. Alexey. M. Glushenkov and Dr. Daniel Fabijanic for their selfless help and important suggestion. Dr. Mateti Srikanth for transferring his knowledge to me. During the experiments, Mateti Srikanth gave me a useful training and assistance. I would like to thank Prof. Xuequan Liu and Ms. Chao Li from Powder Metallurgy Department, Central Iron and Steel Research Institute, China for tribology test. I would like to thank Ms. Helen Woodall for her support during my master study. I would like to thank the help from our technical staff Robert Lovett for lab trainings. I would like to thank Dr. Andrew Sullivan for SEM training, Mr. Rob Pow for XRD and TGA training, and Dr. Jinfeng Wang for BET training. I would like to thank all nanotechnology group’s members for giving me support and valuable advices. My final thanks go to my beloved families specially my parents for their wonderful support and encouragement throughout these years of my study.
Related publication

Yuchen Liu, Srikanth Mateti, Chao Li, Xuequan Liu, Alexey M. Glushenkov, Dan Liu, Lu Hua Li, Daniel Fabijanic, and Ying Chen. Synthesis of Composite Nanosheets of Graphene and Boron Nitride and Their Lubrication Application in Oil, *Advanced Engineering Materials*, 1700488. DOI: 10.1002/adem.201700488.
Abstract

Two-dimensional nanosheets, including graphene and their structural analogues, such as hexagonal boron nitride and transition metal dichalcogenides, have attracted great interest and have been intensively investigated in recent years. Graphene and graphene-like materials have exhibited various extraordinary physical and chemical properties. In parallel, another research field has recently emerged, in which monolayers of nanosheets are reassembled into heterostructures of composite nanosheets that have demonstrated new phenomena and remarkable properties over homogeneous nanosheets.

Various methods have successfully been used to fabricate composite nanosheets, including chemical vapor deposition (CVD), mechanical transfer and facile hydrothermal methods. However, synthesis of composite nanosheets at a large scale remains difficult.

Ball milling can be used to produce homogeneous nanosheets with controlled structures. During ball milling, milling balls provide shear forces that exfoliate nanosheets from bulk materials, while the in-plane structure of the nanosheets is protected by the ammonia in the milling atmosphere. Thus, composite nanosheets can be directly fabricated from ball milling processes, which enable fabrication at large quantities.

Additionally, graphene and BN nanosheets are well-known lubricants as their flake morphology allows penetration and stable deposition into the rubbing area, preventing direct contact between sliding surfaces. However, their composite has not been previously studied as a lubricant. In this thesis, the anti-wear properties of
graphene/BN composite nanosheets are investigated, and it is shown that composite nanosheets have better wear resistance than each individual nanosheets.
List of figures

Figure 2.1 Schematic diagram of the layered structure of graphite and hexagonal boron nitride.

From http://www.substech.com/dokuwiki/doku.php?id=graphite_asSolid_lubricant

Figure 2.2 Graphene monolayers can be seen as the building blocks of the graphite family.[1]

Figure 2.3 Schematic diagram of the layered structure of MoS$_2$.[2]

Figure 2.4 Current 2D material library.[3]

Figure 2.5 Two mechanical routes for exfoliating graphite into graphene flakes and the auxiliary route for fragmentation.[4]

Figure 2.6 Exfoliation of nanosheets via ball milling.[5]

Figure 2.7 Schematic diagram of van der Waals heterostructures.[3]

Figure 2.8 Schematic diagram of the CVD process conducted to synthesize composite nanosheets.[6]

Figure 2.9 Schematic diagram of the mechanical transfer used to synthesize composite nanosheets.[7]

Figure 3.1 Schematic of a ball milling device.

Figure 3.2 Effect of magnet position on ball movement.[8]

Figure 3.3 Photograph of the X-ray diffractometer.

Figure 3.4 Photograph of the Hitachi S4500 Zeiss Supra 55VP.

Figure 3.5 Photograph of the JOEL JEM-2100F.
Figure 3.6 Photograph of the MRS-10A four-ball wear tester.

Figure 3.7 Schematic of a four-ball wear tester.

Figure 3.8 Photograph of the Leica DMI 3000M microscope. From http://www.leica-microsystems.com/products/light-microscopes/industrial-materials/inverted-microscopes/details/product/leica-dmi3000-m/.

Figure 3.9 An example of wear scar photograph.[9]

Figure 4.1 XRD patterns of BN and graphite with different milling times, +: Graphite, *: BN.

Figure 4.2 SEM images of the graphite and BN mixture samples milled for different times: (a) 1 h; (b) 20 h; (c) 40 h.

Figure 4.3 (a) TEM images of graphene/BN composite nanosheets produced by ball milling for 20 h; (b) high-magnification TEM image; (c) enlarged TEM image of the selected area (indicated by the box); (d) EELS spectra of graphene/BN composite nanosheets.

Figure 4.4 Energy-filtered TEM data: (a) an elastic TEM image; (b) an energy-filtered image of the same area with elemental contrast (boron-red, carbon-green); (c, d) individual energy-filtered maps of boron and carbon.

Figure 5.1 SEM images of the graphite and BN mixture samples milled for 20 h: (a) 20 h sample with the oleic acid and carbon coating; (b) the 20 h sample without the oleic acid and carbon coating.

Figure 5.2 Last nonseizure load and weld point of the base oil and the oil containing graphene/BN composite nanosheets.
Figure 5.3 Optical microscopy images of wear scars of the steel balls tested in (a) neat base oil and (b) base oil with graphene/BN composite nanosheets (four-ball method, 1770 rpm, 392 N, 10 second).

Figure 5.4 Average diameters of wear scars under different loads in mineral base oils added with the composite nanosheets prepared using different milling times (a) and in the oils with different nanosheets (b) (four-ball method, 1770 rpm, 10 second).

Figure 5.5 Schematic of possible lubrication mechanism of graphene/BN composite nanosheets as lubricating activities in oils.

Figure 5.6 Friction coefficient for the neat base oil and the base oils containing different nanosheets (four-ball method, 1770 rpm, 200 N, 10 min).
Chapter 1

Introduction

1.1 Overview

The concept of nanotechnology was first introduced in 1959.[10] Inspired by the theory of nanotechnology, nanomaterials then received intensive attention from researchers in the 1980’s. The physical and chemical properties of nanomaterials are significantly different from bulk materials due to their large surface area and to quantum confinement effects that arise when a material’s size is reduced to the nanoscale.[11] Thus, nanomaterials exhibit unique optical, electronic, magnetic or mechanical properties that endow them with diverse applications in aerospace, automobiles, semiconductors, and chemistry.

Nanomaterials can be typically categorized into four spatial scales, from zero-dimensional (0D) to three-dimensional (3D). Nanomaterials with all of their dimensions in the nanoscale are classified as 0D nanomaterials and include nanoparticles, fullerenes, and quantum dots. Nanowires and nanotubes, which have a nanoscale diameter but a length in micrometre range, are categorized as one-dimensional (1D) nanomaterials.[12, 13] Nanomaterials which have only one dimension in the nanoscale are called two-dimensional (2D) nanomaterials and include nanosheets. 3D nanomaterials include piled nanosheets and bundled nanowires.

Because their unique properties have attracted great interest, many reports related to 2D nanomaterials have been published. Recently, the focus has shifted from homogeneous nanosheets to composite nanosheets, which are constructed from van
der Waals heterostructures. In this thesis, it has been demonstrated that the composite nanosheets can be large-scale produced by high-energy ball milling. Additionally, the wear resistance of the composite nanosheets has been investigated.

1.2 Thesis objectives

The objectives of the thesis are summarized as follows:

- To understand how the crystalline structure of composite nanosheets changes during the ball milling process.
- To understand the morphologies of composite nanosheets.
- To explore how the ball milling duration affects the morphology of composite nanosheets.
- To develop optimal ball milling conditions for the mass production of composite nanosheets.
- To study the wear resistance of graphene/BN composite nanosheets as a lubricant additive in oil.
- To study the effects of the size and morphological features of the composite nanosheets resulting from different milling times on their anti-wear properties.
- To study the wear resistance of homogeneous nanosheets and composite nanosheets produced using the same conditions.

1.3 Thesis structure

This thesis is presented in six chapters. The content of each chapter is summarized below:

Chapter 1: Overview of nanomaterials and list of the objectives of this thesis.
Chapter 2: Literature review to provide background information.

Chapter 3: Synthetic methods and characterization techniques used in this thesis.

Chapter 4: Synthesis of composite nanosheets of graphene and boron nitride.

Chapter 5: The lubrication application of graphene/BN composite nanosheets in oil.

Chapter 6: Conclusions and future work.
Chapter 2

Literature review

2.1 Two-dimensional nanosheets

Two-dimensional nanosheets are nanomaterials which have one dimension reduced to the nanoscale. Ideally, the thickness of nanosheets is only a single atom thick, but due to the difficulty of their syntheses, nanoscale thicknesses are also acceptable. These layered materials can be used as raw materials to synthesize nanosheets, such as graphite, hexagonal boron nitride (h-BN) and transition metal dichalcogenides (TMDs). Figure 2.1 exhibits the structures of graphite and h-BN. These materials have strong in-plane chemical bonds but weak interlayered bonds, which are called van der Waals bonds.[14] These interlayered bonds can be easily cut off by shearing force or vertical expansion. Thus, nanosheets can be obtained from the materials held together by van der Waals bonds.

![Graphite structure](image)

![Hexagonal boron nitride structure](image)

*Figure 2.1 Schematic diagram of the layered structure of graphite and hexagonal boron nitride.*

*From http://www.substech.com/dokuwiki/doku.php?id=graphite_as_solid_lubricant*
2.1.1 Graphene

In 2004, graphene was first obtained via mechanically exfoliated graphite; after peeling repeatedly with Scotch tape, the thickness of the graphite flakes shrank to a few atomic layers. This novel material was called graphene.[15] Graphene consists of a flat monolayer of benzene-rings, which has strong sp² covalent in-plane bonds, and exhibits various extraordinary properties such as a high theoretical specific surface area (2630 m²g⁻¹), a high current capacity that reaches up to 10⁹ A/cm²,[16] a high electron mobility (200,000 cm²v⁻¹s⁻¹),[17] a high thermal conductivity (5×10³ Wm⁻¹k⁻¹),[18] quantum Hall effects at room temperature,[19] a strong mechanical strength[20] and many other unique properties. Moreover, the extended honeycomb structure of graphene is seen as a basic building block of other allotropes, such as fullerenes, nanotubes and graphite. For example, it can be wrapped up to make fullerenes, rolled into nanotubes and stacked to form graphite, as shown in Figure 2.2.[1] Hence, graphene shows great promise in applications such as lubrication, biological and chemical sensors, optical devices, photovoltaics and energy storage.

![Figure 2.2 Graphene monolayers can be seen as the building blocks of the graphite family.][1]
2.1.2 Hexagonal boron nitride (h-BN)

Hexagonal boron nitride (h-BN) is a layered material with a honeycomb structure similar to graphite. Hexagonal boron nitride stacks via planar reticulation of BN hexagons, which consist of an equal number of boron and nitrogen atoms alternating around a ring. Structurally, h-BN is an analogue of graphite, which has strong sp\(^2\) covalent in-plane bonds and weak van der Waals bonds between each layer.[21] As graphene has demonstrated several unique properties, its BN counterpart — BN nanosheets in which B and N atoms substitute C atoms — has received intense interest. Similar to graphene, BN nanosheets exhibit high thermal conductivity and high mechanical strength, but they also have distinctly different properties. The electronic properties of BN nanosheets are quite different from those of graphene: compared with the zero band gap of graphene, the wide band gap (approximately 5.9 eV) of BN nanosheets[22] makes them a good insulator, which can be used in electronic equipment as charge leakage barrier layers. Additionally, BN nanosheets have exhibited high thermal stabilities — high-quality BN nanosheets can survive up to 850 °C in air — which is much high than that of graphene, which etches at 450 °C.[23] Moreover, BN nanosheets have exhibited many other excellent properties, such as high CO\(_2\) adsorption,[24] super hydrophobic properties[25] and light emission in the deep ultraviolet.[26, 27]
2.1.3 Transition metal dichalcogenides (TMDs)

Another 2D nanomaterial family is transition metal dichalcogenides (TMDs). The generalized formula of a TMD is MX$_2$, where M is an element from groups 4–7 and X is a chalcogen such as Se, S and Te. Similar to h-BN and graphite, bulk TMD materials contain strong in-plane bonds but weak interlayer bonds. The chalcogen atoms of TMDs are saturated, and therefore individual TMD nanosheets can be obtained from TMD materials. Each individual layers of a TMD nanosheet consists of three single atomic layers, with a transition metal layer between two chalcogen layers.[28] For example, the structure of MoS$_2$ is shown in Figure 2.3.[2] The properties of TMD monolayers were significantly different from their bulk counterparts because the charge carriers were restricted in X- and Y-directions. For example, the band gap dramatically changes when a bulk TMD is reduced to a monolayer. The 1.3 eV indirect band gap of bulk MoS$_2$ is reduced to a 1.9 eV direct gap when MoS$_2$ is reduced to a monolayer, and as a result the monolayer shows strong photoluminescence. Similarly, other TMD materials present this property as well, such as WS$_2$; the band gap of WS$_2$

![Figure 2.3 Schematic diagram of the layered structure of MoS$_2$.][2]
changes from 1.4 eV to 2.1 eV when the structure is reduced to the monolayer.[29]
Moreover, different M atoms have different coordination numbers and oxidation states. For example, TMD sheets are semiconducting when Mo or W was selected for M; in contrast, TMD sheets are metallic when M was Nb or Re.[30] Many other attractive properties of 2D transition metal dichalcogenides have been reported, such as half-metallic magnetism,[31] charge density waves[32] and superconductivity,[33] resulting in a wide array of applications for 2D TMDs, including lubrication,[20] catalysis[34] and photovoltaics.[35] However, not all TMDs can be stable in a free-standing monolayer honeycomb structure. There are 88 possible MX$_2$ compounds, but theoretical calculations based on density functional theory show that only 44 of them can exist in MX$_2$ monolayers.[36]

### 2.1.4 Other 2D nanomaterials

There are also many other 2D nanomaterials that exist under room temperature in the air. Geim and Grigorieva introduced the ‘2D library’ shown in Figure 2.4.[3] The materials that are marked in blue have been proven to be stable in ambient conditions and include graphene and h-BN. The green labels, including MoO$_3$ and WO$_3$, were possibly stable in air. Materials that are steady under an inert atmosphere but unstable in the air are shaded in pink. Those that have been successfully synthesized as single layers but demand further study have been marked as grey.
2.2 Synthesis methodology

Since 2D nanosheets have been brought to the forefront of research efforts, owing to their exceptional properties and promising applications, many methods have been developed to synthesize them. Generally, the synthesis method of 2D nanosheets can be summarized as two major methods: top-down methods and bottom-up methods. Here, graphene is selected as an example to explain these synthetic approaches.

2.2.1 Bottom-up method

Epitaxial growth via chemical vapour deposition (CVD) is the typical bottom-up method, and it relies on the chemical reaction and activation of gaseous reactants to build a 2D structure. High-quality 2D nanosheets with few structural defects were controllably produced using this strategy. The technique for synthesizing few-layer graphene via CVD was first reported in 2006[37] and then continually evolved to control the number of layers and the density of grain boundaries, to prevent defects and so on. Typically, CVD consists of four steps, including heating, annealing, growing
and cooling, and catalytic metals, such as Ni and Cu, are selected as substrates for the graphene to grow.

Graphene was first shown to grow on a Ni substrate via CVD by Reina et al. [38] The reaction occurred in a CH₄ atmosphere, which provided carbon atoms. Firstly, Ni films were annealed in a mixture of argon (Ar) and hydrogen (H₂) gas at 900–1000 °C. The grain size of the Ni films was increased and certain impurities were eliminated during this procedure to improve the quality of the substrate for graphene growth. Secondly, the H₂ and CH₄ were introduced into furnace chamber and heated at 1000 °C for 20 min, and the carbon atoms provided by CH₄ reacted with the Ni atoms to form a Ni-C solid solution. Thirdly, the sample was cooled to room temperature in an Ar atmosphere, during which carbon atoms diffused out from the solid solution to form graphene on top of the Ni film. Finally, the graphene film was transferred to another substrate to isolate it. [39] Ni has exhibited excellent properties as a substrate for graphene growth via CVD process because it has similar lattice constants and hexagonal lattices. Moreover, several other metals have been investigated as substrates to produce graphene, such as Ru,[40], Pt[41] and Cu.[42] Cu was investigated because it is economical and shows good controlling capabilities of graphene growth. Similarly, Cu foil was annealed in H₂ gas at 1000 °C. A mixture of H₂ and CH₄ gas was passed through the furnace, and graphene was grown continuously on the foil’s surface. After cooling the foil to room temperature, graphene was obtained.[42] However, the CVD process can only produce one film in each experiment and has limited production.
2.2.2 Top-down method

The top-down method is the simple and reliable strategy, which was the first synthesis method. The top-down method relies on mechanical exfoliation due to the weak interlayer van der Waals bonds. Generally, mechanical exfoliation occurs via two routes: normal force and shear force. Fragmentation can occur during mechanical exfoliation if the normal force is too strong. A schematic diagram of these forces is illustrated in Figure 2.5.[4]

![Schematic diagram of normal force, shear force, and fragmentation.](image)

Figure 2.5 Two mechanical routes for exfoliating graphite into graphene flakes and the auxiliary route for fragmentation.[4]

Normal forces, for example, from micromechanical cleavage, is responsible for tearing van der Waals bonds between each graphite layer to obtain graphene. In 2004, Novoselov and Geim first reported graphene prepared by the micromechanical exfoliation of graphite. Highly ordered pyrolytic graphite (HOPG) was chosen as the raw material, and Scotch tape was used to divide graphene flakes from the HOPG. Scotch tape provides a normal force to the surface of graphite, and after several iterations, the HOPG flake was reduced to only a single layer, i.e., graphene was obtained.[15, 43] However, this method costs time and is repetitive, which unsuitable
for large scale graphene production, so many researchers focus on methods to increase graphene production. Sonication of graphite in a liquid can provide large-scale production. This method was first presented by Coleman’s group in 2008,[44] who dispersed graphite powders in N-dimethylformamide (DMF) and N-methylpyrrolidone (NMP) (organic solvents) and then sonicated the mixture. This method can reduce the cost of graphene production, but the quality of the product is unsatisfactory.[45]

Shear force is another route for exfoliating layers from bulk graphite and is used by fluid dynamics methods and ball milling. Fluid dynamics strategies rely on mechanical exploitation provided by moving liquid to break van der Waals bonds. Two different peeling processes were developed to exfoliate graphene from graphite. The first approach was introduced by Chen et al. and is called vortex fluidic exfoliation. In this process, graphite was dispersed into an organic solvent, transferred into a tube and then rotated rapidly. During this rotating, friction occurs on the tube wall, causing the graphite to peel into graphene.[46] The second technique, in which the organic solvent with graphite is pressurized into a channel, also uses shear forces. Graphite was exfoliated to form graphene via the mixture slipping against the channel.[47]

Moreover, controlled ball milling using ammonia or hydrocarbon gases as exfoliation agents has been found to be an efficient and high-yielding method to produce to nanosheets[48] that are flat and maintain their single-crystalline structure and low defect density even after a long period of milling. During the ball milling process, NH₃ and C₂H₄ molecules chemically adsorbed onto the nanosheet surfaces and acted as a lubricant that reduced the milling impact on the nanosheets. The gas molecules attached at the edges and at defect sites underwent chemical reactions, healing the
defects by saturating the dangling bonds. Two different forces, shear force and fragmentation force were present during the ball milling procedure. The shearing force is responsible for peeling layers from the bulk graphite, in which van der Waals bonds were cut by the shearing force, as shown in Figure 2.6.[5] The fragmentation appears due to normal force from the milling ball collision, resulting in the small graphene flakes. If the fragmentation force can be decreased, the size of graphene will be larger.

![Figure 2.6 Exfoliation of nanosheets via ball milling.[5]](image)

In summary, 2D nanosheets can be synthesized from either bottom-up and top-down approaches. The top-down method is economical and effective compared to the bottom-up method. In top-down strategies, mechanical exfoliation from either normal or shear forces have been used to produce single-layer or few-layer nanosheets, and these methods have potential for the industrial fabrication of nanosheets. This project investigates production of nanosheets with the ball milling method.

### 2.3 Composite nanosheets

Although homogenous 2D nanosheets have demonstrated outstanding properties, composite nanosheets, combinations of different nanosheets, have been reported to have various enhanced properties compared with homogenous nanosheets. Xie et al. demonstrated that MoS$_2$ and reduced graphene oxide (rGO) composite nanosheets could be used as anodes in sodium-ion batteries as the heterointerface in the MoS$_2$...
and rGO composite nanosheets significantly improved the electronic conductivity and storage of Na ions, which significantly improved the performance of the batteries.[49] Yang et al. have reported that WS$_2$ and reduced graphene oxide composite nanosheets demonstrated higher activity for the hydrogen evolution reaction than pure WS$_2$ nanosheets.[50] Leven et al. reported that a stable superlubricity state occurred between the sliding interface of sufficiently large graphene and BN layers, which was almost impossible at the interfaces of homogenous graphene.[51] In addition to the aforementioned properties, other excellent properties of composite nanosheets have been studied in applications such as electronic devices,[52] photocatalysis[53] and biomedicine.[54] These hybrid materials have exhibited unique properties, so it is important to understand their composite structure.

The fundamental principle of composite nanosheets is simple. The composite nanosheets are made by stacking different nanosheets on the top of each other. In this hybrid structure, strong in-plane chemical bonds ensure each layer is stable, and van der Waals bonds keep each layer stacked together. Ponomarenko et al. first described a novel van der Waals heterostructure and suitably named it a ‘sandwiched structure’.[55] This ‘sandwiched structure’ consisted of two monolayers of graphene with one monolayer of BN nanosheets in the middle. Furthermore, various composite nanosheets could be obtained via combining different individual nanosheets, as shown in the schematic diagram of composite nanosheets in Figure 2.7.[3]
2.3.1 Anti-wear properties of the composite nanosheets

2D nanosheets have a lamellar crystalline structure in which the bonding within each layer is strong and covalent but the interlayered van der Waals bonds are weak. 2D nanosheets such as graphene and BN nanosheets have flat, plate-like shapes, and can easily shear at their contact interfaces. Because of their excellent mechanical strengths, high thermal stabilities and resistance toward oxidation, homogenous 2D nanosheets already show excellent performance for lubricant applications.

Although homogeneous nanosheets are well-known lubricants, composite nanosheets may surpass their anti-wear properties. Wang et al. have reported that the interlayer friction of fluorographene and MoS$_2$ composite nanosheets is reduced to 1/40 of that in fluorographene homogenous nanosheets and 1/160 of that in MoS$_2$ homogenous nanosheets.[56] Furthermore, Leven et al. have suggested via first principle calculations and modelling that a robust superlubricity state occurred in van der Waals heterostructures. They found that the friction was vanishingly small when
graphene slides on top of BN layers. However, these studies were focused on the interlayer friction of composite nanosheets, and the wear resistance of composite nanosheets as a lubricant in oil still requires experimental verification.

### 2.3.2 Synthesis of the composite nanosheets

Using heterostructures, various strategies similar to those used to synthesize homogenous nanosheets were successfully used to produce composite nanosheets, such as CVD, mechanical transfer and facile hydrothermal methods. The CVD process was based on the principle of heterostructures, in which composite nanosheets were grown by one-nanosheet on top of the surface of others nanosheets. As a typical example, Yunus et al. reported a vertical heterostructures of MoS$_2$ and graphene nanoribbons using a two-step CVD strategy, as shown in Figure 2.8. The graphene nanoribbons were first synthesized on Cu films at 975 ℃, and then the graphene nanoribbons were transferred onto a SiO$_2$/Si substrate. The graphene nanoribbons were used as a template and the MoS$_2$ was directly grown onto their surface by a second CVD process.

![Figure 2.8 Schematic diagram of the CVD process conducted to synthesize composite nanosheets.][6]
Similarly, many studies have reported that composite nanosheets have been successfully produced by mechanical transfer or facile hydrothermal strategies. Figure 2.9 illustrates the use of a mechanical transfer process to synthesize graphene and h-BN composite nanosheets.[7] In this method, h-BN nanosheet monolayers were obtained via mechanical exfoliation and were transferred onto a silicon wafer; the graphene was exfoliated onto a PMMA polymer stack. The bottom polymer layer is dissolved by DI water, and then the graphene with the hydrophobic PMMA layer floated to the top of the water. Transferring the graphene to the h-BN substrate was accomplished using a micromanipulator, and once the PMMA membrane was removed, the graphene and h-BN composite nanosheets were obtained. Furthermore, Xie et al. reported that sheet-on-sheet MoS$_2$ and reduced graphene oxide composite nanosheets can be produced by a facile hydrothermal method.

![Figure 2.9 Schematic diagram of the mechanical transfer used to synthesize composite nanosheets.][7]

Although the various methods have successfully produced composite nanosheets, synthesizing composite nanosheets in a large quantity is still a challenge. CVD, mechanical transfer and facile hydrothermal methods, cannot use for high-yield production. Constrained by limited production, a few researcher focus on the
application of composite nanosheets. Thus, exploration of an efficient method to produce a large quantity of composite nanosheets, and their possible application will be the main aims of my master study.
Chapter 3

Synthetic methods and characterization techniques

3.1 Synthetic methods

Composite nanosheets can be synthesized by several methods, but improving the production yield remains difficult. Inspired by the techniques used to synthesize homogenous nanosheets, ball milling is one possible candidate for producing composite nanosheets.

Bulk graphite and hexagonal boron nitride were chosen as the starting materials due to being weakly bound by long-range van der Waals forces between layers, and high-energy ball milling was selected to produce the nanosheets. The milling conditions are very important to the milling process and include the milling time, milling speed, milling medium, the ratio of the ball and the materials.

During the high-energy ball milling process, the materials are subject to large amounts of energy from the collisions between the balls and the walls of jars, which can result in structural changes and chemical reactions. This energy permits the 2D bulk materials to be broken into nanosheets. Moreover, adding an external magnet to the ball milling device can control the ball movement and further increase the energy. In 1991, Calka and Radlinski introduced a ball milling device with an external magnet that could control the rolling route of the balls and increase the energy, as shown in Figure 3.1. The ball milling process was affected by two major factors: the ball rolling route and the energy. Through changing the position of the magnet, the rolling route of the balls could be controlled. A controlled ball milling process can not
only reduce the fragmentation force but also increase the shear force by directing the balls’ movements, as shown in Figure 3.2.[8]

*Figure 3.1 Schematic of a ball milling device.*

*Figure 3.2 Effect of magnet position on ball movement.[8]*

In this project, high-energy vertical-rolling ball mill was used to directly synthesize the composite nanosheets.
3.2 Characterization techniques

3.2.1 X-ray diffraction (XRD)

X-ray diffraction was conducted using a PANalytical X’pert Powder instrument as shown in Figure 3.3. The operating voltage was 40 kV, the current was 30 mA and the radiation source was Cu K-alpha $\lambda = 0.15418$ nm. The samples were scanned from 20° to 60° with a 0.02° step size and 150 sec step durations. The phase, crystal structure and crystallite size of the composite nanosheets were analysed using X-ray diffraction.

The X-ray diffraction analysis is based on Bragg’s law:

$$2d \sin \theta = n\lambda$$
θ: the incident angle

n: integral

λ: wavelength of the beam

d: space between the planes of the crystal

3.2.2 Scanning electron microscopy (SEM)

Scanning electron microscopy (Hitachi S4500 Zeiss Supra 55VP) was used to characterize the morphologies of the composite nanosheets, as shown in Figure 3.4. In the SEM analyses, high-energy electrons scanned the surface of samples while secondary electron imaging and an in-lens mode were used to observe the nanosheet samples. Additionally, electron energies equal to or below 6 kV were usually selected for imaging samples. To prepare the samples, a ball milling sample was first sonicated with ethanol and then deposited on a silicon wafer. After volatilization of the ethanol, the sample was coated with 1–3 nm of carbon using a Leica EM ACE600 sputter coater.

Figure 3.4 Photograph of the Hitachi S4500 Zeiss Supra 55VP.
3.2.3 Transmission electron microscopy (TEM)

**Figure 3.5 Photograph of the JOEL JEM-2100F.**

TEM studies were conducted on JOEL JEM-2100F instrument, as shown in Figure 3.5. In this characterization, high velocity electrons penetrated through the samples and were captured by detectors beneath the sample. TEM testing can provide high-resolution images with crystallographic information of the samples, which can be used to deeply understand the morphologies of the composite nanosheets. For the TEM sample preparation, because the signals were collected blow the samples, the ball milling nanosheets were first ultrasonicated in ethanol and then drop-cast onto the holey carbon film. Electron energy loss spectroscopy (EELS) is the use of energy distribution of electrons that pass through the sample to analyse the elemental content, and the EELS instrumentation is incorporated into the TEM. Energy-filtered
TEM was used to visualize the elemental distribution in the samples, and different elements were marked in different colours.

### 3.2.4 Four-ball wear testing machine

![Four-ball wear testing machine](image)

*Figure 3.6 Photograph of the MRS-10A four-ball wear tester.*

The four-ball method is a common technique for measuring the extreme-pressure behaviour of lubricating fluid. The measurements were conducted using a MRS-10A four-ball wear testing instrument produced by the Jinan Shidai Shijin Testing Machine Group Co., LTD. China, as shown in Figure 3.6. The machine is operated with one upper rotating steel ball under loading against three lower stationary steel balls. The contact area between the four balls was immersed in the testing lubricant. The main spindle was rotated with the upper ball to provide a load against the lower balls, and the centre of rotation is along the axis of symmetry of the upper and low balls. The schematic of the four-ball wear tester is presented in Figure 3.7.[59] During testing,
the load was varied from low to high, and after each test the circular wear scars on
the three stationary balls were observed. The load-carrying capacity and abrasion-
resistance of the lubricant were evaluated via the diameter of the circular wear scar.

Figure 3.7 Schematic of a four-ball wear tester. [59]

The four-ball wear testing procedure followed the ASTM D2783 standard method,
which details the measurement of the extreme-pressure properties of lubrication
fluids.

To prepare the ball milled samples, they were first dispersed in the mineral base oil
then stirred and ultrasonicated. Then, the mixture was transferred into the test-
lubricant cup and the contact area of three lower balls and the one upper ball were
confirmed to be immersed in the mixture oil.
3.2.5 Optical microscope

The image of worn surface of steel balls was collected using a Leica DMI 3000M optical microscope, shown in Figure 3.8. The wear scar picture was photographed using the digital camera of the microscope, the example of wear scar photo as shown in Figure 3.9.[9] After testing, the worn surfaces of the steel balls were observed using the microscope, where smaller and smoother wear scars indicated that the lubricant had better friction-reduction properties.
Figure 3.9 An example of wear scar photograph.[9]
Chapter 4

Synthesis of composite nanosheets of graphene and boron nitride

4.1 Introduction

Since graphene was discovered in 2004,[15] it has attracted considerable attention due to extraordinary physical and mechanical properties, such as high surface area, high Young’s modulus and high thermal conductivity.[18, 60] Similarly, 2D structural analogues including hexagonal boron nitride (h-BN) nanosheets and transition metal dichalcogenides (TMDs) nanosheets also have exhibited many distinct properties,[23, 61-67] affording a wide potential application range.[68-71]

Chemical vapor deposition (CVD),[6] hydrothermal[49] and mechanical transfer[58] methods can be used to produce various composite nanosheets on substrate surfaces at a small scale. However, synthesis of a large quantity of composite nanosheets is still a considerable challenge. Recently, controlled ball milling using ammonia or hydrocarbon gases as exfoliation agents has been found to be an efficient and high yield production method to produce pure nanosheets of graphene, BN, MoS$_2$ and WS$_2$.[48] In this process, the obtained nanosheets remained flat and maintained their single-crystalline structure with a low defect density, even after a long period of milling. During the ball milling process, NH$_3$ and C$_2$H$_4$ molecules were chemically adsorbed on the nanosheet surfaces and acted as a lubricant to reduce the milling impact on the nanosheets. The gas molecules attached at edge and defect sites underwent chemical reactions and healed the defects by saturating the dangling bonds.[48]
In this study, an optimized high-energy ball milling process was employed for the first time to produce composite nanosheets of graphite and boron nitride.

### 4.2 Experimental Section

The commercial graphite and h-BN powders with diameters of less than 40 μm were chosen as starting particles. An optimized high-energy ball milling process was conducted to produce the graphene and h-BN composite nanosheets in an ammonia atmosphere. Several grams of a 1:1 graphite and h-BN mixture were added into a steel vial. 25 mm steel balls were loaded in the vial with a ball-to-powder weight ratio of 64:1. The rotating speed was 140 rpm. The vial was sealed and filled with 310 kPa of ammonia (NH\(_3\)) gas, which is a critical atmosphere for nanosheet production.

The structure of the synthesised composite nanosheets was examined using X-ray powder diffraction (PANalytical X’pert Powder, Cu K-alpha radiation, \(\lambda=0.15418\) nm). A scanning electron microscope (Hitachi S4500 Zeiss Supra 55VP) and a transmission electron microscope (JOEL JEM-2100F) were used to characterize the morphologies and structures of composite nanosheets. To examine the synthesised composite chemical composition, electron energy loss spectroscopy (EELS) and energy-filtered transmission electron microscopy (EFTEM) were performed using a Gatan Quantum ER 965 Imaging Filter attached to a JEOL JEM-2100F instrument. EELS spectra were acquired in the imaged-coupled mode (TEM was in diffraction mode with an area of interest defined by a selected area diffraction aperture), and the elemental maps were acquired using the three-window method.
4.3 Results and discussion

Figure 4.1 XRD patterns of BN and graphite with different milling times, +: Graphite, *: BN.

Figure 4.1 shows the XRD spectra of graphene and BN powder mixtures milled for different periods of time. After being ball milled for 1h, the XRD spectra of the graphite and BN mixture show two strong (002) characteristic peaks between 26° and 27°. By referring to the XRD spectra of commercial graphite and BN, the peaks located at 26.5° and 54.5° can be identified as originating from graphite, and the peaks at 26.7° and 56° belong to h-BN phase. With increasing milling time, the characteristic peaks of hexagonal structures ((002) and (004)) are weaker and broaden because of particle size reduction, and the (100), (101) and (004) peaks almost vanish. This result suggests that the thickness-to-size ratio of the starting particles were reduced and the nanosheets were exfoliated from bulk materials after ball milling for 20 h or 40 h. Additionally, the two individual (002) and (004) peaks combined to one peak,
suggesting the homogeneous graphene and BN nanosheets combined into graphene/BN composite nanosheets.

Figure 4.2 SEM images of the graphite and BN mixture samples milled for different times: (a) 1 h; (b) 20 h; (c) 40 h.

SEM images revealing the morphologies of composite nanosheets synthesized after different ball milling times are shown in Figure 4.2. A thin carbon coating was used to reduce the charging effect from the electrically insulating BN samples. After the BN and graphite mixture was ball milled for 1h the particles were thick and blocky, and the diameter was still greater than 2 µm (Figure 4.2(a)). However, as the milling time increased the layered structure was extensively exfoliated. After 20 h of milling nanosheets with a large surface area and uniform size can be seen clearly in Figure 4.2(b). Multiple composite nanosheets were loosely stacked with distinct edges, and
the nanosheets had diameters larger than 200 nm. Extending the milling time to 40 h further reduced the size of individual composite nanosheets to a diameter of ~100 nm (Figure 4.2(c)). These 40 h milled graphene/BN composite nanosheets were compactly stacked together, and loose individual composite nanosheets agglomerated to form clusters. It is known that the starting particles are subjected to shear and fragmentation forces during the ball milling procedure.[4, 5, 72, 73] When the shear force exceeds the weak interlayer van der Waals bonds, the bulk materials exfoliate into nanosheets. Therefore, excessive milling times (e.g., 40 h) results in the reduction in the size of individual nanosheets and causes the nanosheets to agglomerate tightly.

![Figure 4.3](image_url)

**Figure 4.3** (a) TEM images of graphene/BN composite nanosheets produced by ball milling for 20 h; (b) high-magnification TEM image; (c) enlarged TEM image of the selected area (indicated by the box); (d) EELS spectra of graphene/BN composite nanosheets.
20 h milled samples were investigated using TEM and EELS to further reveal the microstructure and elemental distribution of the graphene/BN composite nanosheets. Figure 4.3(a) exhibits an edge of a composite nanosheet suspended on a holey carbon film. It is apparent that multiple nanosheets were irregularly stacked together and the degree of transparency is indicative of the number of stacked sheets. The thickness of the nanosheets can be estimated from a side view of the structure in a high-magnification TEM image shown in Figures 4.3(b) and 4.3(c). Each individual graphene or BN nanosheets is composed of approximately 10 layers of graphene or BN, and the typical thickness of the nanosheets is less than 10 nm. The EELS spectrum in Figure 4.3(d) shows the elemental edges of B, C, and N, indicating that the composite nanosheets were formed from BN and graphene.
EFTEM was used to visualize the elemental distribution in a region of the sample suspended over a hole in a holey carbon film (Figure 4.4(a)). The distribution of elements is shown in an energy-filtered image (Figure 4.4(b)), where boron is marked in red and carbon is depicted in green. The individual energy-filtered maps of boron and carbon are displayed in Figure 4.4(c) and 4.4(d). The boron and carbon coloured regions are overlapping, but discrete graphene and BN nanosheets can also be identified at the particle edges. It can be concluded that the composite nanosheets are constructed by stacking of multiple graphene and BN nanosheets together.
4.4 Conclusions

Large-scale production of graphene/BN composite nanosheets has been achieved via a high-energy ball milling process conducted on graphite and h-BN powders in an ammonia gas atmosphere. The milling time significantly influences the size and morphologies of the composite nanosheets.
Chapter 5

The lubrication application of graphene/BN composite nanosheets in oil

5.1 Introduction

2D nanosheets offer many advantages in tribological applications. Their layered structure consists of strong $sp^2$ covalent in-plane bonds and weak van der Waals interlayer bonds, which facilitates inter-plane sliding and low friction. Further, the flake morphology allows penetration and stable deposition into the rubbing area, avoiding direct contact between the sliding surfaces. As additives, these features conspire to significantly improve the anti-wear and friction-reducing lubrication performance of oil.[74-78] Huang et al. reported an over 50% reduction in wear scar diameter and reduced coefficient of friction (0.06 $\mu$ - 0.08 $\mu$ to 0.01 $\mu$ - 0.02 $\mu$) for paraffin oil containing graphene, relative to natural flake graphite powder additives.[79] Due to the hybridization of different material properties composite nanosheets of graphene and BN nanosheets may overcome the limitations of graphene. In particular, BN nanosheets have higher thermal and chemical stability than graphene and very different surface property. Both materials are well-known lubricants, however, their composites have not been previously studied as lubricants. This requires experimental verification and is the focus of this present work.

The graphene/BN composite nanosheets were fabricated via ball milling in this study, the wear resistance and friction reducing performance of the composite nanosheets as a lubricant additive evaluated via a four-ball method are presented in this chapter.
5.2 Experimental section

The tribology testing of the composite nanosheets was carried out via a MRS-10A four-ball wear tester (Jinan Shidai Shijin Testing Machine Group Co., LTD. China), according to the National Standard of the People’s Republic of China GB/T 12583-1998 “Standard test method for measurement of extreme-pressure properties of lubrication fluids (four-ball method)”, which is equivalent to the standard ASTM D2783-88. The composite nanosheets were dispersed by stirring and ultrasonication in mineral base oil (500 N mineral base oil produced by China Daqing petrochemical company, whose viscosity is 10-12 cSt at 100 °C, pour point -12 °C, flash point 230 °C, Aromatics less than 1 wt%). Four 12.7 mm diameter steel balls made of GCr15 bearing steel (AISI-52100) with the hardness of 64-66 HRC, Grade 25 EP (Extra Polish) were used for testing. The measurement of scar diameters in our experiments was performed following the standard procedure ASTM D2783-88. The balls were left clamped in the cup and washed using cleaning solvent and rinse solvent. The scar diameters of the three test balls were measured under an optical microscope; an average scar diameter was obtained from several measurements in different directions. An ocular micrometre equipped with a calibrated measuring scale (±0.01 mm) was used to determine the average wear scar diameter on the three lower ball, and repeat each test three times at each load and take the mean to eradicate any discrepancies. During the test, the rotating speed of the main spindle was maintained at 1770 rpm, a timer with the accuracy of 0.1 s was employed and the testing temperature was ambient 25 °C. The wear scars were observed using an optical microscope (Leica DMI 3000M).
5.3 Results and discussion

An optimized high-energy ball milling process was employed to produce graphene/BN composite nanosheets. For tribology studies, the graphene/BN composite nanosheets made by 1 h, 20 h, and 40 h ball milling were selected as a lubricant additive (for characterization details see Chapter 4). Additionally, homogeneous graphene and BN nanosheets made by 20 h ball milling were selected as controls.

![SEM images](image)

*Figure 5.1 SEM images of the graphite and BN mixture samples milled for 20 h: (a) 20 h sample with the oleic acid and carbon coating; (b) the 20 h sample without the oleic acid and carbon coating.*

Acting as a dispersant, 5 wt% oleic acid was injected into the vials for the purpose of enhancing the mechanical exfoliation process and improving the dispersion of the composite nanosheets in oil for subsequent lubrication testing. However, the acid may obscure features in SEM imaging. Consequently, the 20 h ball milled graphene/BN composite nanosheets were washed by ultrasonic cleaning in petroleum spirit to remove the oleic acid. Figure 5.1(b) shows a SEM image of the graphene/BN composite nanosheets after removing the oleic acid. Relative to Figure 5.1(a) the insulating BN nanosheets (white regions) with a diameter less than 100 nm
are distinct and dispersed homogeneously on the dark graphene to form the stacked composite structure.

The wear resistance of graphene/BN composite nanosheets was evaluated via a four-ball method according to the standard ASTM D2783-88. The four-ball method is a common technique to evaluate the load-carrying capacity and abrasion resistance of a lubricant. An upper rotary ball is connected to a transmission, which can apply various loads to three stationary lower balls and the three contact areas are immersed in the testing lubricant. Friction occurs when the upper ball rotates against the lower balls and wear scars are generated during this procedure. After each loading, the wear scar diameter was measured by an ocular micrometre equipped with a calibrated measuring scale (±0.01 mm). Under the same load and rotary speed, a smaller wear scar diameter indicates is and the better friction-reduction of the lubricant will be. The graphene/BN composite nanosheets made by different ball milling times were selected as lubricating additives and then dispersed into mineral base oil at an addition proportion of 1 wt%, which is the common concentration of nanosheets additives selected for testing.[18, 75, 79, 80]
Figure 5.2 Last nonseizure load and weld point of the base oil and the oil containing graphene/BN composite nanosheets.

The last nonseizure load \((P_B)\) and weld point \((P_D)\) of the mineral base oil containing nanosheet additives were determined according to ASTM D2783-88 standard procedure. \(P_B\) is the last nonseizure load at which the commencement of plastic deformation of the steel balls is observed, and \(P_D\) is the weld point at which the fusion between the rubbing metal surfaces occurs. Figure 5.2 shows the \(P_B\) and \(P_D\) values of the neat mineral base oil and the oil containing 1 wt% of the composite nanosheets. It is seen that both \(P_B\) and \(P_D\) values of the mineral base oil increase significantly (\(P_B\) from 255 N to 392 N and \(P_D\) from 1236 N to 1569 N) with 1 wt% composite nanosheets addition. The typical wear scars of the steel balls after testing are shown in Figure 5.3. The wear scar lubricated by the oil with composite nanosheet additive is smaller and smoother compared with that of neat mineral oil (Figure 5.3). The improvement in wear resistance can be attributed to the composite nanosheets consisting of multiple
layers of graphene and BN nanosheets. The ultrathin composite nanosheets can easily be adsorbed on the rubbing surface, which separates the rubbing surface to avoid direct contact. The layered structure and flexibility of the composite nanosheets can facilitate a mending and polishing effect,[81] similar to reports of nanoparticles used to enhance the anti-wear properties of the mineral base oil.

Figure 5.3 Optical microscopy images of wear scars of the steel balls tested in (a) neat base oil and (b) base oil with graphene/BN composite nanosheets (four-ball method, 1770 rpm, 392 N, 10 second).

Figure 5.4 Average diameters of wear scars under different loads in mineral base oils added with the composite nanosheets prepared using different milling times (a) and in the oils with different nanosheets (b) (four-ball method, 1770 rpm, 10 second).
The effects of the size and morphological features of the composite nanosheets resulting from different milling times on the anti-wear properties were investigated. 1 wt% of the graphene/BN composite nanosheets were dispersed into neat mineral base oil and tested by the four-ball method. The wear scar diameters of the testing steel balls in the oils with different additives under varying loads were measured, and the results are plotted in Figure 5.4(a). The average wear scar diameters of the mineral base oil containing the composite nanosheets produced by 1 h and 20 h ball milling were the largest and the smallest, respectively (Figure 5.4(a)). This indicates that the graphene/BN composite nanosheets produced by 20 h ball milling time possess the best anti-wear properties.

![Schematic of possible lubrication mechanism of graphene/BN composite nanosheets as lubricating activities in oils.](image)

*Figure 5.5 Schematic of possible lubrication mechanism of graphene/BN composite nanosheets as lubricating activities in oils.*

The graphite/BN composite powders produced by 1 h ball milling is not layer structured (see Figure 4.2(a)), which may restrict particle flow into the contact region and result in the larger wear scar diameters. As the milling time increased to 20 h the
layered graphite and h-BN were extensively exfoliated, resulting in a reduced diameter (large than 200 nm) and a thickness of less than 10 nm. This reduced size allowed the nanocomposite to readily enter the gap between rubbing surfaces, as illustrated in Figure 5.5. The layered structure and flexibility of the composite nanosheets can generate the mending effect and the polishing effect,[81, 82] so the wear scar diameters of the oil containing the composite nanosheets decreased. When the milling time was further increased to 40 h, the diameter of the graphene/BN composite nanosheets reduced and individual composite nanosheets agglomerated to form large inflexible nanosheets clusters. These clusters act like large particles and have a limited lubrication effect.

![Friction Coefficient Graph](image)

**Figure 5.6** Friction coefficient for the neat base oil and the base oils containing different nanosheets (four-ball method, 1770 rpm, 200 N, 10 min).
To compare to composite nanosheets, homogeneous graphene and BN nanosheets were produced separately by the same optimised (20 h) ball milling process and dispersed at a concentration of 1 wt% into neat mineral base oil. The wear scar diameters of these oil mixtures under six different loads in the range of $P_B$ and $P_D$ were determined in sequence by four-ball method. Figure 5.4(b) presents the wear scar diameters of the mineral base oil with and without nanosheet additives. Welding of the steel balls in the rubbing surfaces occurs under a load of 1236 N for the neat mineral base oil, and the wear scar diameters of the mineral base oil containing all nanosheets clearly decrease. The reduction in wear scar diameter of the oil with the composite nanosheets under the same load is more remarkable than those of the oil containing homogeneous nanosheets, which indicates that the composite nanosheets possess the better anti-wear properties. Furthermore, the effect of different nanosheet additives on the friction coefficient of different oils was investigated via the four-ball method. Figure 5.6 shows the changes of friction coefficient versus time for neat mineral base oil and mineral base oil containing 1 wt% of three different nanosheets (BN nanosheets, graphene and graphene/BN composite nanosheets). It can be seen that the mineral base oil containing graphene/BN composite nanosheets displays the lowest friction coefficient relative to the neat mineral base oil and mineral base oil containing homogeneous nanosheets.

Different nanosheets exhibit distinct behaviour under external pressure. Thin graphene sheets become stronger compared to thicker graphite sheets,[60] whereas the strength of BN nanosheets is not sensitive to their thickness because of the comparatively stronger interaction between basal planes under applied pressure.[83]
Leven et al. have theoretically predicted that a robust superlubricity state occurs between the sliding interface of sufficiently large graphene and BN layers, leading to a low friction state.[51] This fundamental study is consistent with the experimental results of friction coefficients in the present work.

5.4 Conclusions

The size and morphologies of the composite nanosheets were influenced by varying the milling time, which subsequently affected the wear resistance. The composite graphene/BN nanosheets produced by 20 h of ball milling time have large diameters and thin thickness, which form a better film on the testing ball surface resulting in a lower friction coefficient and improved anti-wear properties.
Chapter 6

Conclusions and future work

6.1 Conclusions

Graphene/BN composite nanosheets were produced by controlled high-energy ball milling. After graphite and BN particles ball were milled in an ammonia atmosphere for 20 h, graphene/BN composite nanosheets were obtained.

XRD spectra revealed that after graphite and BN composite nanosheets had been ball milled for 20 h, the characteristic (002) and (004) peaks of the hexagonal structure are weaker and broadened, while the (100), (101) and (004) peaks almost vanish, indicating that, after ball milling, the thickness-to-size ratio of the particles are reduced and that BN and graphite are exfoliated from their bulk materials. Additionally, individual (002) and (004) peaks from the starting particle are combined into one peak, which indicated that, after 20 h of ball milling, the homogeneous graphite and BN nanosheets had formed graphene/BN composite nanosheets.

Furthermore, after being milled for 20 h, the graphene/BN composite nanosheets had a uniform size with a large surface area and were loosely stacked with distinct edges. The diameter of the composite nanosheets was over 200 nm, and their thickness was lower than 10 nm. EFTEM mapping shows that the composite nanosheets are constructed of stacks of multiple graphite nanosheets and BN nanosheets together.

The wear resistance of the graphene/BN composite made by ball milling for 20 h was evaluated via a four-ball method. The last non-seizure load and the weld point of the
mineral base oil containing 1 wt% composite nanosheets increased significantly relative to the neat mineral base oil. Additionally, the wear scar diameters of graphene/BN composite nanosheets were smaller than those of the homogeneous nanosheets at same load. This remarkable anti-wear and friction-reducing behaviour could be attributed to the different behaviours of the different nanosheets under external pressure. Graphene is stronger than thick graphite sheets, but the strength of BN is not sensitive of its thickness. Thus, the composite nanosheets of thin graphite and BN nanosheets overcame the weaknesses of individual homogeneous nanosheets. The wear resistance of the composite nanosheets was substantially improved relative to that of the homogeneous nanosheets.

### 6.2 Future work

Herein, ball milling was demonstrated to produce graphene/BN composite nanosheets at a large scale, and the tribology studies showed that the wear resistance of these composite nanosheets are further improved relative to homogeneous nanosheets. However, this is an interesting topic which deserves further investigation.

It has been shown that the graphite and BN composite nanosheets can act as lubricant additives in mineral base oil to improve its anti-wear properties. Although oleic acid is used in nanosheet syntheses to improve the dispersion of nanosheets in oil, and the nanosheets were stably dispersed in the oil, a deeper study of the improved distribution of nanosheets remains a challenge. The dispersion effect of other dispersants on nanosheets, such as cetyl trimethyl ammonium bromide (CTAB), sodium dodecyl benzene sulfonate (SDBS) and sorbitan monooleate, need to be investigated. Additionally, although it was demonstrated that composite nanosheets
synthesized in a graphite:BN ratio of 1:1 have excellent anti-wear properties, further study should be conducted to understand the wear resistance of composite nanosheets with different ratios, such as 1:2 and 2:1. Moreover, to elucidate the dominant mechanisms of the lubricating behaviour of these composite nanosheets, various concentrations of composite nanosheets in mineral base oil should be investigated.

Furthermore, it was demonstrated that the composite nanosheets could be produced by ball milling, which suggests that this method may be used to produce other 2D composite nanosheets such as MoS$_2$/BN composite nanosheets, graphene/MoS$_2$ composite nanosheets and MoS$_2$/WS$_2$ composite nanosheets. Additional work should be conducted to optimize the ball milling conditions for the production of different composite nanosheets. Additionally, it would be very interesting to investigate the wear resistance of these other composite nanosheets.

More research on these composite nanosheets should be conducted to explore applications other than lubricants, such as optics and energy storage. These investigations could lead to great advancements in the state of 2D materials.
References


