Nanostructured Carbon Materials: Fabrication and Applications

by

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Deakin University
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I am the author of the thesis entitled

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Abstract

The fabrication of carbonaceous materials with required structures and properties has been intensively investigated in recent years. Among all the efforts, the application of ball milling synthesis in designing nanostructured carbonaceous materials has some advantages in structure control, large production quantities and efficient process. However, the formation mechanism and the detailed influence of treatment conditions on carbonaceous materials are not well established. It is, therefore, very important to perform a systematic study and understand the mechanism of the process, so that ball-milling fabrication can be used more wisely and efficiently in the creation of new carbon nanostructures with desired properties, which is the main goal of this thesis work.

During carbon nanomaterial fabrication with ball-milling method, it is discovered that the atmosphere can significantly affect the structure of the products. Ammonia can protect the in-plane aromatic structure of graphite and form thin graphite flakes, while the same ball milling in argon leads to amorphous structure. Similar influence is also found when ball milling boron nitride and molybdenum disulphide in ammonia. Moreover, it is demonstrated that ethylene and methane can also protect the sample structure during the milling process. It is revealed that the protective gas can be adsorbed on the surface of the milled material and functions as a lubricant, which reduces the damage to the material and achieves the structural control of the products.

Nanostructured carbon has been the main research focus in the past decades, the representatives of which include fullerene, nanotube and graphene. Other nanostructures are also under extensive investigation due to their substantial application in various important fields. Graphite has been the most popular anode of lithium ion batteries (LIB). Recently, it was found that disordered graphitic structures could allow for extra lithium storage. The mechanism, however, still needs to be clarified. By utilising ball milling, two kinds of graphitic structures, i.e.
amorphous and nanoflake structures, are fabricated and these are very good models to study the mechanism of the enhanced storage of lithium in graphitic materials. It is discovered that a capacity-like storage mechanism existing in the ball-milled graphite that has distorted graphitic structures. This storage mechanism contributes to the enhanced capacity of lithium, compared with the intercalation/de-intercalation mechanism.

Nitrogen doped carbonaceous materials have been demonstrated as electro-catalysts for oxygen reduction reaction (ORR). However, how to produce large quantities of the catalysts is still a problem. A new approach to efficiently synthesise nitrogen doped carbon nanoparticles (NDCP) is demonstrated using ball-milling method in nitrogen-containing gases. The synthesised NDCP can be used as electro-catalysts for ORR in alkaline solution after a structural refinement.

In addition to the catalyst synthesis, the mechanism of the catalysis process on nitrogen doped carbonaceous materials is also investigated. Particularly, the function of the nitrogen doping structures in catalysing ORR is still under debate. It is found that after catalysing ORR, the chemical environment of the nitrogen doping in nitrogen-doped graphene has changed. This evidence, determined with ex situ X-ray photoelectron spectroscopy, is very important in determining the catalytic activity of nitrogen doped structures.
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<tr>
<td>AFM</td>
<td>atomic force microscope</td>
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<tr>
<td>CV</td>
<td>cyclic voltammetry</td>
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<td>CNTs</td>
<td>carbon nanotubes</td>
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<td>CVD</td>
<td>chemical vapour deposition</td>
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<td>EIS</td>
<td>electrochemical impedance spectroscopy</td>
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<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
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<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
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<tr>
<td>HRTEM</td>
<td>high resolution transmission electron microscope</td>
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<td>LFM</td>
<td>lateral force microscope</td>
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<td>LIB</td>
<td>lithium ion battery</td>
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<td>NDCP</td>
<td>nitrogen doped carbon nanoparticles</td>
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<td>NEXAFS</td>
<td>near edge X-ray absorption fine structure</td>
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<td>NMR</td>
<td>nuclear magnetic resonance</td>
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<td>ORR</td>
<td>oxygen reduction reaction</td>
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<tr>
<td>RDE</td>
<td>rotating disc electrode</td>
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<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
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<tr>
<td>SIMS</td>
<td>secondary ion mass spectrometry</td>
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<td>SPM</td>
<td>scanning probe microscopy</td>
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<td>TEM</td>
<td>transmission electron microscope</td>
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<td>TGA</td>
<td>Thermogravimetric analysis</td>
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<td>UV-Vis</td>
<td>ultraviolet-visible absorption spectroscopy</td>
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<td>X-ray photoelectron microscopy</td>
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Chapter 1 Introduction

1.1 Overview

Carbon based materials have been widely used in modern society. Due to carbon atoms’ colourful chemistry, namely the ability to form $sp$, $sp^2$ and $sp^3$ bonds, carbon based materials have a wide range of structures, including but not limited to carbon quantum dots (0-D) [1], carbon nanotubes (1-D) [2], graphene materials (2-D) [3], graphite [4] and diamond [5] (3-D). Importantly, it has been discovered that the structures of the carbon based materials can significantly affect their properties, such as electrical [6], optical [7] and electrochemical properties [8]. It is, therefore, very important to control the structure and morphology of the product during the fabrication process of carbonaceous materials. However, despite significant research in this area, it still needs to be further explored, in particular the phase transformation of graphite in ball milling process. Graphitic materials have been used as anodes for lithium ion batteries for decades. Recently, much research has been done to increase the lithium capacity of graphitic materials. It has been discovered that the disordered graphitic structure can store more lithium than the perfect structure [8]. New research suggests that multilayer graphene with high structural disordering can also provide better capacity [9]. However, the mechanism of the enhanced capacity still needs to be further explained. Nitrogen doped graphitic materials have been discovered as alternative catalysts for the oxygen reduction reaction (ORR) [10]. The lack of large quantities production of nitrogen doped graphitic materials, however, hinders the practical application of these materials. In this thesis, it has been demonstrated that mechano-chemical synthesis can be a potential way to synthesis nitrogen doped carbonaceous materials in large scale, which can be used as catalysts for ORR. In addition, the mechanism of how nitrogen doped graphitic materials can catalyse ORR is still
under heavy debate. Particularly, how nitrogen affects the catalytic process is still arguable. To finally solve this problem, new analytical methodologies need to be developed.

### 1.2 Thesis objectives

The aim of this thesis is to solve the problems raised in Chapter 1.1. The objectives of the thesis are summarised as follows:

(a) To understand how the crystalline structure transforms during a ball-milling process.

(b) To explore how the atmosphere affects the structure of the products in a ball-milling process.

(c) To understand the mechanism of the lithium storage in disordered graphitic materials.

(e) To develop a mehano-chemical synthesis route for mass production of nitrogen-doped carbonaceous materials.

(f) To study the ORR mechanism on nitrogen-doped graphene and develop the application of ex situ XPS methodology in studying the mechanism of ORR on nitrogen-doped carbonaceous materials.

### 1.3 Thesis structure

This thesis is presented in nine chapters to show different aspects of the research work within a wide research field. The content of each chapter is summarised below:

**Chapter 1**: overview of this thesis and discussing the gaps in the research, which will be addressed.

**Chapter 2**: reviewing the related literature to provide an in-depth background of the research work in this thesis.
Chapter 1 Introduction

Chapter 3: introducing the methodologies used in this thesis.

Chapter 4: phase transformation in the ball-milling process of graphite.

Chapter 5: influence of atmosphere on the structure of the product during the ball-milling process.

Chapter 6: clarifying the mechanism of the enhanced lithium storage in the disordered graphitic materials.

Chapter 7: mechano-chemical synthesis of nitrogen-doped carbonaceous materials in large quantities, which can be used as electro-catalysts for ORR.

Chapter 8: mechanism of the catalytic process on nitrogen-doped graphene and the application of ex situ XPS in exploring the mechanism of ORR on nitrogen-doped graphitic materials.

Chapter 9: summarising the thesis findings and suggesting future work.
Chapter 2 Literature Review

2.1 Graphite and related graphitic materials

2.1.1 Structure of graphite

Graphite is one of the carbon allotropies that has been used by human beings from 4th millennium B.C [11]. Graphite has unique anisotropic properties. For example, the electrical conductivity parallel to the graphene sheets could be 100 times larger than the one in the vertical direction [12]. This anisotropy is absent in another well-known allotropy of carbon, diamond, and most of the natural carbon containing organic compounds. The mystery of the anisotropy of graphite was not solved until the development of crystallographic techniques and quantum mechanics allowed researchers to understand its physical and electronic structure [13, 14].

It has been found that there are two common graphite structures: hexagonal and rhombohedral. These two structures have the same in-plane six-member aromatic ring structure (the ring showed in Figure 2.1), but different stacking orders among the layers. Moreover, an anisotropic electronic structure and bonding of carbon atoms are found, which can explain graphite’s unique property. The carbon atoms in graphite form two sets of orbitals in the frame of the hybridisation theory [15]. One of the two sets of orbitals is the $sp^2$ hybridised orbitals. These orbitals are found to form the in-plane $\sigma$ bonding between carbon atoms. Another set of orbitals is the $p_z$ orbitals, which form delocalised $\pi$ orbitals and cause the inter-plane $\pi-\pi$ interaction. The $\sigma$ bonding electrons are localised, but the $\pi$ electrons are highly delocalised. Further research in solid state physics finds that the delocalisation of the $\pi$ electrons is the origin of the high electrical conductivity, high thermal conductivity and the visible spectrum absorption of
graphite [13]. However, the delocalised \( \pi \) orbitals are distributed vertically to the \( z \) axis of the crystal and parallel to the graphene sheets, therefore, the properties related with the \( \pi \) orbitals, such as high electrical conductivity and thermal conductivity are only evident in the direction parallel to the graphene plane, but are absent in the vertical one.

![Image of graphite structure]

*Figure 2.1 The six-member aromatic ring in hexagonal graphite.*

### 2.1.2 Other graphitic materials

Another very popular graphitic material is the carbon nanotube (Figure 2.2). The synthesis of single-wall carbon nanotubes was first confirmed in 1991 [16]. Carbon nanotubes with a diameter below 20 nm are seen under the electron microscope after arc-discharge evaporation is applied to the carbon source. The structure of the single-wall carbon nanotube is described as a single graphite layer that is curved around to form a tube. In addition, the synthesis of multiwall carbon nanotubes is also reported [17]. Nanotubes with diameters ranging from tens to hundreds of nanometers can be synthesised by altering the particle size of catalyst, reaction temperature, pressure of the precursor and other experimental conditions [17].
In contrast to the nanotube, graphitic carbon nanofibre (Figure 2.3) can be synthesised with a structure of stacking of graphitic layers vertical to the graphitic plane [18]. Chemical vapour deposition (CVD) is a popular method to synthesise graphitic carbon nanofibre. By controlling the growth of particular direction of the crystal, fibres could be synthesised with different stacking orders. For example, by controlling the growth of the (0 0 2) plane, micrometre long fibres with nanoscale in-plane size can be synthesised (Figure 2.3a) [18].

Recently, the successful fabrication of graphene attracted much attention for the development of two-dimensional (2-D) graphitic materials [19]. Strict 2-D crystal was believed not existing in free state as suggested by both theoretical and experimental studies [20, 21]. However, in 2004, the discovery of free-standing graphene flaunted that common belief [19]. Moreover, a follow-up experiment shows that the charge carriers in graphene are massless Dirac fermions, which was predicted theoretically 20 years ago [22]. This new knowledge about graphene has
attracted much research interest in both the scientific community and industry about the potential application of graphene and other 2-D materials in the development of next generation electronics [23], logic circuits [24], energy storage materials [25] and catalysts [26].

Figure 2.3 Illustration of graphitic nanofibers with different stacking orders. Reprinted with permission from [18]. Copyright 2014 American Chemical Society.

2.1.3 Application of graphite and related graphitic materials in energy storage and conversion

Graphite and related materials have attracted much research interest as potential candidates to solve the existing worldwide energy challenge. Graphitic materials have been used as anodes for lithium ion batteries and there is still much research on improving their performance [27, 28]. Carbon nanotubes (CNTs) have been suggested for use in solar cells as a method of enhancing the efficiency of energy conversion [29-32]. Recently, CNTs and graphene have been found to be electro-catalysts for ORR, which might allow them to be used in fuel cells to replace expensive Pt catalysts [10, 33-42]. The applications of graphitic materials in lithium
ion batteries and fuel cells are reviewed in the following content, where the problems faced are also introduced.

2.2 Introduction to Ball milling

2.2.1 Types of ball mills

Due to the large number of variations of ball mills, here only the common types of lab-based ball mills are introduced, including vibrational ball mill [43], planetary ball mill [44] and rolling ball mill [45].

2.2.1.1 Vibrational ball mill

In a vibrational ball mill (Figure 2.4), the milling mortar vibrates and pushes the grinding ball to vibrate at the same time. Since the motion of the grinding ball and the mortar is not synchronised, the collision between them happens during the vibration of the system and the mechanical impact can be applied to the milled material during the collision [46]. It is reported that after ball milled in a vibrational ball mill, TiO$_2$ can be changed from anatase phase to meta-stable phase, which was found only under high pressure conditions [43]. This result demonstrates the strong impact of the vibrational ball milling.
2.2.1.2 Planetary ball mill

On the other hand, planetary ball milling (Figure 2.5) applies more shearing force than the direct impact in vibrational ball milling [47]. In a planetary ball mill, the ball mill beaker mimics the motion of a planet, which revolves around a star in an elliptical orbit and at the same time spins against an axis through the centre of the sphere. However, in the planetary ball mill, the beaker revolves in a circular orbit and the radii of the orbit is vertical to the spin axis of the beaker. Planetary ball milling can be used to fabricate 2-D materials. For example, it can be used to fabricate boron nitride nanosheets at a large scale [48]. When the ball milling significantly reduces the thickness of the boron nitride sheets, it does not break the in-plane aromatic structure, which is due to the planetary ball milling’s high shearing force and low impact.

Figure 2.4 Photo of Pulverisette 0 vibration ball mill. The ball mill mortar is highlighted by the arrow (http://profilab24.com/FRITSCH-PULVERISSETTE-0-Vibratory-Micro-Mill).
2.2.1.3 Rolling ball mill

A rolling ball mill (Figure 2.6) can provide shearing force. Interestingly, preliminary research shows that the milling atmosphere plays an important role on what force dominates [49], which has also been observed when a planetary ball mill is used [74]. For example, it is reported that graphite milled in Ar and H₂ atmosphere could have very different structures [49]. However, the mechanism of the phenomenon is still not clear. It is suggested that the doping of the active gas on the boundary defects created by ball milling should be responsible for the retarded amorphisation process, but no clear evidence has been found to support this hypothesis. In this thesis, the discoveries on this topic will be introduced and the explanation of this phenomenon will be discussed based on these new findings.
2.2.2 Ball milling induced phase transformation

Ball milling induced phase transformation was discovered thirty years ago [50]. One important finding is that ball milling can be used to prepare magnetic amorphous alloys for soft magnetic applications. Yermakov et al. studied the magnetic properties of amorphous Y-Co alloy prepared by a planetary ball mill [51]. After that, it is reported using ball milling to induce the amorphisation of Co enriched magnetic alloys. Three bi-metallic systems are studied, which are Co-Zr, Co-Nb and Co-Ti. The mixed elemental metals are ball milled in a high-energy ball mill (Mitsui Miike attritor MA1D, Japan) with a content of Co higher than 75 at.%. After more than 20 h, the amorphisation of the metal powders is seen using X-ray diffraction (XRD). After amorphisation, the coercivities of the binary alloys are decreased. Ball milling is also used to fabricate quasi-crystallined materials [52-56]. Mizutani et al. reported the observation of quasicrystal phases after ball milling elemental powders of pure Mg, Al and Zn. After 10 h milling, the phase of quasicrystal can be observed from the XRD. A further Differential
Scanning Calorimetry (DSC) study confirms that the quasicrystal phases are metastable and would transform to stable structures during heat treatment. The formation of metastable quasicrystal is also reported in other systems with ball milling [52]. Al<sub>65</sub>Cu<sub>20</sub>Mn<sub>15</sub> is prepared by ball milling the three metal elements for 90 h, and the formation of the quasicrystal phase is confirmed with XRD and transmission electron microscopy (TEM). Compared with other methods, which are used to prepare metallic quasicrystal, such as liquid phase quenching, vapour deposition and ion bombardment, ball milling does not require extreme conditions such as high temperature. In addition, ball milling can fabricate large quantities of samples, which is more applicable to the real life applications.

Recently, the amorphisation process of ball milling has been used in the fabrication of nanomaterials on a large scale [48, 57, 58]. Chen et al. discovered that ball milling could be used to synthesise chemically active precursors that could be used in the synthesis of boron nitride nanotubes [59]. When boron powder is milled in a high-energy ball mill, it can form an amorphous structure, which is confirmed by XRD. After the milled powder heated to 1300 °C, boron nitride nanotubes are formed. It is found that the meta-stable structure formed under ball milling is essential seeds for the growth of boron nitride nanotubes.

However, it is found that the amorphisation process induced by ball milling could be more complex than a simple one-way process, in which the material keeps disordering [60]. This will be reviewed in Chapter 2.3.1, and in this thesis, the amorphisation process of graphite under ball milling will be discussed.

### 2.2.3 Ball milling induced chemical reactions

The ability of ball milling to trigger chemical reactions has also attracted attention recently [61-65]. Chen et al. reported that ball milling could trigger the reaction between iron and ammonia...
[66]. Four gram of iron powder is milled in ammonia atmosphere up to 200 kPa. After 400 h ball milling, the phase of iron nitride is clearly seen from XRD. Combustion elementary analysis reveals that the nitrogen content increases with the milling time. To 400 h, the nitrogen content is above 5 wt.%. Moreover, the phase of iron nitride is also found by Mössbauer spectroscopy.

Similar gas-solid reaction also occurs when Zr is ball milled in ammonia gas [67]. It is found that the ammonia pressure reduces in the first 30 h of the ball milling. After this stage, the pressure begins to increase until about 100 h. After 100 h, the pressure remains constant in further ball milling. Elemental and structural analyses confirm that when the nitrogen content of the milled sample increases until 70 h, its hydrogen content increases to 0.8% in the first 30 h and then begins to decrease to below 0.1% until 80 h. This mechanism is explained with the experimental evidence. In the first 30 h, Zr reacts with ammonia and forms ZrH₂ and ZrN, which leads to the decrease of pressure. However, after this stage, when the nitridation reaction still happens, the ZrH₂ begins to react with nitrogen or ammonia and emits hydrogen, which causes the increase of pressure. This research shows that the ball milling can induce complex chemical reactions.

In addition to the chemical reactions in metals, it has been reported that carbon based materials could also undergo chemical reactions when ball milled. For example, ball milling can trigger a solvent-free Sonogashira coupling reaction [68]. The Sonogashira reaction is the cross-coupling reactions between a terminal alkyne and an aryl or vinyl halide. Several kinds of terminal alkynes and halides are checked by ball milling. For example, iodobenzene reacts with phenyl acetylene and trimethyl silyl acetylene under high-speed ball-milling conditions with catalysts. It is also found that when copper balls and beakers are used during the ball milling,
the yield of the resultant increases. It is proposed that the ball milling beakers and balls can be the catalyst of the reactions.

A similar reaction with the modification of carbon bonding is also reported [69], where ball milling is demonstrated to trigger the reaction between ketone and aldehyde. In the reaction, the C=O group is reduced to C-OH, with the breaking of C-H and C=O bonds and the formation of C-C bond. This research shows the potential application of ball milling in altering carbon bonding and synthesising chemically modified carbon materials.

In this thesis, ball milling is demonstrated as a mechano-chemical method to synthesise nitrogen-doped carbon nanoparticles.

2.3 Ball milling of graphite

2.3.1 High-energy ball milling of graphite in inert atmosphere

Ball milling is becoming an attractive way of fabricating functional graphitic materials [70, 71]. However, research of ball-milled graphite started much earlier [72]. Due to its lamellar structure, graphite has been used as a solid lubricant (Figure 2.1). Its structural evolution under mechanical forces was first studied in 1986 to further understand its behaviour [72]. By checking the XRD patterns, a conclusion is made that, after ball milling, the (0 0 2) interlayer distance increases from 3.35 to about 3.44 nm and the structure becomes more disordered.

Further research is conducted on the structural changes in the ball-milling process of graphite [73]. XRD shows a broadening of the (0 0 2) diffraction peak, whose full width at half maximum (FWHM) increases from less than 1 degree to about 7 degrees. The crystalline size is calculated on c axis and it is claimed to be down to about 1 nm. However, since the stress and equipment broadening are not taken into account, this calculation might not be very accurate, but a broadening and asymmetric (0 0 2) peak indicates a disordered structure.
Besides XRD, Raman spectroscopy is also conducted to characterise the structure of the milled samples. It is found that the intensity of D band at about 1350 cm\(^{-1}\) increases with the milling time, which indicates the increase of defects in the system.

T.S. Ong and H.Yang checked the effect of atmosphere in this disordering process [74]. With planetary ball milling, they find that different gases could lead to very different structures of the products. When the graphite is milled in inert atmospheres, such as argon or nitrogen, the milled powder has an amorphous structure following 3 h milling. The average \(d_{002}\) spacing is also increased from about 0.3342 nm to 0.3370 nm. At the same time, the BET surface area has a very large increase from about 5 to 400 m\(^2\)/g. The results shows an amorphisation process with the creation of large areas of new surfaces. However, when the graphite is milled in oxygen, the structural evolution is very different. XRD shows crystalline structure after even 10 h of ball milling in oxygen. In addition, the surface area remains almost unchanged after 10 h. It seems that the ball milling in oxygen does not lead to amorphisation as efficiently as the milling in Ar. This is probably due to the oxidation reaction of the active centres on the ball-milled graphite, which suppresses the fracture rate and slows down the amorphisation of the graphite.

In 1999, Chen et al. found that the process might be more complex [60]. It is found that the surface area of graphite increases in the first 15 h ball milling in Ar, which can be explained as the disordering, structural breakage of the starting material and the creation of new surfaces and pores (Figure 2.7). However, after about 15 h, the surface area begins to decrease and never reaches as high as at 15 h. This phenomenon suggests that there could be other processes occurring and after this research, similar results are reported and efforts are made to understand the mechanism [75, 76]. For example, a suggested cause of the mystery decrease of the BET surface area is the oxidation of the surface and the surface physical and chemical adsorption
species, which could hinder the adsorption in the nitrogen adsorption analysis [75]. This explanation is not conclusive, however, as it cannot explain the significant decrease of surface area even when milling in Ar, which is very inert and cannot react with milled graphite. The thermogravimetric analysis (TGA) results also show that the samples milled for 100 h and 1000 h lose about 70% of the weight when heated to 1200 °C, which indicates that oxidation and the content of the surface adsorbed species of two samples are very close.

![Figure 2.7 The BET surface area of ball-milled graphite with different milling durations](image)

*Figure 2.7 The BET surface area of ball-milled graphite with different milling durations [60]. Reprinted with permission from AIP Publishing LLC.*

However, on the other hand, the specific BET surface area of the sample decreases from 320 to 178 m²/g, which is a decrease of 44%. Therefore, the surface area reduction cannot be caused by the chemical and physical adsorption species alone. On the other hand, the structure evolution of the graphite, during the extended ball milling after 100 h, is not discussed in detail.

Recently, the use of ball milling in the synthesis of energy storage materials has been developed, especially the application of ball-milled carbonaceous materials in lithium ion batteries [77-79]. These applications again excites researchers’ interests in understanding the detailed
structural evolution in ball-milling process. This understanding becomes very important in the fabrication of the functional materials with good properties [80].

In this thesis, the structural evolution of ball-milled graphite is carefully studied and the detail of the amorphisation process is explained based on the experimental evidence.

2.3.2 Exfoliating graphite by ball milling

2.3.2.1 Introduction of graphene

Graphene is a single layer of graphite, in which carbon atoms are bonded with each other in a six-member aromatic ring pattern. Recently, researchers have broadened the concept of graphene to include multilayer graphene, which usually has less than 10 layers (Figure 2.8). It has attracted attention in the past few years, due to its unique properties in electronics [81], spintronics [3] and electrochemistry [82]. However, good quality large-scale graphene fabrication remains problematic.

![Graphene Image](image)

*Figure 2.8 AFM image of a multilayer graphene sheet on silicon wafer. The thickness of the graphene was about 3 nm [19]. Reprinted with permission from AAAS.*
2.3.2.2 Synthesis of graphene

Graphene is first fabricated by mechanical exfoliation [19, 83]. Highly oriented pyrolytic graphite is used in the repeated peeling. This method can produce multi or even single layer graphene that contains few defects and has good structure. However, large-scale production of graphene by this method is difficult and other exfoliation methods have been developed in an attempt to solve this problem. Su et al. developed a method that uses an electrochemical reaction to exfoliate a thin layer of graphene [84]. However, the structure of the exfoliated graphene contains many defects, which may be due to the oxidation in the process.

Graphene can be fabricated through sonication and centrifuge in a suitable solvent, as demonstrated by Hernandez et al. [85]. It is suggested that a solvent with a similar surface energy to graphene is the first choice for exfoliation, since the solvation energy of graphene will balance the energy required for the exfoliation. The synthesised graphene is dispersive in the solution, the concentration of which is about 0.01 mg/mL, which is very low for practical use. As the solvents that match the surface energy of graphene usually have high boiling points, this results in solvent deposition on graphene. Some researchers have tried to extend the range of solvents in which graphene can be dispersed. Zhang et al. reported that graphene could be dispersed into ethanol through a solvent exchange method [86]. Lotya et al. further extended the solvent to water containing surfactants [87]. However, these methods cannot fabricate graphene at a reasonable scale even for research purpose (less than 1 mg/mL).

In an effort to solve the problem of low quantity of graphene fabrication, a solvent intercalation process is performed to exfoliate graphene oxide [88]. Graphene oxide is chosen since it is hydrophilic and the interlayer distance is larger than graphite, which leads to a much easier intercalation of water molecules. After that, the thin layers of graphene oxide are reduced to form graphene. However, the oxidation and reduction process can seriously damage the
graphene structure, and it is impossible to fully reduce all the carbon oxide groups. Cristina et al. reported that the fully reduced graphene oxide sheets lag behind graphene in room-temperature conductivity and carrier mobility by 3 and 2 orders in magnitude, respectively [89].

Chemical vapour deposition has also been used to synthesise graphene ready to use on a substrate [90]. Camphor is used as the carbon source with nickel as the substrate. Obraztsov et al. succeeded in producing very thin multilayer graphene with chemical vapour deposition [91]. Nevertheless, some people consider it to be a problem of surface defects of polycrystalline nickel. Reina et al. reported that graphene, the size of which could be as large as 20um, could be fabricated on a refined nickel substrate [92]. Other CVD based synthesis methods have been proposed to increase the quality of graphene. [93, 94].

**2.3.2.3 Production of graphene by ball milling**

Ball milling is also used as a synthesis route to achieve large-scale fabrication of graphene. It has been reported that multilayer graphene could be produced by wet ball milling [95]. The starting material is graphite nanosheets with a thickness of 30 to 80 nm. The graphite nanosheet is dispersed in DMF with a concentration of 0.25 mg/ml. The dispersion is then ball milled in a planetary ball mill for 30 h. After the ball milling, the milled sample is centrifuged at 10 000 rpm for 20 min and the multilayer graphene is found in the supernatant. AFM proves the existence of a thin sheet with a thickness of less than 2 nm (Figure 2.9).
Veronica et al. further studied the influence of the additive when using dry ball milling to produce few-layer graphene [96]. In the experiment, graphite is ball milled with melamine in dry condition with inert atmosphere or air. The milled sample is then dispersed into DMF or water. The authors claim that the ball-milled sample could form a stable dispersion in DMF, which could imply the formation of graphene sheets since the starting graphite would aggregate and could not be dispersed at the same condition. The authors also claim that the intermolecular force between graphene sheets and melamine may help to stabilise the graphene sheets and reduce the interlayer interaction between graphene sheets, which could help the exfoliation process. Nanosheets with wrinkles are captured under TEM, which shows the
exfoliation effect of ball milling. However, the quality and quantity of the graphene synthesised by ball milling is still not satisfactory. Thus, the research of the exfoliation effect of ball milling is essential to develop ball milling’s application in the fabrication of graphene and related 2-D materials.

In this thesis, the protection effect of the active milling atmospheres are studied and the mechanism is discussed, which provides insight to the design of ball milling experiment to fabricate 2-D materials.

2.3.2.4 Other 2-D nanomaterials

Several other materials besides graphene have a similar layered nature. Hexagonal boron nitride has the same layered structure and a six-member aromatic ring system like graphite. The only difference is that, in the crystal, boron and nitride atoms alternatively replace the carbon atoms inside graphite. Recently, research has been conducted to produce single or multilayer hexagonal boron nitride nanosheets and the photonics, mechanical, thermal and hydrophobic properties are studied [48, 97-100]. Another group of materials, the layered metal chalcogenides, has also been studied in recent years. There are reports that it could also form very thin layer of the material that has unique property different from its bulk counterpart [101-105].

In this thesis, ball milling of BN and MoS₂ in different atmospheres is reported. The protection effect is also found in these two cases.

2.3.3 Doping of graphite/graphene by ball milling

As described above, ball milling can be used to trigger the chemical reaction. It can also be used as a chemical way to introduce heteroatoms in the material and form doping structures. Doping metal with ball milling has been studied by several groups, which was described in
Chapter 2 Literature Review

Chapter 2.2.3 [62, 63, 65, 106]. Recently, ball milling has been applied to synthesise functional carbonaceous materials [47, 76, 107, 108]. It is reported that ball milling could dope amino functional groups to CNT, which behaves as an active site to react with silver when the silver nanoparticles are deposited on the ball-milled samples [107]. In the experiment, CNTs are ball milled in the presence of ammonium bicarbonate and the milled sample is then studied by secondary ion mass spectrometry (SIMS). Several molecular fragments containing carbon, nitrogen and hydrogen are captured in SIMS. In particular, the presence of several amine groups, such as –CH4N, -C2H6N and -C3H8N, confirms the doping of CNT by ammonium bicarbonate triggered by ball milling. After functionalised by ball milling, it is found that the introduction of the amine and amino groups can help to increase the interaction between CNTs and Ag nanoparticles during the deposition process of Ag. TEM and X-ray photoelectron spectroscopy (XPS) show the deposition of silver nanoparticles on the surface of modified CNTs. In contrast, the starting CNTs show a much lower interaction with Ag and no evidence of the surface deposition of Ag. Further study suggests that, after the deposition of Ag, the electrical conductivity of CNTs increase $10^4$ times when the flexural modulus changes less than 10%. This work demonstrates the possibility of using the ball mill as a reactor to trigger chemical reactions between ammonium bicarbonate and the surface atoms of CNTs, which dopes nitrogen-containing groups onto the surface of CNTs.

Orimo et al. reported the doping of hydrogen atoms in graphite in a ball milling process [76]. Graphite is ball milled in 1.0 MPa hydrogen gas in a planetary ball mill at 400 rpm for varied periods. Using oxygen combustion analysis, it is found that the hydrogen content in the ball-milled sample increases with prolonged milling from 1 to 80 h. However, at the same time, the BET surface area of the milled sample decreases markedly after 6 h milling. It is only about 8 m$^2$/g after 80 h ball milling, which rules out the possibility of the hypothesis that the hydrogen
is adsorbed on the surface of graphite. The radial distribution study is then applied to study the coordination of the deuterium in the sample. It is found that two types of deuterium coordination are inside the milled sample with three distances between the deuterium and carbon atoms, which are 0.11, 0.22 and 0.18 nm. The first coordination is suggested to be the deuterium atoms covalently bond to the carbon atoms. In this coordination, 0.11 nm is the length of carbon-deuterium bond and 0.22 nm is the distance between the deuterium and its second nearest carbon atoms. With this evidence, the authors claim that during ball-milling process, graphite can react with hydrogen gas, which involves breaking strong bonding between H-H and the C-C in graphite.

In 2013, Jeon et al. expanded the application of ball milling to prepare doped graphitic structures by ball milling graphite within different atmospheres [109]. Hydrogen, dry ice, sulphur trioxide and a dry ice/sulphur trioxide mixture are used in the experiment. By FTIR and XPS analysis, the introduction of dopants is confirmed. For example, XPS analysis shows the presence of C-S bonding in the sample milled in sulphur trioxide. The doped graphitic materials are then tested for their catalytic properties in ORR. It is found that after doping, the catalytic properties are changed. For example, the sample milled in sulphur trioxide shows a more positive reaction onset of ORR, which indicates a lower over-potential of the reactions. This research suggests that ball milling can be used to fabricate electro-catalysts by forming doped graphitic materials.

In this thesis, ball milling is discovered to trigger the reaction between graphite and nitrogen gas, forming nitrogen-doped graphitic nanoparticles.
2.4 Graphite as an anode of lithium ion battery

2.4.1 The introduction of graphite used in lithium ion battery

Graphite has been researched for 30 years as an anode of lithium ion batteries (LIB), due to its ability to store lithium by forming lithium intercalated graphite [110]. Graphite has several advantages, such as low volume expansion, stable charging-discharging plateau and low irreversible capacity [111]. It has been found that graphite undergoes the intercalation storage mechanism of lithium, in which the lithium ions diffuse into graphite and sit in between the graphene layers. The highest intercalation density is achieved by forming LiC₆ [112, 113] (Figure 2.10).

![Diagram showing structure and unit cell of LiC₆](image)

*Figure 2.10 Illustration of (a) structure and (b) unite cell of LiC₆. Reproduced from [113] with permission from Elsevier.*

However, the early attempt to use graphite as the host structure of lithium is not very successful, due to the reactivity of the electrolyte on the graphite surface. For example, it is found that propylene carbonate, which is used as the electrolyte in lithium ion batteries, decomposes on graphite surface and form the propylene gas and carbonate ions [114]. The experiment is performed in the propylene carbonate solution of NaClO₄ with a graphite electrode and a
lithium electrode. The open-circuit voltage is +2.75 V vs. Li reference. However, the potential decreases sharply to about +0.6 V vs. Li when a cathodic current is undergoing. At the same time, there are gaseous chemicals formed. The gas chromatographic analysis reveals the majority of the formed gas is propene. By analysing the resultant of the electrolysis process, it is found that the cumbic efficiency of the process is about 100%, which indicates that the electrolysis of the solvent is favourable on the graphite surface.

The important improvement is made by using binary solvent mixtures that can provide good performance and stability [115, 116]. Ethylene carbonate is mixed with either dimethylcarbonate, diethyl carbonate or ethyl methyl carbonate to form the binary electrolyte, in which lithium salt and lithium hexafluorophosphate are added. It is found that those solvents could be reduced to lithium ion compounds that are not soluble in the electrolyte and would deposit on the electrode [117]. This layer of precipitation is essential to the stability of the graphite electrode at low potential. When this layer grows to a certain thickness, it will stop the electron transport and prevent the further reduction of electrolyte molecules. However, as this layer of precipitation contains mostly lithium salts (ROCO2Li and ROLi, R=alkyl group), it has good lithium ion conductivity. Therefore, the layer of the deposition functions as a solid electrolyte for lithium and a passivation layer of graphite surface that prevents the reduction of the solvent.

Another drawback of perfect graphite is its relatively low specific capacity, which is about 372 mAh/g [118]. In defective or semi-amorphous graphitic structure the specific capacity could be increased [119-121]. For example, mechanical grinding is able to increase the capacity of graphite [120]. In the experiment, two grinding modes are used and compared, which are impact mode and shearing mode. Using the shearing mode of ball milling, both the reversible and irreversible capacity of the milled sample increases. For example, after 80 h milling with
mainly shearing force, the reversible capacity rises to about 1.5 times of the theoretical capacity of perfect graphite. At the same time, the irreversible capacity increases about 10 times. On the other hand, after same 80 h milling with impact mode, the reversible capacity rises to about 1.8 times of the capacity of the starting graphite. However, the irreversible capacity does not increase as much as in the first case, which is only about 4 times of the one shown by the starting sample. The authors try to explain the phenomena with different structural evolutions induced by two ball-milling modes. When using the shearing mode, the interlayer distance increases without much distortion of the graphene layers, so more lithium could be intercalated into the enlarged space between graphene layers. On the other hand, the shock impact could significantly distort both the in- and out-plane graphite structure and creates more disordered phases. The disordered structure could also provide more sites for lithium storage, which leads to the increase storage of lithium. Regarding the irreversible capacity, the authors claim that it is related to the surface area of the sample. The sample prepared with impact mode shows a decrease BET surface area after 20 h, which corresponds to the decreased irreversible capacity of the sample. When using shearing mode, the surface area keeps increasing to 80 h and the new surface formed causes the increase of irreversible capacity. However, the study does not clarify the difference of the structure fabricated under different milling conditions. Moreover, a controversial result is also reported [119]. It is found that the capacity of the ball-milled graphite could be even lower than the starting graphite when a small current is applied. For example, the graphite milled for 10 h has only 90% of the capacity of the pristine graphite.

The solution of the controversial results and explanations lays on the understanding of the storage mechanism of graphitic materials [119, 122-125]. In this thesis, graphitic materials with different structures and disordering are synthesised by ball milling and the link between capacities and structures are discussed.
2.4.2 The mechanism of the enhanced lithium storage in graphitic anode

Several models are suggested to explain the extra capacity of the disordered graphitic materials. Most discussions focus on the disordered structure of the graphitic materials and it is believed that the disordering should contribute to the enhanced lithium storage. However, the details of the discussion are different [123, 124, 126, 127]. Akihiro et al. studied the change of capacity with the annealing temperature of mesocarbon microbeads and suggested that the extra lithium capacity is contributed by pores [126]. The mesocarbon is heated from 700 to 2800 °C. It is found that when comparing the capacity of samples annealed at 700 to 1000 °C, the capacity decreases with the increasing annealing temperature. Especially, the sample shows discharge capacity above 1000 mAh/g, which is much higher than the theoretical capacity of graphite. Then, when the annealing temperature increases, the capacity decreases to be close to the theoretical value. XRD analysis shows that there is not much structural changing on inter-planar distance and crystal size. However, a specific gravity analysis reveals that the specific gravity increases when the annealing temperature rises from 700 to 1000 °C. It is caused by the high temperature annealing, which refines the structure of the material and removes cavities. The authors further correlate the structural refinement and the capacity depletion and suggest that there is another lithium storage mechanism in graphitic materials, which is associated with the cavities. Moreover, this mechanism could store lithium with higher density than normal intercalation, which leads to the increase of the capacity.

Another mechanism shows a partially controversial explanation and implies that the in-depth mechanism of the increased storage could be more complex than what is reported [123, 124]. The graphitised soft carbon is annealed at a different temperature from 2300 to 2800 °C. The XRD analysis shows that different contents of turbostratic stacking are in the material annealed at different temperatures. A negative correlation between the turbostratic stacking and capacity
is observed. For example, comparing the sample heated at 2300 and 2800 °C, the possibility of the existence of the disordered structure is smaller in the sample heated at higher temperature. However, the sample annealed at 2800 °C has about 30% higher lithium storage capacity. The authors explain that the inter-plane space with turbostratic stacking could lead to extra resistance of lithium intercalation, which would have no capacity. This claim partially contradicts to Akihiro’s discovery. Akihiro et al. suggests that the graphite with low density and structure disordering can provide extra lithium storage [126]. However, the second research finds that the turbostratic stacking, which is more disordered and also has a less density than perfect graphitic structure, could not be accessible for lithium storage [123]. The contradiction indicates that the way in which the disordered structure contributes to the lithium storage could be a complex problem and this will be discussed in the thesis.

2.5 Nitrogen-doped graphitic materials as catalysts for oxygen reduction reaction

2.5.1 Introduction of oxygen reduction reaction

Oxygen reduction reaction (Figure 2.11) are chemical process in which the oxygen molecules receive electrons to form the reducing product. This process is the cathode reaction in the fuel cell, which is one of the contemporary solutions for clean energy. However, the absence of good cathodic catalysts hinders the development of the fuel cell technology for the practical uses. Pt is found to be very efficient as the catalyst for ORR. However, restricted by its low reserve on earth, high price and very low tolerance to the fuel toxicity, until now it still cannot be commercialised. Thus, finding alternatives is essential to the development of full cells.
Some researchers try to develop metal catalysts without the use of noble metal to reduce the cost of fuel cell technology [128, 129]. For example, carbon supported cobalt-nitrogen system is found to catalyse ORR [130]. The cobalt is coordinated by four nitrogen atoms, which might enhance the electron donation of cobalt and cause a positive shift of the onset of the ORR. Beside metal catalysts, hetero-atom doped carbon materials have been found to be possible non-metal catalysts that could replace Pt as catalysts for ORR [10, 41, 109, 131].

### 2.5.2 Application of graphitic materials as catalysts for oxygen reduction reaction

Gong et al. reported that vertical aligned nitrogen-doped carbon nanotubes (VA-NCNTs) could be an efficient catalyst for ORR (Figure 2.12) [10]. The VA-NCNTs are synthesised by pyrolysis of iron phthalocyanine and the iron contamination is then removed by electrochemical purification. Comparing with non-aligned CNTs without nitrogen doping, the potential onset of the ORR on VA-NCNTs, which shows the potential for the reduction reaction to start, shifts to a more positive potential, indicating a better catalytic property. At the same time, the current density on VA-NCNT also increases and implies the potential application in
high current output circumstances. Another unique property of this carbon-based catalyst is its strong resistance to the toxicity of fuels. In the real fuel cell, the fuel molecules could penetrate the membrane and contact with the Pt electrode, which causes the poisoning of Pt and reduces its catalytic efficiency [132]. It is found that VA-NCNTs keep their catalytic property in the presence of methanol, which demonstrates their good tolerance to fuel molecules. The authors also try to explain the origin of the catalytic property of the materials by modelling and calculation. It is found that the nitrogen doping induces a dipole among the nitrogen atom and the carbon atoms bonded to it. This dipole can help the dissociation of the bonding of oxygen molecules.

Figure 2.12 the a) SEM b) TEM and c) photo images of the aligned nitrogen-doped carbon nanotubes. From [10]. Reprinted with permission from AAAS.
This article has attracted much interest in the community. Other nitrogen-doped graphitic materials have been shown to have similar catalytic properties [33, 38, 39, 41, 133]. In 2012, it was suggested that the iron co-doping with nitrogen might enhance the catalytic property through a synergistic effect [134]. It is found that iron impurities inside the nitrogen-doped carbon-graphene complex can affect the ORR performance. On the other hand, when testing the ORR on iron contaminated material, adding CN⁻ into the system leads to reduced performance, which can be seen by an approximately -0.1 V shift of the reaction onset. High-resolution EELS reveals the presence of the interaction between the nitrogen doping and the iron. The authors conclude that the cause of the enhanced ORR catalytic performance could be the synergistic effect between iron and nitrogen atoms. This synergistic effect has also been suggested to exist in other co-doping systems [41, 42, 135]. However, since the fabrication of graphene and carbon nanotube is still not fully developed, a new fabrication method of nitrogen-doped carbonaceous materials, which can catalyse ORR with good performance, is still required. In this thesis, ball milling is demonstrated to be able to synthesise nitrogen-doped graphitic nanoparticles, which can be used as catalysts for ORR.

2.5.3 Mechanism of the catalytic process

Recently, the mechanism of the catalytic process on nitrogen-doped graphitic materials has been intensively researched. It has been widely accepted that nitrogen doping affects the charge density distribution of the neighbouring carbon atoms and induces a polarity of charge density distribution in the graphitic materials [10]. The induced polarity would help the de-association of the O-O bonding and the formation of the C-O bonding [136]. The density functional theory (DFT) calculation suggests that there is only a weak ionic interaction between oxygen molecules and pristine graphene and the distance between them is 0.256 nm [136]. However, with 4% nitrogen doping, the calculation suggests that there is a charge transfer of 0.86e from
graphene, and the distance between oxygen and graphene is also reduced to 0.230 nm [136].

In the same paper, the authors also calculate the potential barrier for each step of the reaction. It is found that nitrogen doping can reduce the energy barrier of forming C-O-C intermediate and enhance the efficiency of the ORR comparing with pristine graphene.

Another factor suggested is that the doped nitrogen changed the spintronic distribution at the same time [137]. The spintronic distribution affects the magnetic property of the catalyst core, which influences the interaction between the catalytic core and the intermediate products and the efficiency of the process [137]. The calculation suggests that the nitrogen doping induces an uneven spintronic distribution with a simultaneous uneven charge distribution. The authors find that the atom with highest spin can be the most favourable site for oxygen absorption. On the other hand, the atom that has highest charge distribution but low spin density cannot absorb oxygen efficiently. Therefore, the authors claim that the spin distribution is very important in reducing the reaction barrier by enhancing the absorption of oxygen molecules.

However, the detailed mechanism is still not clear. For example, there are normally three kinds of nitrogen doping structures: pyridinic, pyrrolic and graphitic nitrogen [138]. Recent experimental and theoretical studies on which nitrogen doping is the one that catalyses the ORR obtains controversial results [33, 139-146]. Most of the reports suggest that it is either pyridinic or graphitic nitrogen that has catalytic properties, but there is still no agreement about the function of these nitrogen structures. This suggests that the mechanism is still not well understood and that this may delay the improvement of the performance of the graphitic materials based catalysts for ORR. In this thesis, a new analytic method is proposed that can provide information for the determination of the real catalytic structures from a different angle.
2.6 Summary

This literature review has shown that nanostructured carbon materials have remarkable structures and important applications in energy storage and clean energy. Mass production of fine designed structures remains a scientific and engineering challenge that needs to be solved to develop practical applications in the future. The structural changes from graphite to graphene and to disordered phase need to be investigated in detail for better control of structures and new properties of the products. Further studies are necessary to explore detailed mechanisms of their applications in ORR and Li-ion batteries. These knowledge gaps will be addressed in this study and the obtained results are presented in the following chapters.
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3.1 Synthesis and processing instruments and techniques

3.1.1 High-energy rolling ball milling

High-energy rolling ball mills (Figure 3.1) use the mechanical force of the moving balls to break the chemical bonding in the materials, causing deformation or the creation of dangling bonds and new surfaces. In traditional rolling ball mills, the milling jar rotates vertically. The grinding balls rise to certain level and fall. The kinetic energy of the falling balls is applied to the milled material. In the high-energy rolling ball milling, a magnet is set up in the machine and applies a magnetic field inside the ball-milling jar. Since the milling balls are made by steel, the magnetic field can further increase the energy of the milling balls. The ball-milling jar used is fitted with a gas valve, which controls the inner atmosphere. Several gases, such as Ar, N$_2$, NH$_3$, C$_2$H$_4$ and CH$_4$, are used to study the effect of the atmosphere during the ball-milling process. In this work, a high-energy rolling ball mill was used for the whole research.

Figure 3.1 Image of the high-energy rolling ball mill.
3.1.2 Thermal annealing

In the thermal annealing process, the material is heated at very high temperatures with a high-temperature horizontal tube furnace of maximum temperature at 1500 °C. The Brownian motion of the atoms is excited and the atoms can move out of their potential wells in the crystal. The structure of the material can be changed and some low molecule weight clusters and doping structures can be vaporised from the bulk material. The annealing furnace used in this project was Lindberg/Blue M STF 54233C (Figure 3.2).

![Photo image of the Lindberg furnace.](image)

3.1.3 Battery assembly

In the project, coin cells are assembled to test the performance of the synthesised battery materials. The components of a coin cell are shown in Figure 3.3.
At the bottom is the negative case. Above it is the cathode material, the separator and the anode material for the battery. In the test of half-cell performance, one of the electrodes is lithium plate, which is also the reference electrode. For example, in the case that the anodic performance of graphite is tested, the lithium plate will be the cathode in the battery. Between two electrodes sits the separator. The separator is used to stop the direct electron exchange
between anode and cathode, since it is electrically isolating. However, at the same time, it has tunnels for the lithium ions (in the form of compounds) to migrate from one electrode to another. For instance, when the battery is discharging, the lithium ions migrate from cathode to anode driven by the chemical potential gradient. At the same time, electrons flow from the cathode to the anode via the external circuit and create current to power the electrical appliance and then combine with the lithium ions in the anode material and form lithium atoms again. Above the anode, there are the spring and spacers. They ensure that the components of the battery do not move and at the same time maintain tight contact with the top and bottom cases. The topmost component is the positive case. During assembly, the electrolyte is drop-casted into the cell. The electrolyte is the carrier of the lithium ions, so it needs to soak the cathode, anode and separator so that the lithium can migrate between two electrodes. In the project, the negative, positive cases, spring and spacer were made in stainless steel. The separator was made from polyethylene film. The electrolyte was made by mixing same volume of ethylene carbonate, dimethyl carbonate and diethyl carbonate. The tested material was coated on the copper foil to make the electrode.

Since the coin cell needs to be sealed from oxygen and moisture, the assembling process is conducted in a battery assembling and testing system (Figure 3.4). The system is filled with inert gas, which can prevent the active gas molecules in the air, such as oxygen and water, to reaction with the sample stored inside. The system for battery assembling is filled with Ar gas with oxygen content lower than 5 ppm and moisture level lower than 1 ppm. During the assembling, the components are placed in the order shown above inside the two cases. The whole cell is then moved to a special press to seal. The hydraulic press used in this project was a cell battery press made by MTI Corporation.
3.2 Characterisation methodologies

3.2.1 X-ray diffraction (XRD)

XRD (Figure 3.5) is a very useful characterisation method of the crystallographic structure of materials.
The analysis is based on Bragg’s diffraction condition:

\[ n\lambda = 2d \sin \alpha \]

\( n \): integral
\( \lambda \): wavelength of the X-ray
\( d \): the interplanar space of one group of crystal planes
\( \alpha \): the incident angle of the X-ray on the crystal planes.

From analysing the diffraction pattern, the phase and the structure of materials can be acquired as well as the interplanar spacings of different crystal planes. Besides, the width of the diffraction peak is also related with the structure of the material, for example, the size of the crystal and the stress in the material. In this project, the XRD was used to analyse the crystallinity of the sample prepared. The equipment used was a Panalytical X-ray diffractometer with a Cu target. The minimum step size of the goniometer is 0.0001°.

### 3.2.2 Field emission scanning electron microscopy (FE-SEM)

SEM (Figure 3.6) is the equipment used for visualisation of the morphology of the material at nanometer scale. In SEM, high-energy electrons are used to scan the surface of the material. At the same time, different signals are produced from the materials and can be detected by different detectors. For the visualisation purpose, usually secondary electrons type 1 to 2 are used. The type 1 secondary electrons (SE1) are the electrons excited by the primary electron beam, so they are very local and have high resolution. These electrons are collected by an in-lens detector. Secondary electrons type 2 is the outer electrons that is scattered by the backscattered electrons and can be produced in a larger area compared with SE1, so its resolution is lower. Secondary electrons type 3 (SE3) is the scattered electron from the environment, for instance, from the metal part of the microscope, which is the noise. An
Everhart-Thornley detector is fitted on the right side of the microscope. It could collect all three types of secondary electrons, so its resolution is affected by SE2 & 3 and is lower than the Inlens detector. The SEMs used in the project were the Zeiss Supra 55VP and Leo 1530, both equipped with field emission guns. The field emission gun can produce an electron beam smaller in diameter and more coherent than conventional thermionic emitter, which can provide better resolution. Supra 55VP has a wide acceleration voltage range, which is from 0.1 kV to 30 kV. The probe current is in the range from 4 pA to 20 nA. The resolution is about 1.6 nm at 1 kV. The working vacuum is 2 to 133 Pa. In this work, the imaging was conducted with the electron energy equal to or lower than 5 kV. The sample was usually prepared by being deposited on conductive carbon tape or silicon wafer. For the sample with low conductivity and serious charging problem, the gold coating was applied to increase the conductivity, so the charging would not affect the quality of the images.

Figure 3.6 Photos of LEO-1530 on the left and Supra 55VP on the right.

3.2.3 Transmission electron microscopy (TEM)

TEM (Figure 3.7) is a microscopy that uses very high velocity electrons to penetrate the material and then the interacted electrons are collected below the sample and the crystallographic information of the sample could be extracted from the signal. Because of the high energy, the wavelength of the electron is very small, which makes TEM a very high-
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resolution microscope. In the project, a JEOL-2100 and a JEOL-2100F were used. JEOL-2100F is equipped with a ZrO/W (100) field emission gun. The acceleration voltage is from 80 to 200 kV. The spot diameter of the JEOL-2100F is about 2 to 5 nm in TEM mode. The small beam spot helps the TEM to achieve very high resolution. The point resolution is about 0.23 nm and the line resolution is about 0.1 nm. In the experiment, TEM was frequently used to acquire bright field, dark field images and electron diffraction patterns of samples, which helped to clarify the structures of samples. The sample for TEM analysis needs to be thin, so it is penetrable by the beam. The samples analysed by TEM in this project contained mostly nanoparticles, so they were usually ultrasonicated in water or ethanol and then drop-casted on the TEM grids.

![FE-TEM JEOL 2100F](image)

*Figure 3.7* Photo of the FE-TEM JEOL 2100F.

### 3.2.4 Scanning probe microscopy (SPM)

A Cypher scanning probe microscope (Figure 3.8) was used to characterise the surface property of the material. The working mechanism is illustrated in Figure 3.9. The main part of the SPM includes a cantilever, cantilever holder, laser emitter, position sensitive photodiode, sample stage and data collecting and analysing units. It needs to be emphasised that in Cypher SPM,
the cantilever is kept still during the experiment. Instead, there are four piezo-electric actuators seating at the four directions of the sample stage. During the experiment, electric-potential is applied to the actuator to make them shrink or extend, which moves the stage. By doing this, the cantilever is kept still. Since the cantilever is very light and easy to be perturbed during the movement, keeping it still will reduce the noise related to the cantilever moving and increase the resolution in vertical and horizontal directions. The horizontal resolution can be down to 60 pm and the vertical one is about 50 pm. The position sensitive photodiode in Cypher SPM is built by combining 4 pieces of independent photodiode screens in the pattern shown in Figure 3.10. By measuring the intensity of the laser in each of the photodiode screens and comparing them, the centre of the laser can be known. For example, when the centre of the laser spot is super-positioned with the centre of the four screens, the light intensity on each of the screen is the same. In the simple atomic force microscopy experiment, the sample stage is moving, which causes the cantilever scanning on the surface of the sample. At the same time, the laser spot is positioned on the cantilever and the interaction between the sample and cantilever is set to be constant. By contacting with the sample, the cantilever will be moved up and down to keep the constant interaction with the sample, which causes a change in direction of the laser reflection. This change will be detected by the movement of the laser spot on the position sensitive photodiode quantitatively with the consideration of the geometry of the optical path. In the more complex lateral force microscopy mode, the twist of the cantilever is also monitored by detecting the lateral movement of the laser spot on photodiode screens.

Depending on the conditions, different information can be extracted from the movement of the cantilever and its interaction with the sample surface. In the project, atomic force microscopy and lateral force microscopy have been used to characterise the morphology and the surface friction of samples.
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Figure 3.8 Photo of Cypher SPM.

Figure 3.9 Illustration of the working mechanism of AFM (http://www3.physik.uni-greifswald.de/method/afm/eafm.htm).

Figure 3.10 Illustration of the position sensitive photodiode.
3.2.5 Nitrogen-sorption

Nitrogen-sorption at liquid nitrogen temperature is used to characterise the surface area and pore size distribution of the material. By analysing the adsorption curve with different mathematical models, different properties of the surface can be evaluated. In the project, BET theory was used to calculate the total surface area. BET theory is an extension of Langmuir theory [147]. Instead of considering only single layer absorption in Langmuir theory, BET theory considers the multilayer adsorption with several hypotheses. For example, the adsorption should be physical adsorption and there is no interaction between different adsorption layers. By adopting those hypotheses, the monolayer adsorbed gas quantity can be calculated from the adsorption curve and the surface area can also be acquired. It need to be emphasised that BET theory only holds when the relative pressure is between 0.05 and 0.35 (relative pressure is the actual pressure divided by the saturated vapour pressure at a given temperature). T-plot was used to calculate the pore area and external surface area [148]. The basic concept of T-plot is that by comparing an isotherm curve of a micro-porous material with a standard Type 2 isotherm the information about the pore area can be extracted. By assuming that the thickness of the adsorbed film is uniform, a statistical thickness \( t \) can be calculated from the gas adsorption isotherms and the relationship between \( t \) and the quantity of the adsorbed gas can be built, which is the t-plot. By comparing the t-plot of the sample and the standard t-plot, the area of pore can be calculated. The equipment used was Tristar 3000 (Figure 3.11). Tristar 3000 can measure the pressure from 0 to 999 mmHg with a resolution of 0.05 mmHg. The accuracy of the pressure measurement is within 0.5% of the full scale. The vacuum required for the test is 20 \( \mu \)mHg.
3.2.6 Thermogravimetric analysis (TGA)

In a TGA experiment, the weight changes of the sample induced by chemical reactions or physical changes during the heating process are recorded. From an analysis of the results, the thermal stability of the sample can be evaluated. It is also used to probe the adsorption species in the material since these species are weakly bonded with surface and can be vaporised in the heating process. For example, Ar atmosphere is selected when analysing the content of adsorptive species in milled graphite, since Ar will not react with graphite at high temperature. The equipment used was NETXSCH STA 409 PC (Figure 3.12).

Figure 3.11 Photo of Tristar 3000.

Figure 3.12 Photo of the thermal gravimetric analyser.
3.2.7 Dynamic light scattering

The dynamic light scattering method was used to measure the particle size of samples. In the test, the tested sample needs to be in a solution or dispersion so that the particles perform Brownian motion. The theory is that when the light (the laser light is used in the experiment) is scattered by little particles (smaller than the wavelength), it will cause Rayleigh scattering, in which the scattered light is in all directions. At the same time, particles have relative motion towards or away from each other. The change of the relative position among particles will then lead to an inconstant phase difference among the scattered light, which is interpreted as a fluctuation of the intensity of light detected. Thus, the fluctuation carries the information of the speed of the Brownian motion, which is related to the particle size. This information can be calculated and extracted by a computer program and the particle size can be reported. In this project, this methodology was used to analyse particle size distribution of the samples after different treatments, such as ball milling or annealing. The analyser used in the project was the Malvern Zetasizer nano (Figure 3.13).

Figure 3.13 Photo of the Dynamic light scattering analyser.
3.2.8 Raman spectroscopy

Raman spectroscopy has been demonstrated as a very useful technique in the characterisation of graphitic materials. Single crystals of graphite have a Raman resonance peak at 1575 cm\(^{-1}\), which could be assigned to \(E_{2g}\) vibration mode of the graphite crystal and called the G band [149]. In the same paper, it was also mentioned that there was another peak at about 1355 cm\(^{-1}\) in polycrystalline graphite. The intensity of this band was found to be inverse-proportional to the graphitic in-plane size. In 1977, Hiroshi et al. reported that after neutron-irradiation, the intensity of the band at about 1360 cm\(^{-1}\) increased [150]. In addition, there was another band at about 1623 cm\(^{-1}\) appearing. These two bands were then related with the defect structure or atom clusters introduced by neutron-irradiation. Vidano and Fischbach confirmed that the bands at 1360 and 1623 cm\(^{-1}\) were defect-related and labelled them as D and D’ respectively [151]. They also researched the double-resonance Raman of graphite and found two intensive bands at about 2700 cm\(^{-1}\). In 1979, a more detailed work was conducted to understand the Raman fingerprint of graphite [152]. It has been suggested that the band at about 2700 cm\(^{-1}\) could be the double resonance of the D’ band at about 1350 cm\(^{-1}\), instead of a genuine vibration of perfect graphitic structure suggested before [153]. Willis et al. studied the dispersive property of the Raman band of the graphite. The Raman spectra were recorded using different excitation laser wavelengths from 488 nm to 647 nm. It was found that the Raman bands at 1360 (D), 2720 (2D) and 2950 (D+G) cm\(^{-1}\) shifted with the photon energy. On the other hand, the bands at 1580 (G) and 1620 (D’) cm\(^{-1}\) were not varied. Particularly, it was found that the energy shift of 2D band was approximately twice the shift of D band. This observation implied that the origin of 2D band could be the double resonance of D band.

Ferrari studied different carbon structures and further explained the Raman spectra for disordered graphitic structures [154]. It was suggested that the disordering process of graphitic carbon could be explained with a three-step model. The first step is the change of big graphitic
chunks into nanocrystalline graphite. In the second step, nanocrystalline graphite is changed to amorphous carbon. The amorphous carbon is further evolved into ternary amorphous carbon in the third step. In the first step, $I_D/I_G$ increases due to the boundary atoms creation, which activates the D band. At the same time, the appearing position of G band moves to higher wave number, which is caused by the increasing intensity of D’ band at about 1620 cm$^{-1}$. In this stage there is no dispersion of the G band. In the second stage, it is found that instead of a further increase of $I_D/I_G$, the ratio decreases. The explanation for this phenomenon is that in stage 2, the six-folded ring system begins to be broken and the content of $sp^3$ carbon begins to increase. The origin of D band is the ring-breathing of the aromatic ring in graphite, so with the decrease of the number of the rings, the intensity of D band begins to decrease. On the other hand, G band is associated with the vibration of C=C bonding, which exists even when the ring is broken, so the intensity of G band should keep constant. The decreasing $I_D/I_G$ is explained as an indication of the process, in which the ring system begins to be destroyed when the nanocrystalline graphite is transforming to amorphous carbon. Finally in the third stage, when all the graphitic structure transfers into amorphous phase, the G peak will blue shift as the result of the ring breaking and the formation of olefinic structures. Moreover, the $I_D/I_G$ is close to zero since most of the aromatic rings have been open and very little structure contributes to the D band.

The intensity and the width of the major Raman bands is very sensitive to the structure and chemical composition of the graphitic materials, which makes it a very good technique in studying graphitic materials [155]. The equipment used in this project included The LabRAM HR800 from HORIBA JOBIN YVON S.A.S. and Renishaw inVia micro-Raman system.
3.2.9 Ultraviolet-visible absorption (UV-Vis)

UV-Vis was used to characterise the electronic energy level of the sample. Usually, the molecules containing $\pi$ and/or non-bonding electrons can be excited to the anti-bonding orbitals by the photons in this energy range. For instance, graphite, which has delocalised $\pi$ electrons has a strong absorption of the UV-Vis spectrum. For a sample with an already known absorption in the spectrum, UV-Vis can be used to detect this sample. Varian Cary 3 and the Cary 5000 were used in the project (Figure 3.15).
3.2.10 Synchrotron beam source

The core of a synchrotron beam source is an accelerator that accelerates the charged particles. The basic theory of the synchrotron is that an accelerated charged particle radiates electromagnetic waves, which is described in Larmor formula or relativistic Larmor formula depending on the speed of the motion. In the synchrotron accelerator, charged particles (electrons in Australian synchrotron centre) are moving in a ring, in which they are accelerated at every point of the ring and this causes the change of direction of their velocity. Being accelerated, the electrons radiate electromagnetic wave. The spectrum of the electromagnetic wave is selected by monochromators for different uses. In the soft X-ray beam-line at Australian synchrotron centre, the photon energy is from 100 eV to 2500 eV, which can excite the electron transitions in the materials.

3.2.11 X-ray photoelectron spectroscopy (XPS)

XPS is a technique used to probe the chemical environment of atoms in the materials. In the experiment, the sample is exposed to X-ray radiation. The energy of the X-ray photon can excite electrons to leave the material, if its energy is higher than the gap between the electron’s energy level and the energy level at an infinite point. At the same time, when an inner shell electron is scattered by the X-ray, an outer shell electron may transit and fill the hole. The energy emitted in the process could excite another outer shell electron, which is called the Auger electron, to leave the material. The energy of the photoelectron is related with the kind of the atom and the chemical environment around the atom. Thus, by analysing the energy of photoelectrons, the elemental information and the chemical environment can be acquired. For example, in the project, XPS is used to analyse the nitrogen doping in the ball-milled graphite. A typical spectrum of graphite is shown in Figure 3.16. The peak at about 284 eV comes from the C=C bonding in graphite and the small peak at about 530 eV is due to the oxygen atoms in
the sample. Due to the high-energy resolution of modern XPS, the different nitrogen doping species, such as pyridinic nitrogen and graphitic nitrogen, can be determined after fitting the envelope of the high-resolution N1s spectrum. Moreover, the peak area is proportional to the quantity of the component that it stands for, so the area can be used to calculate the relative quantity for each component. On the other hand, XPS can be used indirectly to monitor the defective structure in the material. An example is using XPS to measure the quantity of \( sp^3 \) and \( sp^2 \) carbon in the ball-milled graphite sample. In the commercial graphite, almost all the carbon atoms are \( sp^2 \). However, after ball milling, the graphitic structure is broken and \( sp^3 \) carbon is formed at the defective sites. Since the energy of the 1s electron in \( sp^2 \) and \( sp^3 \) carbon is different, XPS can qualitatively or semi-quantitatively measure the content of the \( sp^3 \) carbon and help to analyse the defective structure in the material. However, as fitting is needed to differentiate two kinds of carbon and carbon 1s spectrum also receive interference from different carbon oxide groups, this method is not accurate in this circumstance and the result needs to be confirmed by other methodologies before making any assertion. In this project, SPEC-XPS and synchrotron based XPS have been used.

![Figure 3.16 A typical x-ray photoelectron spectrum of commercial graphite.](image)
3.2.12 Near edge X-ray absorption fine structure (NEXAFS)

NEXAFS is the technique similar to XPS in the aspect of the source of excitation and both use monochromatic X-ray. However, in NEXAFS, the X-ray photon energy is scanning instead of being fixed. More importantly, instead of analysing the initial photoelectrons, NEXAFS also monitors the event that happens right after the excitation. Figure 3.17 illustrates three processes that contribute to the NEXAFS spectrum. The photoelectron, fluorescence photon and Auger electron triggered by the incident X-ray can all be detected in NEXAFS experiment. Thus, in contrast to XPS that requires the final detectable state as a free state, NEXAFS can probe even the binding state. The NEXAFS unit used in the project was based on soft X-ray beamline in the Australian Synchrotron Centre.

![Diagram](image)

Figure 3.17 Three processes that contribute to the NEXAFS spectrum, which produce a) photoelectrons, b) fluorescent photons and c) Auger electrons.
In the project, NEXAFS was an effective way to study the structure of graphitic materials. The most significant features in highly crystallized graphite are the transitions at about 285.5 eV and about 291 eV [156]. The transition at 285.5 eV is from the initial 1s state to the final $\pi^*$ state. The transition at 291 eV splits to two peaks at about 291.7 and 292.8 eV in the graphite with good crystallinity. This is caused by the interaction between the $\sigma^*$ orbital and the $p_z$ orbital of the inequivalent carbon atoms in the lattice [157]. The significance of the doublet band is that it requires good alignment between graphene planes, or it cannot be seen in the spectrum [158]. Thus, NEXAFS provides a significant feature that can be used to check the interlayer structure of graphite. Besides, there are two transitions representing the in-plane defects in graphene layers [159, 160]. In conclusion, NEXAFS can be used as a powerful instrumental analysis method to pinpoint the defect structure in graphitic materials.

### 3.2.13 Galvanic charge-discharge

This method is used to test the stability, durability, capacity and columbic efficiency of a battery. In the experiment, the battery is charged and discharged at a fixed current for many cycles. The voltage and the capacity are recorded in the process. The equipment used in the project was LAND battery test system (Figure 3.18). The voltage range of the system is from 5 V to 15 V. The current resolution is 0.001 mA and the voltage resolution is 0.001 V.

![Figure 3.18 Photo of LAND battery test system.](image)
3.2.14 Cyclic voltammetry (CV)

CV is the method used to study the mechanism of an electrochemical reaction. During the experiment, the voltage scans back and forth in a range and at the same time the corresponding current is recorded. CV is helpful in studying electrochemical reactions since it can reveal the potential of the reaction and other properties, such as over-potential and reversibility. In the project, Solartron and Ivium-n-State electrochemical stations were used for the CV test. Ivium-n-State electrochemical station can apply potentials from -10 to 10 V, with a resolution of 0.33 mV. The current range is from 10 nA to 10 A in 10 steps and the current resolution is 0.015% of the current range selected.

3.2.16 Electrochemical impedance spectroscopy (EIS)

EIS is a method to study the mechanism of an electrochemical process. In an EIS experiment, a series of alternating voltage signals with different frequencies is applied. By extending the concept of resistance with the effect in time domain, an extended Ohm theory can be acquired:

\[ Z = \frac{\bar{V}}{\bar{I}} \]

\[ Z_R = |\bar{Z}| \cos \theta \]

\[ Z_I = |\bar{Z}| \sin \theta \]

\( \bar{Z}, \bar{V}, \bar{I} \) are the complex form of impedance, voltage and current. \( Z_R \) is the real part of impedance when \( Z_I \) is the imaginary part. \( \Theta \) is the phase angle of impedance. By analysing the real and imaginary part of the impedance and combining with the equivalent circuit method, it can provide information about the mechanism of chemical reactions. In the project, Ivium-n-State was used to perform EIS experiment. The Ivium-n-State can apply a potential with a frequency range from 10 micro Hz to 250 kHz. The amplitude of the potential is from 0.015 mV to 1.0 V.
3.2.17 Rotating disc electrode (RDE)

RDE is used to study the kinetic of the electrochemical reaction. In contrast to the steady electrode experiment, the working electrode, on which the sample is deposited, is rotating in the electrochemical test. When rotating, the solution around the electrode (hydrodynamic boundary layer) is dragged by the electrode and the forming centrifugal force flings the solution away from the centre of the electrode. The solution beneath the hydrodynamic boundary layer will then move upwards and replace the flung solution. In this way, it builds an electrochemical reaction that is controlled by the solution flow rate rather than the diffusion rate of the reactant. The flow rate is controlled by the rotating speed of the disc. By analysing the reaction at different disc rotating rates, the information of the reaction mechanism can be extracted. For example, in this project, the RDE is used to study the electron transfer number of the nitrogen-doped graphitic materials in catalysing ORR. By applying the Koutecky-Levich equation and plotting the current against rotation speed, the slope of the plot contains the information of the electron transfer number of the reaction, which is valuable information to study the mechanism of electrochemical reactions. In this project, the RDE experiment was carried out with a rotating ring-disk electrode with Pt Ring and GC disc made by ALS Co., LTD.

3.2.18 Fourier transform infrared spectroscopy (FTIR)

Infrared spectroscopy is a very popular methodology used to characterise the functional groups in a wide range of materials. Molecules have different vibrational modes, which can reflect the structure of the molecule. When the molecule interacts with the photon, which carries the energy equal to the energy gap between the ground state and an excited state of one vibrational mode, the photon could be absorbed and the molecule will be excited. The photon energy of the infrared spectrum covers the excitation energy of vibrational modes of many chemical functional groups. Moreover, the excitation energy of vibrational modes of different functional
groups are usually different, so by analysing how the infrared light is absorbed by the molecule, the information of the structure of the molecule can be extracted. The traditional infrared spectroscopy (dispersive spectroscopy technique) needs the sample to be exposed to a monochrome infrared light, the frequency of which is changing during the experiment. It is usually slow. In FTIR, the spectrometer simultaneously detects the spectrum in a wide spectral range. During the data collection, the combination of the frequency in the beam is modified in different exposures to get many data points. The whole data is then processed by Fourier transform to transform the data from time domain to frequency domain. This process is usually done by computer and it dramatically shortens the time needed for the test comparing with the dispersive spectroscopy technique. A typical FTIR spectrum is shown in Figure 3.19. The major peaks at 1200, 1600 and 3400 cm\(^{-1}\) indicate that in this sample there are mainly C-O-C, C=C and -OH functional groups. The equipment used in this project was a Bruker Vertex 70 infrared spectrometer. The instrument has a spectral range from 400 and 4000 cm\(^{-1}\), with a resolution down to 0.4 cm\(^{-1}\).

![Figure 3.19 A typical FTIR spectrum of graphene sample after oxygen reduction reaction.](image-url)
3.2.19 Nuclear magnetic resonance (NMR)

The basic theory of NMR is that when a nonzero spin nuclei is in a magnetic field, the spin energy state of the nuclei will split. The nuclei, then, can absorb and re-emit the electromagnetic radiation to be excited or back to ground state respectively. The energy gap between the excited state and ground state is influenced by the property of the nuclei and the strength of the external magnetic field. NMR can be used as a method to characterise the chemical environment of the nuclei, since the nuclei is shielded by the electron in the atom, which will also response to the magnetic field and produce an induced magnetic field. The induced field will enhance or decrease the applied magnetic field ‘felt’ by the nuclei, which alters the energy gap between the excitation state and the ground state. Therefore, by analysing the frequency of the electromagnetic field, which will resonate with the nuclei, the chemical environment of the nuclei can be characterised. In solid state NMR, the sample is prepared in solid state, which leads to a more complex situation than liquid NMR due to the anisotropic influence of solid. However, several methods, such as magic angle spinning (MAS), have been developed to reduce the negative influence and to get analysable spectra. The equipment used in this project was BRUKER Avance3 NMR spectrometer (Figure 3.20).

![BRUKER Avance3 NMR spectrometer](image)

*Figure 3.20 BRUKER Avance3 NMR spectrometer.*
Chapter 4 Disorder in ball-milled graphite revealed by Raman spectroscopy

4.1 Introduction

As discussed in Chapter 2, the modern high-energy mechanical milling technique has been used to produce graphitic materials with disordered structures [60, 73, 161]. Phase transformation sequence from hexagonal structure to turbostratic, nanocrystalline and amorphous structures has been found [73, 161]. A porous structure is found in graphite after ball-milling treatment in Ar atmosphere because of severe plastic deformation and defect creation [60]. During the ball milling, the surface area of the graphite increases first and then decreases during further milling. This increase can be explained by the particle size reduction, but the later reduction of the surface area has not been well understood. Further characterisation with other analysing techniques is needed to reveal detailed structural changes. Raman spectroscopy is a powerful tool to examine carbon structures and especially in disordering and amorphisation processes [149, 155, 162, 163]. Band intensity ratio $I_D/I_G$ has been found to reflect the different disordering stages in ion-beam bombarded graphite [164]. The phase transformation in graphite under ball milling has not been carefully investigated using Raman spectroscopy. This chapter shows Raman spectroscopy analysis can reveal detailed phase transformations during milling processes.

4.2 Experimental

Crystalline graphite powders from Sigma Aldrich (particle size < 20 μm) were used as the starting material. Ball milling was performed with a high-energy rolling ball mill. A magnet
was used to control the milling energy [165]. 4 g of graphite were milled with 4 hardened steel balls of 2.5 cm in diameter. The powder to ball weight ratio was 1:66. The rotating speed was 150 rpm and milling atmosphere was Ar gas at 300kPa. The purity of the Ar used is 99.99%.

Raman spectroscopy characterisation was performed using a LabRAM HR800 instrument from HORIBA JOBIN YVON S.A.S. with a laser of 532 nm and a power at 50 mW. The spectral resolution of the equipment is 0.3 cm$^{-1}$. The spectra were taken from 200 to 3500 cm$^{-1}$ with a signal collection time of 15 s and two collections were added to generate the final spectrum. To quantitatively analyse the band changes, the D and G bands were fitted with Lorentz peaks so that the position, height and the full width at half maximum (FWHM) of each band can be determined.

X-ray powder diffraction (XRD) was performed using a PANalytical X’Pert Pro diffractometer (Cu K-alpha radiation, $\lambda = 0.15418$ nm). The step size was 0.05° and the collection time was 1.5 s for each step.

Nitrogen-sorption test was carried out using a Tristar 3000 (Micrometrics) system at 77 K. Branauer-Emmett-Teller (BET) theory and t-plot method were used to calculate BET, external and internal surface areas.

Scanning electron microscopy (SEM) images were obtained from a Zeiss Supra-55VP instrument and 3 kV was used as the acceleration high voltage. The working distance was 5 mm. The transmission electron microscopy (TEM) imaging and electron diffraction were performed with a JEOL-2100F microscope at 200 kV.
X-ray photoelectron spectroscopy (XPS) analysis was performed with a SPECS system with the Phoibos MCD 100 electron analyser and monochromatised Al K$_\alpha$ X-rays of 1486.74 eV. The photoemission spectra were simulated with several sets of Gaussian-Lorentzian functions with Shirley background. Four peaks were used to fit the XPS data. The position of the four peaks are at 284.3, 285.0, 285.8 and 287 eV, representing $sp^2$ carbon, $sp^3$ carbon, C-O and C=O, respectively. The ratio of $sp^3$ carbon to $sp^2$ carbon can be calculated by dividing the area of the peak at 285.0 eV by the area of the peak at 284.3 eV.

### 4.3 Results and discussion

![Raman spectra of the graphite milled in Ar gas with different milling periods.](image)

Figure 4.1 Raman spectra of the graphite milled in Ar gas with different milling periods.

The evolution of the Raman spectra during milling process is illustrated in Figure 4.1. Three well defined bands can be seen in the spectrum of the starting graphite (0 h), which are generally called D, G and 2D bands [154, 166], at the positions of around 1350, 1582 and 2718
cm\(^{-1}\), respectively. The strong G band originates from the \(E_{2g}\) vibration mode, corresponding to the relative motion between 2 \(sp^2\) carbon atoms. The D band comes from \(A_{1g}\) ring breathing mode and importantly, this mode is symmetrically forbidden in perfect graphite. The very low intensity of the D band indicates the starting graphite has relatively good graphitic structure. During the first stage of milling (up to 20 h), the intensity of the G band decreases as the milling time increases, while the D band intensity increases rapidly. Significant changes of the bands as a function of milling time are plotted in Figure 4.2. Figure 4.2a shows the changes of the intensity ratio of D over G band (I\(_D\)/I\(_G\)) during the milling process. I\(_D\)/I\(_G\) rises from 0.28 to a peak value of 1.26 at the end of 15 h and then decreases to 1.07 during further milling to 40 h. It becomes almost unchanged during extended milling to 100 h. Such a complicated variation implies some interesting phase changes, which will be discussed later. Figure 4.2b shows that the G band shifts from 1581 to 1590 cm\(^{-1}\) within the first 30 h of milling and then slowly shifts back to 1587 cm\(^{-1}\) during further milling. In contrast, the D band position does not change much. The band width changes are compared between the D and G bands in Figure 4.2c. A small increase of the FWHM of the G band (from 25 to 80 cm\(^{-1}\)) is observed only during the first 15 h of milling. The FWHM of the G band does not change much during further milling. In contrast, the FWHM of the D band increases rapidly from 50 to 220 cm\(^{-1}\) within the first 40 h and then slowly increases to 240 cm\(^{-1}\) at the end of 100 h milling. The large FWHM of D band is generally considered as a result of the distribution of clusters with different dimensions and orders in amorphous phases [155, 167]. The intensity of the 2D band decreases with the increase of ball-milling time, which is attributed to the disorder in c axis and the formation of turbostratic structure [166] and proportion to the crystal size [168]. Because of the weak bonding between the (0 0 2) basal planes, high-energy ball milling actions can easily destroy the original ordering between the basal planes and even large starting crystal down to very
small size within the first milling stage. A 2D band thus cannot be seen from the samples milled for 20 h or longer.

Figure 4.2 The milling time dependence of a) \( I_D/I_G \); b) position of the G bands; c) FWHMs of the G and D bands. The error bars represent standard deviations.

XRD patterns of the milled graphite samples as displayed in Figure 4.3 show that the diffraction peaks of the milled samples become weak and broaden as the milling time increasing, indicating a gradual disordering process. For the samples milled for 15 and 20 h, the asymmetric shape of the (0 0 2) peaks at about 25.6 degree is due to the mixture of amorphous and nanocrystalline phases. The amorphisation of graphite seems to be complete after 40 h of milling as only one single and broad diffraction peak is observed in the corresponding XRD pattern. No further change can be seen from the XRD patterns for the samples milled for longer time (70 and 100 h). TEM analysis confirms the phase changes. The unmilled graphite has a
well-crystallised hexagonal structure as evidenced by the sharp and dotted (0 0 2) diffraction rings (Figure 4.4a). The TEM image of the 15 h milled sample (Figure 4.4b) shows parallel fringes with a thickness of about 4 nm (indicated by arrows), confirming a mixture of nanocrystalline structure and disordered phases. No parallel fringes can be found in the TEM image in Figure 4.4c and 4.4d taken from the longer milled samples, suggesting disappearance of nanocrystalline structures and full amorphisation after 40 h milling. Dense and compacted clusters can be seen on the TEM image as shown in Figure 4.4d (indicated by arrows). The small clusters are formed by high-energy ball impacts and they are popular in the samples milled for extended periods of time (i.e. 70 and 100 h).

![Figure 4.3 X-ray diffraction patterns of the graphite milled for different periods.](image)

The intensity and shape changes of the D and G bands of the Raman spectra in Figure 4.1 should be associated with the structural changes created by ball milling. When the ball milling begins, the milling actions cut down large graphite particles to small flakes and peel the flakes
into thin sheets, as revealed by the TEM image and the inserted electron diffraction in Figure 4b. The generation of structural defects by milling actions activates the D mode resulting in a rapid rise of the band intensity during the first period of milling (20 h). During further milling, the ball milling actions break up the $sp^2$ bonds of six-member-rings, the D band intensity starts to decrease as the intensity depends on the number of the rings. During the extended milling up to 100 h, the D band intensity remains almost unchanged, implying the disordering process is balanced by an ordering process that will be discussed later.

Figure 4.4 TEM images and electron diffraction patterns of the graphite samples milled for different periods of time: (a) 0 h, (b) 15 h, (c) 40 h and (d) 70 h.

While G band is only related to the $sp^2$ carbon-carbon bonding, the broadening of G band is possibly contributed by electron-photon coupling, which is sensitive to the size and conductivity of the materials [169]. When the milling actions severely damage the crystallinity of graphite, the relative position between carbon atoms is slightly changed. A wider distribution of the parameter of $sp^2$ bonding could also lead to widening of the frequency of $E_{2g}$ vibrational mode and a wider G peak during the first stage of ball milling. The band widening might also
be the result of the merge of D' band into G band. The D' band appears as a small shoulder peak of G band in the 15 h milled sample (Figure 4.1) and cannot be separated from the G band in the Raman spectra of the samples milled for longer time. The large broadening of the D band is associated with the disordered graphite structure [167, 169]. Ball milling actions distort the aromatic rings, which results in the widening of the D peak. When the milling time increases, ball milling could not effectively break the graphite particle further down or thinner as large clusters are formed due to welding effect [60, 74]. A typical SEM image of the clusters is displayed in Figure 4.5. The formation of these clusters is responsible for the complicated specific surface area change as shown in Figure 4.6. The specific surface area increases to 400 m²/g during the first 15 h of ball milling. During this period, particle reduction and new surface generation are dominant [60]. During the further milling stage from 15 to 40 h, the specific surface area begins to drop and stabilises during extended milling period up to 100 h. The specific surface area of milled graphite has the same evolution as I_D/I_G, implying that both evolutions are related to the ball-milling induced phase transition.

Figure 4.5 SEM image of the clusters formed in the graphite sample milled for 100 h.
Figure 4.6 Specific surface area change as a function of milling time.

ID/IG changes are found to relate to the different stages of disorder and amorphisation processes of various carbon materials [150, 154, 155, 164, 170]. ID/IG increases when the bulk hexagonal structure becomes nanocrystalline structure; ID/IG decreases to zero when nanocrystalline structure becomes fully amorphous. In the current ball-milled graphite, the disordering and amorphisation processes have similar ID/IG evolution as other carbon materials, but ID/IG does not decrease to zero when the graphite becomes amorphous. It decreases slightly from 1.28 to 1.07 over the extended milling up to 100 h. The high ID/IG ratio might be due to two reasons. First, the milling intensity used is not high enough to break most of the six-member rings. Most milling energy is lost during breaking up of the large clusters so the energy is no longer sufficient to break all \( sp^2 \) bonding. This is confirmed by the low \( sp^3/sp^2 \) bonding ratios estimated from XPS analysis. The highest \( sp^3/sp^2 \) ratio is about 25% in the sample milled for 70 h. Second, the formation of dense and relatively ordered structures found in the samples milled for 70 and 100 h (TEM image in Figure 4.4d). The ball-milling actions can impact disordered nanostructures into relatively ordered structure at nanometre scale. Equilibrium
might be established between disordering and ordering processes. The similar changes in ID/IG and specific surface area during the ball-milling process are caused by the same structural reasons—an equilibrium disordered structure.

### 4.4 Conclusions

Raman spectroscopy has revealed a detailed phase transformation of graphite during an extended milling process. ID/IG increases during the disordering process from hexagonal to nanocrystalline structure, and it decreases slightly during the amorphisation process and remains unchanged during extended milling up to 100 h. The stabilised ID/IG for the amorphous phase might be due to two reasons: (1) The ball-milling conditions used in this experiment cannot provide sufficient energy to break most of the six-member rings; (2) The formation of new clusters leads to equilibrium between disordering and ordering processes. This finding can explain why the surface area increases at the beginning of the ball milling process and then begins to reduce after 15 h. The ball milling firstly creates new surface by breaking the large graphite particles into smaller pieces. However, when the ball milling cannot further break the particles, it begins to distort the graphite flakes to form compacted clusters, which leads to a reduction of the surface area. This finding is also supported by the XPS characterisation and electron microscopy imaging, which proves that the majority of the carbon atoms are still in \(sp^2\) hybridisation state and the sample milled for long time contains mainly carbon clusters.
Chapter 5 The lubricant effect of milling atmosphere on nanostructures

5.1 Introduction

Mechanical forces have been used in different ways since the Stone Age to produce tools, materials and other goods in human society. Mechanical grinding has been demonstrated as an efficient way to fabricate functional 2-D nanomaterials on a large scale [47, 48, 95, 171]. It can also be used to synthesise electro-catalysts for oxygen reduction reaction [108, 172, 173]. Mechanical milling is also involved in developing new electrode materials for lithium ion batteries with better performance [174, 175]. However, in most of these attempts, the milling atmosphere was not carefully selected and little attention was paid to the relationship between the structure of the final products and the atmosphere.

On the opposite side of utilising mechanical forces, it is important to reduce the friction forces among the parts of a mechanical system to increase the life-time. Dry lubricants have been used for this purpose in the extreme environments, such as high temperature, vacuum or with intensive radiation [176-178]. It has been demonstrated that the performance of the dry lubricant could be closely related with the atmosphere [179-181]. In addition, in the ball-milling processes different atmospheres lead to different structures of milled powder and an hypothesis is raised to explain the phenomenon, which suggests that the milling in active atmosphere could lead to boundary doping and stabilisation of the structure [49, 74, 182-185]. However, the mechanism of the interaction between the atmosphere and the solid lubricant and the way in which it affects the lubrication has not been well studied.
In this Chapter, by analysing the properties and structures of the materials that are ball milled in different atmospheres, the way in which the atmospheres affect the final structure of milled materials and its relationship with lubrication is studied. An increased understanding of the interaction between the atmosphere and solid lubricants may help to develop more efficient solid lubricants, in order to meet specialised needs in, for example, space exploration and other challenging environments.

5.2 Experimental

Crystalline graphite (particle size <20 um), MoS₂ powder (particle size <20 um) (Sigma Aldrich) and hexagonal boron nitride (BN) (particle size ~ 40 um) (Momentive) were used as starting materials. N₂ and N₂/15% H₂ gases used in the experiment had a purity of 99.99%.

The ball-milling experiment was conducted with a high-energy ball mill with an external magnet [165]. In a typical experiment, 4 g graphite (BN or MoS₂) was loaded in the ball-milling jar with four hardened steel balls. The steel balls were weighted 66 g each, with a diameter of 2.5 cm. The milling rotating speed was 150 rpm. At the beginning of the experiment, the milling jar was vacuumed and then filled with the selected atmosphere at 300 kPa.

The structure of the samples was studied with X-ray powder diffraction (XRD), which was carried out using a PANalytical X’Pert Pro diffractometer (Cu K-alpha radiation, \(\lambda = 0.15418\) nm). The step size was 0.05° and the collection time was 1.5 s for each step. The morphologies of the samples were studied with a scanning electron microscope (SEM, Supra 55VP) and transmission electron microscope (TEM, JEOL 2100F).

The nitrogen content was measured by LECO TC 600 Oxygen and Nitrogen Determinator. During the experiment, the sample was heated in a high-purity graphite crucible and the oxygen in the sample reacted with graphite to form CO and CO₂. At the same time, the nitrogen atoms formed stable N₂ gas, which was released from the sample. The released CO and CO₂ was
detected quantitatively by an infrared absorption unit, when the nitrogen was measured by thermal conductivity method.

Near edge X-ray absorption fine structure (NEXAFS) was conducted at the Australian Synchrotron Centre with a synchrotron based X-ray source. The experiment was carried out in the high-vacuum chamber with the pressure at about $10^{-10}$ mbar. The total electron yield was recorded. The step of photon energy was 50 meV for carbon and nitrogen edge and 20 meV for boron edge. The results were normalised by the photon intensity. When collecting the spectra for BN, an electron gun was used to neutralise the positive charge on the sample surface.

Cypher scanning probe microscope (SPM) was used to measure the surface friction force of samples. The SPM was located inside a clean room. In a typical experiment, a sample was exfoliated before the measurement by scotch tape method [186]. It was then deposited on the silicon wafer and moved inside the selected atmosphere with 350 kPa pressure for 24 h. Finally, it was transferred to the SPM and the friction force was measured on a flat flake of sample that was approximately $1 \text{ um} \times 0.5 \text{ um}$. This friction was the approximation of the friction inside the atmosphere. The sample was left in the atmosphere for 24 h. The surface friction was measured again at the same place. The difference of the two measurements was the friction deviation of the surface in the selected atmosphere and in the air.

5.3 Results and discussion

The structure changes of graphite milled in NH$_3$ was revealed by XRD (Figure 5.1 and 5.2). The starting graphite powder has a typical hexagonal structure with two characteristic diffraction peaks ((0 0 2) at about 26.5° and (0 0 4) at about 54.5°). When ball milled in NH$_3$ atmosphere, the diffraction peaks become broad and weak with the increasing milling time up to 70 h, which is associated with the reduction of grain size. However, the (002) peak still can be seen clearly and the FWHM increases from about 0.45° to 1.55°. Conversely, samples milled
in Ar show a disordered and semi-amorphous structure after only 20 h milling. The (0 0 2) peaks of the samples milled in Ar almost disappear and the FWHM increases to about 8°, indicating a semi-amorphous structure [187]. At the same time, (0 0 4) diffraction peak at about 56° exists after 30 h ball milling in NH₃, which indicates that the sample still has good long distance periodic structure on z-axis of graphite. In contrast, the samples milled in Ar for more than 10 h have no (0 0 4) diffraction peak.

Moreover, the position of the (0 0 2) diffraction of samples milled in NH₃ shifts from 26.5° to 26.3° after 70 h milling (Figure 5.3), which suggests a slight increase of inter-plane distance of the (0 0 2) basal planes (Figure 5.4). This increase may be a result of mechanical impact or NH₃ intercalation.

Figure 5.1 XRD of graphite milled in NH₃.
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Figure 5.2 XRD of the graphite milled in Ar.

Figure 5.3 The shift of the (0 0 2) peak position.
The SEM images confirm the different structure evolutions when using NH$_3$ and Ar as the atmosphere (Figure 5.5). In Figure 5.5a, the starting material is large graphite chunks with a particle size of about 6 μm. After being ball milled in NH$_3$ for 15 h, the graphite chunks are exfoliated and many thin nanoflakes are in the samples. An additional 15 h of milling does not significantly alter the morphology of the nanoflakes (Figure 5.5c). When using Ar as the atmosphere, the change is more significant and the structure is broken down more quickly. After 5 h milling in Ar, the sample is still flake-like. However, the high-resolution SEM image shows that most of the flakes are showing signs of distortion that is not typical of the graphitic structure (Figure 5.5d, pointed by an arrow). This may be a sign of the introduction of structural defects. When the milling time was increased to 15 h, the morphology was significantly changed (Figure 5.5e). No graphitic flake remained in the sample and the sample changed to
nanoparticles. Another 15 h milling does not significantly alter the morphology (Figure 5.5f). TEM provides more evidence of the structural change (Figure 5.6). Samples milled in NH₃ for 15 h and 70 h have the flake structure and show the diffraction pattern of polycrystalline materials. However, in the case of Ar, after 15 h milling, the sample begins to lose the flake-like structure and the diffraction is a very weak dotted pattern with diffraction rings. After 70 h milling, only the diffused diffraction rings can be seen and the sample is particle like, which means the sample is disordered and semi-amorphous in structure. The comparison shows that the structure of the graphite samples milled in NH₃ are protected and do not undergo the amorphisation process, like the samples milled in Ar.

Figure 5.5 SEM images of ball-milled graphite produced under different conditions.
Figure 5.6 TEM images and electron diffraction of graphite milled in NH$_3$ and Ar.

Interestingly, this atmospheric protection effect is not restricted to graphite. The milling of h-BN and h-MoS$_2$ in NH$_3$ shows a similar protective effect. The h-BN is called ‘white graphite’, since it has the same lamellar structure of graphite, but with one boron and one nitrogen atom substituting the two carbon atoms in the unit cell. Figure 5.7 shows the structure of the BN sample milled in NH$_3$ and Ar atmosphere. Samples milled in NH$_3$ for 15 and 70 h still have sharp (0 0 2) and (1 0 0) diffractions at 25.5° and 38°. However, after only 15 h milling in Ar, the diffraction peaks broaden greatly and the intensity is much lower than the one milled in NH$_3$. The FWHM of (0 0 2) peak of Ar 15 h is about 5°, which is about two times wider than the FWHM of the sample milled in NH$_3$ for 70 h.
Figure 5.7 XRD of the milled BN samples.

SEM image shows the starting materials are large BN discs (Figure 5.8a). After being milled in NH₃ for 20 h, the sample contains mainly nanoflakes (Figure 5.8b), whereas the sample milled in Ar for the same duration has lost the lamella structure (Figure 5.8c). These results clearly show that the sample milled in NH₃ has much better crystallinity than the one milled in Ar, due to the protective effect of NH₃.
Figure 5.8 SEM images of (a) the starting material before ball milling and the ball-milled BN in (b) NH$_3$ and (c) Ar for 20 h.

NH$_3$ can also protect the structure of MoS$_2$ during the ball-milling process but in a more complex way. The samples milled in NH$_3$ show broadened XRD diffraction peaks compared with the starting material (Figure 5.9). After 200 h ball milling, several diffraction peaks can be seen: (0 0 2) at 14.5°, (1 0 0) at 33°, (1 0 3) at 39.5°, (1 0 5) at 50°, (1 1 0) at 58° and (1 1 2) at 61°. Conversely, samples milled in Ar for more than 100 h lose the (1 0 3) and (1 0 5) diffraction peaks and the (1 1 0) and (1 1 2) diffraction peaks are broadened and merge to one peak at 60° (Figure 5.10). This absence of (1 0 3) and (1 0 5) diffraction peaks is caused by the interlayer rotation of the crystal planes in the nanocrystal [188]. However, in the case of NH$_3$, the sample milled for longer time of 200 h has observable (1 0 3) and (1 0 5) diffraction, which means that NH$_3$ protects the nanocrystal in the ball-milling process and reduces the rotational disordering of the crystal. The SEM images reveal that in this case, both samples contain nanoparticles of MoS$_2$ (Figure 5.11).
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Figure 5.9 XRD patterns of the MoS$_2$ milled in NH$_3$.

Figure 5.10 XRD patterns of the MoS$_2$ milled in Ar.
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Figure 5.11 SEM images of the MoS₂ milled in NH₃ and Ar.

Not only can this protective effect be applied to different materials, but this protection can be provided by gases other than NH₃. Figure 5.12 shows the XRD of graphite milled in different atmospheres. The graphite samples milled in NH₃, C₂H₄ and CH₄ have sharp (0 0 2) diffraction peaks (Figure 5.12 a-c). Especially in (a) and (b), the (0 0 4) diffraction is still observable at about 55°, which indicates good ordering on z-axis. All three diffraction patterns are different to the one milled in Ar (Figure 5.2) and prove that these gases reduce damage to the material structures. The ball milling in the N₂ and N₂/H₂ mixture, however, does not show the same effect (Figure 5.12 d-f). These three samples have very wide (0 0 2) diffraction peaks, which are similar to the sample milled in Ar.

As the protection can be a universal phenomenon in a mechanical system, understanding its mechanism is essential to further develop its application. It has been reported that H₂ could also have a protective effect [49]. Thus, milling in N₂/H₂ mixture was conducted to determine whether the protective affect is due to the decomposition of the hydrogen-containing gases that can form H₂. This possibility was rejected by the results. The XRD pattern shows that H₂ can slightly protect the structure comparing with nitrogen and Ar gas. However, even with 15% H₂, after only 20 h milling, the (0 0 2) peak becomes wider (Figure 5.12d) than the one milled in
NH₃ for 70 h (Figure 12e). This demonstrates that it is not hydrogen that protects the structure of the milled samples.

*Figure 5.12 XRD patterns of the graphite milled in different gases.*

The gas pressure change during the ball milling also rejects the hypothesis that the gas decomposition and hydrogen molecules contribute to the protective effect. When milling graphite in NH₃, the pressure decreases from 300 kPa to 156 kPa after 72 h (Figure 5.13). However, as reported previously, the decomposition of NH₃ should have caused an increase of inner pressure by forming H₂ [189-191]. Thus, the protection is not related to the gas decomposition of NH₃. At the same time, the increase of nitrogen content is found in the samples milled for longer periods. This suggests that there may be NH₃ reacting with the milled graphite.
Chapter 5 The lubricant effect of milling atmosphere on nanostructures

NEXAFS is conducted on the graphite and BN samples milled in NH₃ and Ar for different durations to characterise the influences of these two gases in ball milling. Figure 5.14 shows the C K-edge of different samples. In the spectrum of the starting graphite, there is a peak at about 285 eV and a doublet peak at about 291 and 292 eV. In addition, there is a very small peak at about 289 eV (pointed by arrow). The doublet transition is evidence of the ordered structure on z-axis of graphite. The splitting is caused by the interaction of the $p_z$ orbitals with the $p_x$ and $p_y$ orbitals in the neighbour graphene sheets [158]. It only exists in the graphitic structure with good z-axis ordering [160, 192]. For the sample milled in NH₃, up to 70 h the shape of the doublet transition exists and no significant broadening is observed. This indicates that the NH₃ could protect the sample in ball milling and preserve its ordering structure. However, the doublet transition cannot be seen from the envelope of the spectra of samples.
milled in Ar. The transition at about 298 eV is related with the in-plane defect sites [159, 160]. Compared with the starting material, the intensity of the transition does not increase in the sample milled in NH₃, which proves that NH₃ can protect the in-plane structure of the graphite. On the other hand, samples milled in Ar have a stronger and wider peak at 289 eV than the starting material, which means in-plane defects have been introduced by the ball milling. N K-edge is performed to characterise the nitrogen content in the sample milled in NH₃ (Figure 5.15). Two transitions appear at 399.70 eV and 401.55 eV. These transitions may belong to the trapped NH₃ molecules in the milled graphite and are related to the transition from N 1s to one anti-bonding orbital with $a_1$ symmetry and another one with $e$ symmetry [193, 194]. It may explain the decrease of gas pressure during the ball milling (Figure 5.13) and the increase of the interplanar distance of (0 0 2) crystal planes (Figure 5.4). During the ball milling, NH₃ molecules interact with graphite and adsorb or intercalate into the graphitic structure.

![Graphite C k-edge](image)

**Figure 5.14 C K-edge NEXAFS of ball-milled graphite.**
The similar protective effect of NH₃ is also supported by the N K-edge NEXAFS of BN. (Figure 5.16) The FWHM of the transitions at about 407.5 eV of the samples milled in NH₃ is narrower than the samples milled in Ar, which is a sign of better crystallinity [195].

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**Figure 5.15** N K-edge NEXAFS of graphite milled in NH₃.

**Figure 5.16** N K-edge NEXAFS of ball-milled BN.
B K-edge spectra of the milled BN confirm the less defective structure of samples milled in NH₃, and at the same time provides more information. A high resolution B K-edge NEXAFS reveals four transitions between 192 and 195 eV (Figure 5.17). From the low to high energy, the four transition peaks present boron atoms bonded to three, two or one nitrogen atom, and boron-boron bonds, respectively. The first peak is the native transition in h-BN, when the other three are taken as a sign of defects in the structure [196]. The relative intensity of the defect bands to the native band is found proportional to the quantity of the defect structures. Comparing the sample milled for 15 h, the sample milled in Ar has greater defect peaks than the sample milled in NH₃. However, when comparing the samples milled for 70 h, the sample milled in NH₃ has a similar content of the peak at 194.3 eV, but lower content of the peaks at 193 and 193.6 eV. This is due to the protective effect of NH₃, but more importantly, it may provide evidence to further study the mechanism. The previous research explained the protection of H₂ and O₂ atmosphere as the doping on boundary, which could stabilise the boundary and the structure of the material [74, 183]. However, NEXAFS shows that after the ball milling in NH₃, when the in-plane structure is protected, there are defective boron atoms that are not bonded with three nitrogen or hydrogen atoms, since the spectra show strong peaks above 193 eV (strong peak at 194.3 eV in Figure 5.17). This suggests that most of the defective structure in the sample milled in NH₃ sits on boundaries, which is different to the sample milled in Ar. However, those defective boundary boron atoms are not saturated by the nitrogen or hydrogen from NH₃. This implies that while the reaction between the boundary atoms with NH₃ molecules still needs to be considered, this reaction might not be the main reason for the protection in the ball-milling process.
Since the samples milled in NH$_3$ retain the in-plane structure, the protection of the (0 0 2) plane is studied with lateral force microscopy, by scanning the friction force in an area and calculating the average friction. The friction of the surface in NH$_3$ and C$_2$H$_4$ is 1.56 and 1.96 mV lower than the friction in the air. At the same time, the friction in Ar has only 0.29 mV deviation from the one in air, which is very close with the absolute friction deviation of the control group and contributed most probably by the systematic error of the experiments. An example is given in Figure 5.18. The friction of the surface is 2.6 mV in NH$_3$. However, after left in air for 24 h, the friction increased to 4.2 mV, which is about 60% greater. These results indicate that NH$_3$ and C$_2$H$_4$ functions as lubricant and reduces the friction of h-BN (0 0 2) surface, so it can reduce the impact and shearing force applied on (0 0 2) surface in the ball-milling process and protect the in-plane structure. This explanation is also supported by the pressure drop, shown
in Figure 5.13. The pressure drop of active gases during ball milling is observed in other cases too. For example, using NH₃ as the atmosphere, the pressure dropped by 120 kPa and 140 kPa when milling 4 g BN and MoS₂ for 20 h respectively. This pressure drop can be caused by the adsorption on a particular surface of the milled materials. The adsorbed molecules then function as lubricant and protect the surface from the damage of ball milling. This explanation is also supported by the strong interaction between NH₃ and solid surfaces investigated theoretically [197, 198]. It is reported that the NH₃ molecules can interact with the graphene orbitals and cause charge transfer, which leads to an increased adsorption energy. A visual inspection of the surface of the ball-milling balls after ball milling also supports this finding (Figure 5.19). The balls used to mill graphite in NH₃ still have a reflective surface after 70 h ball milling, which suggests a relative smooth surface (four balls on the left side in Figure 5.19). On the other hand, the balls that mill graphite in Ar are much less reflective, which means that the surface is much rougher than the balls milling in NH₃. This is caused by the lubrication of the NH₃, which reduces the abrasion and impact during the ball-milling process.

Table 5.1 the decrease of the (0 0 2) surface friction of BN in selected atmospheres comparing with air.

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>Reduced surface friction compare with air (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>1.56</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>1.96</td>
</tr>
<tr>
<td>Ar</td>
<td>0.29</td>
</tr>
<tr>
<td>Air</td>
<td>-0.20</td>
</tr>
</tbody>
</table>
Figure 5.18 Lateral friction force of boron nitride (0 0 2) surface scanned after taking out from NH$_3$ atmosphere for a) 3 mins, b) 1 day.

Figure 5.19 Image of the ball-milling balls after 70 h ball milling of graphite in NH$_3$ (on the left) and Ar (on the right).
5.4 Conclusions

In this Chapter, the lubricant effect of the atmosphere was studied in a ball-milling system. It was discovered that when ball milling graphite, h-BN and MoS2, NH3 atmosphere can protect the structure of the milled materials. Further study demonstrates that this protective effect is not limited to NH3, but also applies to C2H4 and CH4. Further investigations on the origin of this protection suggested that the strong adsorption of the gas molecules on the surface of the materials increased their lubrication. This finding may help to fabricate nanomaterials with controlled structure by ball-milling synthesis. In addition, this research demonstrates that, by selecting the right atmosphere, the lubrication effect of the dry lubricates can be enhanced.
Chapter 6 The structure influence of ball-milled graphite on lithium storage

6.1 Introduction

The lithium ion battery has become a very popular power source nowadays. Its performance, however, hinders its practicality in high-power and/or high-energy output application, such as in electrical cars. One potential solution is to design electrode materials with higher capacities and better performances [118]. Graphite is a currently widely used anode material for the lithium ion battery, but the theoretical intercalation capacity of perfect graphite is only 372 mAh/g [27].

In the 1990s, it was discovered that the modified graphitic structure could lead to higher capacity than the theoretical value of the perfect graphite [119-121]. Several hypotheses have been suggested to explain the enhanced capacities, but the mechanism remains unclear [122, 123]. Moreover, several recent works report enhanced lithium storage in graphene, in which the graphene shows steep discharge-charge curves instead of the normal interaction/de-intercalation plateau [9, 199, 200]. These results, however, is still not very well understood and need to be researched and further explained. In this chapter, different graphitic structures are produced by ball milling and their lithium ion storage properties are studied. By linking the structure and the lithium ion storage properties, the mechanism of enhanced lithium storage is explained. It is also found that the enhanced lithium storage might be quantitatively linked to the structural disordering, which could be extract from the Raman fingerprint.
6.2 Experimental

The graphite samples ball milled in Ar and NH₃, which have been introduced in Chapter 4, were used for Li storage investigation and the detailed preparation process has also been described in Chapter 4.

The battery test cells were assembled in an Ar glovebox. The anode was made by mixing the sample, carbon black and polyvinylidene fluoride (80:10:10 by weight ratio), in N-methyl-2-pyrrolidone. The slurry was then coated on copper foils by 1*1 cm². The electrodes were dried in a vacuum oven, weighed and moved into the glovebox. The bulk electrode made for NMR experiment was prepared with Teflon as binder. The electrolyte used was a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) by 1:1:1 volume ratio. The cathode is lithium plate, which is also the reference electrode in the system.

The galvanic charge-discharge capacities were measured by a Land CT2001A system. The CV and EIS were conducted with Ivium-n-Stat. In both experiments, the cells were preconditioned by a 3-cycle charge and discharge before the test to avoid the influence of solid electrolyte formation. The CV tests were performed at 50 mV/s. The EIS were measured from 0.1 to 10⁵ Hz. The charge-discharge results showed were from the third cycle.

Solid-state NMR experiments were carried out on a BRUKER Avance3 NMR spectrometer, operating at 500.13 and 194.2 MHz for ¹H and ⁷Li, respectively. Samples were packed in standard 4 mm MAS rotors under Ar atmosphere, mounted in a BRUKER triple-resonance 4 mm MAS probe. Magic angle spinning (MAS) for the commercial graphite (CG) was set to 5 and 7.5 kHz for ¹H and ⁷Li experiments, and to 13 kHz for the ball-milled carbon sample. A single 90 degree pulse with a nutation frequency of 125 kHz and 100 kHz was used for proton and lithium excitation, respectively. Recycle delays were set to 4 – 6 sec as determined beforehand.
Chapter 6 The structure influence of ball milled graphite on lithium storage

All $^1$H chemical shifts are given relative to TMS using adamantane (d=1.8ppm) as secondary reference and $^7$Li shifts are given with respect to 1M LiCl solution.

6.3 Results and discussion

Figure 6.1 shows the discharge-charge capacity of several ball-milled graphite samples at 0.1 C. The samples milled in Ar atmosphere are shown in Figure 6.1a, which shows the capacity increases with the milling time and all three milled samples have higher capacities than commercial graphite (CG). However, in both discharge and charge curves of the milled samples, there is no intercalation or de-intercalation plateau [27]. Instead, the curves are steep indicating different charge/discharge mechanisms from graphite. On the other hand, samples milled in NH$_3$ show different performance (Figure 6.1b). All three milled samples have lower capacities than CG. The discharge capacity drops to about 305 mAh/g, after 15 h milling and further milling up to 70 h leads to a lower capacity around 240 mAh/g. The curves show the intercalation-deintercalation plateaus, but the plateaus shrink with the increasing milling duration.

Figure 6.1 Charge-discharge curves of samples milled in a) Ar and b) NH$_3$ at 0.1C.
A charge-discharge experiment with a higher current rate was also conducted on selected samples. Figure 6.2 shows the results of 0.5 C charge-discharge of CG, Ar 15 h and NH$_3$ 15 h samples. The results show a similar trend with 0.1 C experiments. Ar 15 h has a much higher capacity of 285 mAh/g, when CG’s capacity shrinks to about 175 mAh/g. The capacity of NH$_3$ 15 h drops to only about 130 mAh/g. The stability of the materials is also studied at 0.5 C. The capacity decreases during the recycling for all three testing samples. One example is shown in Table 6.1. It could be seen that all samples show less capacity in the 90$^{\text{th}}$ cycle comparing with the 1$^{\text{st}}$ cycle.

![Figure 6.2 Charge-discharge of the selected samples at 0.5 C.](image)
Chapter 6 The structure influence of ball milled graphite on lithium storage

Table 6.1 Charge stability of the selected samples at 0.5 C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Capacity (3rd cycle) mAh/g</th>
<th>Capacity (90th cycle) mAh/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>CG</td>
<td>174.6</td>
<td>101.3</td>
</tr>
<tr>
<td>Ar 15 h</td>
<td>285.1</td>
<td>220.7</td>
</tr>
<tr>
<td>NH3 15 h</td>
<td>126.7</td>
<td>71.5</td>
</tr>
</tbody>
</table>

The CV curves of various samples are shown in Figure 6.3 to study the charge-discharge mechanism. In CG, there is a strong intercalation peak appearing below 0.17 V [201]. In charging half-cycle, the corresponding de-intercalation peak appears at about 0.35 V. After being ball milled in Ar, the CV profile changes significantly. The sample milled for 15 h in Ar shows a much wider CV profile than CG, which is caused by greater specific currents in both charging and discharging half-cycle. An extended milling leads to even wider CV profile. After being ball milled in Ar, the samples show CV profiles similar to the ones of capacitors while the intercalation/de-intercalation peaks disappear [202, 203]. This implies that the storage mechanism is changed and intercalation/de-intercalation is no longer the major mechanism that contributes to the lithium storage. The samples milled in NH3 still have intercalation and de-intercalation peaks and the widening of CV profiles is not significant.
Figure 6.3 CV of the ball-milled samples.

XRD was used to characterise the change of the crystallinity in the ball-milling process. Samples milled in Ar show very broad (0 0 2) peaks at about 25° (Figure 6.4). This is a sign of the amorphisation of graphite and the severe disruption of the graphitic structure [187]. On the other hand, samples milled in NH₃ also show a widening (0 0 2) peak. The diffraction peaks, however, are much narrower than the peaks of samples milled in Ar, which indicates that samples milled in NH₃ have better crystallinity. The same increase of interlayer distance, which is introduced in Chapter 5 (Figure 5.3), is also observed in the samples milled in NH₃.
Figure 6.4 XRD patterns of the ball-milled samples.

Raman spectroscopy confirms the different structures of samples milled in Ar and NH₃ (Figure 6.5). The Raman spectroscopy of graphite contains four bands, labelled as D, G, D’ and 2D band [155, 204]. In samples milled in Ar, only two bands can be seen, which are D and G bands. G and D’ bands merge and cannot be separated. 2D bands are very weak in Ar 15 h and completely disappear in samples milled for 30 and 70 h. D, G and D’ bands are fitted to extract the information of the structure changing. I_D/I_G is an indication of the structure defects in graphitic materials [154]. I_D/I_G is about 0.3 in CG, which indicates a good crystallinity and low
level of defects. When ball milled in Ar, $I_D/I_G$ rises from 0.3 to about 1.7 after 15 h milling. Then, $I_D/I_G$ decreases with further milling. This evolution has been studied before [187]. This feature means that, in this ball-milling process, after 15 h the ball milling cannot break down the graphitic flakes further. Instead, the ball milling distorts the graphitic structure and produces clusters of $sp^2$ carbon or even $sp^3$ carbon atoms. This is also confirmed by the evolution of FWHM of D bands (Figure 6.6b). The FWHM of D bands increase from 45 to 110 cm$^{-1}$ after 15 h ball milling and finally reach 220 cm$^{-1}$. This widening also points to a disordered and distorted ring system. On the other side, the sample milled in NH$_3$ shows very different Raman spectra (Figure 6.6a). $I_D/I_G$ increases from 0.3 to about 2.1 monotonically with milling time. There is, however, no significant widening of the peaks appearing. For example, FWHM of D bands is shown in Figure 6.6b. It only increases from 43 to 47 cm$^{-1}$ after 70 h milling. This indicates that the milling in NH$_3$ could produce more defective aromatic rings that contribute to the intensity of D bands. However, the milling does not distort the ring system greatly; therefore, the Raman bands are not widened.

![Figure 6.5 Raman spectra of the ball-milled samples.](image)
EIS is shown in Figure 6.7. CG, NH$_3$ 15h and NH$_3$ 70h have typical Warburg impedance in low frequency whereas the samples milled in Ar do not [205]. Samples milled in Ar have much lower resistance than CG and samples milled in NH$_3$ in the mid to low frequency range. To understand the reason for this difference, the equivalent circuit has been used to fit the data. An example has been shown in Figure 6.8, which is the fitting of the EIS of Ar 70 h. The model used is a two semi-circle model (each is represented with a RC (R represents resistor; CPE represents constant phase element) component), which describes the electrochemical property of the solid-state electrolyte interface (SEI) and sample surface [205]. The first RC component represents the impedance of lithium migration from solution to the solid electrolyte interface (SEI). The second semi-cycle represents the impedance of the lithium migration from SEI to graphite surface. The Warburg impedance characterises the lithium diffusion into graphitic structure. R4 represents the resistance of the charge transfer between graphite and lithium.
atoms and CPE2 characterises the capacitance of graphite surface. When the circuit in Figure 6.8a is the normally used circuit, another parallel circuit has been added to analogue the observed capacitor-like storage mechanism (Figure 6.8b). In this parallel circuit, the first semi-cycle describes the SEI and the resistor analogues the resistance when the lithium migrates in the electrode material. The capacitor (C2) in this circuit is corresponding to the capacitive storage of lithium. The fitting in 6.8b is better than the one in 6.8a at mid frequency range. An interesting finding with the new fitting is that for CG and samples milled in NH₃, C2 is smaller than 10⁻⁵ F. However, in the samples milled in Ar, C2 is higher than 10⁻² F, which is 10³ times larger than the ones in CG and NH₃ cases. The equivalent circuit method is not always quantitatively accurate; however, such a large difference may be meaningful. It implies that there is a capacitor-like storage mechanism in samples milled in Ar, but this is absent in CG and samples milled in NH₃. CV and discharge-charge experiments also support this hypothesis. This capacitor-like storage mechanism causes the increased capacity of samples milled in Ar.

Figure 6.7 EIS of the ball-milled samples.
Chapter 6 The structure influence of ball milled graphite on lithium storage

Figure 6.8 Fitting of the EIS data by equivalent circuit method.

$^7\text{Li}$ solid state NMR clearly demonstrates the different lithiated carbon products formed in the graphitic samples with different disordering after being fully discharged (Figure 6.9). Figure 6.9a shows the $^7\text{Li}$ solid state NMR spectrum of CG after discharging. Three actual lithium signals are collected, which are highlighted in Figure 6.9b. The peak with the largest area at about 43.6 ppm is corresponding to LiC$_6$, which is formed by the lithium intercalation into the well organised graphitic structures [206, 207]. The peak at about 4.4 ppm is due to the defect related storage of lithium [125]. The sharp peak at about -1 ppm represents the lithium in the electrolyte [125]. After ball milling in Ar for 70 h, the lithium storage sites have been changed significantly. Figure 6.9 a and b show the spectra of lithium in Ar 70 h after fully discharged. There are much more spinning sidebands observed in this case than in CG, which means that, in Ar 70 h, the lithium is stored in a much more disordered and anisotropic environment [208]. Figure 6.9 b highlights the only actual signal in this case, which is a broad peak at about 1 ppm. This is a strong evidence that, in this material, the mechanism of the lithium storage is defect-related storage, which shows a broad peak at about 1 ppm [206]. Moreover, typical signals for the lithium intercalated graphite are not observed, which confirms that lithium storage in this case is barely through intercalation mechanism, but through the storage at defect sites.
Figure 6.9 $^7$Li solid state NMR spectra of CG in a) and b); the spectra of Ar 70 h are shown in c) and d). ‘Real’ signals representing lithium in different chemical environments are labelled by ‘*’ to distinguish from spinning sidebands. Multiple spinning frequencies are used to differentiate the actual signal and spinning sidebands.

A closer look at the capacity and the Raman spectroscopy evolution of the samples provides an indication of the relationship between the disordered structure and capacitor-like storage. When the ball milling in both gases created defects, only the milling in Ar produces a distorted ring system in graphite. These samples milled in Ar also have the increased capacity than CG and different storage mechanism. This increased capacity and changed mechanism, therefore, may be related with the distortion of the graphitic structure rather than the simple point or boundary defects. A dimensionless quantity $Dis$ is built to describe the distortion of the graphitic system:

$$Dis = \frac{ws - wp}{ws} \times \frac{A_{Ds}}{A_{Gs}}$$

ws: FWHM of D band of the sample;
wp: FWHM of D band of graphite that contains no distorted aromatic ring;

$A_{D\theta}$: Area of D band of the sample;

$A_{G\theta}$: Area of G band of the sample;

The wider the D peak, the more distorted the graphitic ring system is. Moreover, $A_{D}/A_{G}$ should be considered since it indicates the quantity of the distorted rings [154, 187].

At the same time, the intercalation and non-intercalation capacities are differentiated. By analysing the CV and galvanic discharge results, for CG and samples milled in NH$_3$ the capacities below 0.2 V are intercalation capacity, when the ones above are contributed by non-intercalation process [205, 209]. For the samples milled in Ar, since no intercalation-deintercalation couple can be seen in CV and their capacities below 0.2 V are also very low, all the capacities are approximately taken as non-intercalation capacities. Afterwards, the excessive non-intercalation capacity of the sample is calculated:

$$C_{en} = C_{sn} - C_{gn}$$

$C_{en}$: excessive non-intercalation capacity of the sample;

$C_{sn}$: non-intercalation capacity of the sample;

$C_{gn}$: non-intercalation capacity of CG;

Excessive non-intercalation capacities of samples milled in Ar are plotted against $D_{is}$ (Figure 6.10a). A positive correlation can be seen between two quantities. It need to be emphasised that since $I_{D}/I_{G}$ decreases after 15 h milling in Ar, there is no simple relationship between $I_{D}/I_{G}$ and the excessive non-intercalation capacity. It implies that the capacitor-like storage can only happen in the distorted graphitic structure, rather than edge-site or simple-defect site that can
cause the increase of $I_D/I_G$ but not the widening of the bands [155, 187]. This is further supported by the analysis of the samples milled in NH$_3$ (Figure 6.10b). A similar positive correlation can also be built. Furthermore, linear fitting is given in both cases (red line in Figure 6.10). In both cases, $R^2$ is bigger than 0.96, which suggests that the excessive lithium storage might have a linear relationship with $Dis$.

![Graph showing the relationship between excessive non-intercalation capacity and $Dis$ for samples milled in Ar and NH$_3$.](image)

*Figure 6.10 The plot of excessive non-intercalation capacity against $Dis$ of a) samples milled in Ar and b) samples milled in NH$_3$.***

When non-intercalation capacity is due to the distorted graphitic structure, intercalation capacity is related with normal graphitic structure. Figure 6.11 shows the evolution of $I_G/I_D$ and intercalation capacity. $I_G/I_D$ can qualitatively describe the perfection of the graphitic structure in the samples milled in NH$_3$. $I_G/I_D$ has the similar evolution trend with the intercalation capacity. The different electrochemical performance of samples milled in Ar and NH$_3$ can be understood. In Ar cases, the ball milling is very efficient in creating a distorted graphitic structure, so there is no intercalation-deintercalation plateau and only very small peaks in CV. However, the distorted graphitic structure provides another storage mechanism, which provides more lithium storage sites than the depleted intercalation sites and causes an increase in capacity. In contrast, in the case of NH$_3$, it does not cause significant distortion to the graphitic structure. Thus, until 70 h milling, the main effect of ball milling is cutting down the big
graphite chunk, which raises the intensity of $I_D$, but does not widen the Raman band. In these samples, the intercalation-deintercalation capacity keeps decreasing. The total capacity also decreases.

![Graph showing the relationship between $I_G/I_D$ and intercalation capacity.](image)

*Figure 6.11 The relationship between $I_G/I_D$ and the intercalation capacity.*

It is found that the capacity of the material does not have a simple relationship with the surface area, as reported before [120, 121]. Figure 6.12 shows the BET surface area of samples milled in Ar and NH$_3$. The BET surface area begins to decrease when CG is milled in Ar for longer than 15 h, but the capacity still increases with the milling duration. The samples milled in NH$_3$ have BET surface areas about 10 times larger than CG. Their capacities, however, are much lower than the capacity of CG. Comparing samples milled in Ar and NH$_3$, samples milled in Ar have larger capacities and surface areas, but as discussed before it is caused by the distorted graphitic structure rather than the simple surface area increase. The increase of capacity with inter-plane distance, which was suggested by previous work [9], has not been observed in this work. The inter-plane distance increases with longer milling duration in NH$_3$ (Figure 5.4). However, the intercalation/de-intercalation capacity keeps decreasing with the increase of the inter-plane distance. These results are consistent with the early finding that the inter-plane
space with turbostratic stacking can lead to a decrease in lithium storage [123]. The performance of graphene may also be explained with the mechanism suggested [9, 199, 200]. In the reported results, the Raman spectra of the used graphene samples all showed very broad and intensive D peaks, which indicated a highly disordered graphitic structure. The enhanced capacity is highly likely to be contributed by these distorted graphitic structure with the capacity-like mechanism. This could also be the reason why the published results of graphene all show steep charge/discharge curves and very low capacity below 0.2 V, rather than the plateau of graphite, which are similar with the performance of the sample milled in Ar.

![Graph showing BET surface area vs. milling duration](image)

**Figure 6.12 BET surface area of the ball-milled samples.**

### 6.4 Conclusions

In this chapter, the lithium storage mechanism in graphitic structures was studied. It is discovered that the distorted graphitic structure has a lithium storage mechanism that performs similarly to the electrochemical capacitor instead of intercalation. This mechanism can provide
a greater capacity than intercalation/de-intercalation. The samples milled in Ar have a very disordered structure and show much larger capacity than CG. However, among these samples, the enhanced capacity does not show dependence on the surface area, but increases with the disordering of the structure. On the other hand, the milling in NH$_3$ does not introduce much disordering and the capacity decreases after ball milling. It needs to be emphasised that the inter-plane distance of these samples increases with longer ball-milling duration, but the capacity decreases, which shows that in this case the capacity is not positively correlated with the inter-plane distance.
Chapter 7 A green mechano-chemical approach for synthesis of nitrogen-doped carbon nanoparticles

7.1 Introduction

Pt-based materials have been scientifically demonstrated as effective electrocatalysts for oxygen reduction reaction (ORR) [10], yet large-scale commercial use has been precluded by the high cost, limited supply, and weak durability of platinum. Recent intensive research efforts directed at reducing or replacing Pt-based electrodes in fuel cells have led to the development of new metal-free ORR electrocatalysts [38, 41]. In particular, nitrogen-doped carbon nanomaterials have been reported to have better resistance to poisoning [10, 38, 131] and relatively cheaper to fabricate [210] than Pt-based catalysts. Thus, nitrogen-doped carbon materials have been investigated as potential candidates for replacing Pt to achieve the commercialisation of fuel cell technology. Nevertheless, most of the current methods to synthesise nitrogen-doped carbon materials face problems like low production yield. Therefore, the development of improved fabrication method is still required for large-scale application. This chapter reports a ball-milling assisted N doping process, which can produce nitrogen doped carbon catalyst for ORR.

Ball milling is a process, in which the moving balls apply their kinetic energy to the milled material, break the chemical bonding and produce fresh surfaces. These dangling bonds and fresh surfaces are usually very chemically reactive to small gas molecules such as nitrogen. Also, it has been reported that the milling impact sometimes can create local high temperatures [211] and/or high pressure up to several GPa [212]. Due to this nature of the ball-milling process, the process has been used as a mechano-chemical synthesis method [211, 213] for the fabrication of unique nanostructures with new chemical properties. Solid-gas reaction was
researched by milling titanium and zirconium in nitrogen-containing atmosphere to produce the nitride species [63-65]. It also has been showed that nitrogen can be effectively doped into materials by ball milling in presence of nitrogen gas [214, 215]. It was demonstrated that mechanical energy of ball milling can break the chemical bonds in solid materials and produce dangling bonds, which are very active to chemical reactions [165, 213]. Simultaneously, gas molecules react with the solid atoms with dangling bonds. Graphite has a layered structure of aromatic rings. Numerous strong bonds are broken upon disruption of the layers producing free valences along the fresh borders. This would open the way for the formation of carbon nanostructures with new functionality. In the previous work [60]. It has been demonstrated that a nanoporous carbon structure can be produced in the graphite samples after ball milling at ambient temperature. Formation of the nanoporous structure is associated with that of the disordered carbon. The disordered and nanoporous structure is probably fullerene-like in nature. Subsequently, it has also been showed that annealing of disordered carbon nanostructure at 1400 °C produced carbon nanotubes [216].

In this chapter, it is introduced that ball milling can be used as a green method to synthesise nitrogen-doped carbon nanoparticle (NDCP), which can be used as an electrochemical catalyst for ORR. The resulting carbon nanoparticles exhibit improved catalytic activity and excellent methanol tolerance comparing to a commercial Pt/C catalyst.

### 7.2 Experimental

Nitrogen-doped carbon nanoparticles (NDCP) was prepared by ball milling pristine graphite in high-energy rolling ball mill in the presence of nitrogen (300 kPa) at room temperature. In a typical experiment, 2g of graphite powders (< 20 micron, synthetic) were placed into a milling jar with four stainless steel balls. The sample to ball mass ratio is 1:132. The ball-milling process lasted for 24 hours with a rotation speed as 150 rpm. The milled samples were then
heated in a horizontal tube furnace (Lindberg) from room temperature to 700 °C, at a rate of 25 °C/min and then annealed for 3 hours. After that, the sample was cooled to room temperature in 16 hours with a cooling rate about 42 °C/hour. N2-15% H2 mixture gas was used as annealing atmosphere with a flow rate at 0.05 L/min.

The samples were characterised using X-ray diffraction (PANalytical X’Pert Pro diffractometer) with Cu K-α radiation (λ= 0.15418nm). The sample morphologies were studied using a scanning electron microscope (SEM, Supra 55VPP) at 3 kV and a working distance of 4.6 mm. Particle size was measured by a dynamic light scattering method (Malvern ZETASIZER). 0.5 mg samples were added into 5 ml deionized water to make dispersions. The dispersions were ultrasonically treated for 30 mins before the test.

Ultraviolet-visible (UV-Vis) spectroscopy was used to characterise the dispersive ability of the samples in water. The dispersions were made by adding 20 mg of samples to 5 ml deionised water. Then, dispersions were ultrasonically treated for 30 min. After that, they were diluted by 50 times to make adequately transparent solutions for UV-Vis test. The scans were from 200 nm to 800 nm with a scan rate of 600 nm/min and a scan step of 1 nm. Water and a completely opaque cell were used as 100% and 0% transmittance standards, respectively, to correct the baseline.

X-ray photoelectron spectroscopy (XPS) system, (model: SPECS-XPS, from SPECS, Germany) was used to analyse the concentrations of elements and binding energies on the sample surface. The XPS system was equipped with a high sensitivity PHOIBOS 150-9 MCD energy analyser. An Al K-alpha X-ray source (1486.74 eV) was used for the analysis.

The catalyst suspension was prepared by sonication (Soniclean 160T, Soniclean Pty Ltd) of the sample with tetrahydrofuran (THF, 99.9+%, Sigma-Aldrich) for 1 h, resulting in the ink with final concentrations of 5 mg sample/mL. An aliquot of 4 μL of suspension was drop-casted
onto a glassy carbon (GC) disk electrode (4 mm diameter, 0.126 cm\(^2\) area, rotating ring-disk electrode (RRDE) Pt Ring/GC disk electrode, ALS Co., Ltd). The electrode was previously polished with 0.05 \(\mu\)m alumina slurry (Buehler) on a clean polishing cloth (Buehler); it was sequentially rinsed with distilled water and acetone, and then dried with lint-free tissue paper. After slow evaporation of the solvent, 1 \(\mu\)L of Nafion\(^\text{®}\) solution (5 wt.\%, Fluka) was drop-casted on the electrode surface and dried slowly overnight inside a closed beaker to attach the catalyst particles onto the glassy carbon disk electrode. Based on the density of Nafion\(^\text{®}\) solution of \(\sim 0.874 \text{ g cm}^{-3}\) and density of Nafion\(^\text{®}\) film of \(\sim 2.0 \text{ g cm}^{-3}\) [217], an estimated Nafion\(^\text{®}\) film thickness of \(\sim 1.74 \mu\text{m}\) is obtained. The thickness of the film is reasonably thin to render a negligible \(\text{O}_2\) transport resistance within the film [218].

Voltammetric experiments were performed with a Biologic VMP2/Z multichannel potentiostat. Rotating disk electrode (RDE) voltammograms were obtained in a 0.1 M potassium hydroxide (KOH) prepared from deionised water and potassium hydroxide pellets (KOH, 99.99%, Sigma-Aldrich) at a scan rate of 20 mV s\(^{-1}\) in either \(\text{N}_2\) or \(\text{O}_2\) (ultrahigh purity grade, BOC) saturated atmosphere at room temperature (which corresponds to electrolyte temperature of \(\sim 17 \pm 1 ^\circ\text{C}\)). Voltammograms for the reduction were obtained using a three-electrode arrangement in a 100 mL glass cell vial utilising RRDE-3A rotating ring/disk electrode apparatus (ALS Co., Ltd, Japan). This consisted of a glassy carbon disk electrode (0.126 cm\(^2\) area, ALS Co., Ltd, Japan), a platinum wire counter electrode and an Ag|AgCl (3M NaCl) reference electrode (RE-1B, ALS Co., Ltd, Japan).

The background capacitive current contribution (obtained from \(\text{N}_2\) saturated experiment) was subtracted from each voltammogram. Three catalyst films were prepared for each sample to check the reproducibility of the film quality and performance; the results of those vary within the experimental error. The current density values were obtained assuming effective disk surface area of 0.1257 cm\(^2\) (diameter of 4 mm) for all samples.
7.3 Results and discussion

The preparation of NDCA and its ORR catalytic property is shown in Figure 7.1. Ball-milled graphite (C2) is fabricated by milling the commercial graphite (C1) in nitrogen atmosphere. Then, C2 is annealed to produce the NDCA (C4) with catalytic property. For comparison purpose, C1 is also annealed directly without milling treatment at the same condition to produce annealed commercial graphite (C3). SEM image (Figure 7.2) shows a total breakdown of graphitic layer structure after ball-milling treatment. Furthermore, XRD patterns (Figure 7.3) confirm the crystalline structure break-down from the significant widening of the diffraction peaks of graphite [73]. These results imply a wide introduction of dangling bonds and the potential to trigger the gas-solid reaction.

![Diagram](image)

*Figure 7.1 Fabrication of the nitrogen-doped carbon nanoparticles (NDCA) and its ORR catalytic property.*

The high-resolution SEM images show the different morphologies of four samples. Original commercial graphite (Figure 7.2a) has a flake-like shape. Annealing does not change this morphology, which can be seen from the SEM image of annealed commercial graphite (Figure 7.2c). However, ball milling has changed the morphology substantially. There is no typical
flake-like structure in milled graphite samples (Figure 7.2b). Instead, the milled samples contain irregular sphere-like structures with a wide distribution of particle sizes. After annealing of the milled graphite, no significant change occurs in morphology (Figure 7.2d).

![Figure 7.2 Typical SEM images of a) starting graphite, b) milled graphite, c) heated graphite without milling treatment and d) heated graphite after milling treatment.](image)

XRD patterns of the four samples are consistent with the SEM imaging results (Figure 7.3). The starting (C1) and heated (C3) graphite samples have similar XRD patterns, showing a most intensive peak (002) at ~26.5 degree and some other weak peaks at ~45 degree (100, 101), 55 degree (004) and 77 degree (110). However, after ball milling, the XRD pattern of C2 shows a much broader peak of (002), which suggests a serious damage of graphite inner plane aromatic ring structure. Comparing C4 with C2, the FWHM of peaks becomes narrower after annealing; indicating that annealing refines the graphitic structure. This structure refinement is expected to increase sample's conductivity [219].
XPS is used to characterise the element contents of samples. As expected, in the XPS analysis of sample C₁, C₁s peak (for carbon) was the only intensive peak found with a very small O₁s peak, corresponding to approximately 2.2% oxygen. After ball milling treatment (sample C₂), there were approximately 7.5% oxygen and 6.3% nitrogen found. The high nitrogen content in the sample after ball-milling process in nitrogen atmosphere indicates that the milling process leads to nitrogen incorporation. The rise of oxygen level in C₂ may also support the hypothesis that the ball-milling treatment produces a more active surface. Both nitrogen and oxygen contents are reduced after annealing (sample C₄), approximately 1.0% for nitrogen and 0.7% for oxygen (sensitivity of the analysis is about 0.1%) (Figure 7.4). This loss of nitrogen
and oxygen functional groups is also confirmed by the TGA characterisation (Figure 7.5), which shows a 24% weight loss when the sample is annealed to 700 °C. As a comparison, direct annealing of C_1 in N_2/H_2 mixture (sample C_3) does not introduce detectable nitrogen using XPS. The possible mechanism of the ball milling in nitrogen atmosphere in the synthesis of N doped graphite catalyst is that the mechanical milling process introduces active sites such as unpaired bonds during the milling, resulting in nitrogen covalent bonding to the carbon surface [211].

Figure 7.4 XPS surveys of C_1-C_4.
Figure 7.5 TGA of the ball-milled graphite (C2) in N₂/15%H₂ mixture.

XPS N₁s spectra are analysed to characterise the bonding nature of the nitrogen in the catalysts since different states of nitrogen result in different catalytic properties [220]. The N₁s spectrum of sample C₂ (Figure 7.6a) can be fitted by 4 components at 398.8eV, 399.7eV, 401.1eV and 403.6eV, corresponding to nitrogen in pyridinic (N1), pyrrolic (N2), graphitic (N3) and nitric oxide (N4) structures [138, 210]. After annealing (Figure 7.6b), three components remain while pyrrolic structure (N2) disappears and the relative amount of graphitic structure (N3) increases from 43% to 66%, which is calculated by dividing the area of N3 by the total area of all components. This phenomenon is consistent with previous research that the graphitic structure (N3) has better thermal stability than pyridinic and pyrrolic structures [220].
Figure 7.6 High resolution N1s XPS of a) C2 and b) C4. The signal of C2 can be fitted with 4 components at 398.8, 399.7, 401.1, 403.6 eV, which correspond to pyridinic N (N1), pyrrolic N (N2), graphitic N (N3), and nitric oxide (N4), respectively. After annealing, pyrrolic N (N2) is disappeared and nitric oxide (N4) peak shifts to 403.1 eV.

The particle size distribution test is to show how particle size changes after annealing (Figure 7.7). C2 had an average particle size as 210 nm when in C4, after annealing, the particle size becomes 348 nm. This phenomenon might be caused by the agglomeration and the refinement of graphitic structure in high temperature annealing [221].

Figure 7.7 Particle size measurement of a) C2 and b) C4. The average particle size is 210nm for C2 and 348nm for C4.
Visible-ultra violet (UV-Vis) absorption spectroscopy is used to characterise the dispersive and hydrophilic property of samples (Figure 7.8). C₁ and C₃ cannot form stable dispersion in water. However, C₂ and C₄ can be dispersed in water, as reflected by the presence of UV-Vis absorption band of the aromatic system in graphite [222]. This enhanced dispersive ability and hydrophilicity is likely to be due to the changed surface property and the decreased average particle size during the ball milling [223]. Indeed, the introduction of N and O doping [215] has been proved to increase the hydrophilicity. This increased hydrophilicity may be responsible for the improved catalytic property by enabling enhanced mass exchange rate and the stability of the three-phase zone, which is the zone including the surface of the catalyst, the electrolyte right above the surface of the catalyst and the dissolved oxygen molecules in the electrolyte. [224, 225].

Figure 7.8 UV-Vis absorption of the four samples after ultrasonic treatment. C₁ and C₃ quickly precipitate after ultrasonic treatment and indicate no Uv-Vis absorption (inset photo: C₁-C₄ from left to right taken after 30 mins of ultrasonication).
Figure 7.9 shows ORR in 0.1 M KOH using a thin film of C1, C2, C3 and C4 deposited on the rotating disk electrode rotated at 1600 rpm. As a control experiment, Figure 7.10 is obtained at the same condition confirming the absence of reduction currents for typical carbons e.g. C2 and C4 in the absence of oxygen. The ORR activity is enhanced in the order of C3, C1, C2 and C4. The ORR enhancement is evident in both the current onset and density e.g. sample showing more positive onset potential value exhibits larger current density. C4, in particular exhibits an onset potential value about 0.1 V more negative comparing to Pt/C (60 wt.% C), the standard benchmark for ORR in conventional fuel cells; implying the remarkable potential of the proposed doping method to synthesise alternative ORR catalysts. However, it also could be seen that for all 4 samples tested, there are current plateaus around -0.3 V to -0.45 V (Figure 7.9). These plateaus suggest that the mechanism of the reaction is not fully 4-electron mechanism at this potential window. The improved catalytic performance is due to the doping of nitrogen and the breaking of graphite basal plane structure. Nitrogen-doped carbon materials have been reported to have unique ORR catalytic property by previous researches from both theoretically and experimentally aspects [10, 38, 41, 131, 220, 226-228], and because basal-plane aromatic ring structure of graphite is very inert to chemical reaction and electron transfer [229-232], defect and boundary carbon atoms are the real active sites where chemical reactions and catalytic processes take places. As demonstrated, ball milling creates a large quantity of structural defects and even changes the morphology, which increases the quantity of active catalytic sites. However, it is interesting to compare the RDE results of C1, C2 and C4. In fact, the catalytic performance does not change much after only ball-milling process. One reason may be that the damaged structure leads to reduced conductivity. The reduced conductivity leads to more energy consumption when charge transfer occurred in the material, which can compensate the energy saving brought by the catalytic process. Another possible reason is that although the ball milling causes nitrogen doping, the structure of most of these nitrogen is not
catalytically active. XPS uses bonding energy to differentiate different nitrogen doping structures. It is possible that there is nitrogen doping or adsorbed nitrogen with no catalytic contribution (which has bonding energy within the fitting area) to the extent that the catalytic nitrogen doping might be less than the fitting shows (Figure 7.6). After annealing, the catalytic property appears strongly even though the nitrogen content is much lower, reduced from 6.3% to 1%. Previous research suggests that the nitrogen doping which has catalytic property are pyridinic and graphitic nitrogen [220]. However, in this case, XPS shows that the content of all kinds of nitrogen doping decreases after annealing. Thus, in this work, the catalytic property of the sample is not quantitatively related with the nitrogen content.

![Graphical representation of RDE voltammograms](image)

*Figure 7.9 Rotating disk electrode (RDE) voltammograms of C1-C4 and Pt/C reference at 1600 rpm in O2 saturated 0.1 M KOH at a scan rate of 20 mV/s.*
To determine the ORR characteristics, the relationship between the current density and the rotation rate was examined. The typical ORR current density profile versus rotation rate is shown in Figure 7.11 for C₄. Figure 7.12 plots the typical inverse of the current density as a function of the inverse of the root square of the rotation rate e.g. the Koutecky-Levich plots [233, 234]. The slope contains the information of the reaction mechanism, for instance, whether the reaction follows four-electron or two-electron pathway. When the solvent and the temperature of the experiment are same, the reactions which have the same electron transfer number will show the same slope in Koutecky-Levich plots. The slope seems to vary between C₃/C₁ and C₂/Pt/C/C₄. Considering the widely established facts that ORR on Pt/C occurs through four-electron mechanism whereas conventional carbon through two-electron mechanism [233, 235], it is most likely that (within the experimental error), ORRs on C₃ and
C$_1$ follow two-electron mechanism while ORRs on C$_2$, Pt/C and C$_4$ follow four-electron mechanism pathway. The shift of the mechanism from two-electron to four-electron is consistent with the ORR activity enhancement trend observed above. Also, the kinetic current density ($J_k$) can be calculated from the y-axis intercept of Koutecky-Levich plots. The $J_k$ increases in the order of C$_3$, C$_1$, C$_2$ and C$_4$, same with the order of potential onset increasing. The $J_k$ of C$_3$ is 4.2 mA cm$^{-2}$ and for C$_4$ it is 5.2 mA cm$^{-2}$, which is approaching to that of Pt (7.5 mA cm$^{-2}$).

Figure 7.11 Rotating disk electrode (RDE) linear sweep voltammograms of C$_4$ in O$_2$ saturated 0.1 M KOH with different rotation rates at a scan rate of 20 mV/s$^{-1}$. 
Figure 7.12 Koutecky-Levich plots derived from RDE voltammograms of different materials.

For C3 and Pt+C sample, the current at -0.4 V is used to avoid a mass transport controlled reaction plateau at -0.5 V.

In real fuel cells, the organic compounds like methanol at anode would penetrate the membrane and reach Pt cathode, which could change the chemical reaction of oxygen reduction to the oxidation of those organic compounds [236]. This phenomenon is called the poisoning of catalyst. The advantage of carbon-based materials becomes apparent in terms of its methanol resistance. The chronoamperometric response is obtained at -0.35 V (Figure 7.13). It was discovered that introducing methanol leads to slight deterioration of ORR current for C4. For Pt/C, however, methanol oxidation occurs and causes total loss of cathodic current. This indicates a much better stability of reaction sites in C4 than Pt/C in alkaline environment, of interest for advanced fuel cells.
7.4 Conclusions

High performance ORR electrocatalysts can be synthesised based on nitrogen-doped carbon nanoparticles by ball milling and annealing processes. The nitrogen-doped carbon nanostructures exhibit a high activity, excellent tolerance to methanol in comparison to other non-precious metal catalysts. The synthesis strategy demonstrated here exploits novel carbon-based structures, and represents a general approach to the fabrication of efficient electrocatalysts for a range of electrochemical reactions. This strategy is low-cost and easy to scale up, so it provides a feasible synthesis method for the large-scale practical electrocatalysts.
Chapter 8 Direct observation of active sites for oxygen reduction reaction on nitrogen-doped graphene

8.1 Introduction

Fuel cells are a promising sustainable and renewable energy source. The practical use of fuel cells highly depends on the development of suitable catalysts for oxygen reduction reaction (ORR). Nitrogen-doped graphene is a potential carbon-based ORR catalyst of low cost, high stability and high efficiency [10, 38, 48, 210]. In spite of extensive studies, the exact catalytic mechanism of nitrogen-doped graphene is still under debate. A fundamental disagreement lies in how nitrogen contributes to the catalysis. To answer the question, the key is to determine the contribution of three nitrogen doping configurations, namely pyridinic, graphitic and pyrrolic, to the catalytic performance, which is still inconclusive. Some studies support that pyridinic nitrogen is catalytically active [33, 41, 137, 140, 141, 237]; while others suggest graphitic nitrogen is effective [139, 143, 145, 238-241]. There are also claims that both pyridinic and graphitic nitrogen contribute to the catalytic property but with different roles [242, 243]. To date all the experimental determinations of the active sites in nitrogen-doped graphene are indirect. The controversial results from the previous experiments suggest that there is a need to develop a method that is able to observe the active sites and elucidate the catalytic mechanism. It has been demonstrated before that intermediates of a catalytic reaction could be ex situ detected on the surface of the catalyst, e.g. using X-ray photoelectron spectroscopy (XPS) [125, 207]. In this chapter, it is reported that chemically adsorbed oxygen reduction intermediates are found on the nitrogen-doped multilayer graphene after ORR. This not only implies that nitrogen close to carbon in nitrogen-doped graphene is involved in the catalysis of ORR process
and, more importantly, can be used to observe the active nitrogen sites and pinpoint the ORR pathway.

8.2 Experimental

The graphene oxide (GO) was prepared from graphite flakes (Sigma, 325 mesh) using a slightly modified Hummers’ method [244, 245]. The GO powder was collected by lyophilisation. Three types of N-graphene were synthesised via different nitrogen sources and incorporation methods. For G-NH$_3$$\cdot$H$_2$O, the initial GO solution (~1 mg/mL) was mixed with 5 mL 25% NH$_3$$\cdot$H$_2$O, then the mixture was stirred and heated at 90 °C for 12 h to complete nitrogen incorporation. Resultant solution was then washed by water to remove base and lyophilised to get the final product in a dry powder form. G-NH$_3$ was prepared by annealing GO powder in 20% NH$_3$/Ar at 600 °C for 5 h. G-C$_3$N$_4$ was prepared by mixing initial GO with melamine at a mass ratio of 1:10 and the mixture was annealed in Ar to 950 °C for 3 h.

All electrochemical measurements were performed under identical conditions (the same catalyst mass loading). Taking G-NH$_3$$\cdot$H$_2$O electrode as an example, the catalyst was first ultrasonically dispersed in distilled water (Milli-Q). Aqueous catalyst solution dispersion of 20 μL (2.0 mg/mL, with 0.5 wt% Nafion$^\text{®}$ solution) was then transferred onto the glassy carbon electrode (GC, 0.196 cm$^2$, Pine Research Instrumentation, USA) via a controlled drop casting approach then dried in air for 12 h served as a working electrode. The reference electrode was an Ag|AgCl in saturated AgCl-KCl solution and the counter electrode was platinum wire. A flow of O$_2$ was maintained over the electrolyte (0.1 M KOH) during the recording of electrochemical measurements in order to ensure its continued O$_2$ saturation. Cyclic voltammograms (CVs), linear sweep voltammograms (LSVs) and rotating disk electrode (RDE) tests were carried out using a glassy carbon rotating disk electrode. The scan rate of CVs was kept at 100 mV/s while that for LSVs and RDE tests was 10 mV/s. The data were recorded
using a CHI 760D potentiostat (CH Instruments Inc., USA). Electrochemical impedance spectroscopy of the three nitrogen-doped graphene samples in 0.1 M KOH; data were collected using electrodes under electrode potential = −0.5 V vs Ag/AgCl.

The samples used for XPS were prepared in the same way described above, which were dispersed in distilled water and then drop-casted on the electrode. They were then under continuous CV scan for 200 cycles from +0.2 V to −1.0 V (vs. Ag|AgCl), in which only reduction of oxygen occurs and no electrolysis of water happens. The samples were removed and collected from the electrode by ultrasonication after the reaction. The resultant samples were washed by Milli-Q water and separated for three times by centrifuge at 14,800 rpm to remove alkaline electrolyte. The samples were drop-casted on the gold plate for XPS. No potassium hydroxide (KOH) is detectable by XPS. The XPS analyses were conducted in an ultrahigh vacuum chamber (~10⁻¹⁰ mbar) of the undulator soft x-ray spectroscopy beamline at the Australian Synchrotron, Victoria, Australia. The photoelectrons were collected by a high-resolution and high-sensitivity hemispherical electron analyser with nine channel electron multipliers (SPECS Phoibos 150). In the scans, the excitation energy was 700 eV for better signal-to-noise ratio and the E-pass was set to 5 eV for optimum energy resolution. To evaluate the signal contribution from Nafion and gold plate, the XPS spectra of pure Nafion and a clean gold plate were also recorded. It is found that for all samples, the N and C contributions from the Au plate are negligible (less than 5% and 1%, respectively). The excitation photon energies were calibrated by the photon energy measured on a reference Au sample and the binding energies were collated by the C–C peak at 284.6 eV.

The measured C 1s XPS spectrum of G-NH₃·H₂O after ORR was partially contributed by Nafion residues. The removal of Nafion’s contribution from the XPS spectra is described below. Pure Nafion shows three intensive peaks at around 291, 293 and 295 eV, standing for carbon fluoride backbone of Nafion. After comparing the C 1s spectrum of the G-NH₃·H₂O after ORR
and pure Nafion, Nafion’s contribution is determined mainly at the high energy side of the C 1s spectrum of the G-NH₃·H₂O, i.e. around 291, 293 and 295 eV. The three Nafion peaks at around 284.6, 288.1 and 297.5 eV are found to be either too weak to affect the fitting or out of the scan range, which therefore are not introduced in the fitting. In the fitting, the area ratio and bonding energy difference among the Nafion peaks were set to be same as those in the pure Nafion. Different carbon peaks in nitrogen-doped graphene were then introduced to fit the data. The C 1s XPS spectrum after ORR can be obtained by subtracting the Nafion’s contribution and then least-square fitted.

¹H solid-state NMR was conducted on G-NH₃·H₂O after ORR and vacuum drying at 65 °C for 24 hours. Because only a small amount of sample could be collected after ORR, it is found that background signals contribute significantly to the ¹H NMR spectrum. The ¹H NMR spectrum after background subtraction is shown in Figure 8.6.

Transmission infrared spectra were collected using a Bruker Vertex 70 infrared spectrometer. The multilayer graphene samples before and after ORR were vacuum dried at 65 °C and then mixed with FTIR grade KBr (Sigma-Aldrich), ground and pressed to make pellets. During the experiment, the pure KBr was used as a reference. Total 32 scans were collected for both the reference and the samples. The reference spectrum was then subtracted from the sample spectrum to reduce the interference from the atmosphere and the equipment. The resolution was 4 cm⁻¹ and the scan range is from 600 to 4000 cm⁻¹.

### 8.3 Results and discussion

Three multilayer graphene samples were prepared from graphene oxide using different nitrogen sources and doping methods for different nitrogen doping configurations and concentrations: treatment by ammonium hydroxide, heating under ammonia (NH₃) gas and reaction with
melamine. For simplicity, the three samples are named G-NH$_3$·H$_2$O, G-NH$_3$ and G-C$_3$N$_4$, corresponding to the nitrogen doping methods. Typical transmission electron microscopy (TEM) images of the nitrogen-doped multilayer graphene nanosheets, which are a few nanometer thick are shown in Figure 8.1.

![Figure 8.1 TEM images of G-NH$_3$·H$_2$O, G-C$_3$N$_4$ and G-NH$_3$ nitrogen-doped multilayer graphene samples.](image)

Synchrotron-based XPS of high resolution and high sensitivity was used to investigate the chemical composition change in the three nitrogen-doped multilayer graphene samples before and after ORR. Before ORR, the nitrogen contents in G-NH$_3$·H$_2$O, G-C$_3$N$_4$ and G-NH$_3$ are 6.0%, 5.7% and 6.8%, respectively. The least-square fittings of the XPS spectra in the nitrogen 1s region before ORR are displayed in Figure 8.2 (upper row). It can be seen that G-NH$_3$·H$_2$O and G-NH$_3$ samples have relatively higher contents of pyrrolic nitrogen at 399.8 eV (red), slightly less pyridinic nitrogen at 398.5 eV (blue), and much less graphitic nitrogen at 401.2 eV (purple). G-C$_3$N$_4$, on the other hand, contains more pyridinic nitrogen and less but comparable amounts of pyrrolic and graphitic nitrogen. After ORR, the three samples show different changes of pyridinic, pyrrolic and graphitic nitrogen contents (lower row in Figure 8.2). For G-NH$_3$·H$_2$O, the pyridinic nitrogen peak decreases while the “pyrrolic” peak increases (the reason to use parenthesis here will be explained later); for G-C$_3$N$_4$, the graphitic content increases and the pyridinic and “pyrrolic” contents are steady; G-NH$_3$ shows a depressed
“pyrrolic” peak. As shown below, these changes correspond to very different catalytic behaviors and functions of the different nitrogen configurations during the ORR process.

![Figure 8.2](image)

**Figure 8.2 Nitrogen 1s XPS spectra of the three multilayer graphene samples before and after ORR. The least-square fitted peaks are pyridinic nitrogen at 398.5 eV (blue), “pyrrolic” nitrogen at 399.8 eV (red), graphitic nitrogen at 401.2 eV (purple) and nitrogen oxide at 403 eV (green).**

The observed nitrogen content change cannot be attributed solely to nitrogen loss. Nitrogen may be lost via a nitrogen oxidation process during ORR, which could change the contents of the different nitrogen configurations. Generally, pyrrolic nitrogen is less stable than pyridinic and graphitic nitrogen and more prone to the oxidation and loss during ORR process [138, 246]. In other words, the pyrrolic nitrogen peak should relatively decrease after ORR. However, G-NH$_3$·H$_2$O shows the opposite trend with an increased “pyrrolic” peak after ORR.

For clues to the reason for the relative change of the nitrogen contents, we can turn to the carbon and oxygen XPS results. Both the oxygen and carbon 1s XPS spectra reveal that the content of –OH, one of the intermediate products of ORR, increases after ORR. Figure 8.3 compares the oxygen 1s XPS spectra of G-NH$_3$·H$_2$O before and after ORR. It can be seen that after ORR the
C(aliphatic)–OH/C(aliphatic)–O–C(aliphatic) peak at 532.0 eV (red) relatively decreases in intensity and the C(aromatic)–OH at 533.3 eV (blue) increases in intensity [247, 248]. This suggests that compared to the other oxygen-containing groups, the relative content of –OH group attached to aromatic carbon rises after ORR. The carbon 1s XPS spectra also show that the C–OH peak at 285.4 eV [247] (purple) dramatically strengthens in G-NH$_3$·H$_2$O after ORR (Figure 8.4). The increased content of –OH after ORR has also been confirmed by Fourier transform infrared spectroscopy (FTIR) [205, 206]: the characteristic –OH peak centred at ~3440 cm$^{-1}$ is much stronger for the sample after ORR, as shown in Figure 8.5. Besides, solid-state nuclear magnetic resonance (NMR) spectroscopy shows that most of hydrogen is in the form of C–OH in G-NH$_3$·H$_2$O after ORR (Figure 8.6) [208, 249]. The spectrum shows a relatively strong peak at about 1 ppm which represents –OH groups and a weaker peak at about 8 ppm which should be hydrogen attached to aromatic carbon in graphene. This confirms that most of the hydrogen is in the form of C–OH on G-NH$_3$·H$_2$O.

**Figure 8.3** Oxygen 1s XPS spectra of G-NH$_3$·H$_2$O a) before and b) after ORR. The fitted peaks are C=O at 530.8 eV (green), C(aliphatic)–OH/C(aliphatic)–O–C(aliphatic) at 532.0 eV (red), C(aromatic)–OH at 533.3 eV (blue) and chemisorbed water molecules at 535.7 eV (purple).
Figure 8.4 Carbon 1s XPS spectra of G-NH$_3$·H$_2$O a) before and b) after ORR. The fitted peaks are C–C/C=C at 284.6 eV (blue), C–OH at 285.4 eV (purple), C–O–C at 286.5 eV (cyan), C=O at 288.1 eV (green) and –COOH at 290.8 eV (red).

Figure 8.5 FTIR spectra of G-NH$_3$·H$_2$O before (blue) and after (red) ORR. The O–H signal is not due to water.
The changes of the nitrogen 1s XPS profile in Figure 8.2a and b therefore could be caused by the chemical environment change of the doped nitrogen during ORR, i.e. the attachment of –OH to the carbon atoms bond to the nitrogen. It has been reported that the attachment of –OH to pyridone can cause an upshift of the nitrogen binding energy from 398.8 to 400.2 eV [138, 250, 251]. Similarly, when an –OH attaches to the carbon neighboring pyridinic nitrogen in graphene, the nitrogen binding energy should shift upwards to an energy very close to the 399.8 eV position of the pyrrolic peak. Therefore, the observed intensity decrease of the pyridinic peak and intensity increase of the “pyrrolic” peak in G-NH₃·H₂O after ORR could be caused by the change of the pristine pyridinic nitrogen to the pyridinic nitrogen with a neighboring carbon attached to –OH, as illustrated in Figure 8.7. In other words, the increase of the “pyrrolic” nitrogen after ORR in XPS is not caused by the increase of pyrrolic content, but the increased content of the –OH attached pyridinic nitrogen which has a very similar XPS peak position to the pyrrolic nitrogen. The existence of the –OH attached pyridinic nitrogen is also supported by the increased full width at half maximum (FWHM) of the least-square fitted “pyrrolic” peak at 399.8 eV from 1.61 eV before ORR to 1.71 eV after ORR, suggesting the existence of the –OH attached pyridinic nitrogen peak in the region. The unchanged and decreased intensities of the 399.8 eV peak in G-C₃N₄ and G-NH₃ suggest that much less –OH attachments are formed to the carbon atoms neighboring pyridinic nitrogen in the two graphene samples and pyrrolic nitrogen is slightly lost during ORR.

Figure 8.6 $^1$H solid-state NMR spectrum of G-NH₃·H₂O after ORR and vacuum drying.
Intriguingly, G-NH₃·H₂O which experiences the highest increase of the –OH attachment to pyridinic nitrogen after ORR shows the best catalytic performance; G-C₃N₄ and G-NH₃ which have no increase or even decrease in the 399.8 eV peak after ORR show much worse ORR properties. The ORR catalytic performances of the three samples in alkaline electrolyte are tested by RDE voltammetry (Figure 8.8) and summarised in Figure 8.9. For G-NH₃·H₂O, the onset potential of ORR is about –0.13 V and the electron transfer number is 3.75 with a dynamic limiting current ($J_k$) of about 15 mA cm⁻² at 0.6 V vs Ag/AgCl. Both G-C₃N₄ and G-NH₃ show more negative onset potentials, lower electron transfer numbers and $J_k$. The correlation between the increased content of the –OH attached pyridinic nitrogen and the ORR performance can be used to determine the active sites for ORR on nitrogen-doped graphene.

Figure 8.8 RDE tests of three nitrogen-doped graphene samples.
In the commonly accepted four-electron associative ORR mechanism of nitrogen-doped graphene in alkaline solution, intermediate OH(ads) is formed from O(ads) with the addition of H$_2$O and one electron [142, 210]. It is predicted that the OH(ads) is attached to the catalytic core or active site via a chemical bond [136, 137, 142]. Therefore, the ORR active sites can be determined from the presence of intermediate OH(ads). Our observation of the –OH attached pyridinic nitrogen after the electrochemical reaction suggests that pyridinic nitrogen plays an important role in the ORR process and the nearby carbon should be the main active sites, in a good agreement with some of the previous theoretical calculations and experimental studies [33, 41, 137, 140, 141, 237, 252, 253]. According to these studies, the neighbour carbon atoms of pyridinic nitrogen have favoured atomic charges that can induce the ORR process: the absorption of the intermediate products, the formation of C–O bond and the disassociation of O–O bond [136, 137]. The carbon bond to graphitic nitrogen should not be the main active site in the three tested samples, because the content change of graphitic nitrogen before and after ORR is much less significant and therefore presents no strong relation with the catalytic performance.
Another very interesting point from this study is that the dominant type of nitrogen doping configuration may not necessarily correlate with the ORR performance of nitrogen-doped graphene. Before ORR, G-NH$_3$·H$_2$O and G-NH$_3$ have similar contents of nitrogen and oxygen (about 13% in G-NH$_3$·H$_2$O and 14% in G-NH$_3$). The contents of pyridinic, pyrrolic and graphitic nitrogen in the two samples are similar too (Figure 8.2a and e). In addition, the three samples show similar electrochemical impedance values, indicating their similar electrical conductivity (Figure 8.10). The electrochemical impedance tests also imply comparable wettability of the three samples, consistent to their capability to be dispersed in water. However, the two samples show dramatically different catalytic properties (Figure 8.9). This clearly shows that the pyridinic or graphitic nitrogen content before ORR cannot be used to predict or explain ORR performance. This also raises a question: why do the two samples with similar pyridinic contents show dramatically different ORR performance if the pyridinic sites are the main catalytic active sites? One assumption is that pyridinic nitrogen in graphene may have different ORR properties. It has been demonstrated by theoretical calculations that the microstructure of nitrogen dopings, for instance, the location of the doping, and the graphene edge type (zigzag or armchair) could lead to different ORR activities [143, 144, 146]. Our oxygen 1s XPS spectra in Figure 8.3 show that the –OH is mainly attached to aromatic carbon rather than aliphatic carbon in the ORR, suggesting that the pyridinic nitrogen on the edge should be more likely to involve in the catalytic process and the previous proposition that the nitrogen doping microstructure is vital for ORR activity is reasonable. Although the total amounts of pyridinic nitrogen are similar in G-NH$_3$·H$_2$O and G-NH$_3$, the pyridinic nitrogen in the two samples have different fine structures (e.g. on the edge or not) and different ORR activities due to the different nitrogen doping methods used. In contrast, the examination of nitrogen-doped graphene after ORR can reveal the active sites via the appearance of oxygen reduction intermediate, i.e. OH(ads).
8.4 Conclusions

In summary, the examination of chemical composition change of nitrogen-doped multilayer graphene before and after ORR can be used to detect the chemically attached ORR intermediate i.e. OH(ads) and determine the catalytic active sites. The good correlation between the amounts of the OH(ads) attachment and the ORR performances from the three nitrogen-doped multilayer graphene samples suggests that the carbon atom neighboring pyridinic nitrogen plays an important role in the ORR process and should be the main active sites in the tested samples. This study also implies that the location of pyridinic nitrogen can affect its catalytic efficiency.
Chapter 9 Conclusions and Future work

9.1 Summary

The disordering and phase transformation of graphite was created using the ball-milling process and carefully revealed by Raman spectroscopy. The ratio of two main bands (D and G), $I_D/I_G$, increases in the first 15 h of ball milling and then gradually reduces until 40 h. The longer milling does not significantly change the ratio. In the 15 h ball milling, the ball milling breaks the graphite and creates defects that activate the D band. After 15 h ball milling, the grain size of the sample is significantly reduced and further ball milling cannot cut these samples further. The impact, however, can still induce the phase transition of the sample, but instead of cutting the sample, it begins to distort the graphitic planes. The distortion of the graphitic plane causes the rapid broadening of the G and D bands in Raman spectroscopy and the reduced $I_D/I_G$. Since the nano-sized graphitic planes are wrapped and packed into clusters in the distortion, the total surface area decreases. Further ball milling does not significantly change the sample structure and morphology. Since the D band is still intense compared to the G band in all the samples, it implies that the ball-milling condition used cannot break all aromatic rings. It only leads to an equilibrium state of disordering and ordering by destroying and forming clusters at the nanometre scale.

Further research found that the ball milling in different atmosphere can cause entirely different results. Ball milling of graphite, BN and MoS$_2$ in Ar gas can destroy the structure of the milled samples within a short period time, but not in NH$_3$ gas. Principally, NH$_3$ significantly protects the in-plane structure of graphite and BN and leads to nanoflakes, rather than a semi-amorphous structure. MoS$_2$ can also be protected, but not as significantly as the other two materials. The NH$_3$ reduces the rotation disordering of the nano-crystal of MoS$_2$. Furthermore, this protective
effect is not restricted to NH$_3$. C$_2$H$_4$ and CH$_4$ are also demonstrated to protect the milled material. Further investigation suggests that the nature of the protection is the lubrication effect provided by the surface adsorbed gas molecules. This finding can lead to a better understanding of the lubrication effect of the popular solid lubricants (graphite, BN, MoS$_2$). This effect can also be utilised in fabricating multilayer 2-D materials with controlled in-planar structures.

Enhanced reversible lithium storage in graphitic materials was found with ball-milled graphite with different structures. The capacity enhancement was caused by the distorted graphitic structures. Electrochemical characterisation shows that the increased lithium storage happens above the intercalation/de-intercalation voltage and this mechanism has some characteristic feature of the capacitor. This capacitor-like storage increases with the distortion of the graphitic structure. On the other hand, the intercalation/de-intercalation capacity is found to reduce with the distortion of the structure.

Nitrogen-doped carbon nanoparticles are fabricated by ball milling, which can catalyse ORR after a structure refinement. Ball milling for 20 h dopes the graphite with about 8% nitrogen. One drawback is that same with most of the other methods in producing nitrogen-doped graphitic materials; ball milling cannot control the doping structures. Pyridinic, pyrrolic and graphitic nitrogen were all found in the doped samples. The doped samples showed more electron transfer number than CG, but it does not show a more positive reaction onset. It was found that ball-milled samples had very poor graphitic structure, which leads to a high resistance of the catalyst. After the structure is refined by annealing, the sample shows a much more positive onset and higher current density than the starting material.

Moreover, the mechanism of the catalysis process on nitrogen-doped graphene is studied by Synchrotron based XPS. It was found that after catalysing ORR, the samples showed that the XPS spectra of the doped nitrogen changed. This change may be caused by the formation of
the pyrrolidine structure. This phenomenon is further linked with the catalytic performance of three samples with different structures and the results suggest that pyridine nitrogen is the most active nitrogen structure in catalysing ORR. The intermediates of the reaction can form chemical bonds with the neighbouring carbon of the pyridine nitrogen.

9.2 Future work

Ball milling is demonstrated to produce disordered graphitic nanoclusters. The Raman spectroscopy, however, confirms the existence of aromatic rings in the products. This means that ball milling can be further studied and developed in producing graphitic nanomaterials using a top-down strategy. For example, recently graphitic quantum dots have been suggested to have very interesting properties, but a large-scale synthesis strategy is still absent. Ball milling is demonstrated in Chapter 4 that produces the nanocluster smaller than 50 nm. This, therefore, may be a potential way to fabricate 2-D or 3-D nano quantum dots in large quantities. On the other hand, the mechanism of the ball milling should be studied further. In this experiment, the energy of the ball milling was not high enough to break all the aromatic ring system and form chain-like carbon. It is a very interesting topic to investigate whether a high-energy ball milling could provide enough energy to change the graphitic carbon into chain carbon, which is a 1-D material and could have very unique properties. The lubrication of the atmosphere should be further investigated to determine whether this phenomenon also exists when the material has no lamella structure. It would be very interesting to investigate, instead of the mechanical property, whether this adsorbed molecule can change other properties of the material. It was demonstrated that with a proper atmosphere, ball milling is a good tool to fabricate 2-D materials in large quantities. More work should be done to optimise the conditions, for example, the pressure of the atmosphere and the type of ball milling, for
producing the material with a better-controlled structure. Ball milling is demonstrated to be an efficient method to trigger chemical reactions between carbon and nitrogen. How to precisely control the chemical reaction and the chemical composition of the products is a very exciting topic. Almost all the current synthesis methods have difficulties to synthesise the nitrogen-doped carbonaceous materials with only one kind of nitrogen doping. If it is achievable, it could lead to great advancements in the mechano-chemical theory, as well as technological breakthroughs, since ball milling has been widely used in industry already. The mechanism of ORR on nitrogen-doped graphene still needs further investigation, since the current understanding is still not detailed enough to answer the question of how to further improve the performance, or whether it could eventually surpass the metal catalysts and be used in real-world applications.
References


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