Deformation of Hexagonal Boron nitride

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# Table of contents

LIST OF FIGURES ........................................................................................................... 6

LIST OF TABLES .............................................................................................................. 17

ABSTRACT ......................................................................................................................... 19

DECLARATION .................................................................................................................... 20

COPYRIGHT STATEMENT .................................................................................................. 21

ACKNOWLEDGEMENTS .................................................................................................... 22

CHAPTER 1: INTRODUCTION ............................................................................................ 23

1.1 AIMS AND THESIS STRUCTURE .................................................................................. 25

CHAPTER 2: LITERATURE REVIEW .................................................................................... 27

2.1 INTRODUCTION ........................................................................................................... 27

2.2 STRUCTURES ............................................................................................................... 27

2.2.1 Hexagonal boron nitride ......................................................................................... 27

2.2.2 Boron nitride nanosheets (BNNSs) .......................................................................... 30

2.2.3 Boron nitride nanotubes (BNNTs) ........................................................................... 32

2.3 SYNTHESSES ............................................................................................................. 34

2.3.1 Hexagonal boron nitride (h-BN) ............................................................................. 35

2.3.2 Boron nitride nanosheets (BNNSs) ........................................................................ 36

2.3.2.1 Self-Assembly .................................................................................................... 36

2.3.2.2 Mechanical cleavage ......................................................................................... 37

2.3.2.3 Chemical exfoliation .......................................................................................... 38

2.3.2.4 Other methods .................................................................................................... 39

2.3.3 Boron nitride nanotubes (BNNTs) ........................................................................... 42

2.3.3.1 Arc discharge ..................................................................................................... 42

2.3.3.2 Laser ablation .................................................................................................... 42

2.3.3.3 Carbothermal methods ....................................................................................... 43

2.3.3.4 Chemical vapour deposition (CVD) .................................................................... 45

2.3.3.5 The inductive thermal plasma method ................................................................. 46

2.3.3.6 Other methods .................................................................................................... 49
5.2.1 Optical microscopy ................................................................. 97
5.2.2 Raman spectroscopy ................................................................. 99
5.3 BORON NITRIDE (BN) POWDER AND EXFOLIATED BN SHEETS ........................................ 100
5.3.1 X-ray diffraction (XRD) .......................................................... 100
5.3.2 Scanning electron microscopy (SEM) ......................................... 101
5.3.3 Transmission electron microscopy (TEM) ................................... 103
5.3.4 Atomic force microscopy (AFM) ................................................ 103
5.3.5 Optical microscopy .................................................................. 104
5.3.6 Raman spectroscopy ................................................................. 106
5.4 BORON NITRIDE NANOTUBE BUCKYPAPER AND EXFOLIATED BNNTs ................................. 108
5.4.1 Scanning electron microscopy (SEM) ......................................... 108
5.4.2 Transmission electron microscopy (TEM) ................................... 109
5.4.3 X-ray diffraction (XRD) .......................................................... 110
5.4.4 Optical microscopy .................................................................. 111
5.4.5 Raman spectroscopy ................................................................. 112
5.5 SUMMARY .................................................................................. 113

CHAPTER 6: DEFORMATION OF HEXAGONAL BORON NITRIDE (H-BN) ...................... 115
6.1 INTRODUCTION ........................................................................... 115
6.2 EXFOLIATED H-BN FLAKES ........................................................ 115
6.2.1 Thick region (Δ) of the exfoliated h-BN flake .............................. 118
6.2.2 Thin region (□) of the exfoliated h-BN flake .............................. 120
6.3 H-BN/Glass based composites ..................................................... 122
6.3.1 h-BN/glass (I) composites ....................................................... 123
6.3.2 h-BN/glass (II) composites ...................................................... 125
6.4 DISCUSSION ................................................................................ 126
6.4.1 Exfoliated h-BN flake .............................................................. 127
6.4.2 H-BN/glass based composites ................................................. 128
6.5 SUMMARY .................................................................................. 129

CHAPTER 7: DEFORMATION OF BORON NITRIDE NANOSHEETS (BNNSS) GLASS BASED NANOCOMPOSITES ................................................................. 130
7.1 INTRODUCTION ........................................................................... 130
7.2 BNNSs/ BOROSILICATE NANOCOMPOSITES ................................................................. 130
7.3 BNNSs/ GLASS (II) NANOCOMPOSITES ................................................................. 136
7.4 DISCUSSION .................................................................................................................. 139
7.5 SUMMARY ..................................................................................................................... 141

CHAPTER 8: DEFORMATION OF BORON NITRIDE NANOTUBES (BNNTs) .................... 142
8.1 INTRODUCTION .............................................................................................................. 142
8.2 EXFOLIATED BORON NITRIDE NANOTUBES (BNNTs) ........................................... 143
8.3 BNNT/GLASS (II) NANOCOMPOSITES ................................................................. 145
8.4 DISCUSSION .................................................................................................................. 148
8.5 SUMMARY ..................................................................................................................... 150

CHAPTER 9: CONCLUSION AND FUTURE WORK .......................................................... 151
8.1 CONCLUSION ................................................................................................................ 151
8.2 RECOMMENDATIONS AND FURTHER WORK ..................................................... 152

REFERENCES: ..................................................................................................................... 154
List of Figures

**Figure 1.1**: Hexagonal boron nitride published documents. (Data analysis based on the Scopus database) .......................................................... 24

**Figure 2.1**: The layered structure of hexagonal boron nitride. Boron (B) and nitrogen (N) atoms connect in-plane with covalent bonds and out-of-plane with van der Waals bonds. The nearest neighbour distance between B and N is 0.1446 Å. The space between layers is 0.333 nm as the c-axis of the lattice is 0.6661 Å [55]. .................................................. 28

**Figure 2.2**: Structural stacking differences between graphite (left) and hexagonal boron nitride (right). The hexagons of neighbouring plans are shifted by a half hexagon in graphite (i.e. AB stacking), while they are superimposed in hexagonal boron nitride (h-BN), where B and N atoms are in succession along the c axis (i.e. AA’ stacking) [60]. ........................................... 29

**Figure 2.3**: Schematic of 2D BN nanostructures, the distance between the centres of neighbouring hexagons is 2.50 Å and between two layers is 3.33 Å. The edge of a monolayer BNNS can be either zigzag (B- or N-edge) or armchair (BN pairs) [62]. ........................................... 31

**Figure 2.4**: (a) and (b) Models of the bi-layered h-BN and graphite sheets that display the difference in their stacking sequence respectively. (c) and (d) The atomic structural representation of AA’ and AB stacked BN bilayer with corresponding HRTEM image simulations respectively. The grey area indicates the size of the top BN sheet ....... 32

**Figure 2.5**: (a) A layer of hexagonal boron nitride (h-BN) with possible direction of wrapping for zigzag and armchair configurations. The structural models of single-walled boron nitride nanotubes (SWBNNTs) with (b) zigzag, (c) armchair, and (d) chiral configurations [73]. .... 33

**Figure 2.6**: (a) Side and top view of the flat tip of (12, 0) BN nanotube. (b) Side and top view of the pencil-like (conical) tube closing of the (5, 5) arm-chair tube [79]. (c) Buckling shell thickness (RN-RB) in single-walled BN nanotubes as a function of tube diameter [78]. .... 34

**Figure 2.7**: An optical image of hexagonal boron nitride (h-BN) single crystals. This is the final product of using a temperature gradient method with (HP/HT) technique and the solvent was Ni-Cr system [12]. .............................................................. 36

**Figure 2.8**: (a) and (c) SEM images which observed exfoliation mechanism by the shear force of milling balls; (b) and (d) are the corresponding diagrams for (a) and (c) images respectively [92] ............................................................................. 37
Figure 2.9: Schematically illustrates the microfluidic flow velocity indicated by red arrows for a section of the rotating tube at $\Omega = 8000$ RPM and $\Theta = 45^\circ$, and the exfoliation process with slippage of BN layers on the inner surface of the tube [93].

Figure 2.10: (a) and (b) SEM images of folded BN nanosheets, which are so-called nanoscrolls. (c) The exfoliation process of molten hydroxides [105].

Figure 2.11: (a) AFM image with a line-scan profile of a few-layered BN film with thickness of $\sim 1$ nm, which was grown by CVD method [106]. (b) A scheme of BN nanosheets synthesis by the chemical blowing method [116].

Figure 2.12: (a) A 200 mg product of boron nitride nanotubes (BNNT) by the PVC method. (b) A PVC-grown BNNT yarn, 3 cm long and $\sim 1$ mm in diameter [128].

Figure 2.13: (a) SEM image of boron nitride nanotubes (BNNTs) synthesis by born oxide (BO)-CVD method [35]. (b) The experimental schema for growth of boron nitride nanotubes (BNNTs) in tube furnace by growth vapour trapping (GVT) technique [139]. (c) Patterned boron nitride nanotubes (BNNTs) grown on substrates by using catalytic films [140].

Figure 2.14: Images of an induction plasma process for high production of boron nitride nanotubes (BNNTs). (a) Schematic of the three main parts of the induction plasma system: an induction plasma torch, a reaction chamber, a filtration chamber, and growth mechanism of BNNT from boron (B) droplets [144]. (b), (c) Photographs of as-grown BNNTs after an 11 h operation. In total, 192 g of BNNTs were synthesized in a single experiment. (d)–(f) SEM and TEM images of as-produced BNNTs. The walls of the BNNTs are defect-free, demonstrating their high structural quality and a bundle of BNNTs is illustrated with a scale bar of 20 nm [143].

Figure 2.15: (a) A TEM image showing boron nitride nanotubes (BNNTs) grown from boron (B) nanoparticles [143]. (b) A TEM image for a bamboo-like structure of boron nitride nanotubes synthesised by ball milling method [146].

Figure 2.16: Schematic diagram showing the four steps involved in the B ink painting method. (a) Ball-milling of boron (B) powder in a NH$_3$ atmosphere to produce boron (B) nanoparticles. (b) Mixing milled B nanoparticles with metal nitrate in ethanol to form B ink. (c) Painting the B ink on the substrate. (d) Annealing of the painted substrate in a nitrogen-containing atmosphere to grow the boron nitride nanotubes (BNNTs) film.
Figure 2.17: (a) The thermogravimetry (TGA) for BNNTs and CNT in air, which shows the high thermal stability of BNNTs up to ~ 1000 °C [165, 166]. (b) The ultraviolet–visible absorption spectrum with a peak at ~203 nm for boron nitride materials [163].

Figure 2.18: (a) Optical contrast for mono- and bi-layer boron nitride on SiO2 layer with 290 nm in thickness [88]. (b) Boron nitride flake with monolayer regions on SiO2 layer with a thickness of 90 nm [88]. (c) The optical contrast as a function of the wavelength and the thickness of hexagonal boron nitride (h-BN) from 1-80 layers on a 282 nm SiO2 layer [164]. The line indicates the change in contrast along the thickness from 1 to 80 layers of boron nitride (BN) with 516 nm wavelength.

Figure 2.19: (a) Schematic of AFM nanoindentation on suspended BN nanosheets [106]. (b) Force vs. indentation curves of two films of BN [106]. (c) Schematic of AFM bending test for a clamped BN film [190]. (d) Measured-bending modulus vs. thickness of BN nanosheets, where the dashed line indicates to the theoretical value of bulk hexagonal boron nitride (h-BN) [190].

Figure 2.20: Mechanical properties of few layered graphene and boron nitride [192]. Load vs. displacement curves for 1-3L (a) graphene and (b) boron nitride (BN). Changing 2D Young’s modulus (E2D) and Young’s modulus (E) in (c) and (d) respectively with layer numbers of graphene (G) and boron nitride (BN). (e) Fracture load and (f) breaking strength as functions of layers numbers of graphene (G) and boron nitride (BN). The dashed lines in (c) and (e) are based on the multiplication of the values of monolayers by the number of layers of graphene and boron nitride, while in (d) and (f), they indicate the values of monolayers of graphene and boron nitride (BN).

Figure 2.21: (a) Stress–strain curves for pure poly(vinyl alcohol) (PVA) polymer, unmodified BNNSs-PVA nanocomposites and functionalised OH-BNNSs-PVA nanocomposites [205]. (b) Stress vs. strain curves of pure aluminium (Al) and Al-BNNTs nanocomposites with 0.5 wt%, 1 wt% and 3 wt% concentrations of BNNTs at room temperature [218]. (c) Improvements of fracture toughness and flexural strength of BNNSs-BS glass composites with different concentration of BNNSs [214].

Figure 2.22: Schematic of high performance of nanostructured boron nitride compared with traditional BN particles [25]. It would be have poor enhancements of mechanical properties along C axis of BN particles (a), while good enhancements of mechanical properties can be achieved along the axis of BNNTs (b) or the basal planes of BNNSs (c).
Figure 2.23: The geometry of (a) nanotubes and (b) nanoplatelets, where d and t should be in order of nanometers to achieve high aspect ratios [222]........................................................................61
Figure 2.24: Schematic of reinforced nanocomposites by (a) aligned fibre, (b) randomly oriented fibre, (c) aligned nanoplatelets and (d) randomly oriented nanoplatelets [222].........................62
Figure 2.25: Schematic diagrams of the basis of the shear lag model showing: (A) unstressed system and (b) a deformation pattern for a discontinuous flake in a polymer matrix [48]...64
Figure 2.26: (a) A model of single monolayer graphene nanocomposites (not to scale) and (b) the strain distribution in the graphene monolayer at 0.4 strain and calculated curves with different values of Ns [29]. .........................................................................................65
Figure 2.27: Polymer matrix of nanocomposites with randomly dispersed nanoparticles (left) and a nanoparticle is coated by interphase (right) [240]. ..........................................................66

Figure 3.1: The energy level diagram of scattering process types [243], $E_0$ is the ground state of the molecule, incident photons (up green arrows) and Rayleigh scattering photons (down green arrow) have the same frequencies $N_0$, while scattered photons in Stokes (red arrow) and Anti-Stokes (blue arrow) scattering are down-shifted and up-shifted of frequencies respectively .................................................................68

Figure 3.2: The induced dipole moment, P, by incident oscillating electric field, E, of laser radiation. Scattering waves in two directions are shown as well (i.e. back scattering (180°) or right angle (90°)) [242]........................................................................................................69

Figure 3.3: The hexagonal structure and the first Brillouin zone of monolayer hexagonal boron nitride (h-BN). (a) The real lattice unit vectors $A_1$ and $A_2$ in the primitive cell. (b) The reciprocal lattice vectors $B_1$ and $B_2$ in 2D Brillouin zone [246]......................................................71

Figure 3.4: Raman spectrum of hexagonal boron nitride (h-BN). This spectrum exhibits the low frequency lines at $-52.5 \text{ cm}^{-1}$ (anti-Stokes) and $52.5 \text{ cm}^{-1}$ (Stokes) with a width of $\sim 1.1 \text{ cm}^{-1}$ and a high frequency line at $1366 \text{ cm}^{-1}$ (Stokes) with a full width at half maximum (FWHM) of $\sim 8 \text{ cm}^{-1}$. The insets show the in-plan displacements of B and N atoms that correspond to the two Raman-active $E_{2g}$ modes [252]. ..................................................................................73

Figure 3.5: Raman spectra of 1-3 layer boron nitride (BN) nanosheets and bulk h-BN based on experiments in (a) [88] and (b) [6], and on theoretical calculations in (c) [2]. (d) The change in the G band intensity of boron nitride (BN) with the number of layers (N) and the inset shows the phonon mode responsible for the Raman peak [88]. ....................................................75
Figure 3.6: (a) The frequency of the radial breathing mode (RBM) vs. tube radius in range between 5 and 25 Å [76]. (b) Calculated frequencies of the Raman optical A₁ mode for different (n,0) zigzag BNNTs, where the dashed lines shows the frequencies of h-BN sheet, BNNTs and bulk h-BN [266]. ........................................................................................................77

Figure 3.7: (a) The calculated Raman intensities for three different zigzag BNNTs and the (10,10) armchair BNNT [283]. Sketch of high frequency A modes in a zigzag BNNT [78]: (b) radial buckling (R) mode, (c) bond-stretching or longitudinal (L) mode and (d) bond-bending or tangential (T) mode. ........................................................................................................77

Figure 3.8: (a) Phonons energy (frequency) of the shear type and G band modes of hexagonal boron nitride (h-BN) vs. pressure [284]. Raman G band peak frequency as a function of pressure are (b) for MWBNNTs and (c) for h-BN and the phase transition from h-BN to W-BN was noticed at ~ 13 GPa in (c), where filled and open circles correspond to increasing and decreasing the pressure respectively [270] ........................................................................79

Figure 3.9: (a) Raman peak frequencies as a function of temperature for the shear type and G band modes of hexagonal boron nitride (h-BN) [252]. (a) The frequency shift of E₂g mode for multi walled boron nitride nanotubes (MWBNNTs) as function of temperature [263]. (c) Raman peak position of G band mode for 1-3L boron nitride (BN) before and after heat treatment, where Raman peaks upshifted to higher frequencies after heating effect due to biaxial compressive strain in the nanosheets during the cooling down stage [2] .................80

Figure 4.1: The Axio Imager Pol optical microscope with the AxioCam ICC5 ZEISS camera and the parts of the microscope with one of the possible light path [290] .............................................. 83

Figure 4.2: Differences between Light Microscope and Transmission and Scanning Electron Microscopes (i.e. TEM and SEM) [295] .............................................................................85

Figure 4.3: (a) The biasing circuit for a thermal field-emission electron gun [296]. (b) Types of interaction between electron beam and the specimen in the scanning electron microscopy (SEM) ................................................................................................................85

Figure 4.4: Schematic diagram of the Renishaw Raman spectrometer, the laser source is not shown here ..................................................................................................................86

Figure 4.5: Schematic diagram showing the principle working of the atomic force microscopy (AFM) [298] ...........................................................................................................87

Figure 4.6: Schematic drawing for the principal of X-ray diffraction techniques [300] with illustration of the in phase reflection of waves 1 and 2 from two parallel atomic planes in a
crystal structure. The difference in path between wave 1 and wave 2 is \(2d \sin \theta\).

Figure 4.7: Schematic representation of the standard procedure of mechanical cleavage technique for hexagonal boron nitride (H-BN) crystals [54].

Figure 4.8: A single crystal of H-BN was coated on the surface of Scotch tape by repeated mechanical cleavage technique.

Figure 4.9: Schematic diagram for exfoliation process of the boron nitride nanotubes (BNNTs).

Figure 4.10: Three samples of dispersed solutions for boron nitride nanostructures, boron nitride nanosheets (BNNSs) and boron nitride nanotubes (BNNTs).

Figure 4.11: A diagram of the experimental procedure for BN/glass composites fabrication.

Figure 4.12: An optical image of exfoliated H-BN flake with two regions (i.e. thick (Δ) and thin (□)) on a PMMA beam with a strain gauge, which attached parallel to the beam axis. Arrows indicate the direction of tensile strain in the deformation experiments.

Figure 4.13: A boron nitride (BN)/glass composite disk, when it was attached to the PMMA beam before the polishing process.

Figure 4.14: Shows the setup of four-point bending rig where the BN specimen was placed between the fixed and adjusted bars in tension case and the up and down arrows indicates the opposite movements of the bars.

Figure 5.1: Optical images of a single crystal of hexagonal boron nitride (H-BN). (a) The top view of the BN single crystal and (b) its edge.

Figure 5.2: Optical images of H-BN flakes. (a) Thin BN flakes, (b) thin and thick BN flakes and (c) a long BN flake with thin and thick regions. They were exfoliated from a signals crystal of hexagonal boron nitride and transferred to PMMA beams as substrates and the BN flakes have different thickness, where thick flakes appear in white colour while thin flake tend to be transparent.

Figure 5.3: Optical micrographs of hexagonal boron nitride (H-BN) flakes on SiO2/Si substrate in (a) which illustrates the white appearance in thick region and transparency in thin region, and on a PMMA beam in (b). (c) and (d) are a H-BN flake with bright and dark fields of illumination respectively.

Figure 5.4: A typical Raman spectrum of hexagonal boron nitride (H-BN) in range of 200-2000 cm\(^{-1}\), and the G band peak at position of 1366.6 cm\(^{-1}\) with full width at high maximum (FWHM) of 8.1 cm\(^{-1}\).
Figure 5.5: An XRD pattern of boron nitride (BN) powder. The scattering angle (2θ) is plotted in degrees from 20° to 90°. The (002) peak is located at 26.5° in the XRD pattern. .......................... 100

Figure 5.6: SEM images of hexagonal boron nitride (h-BN) powder with particle size of ~ 45µM. The edge of h-BN flake with thickness of ~ 3 µm in the lower inset. The arrows show the twinned structure of h-BN as well as in the upper inset with an angle of ~ 58°. The scale bars are 20 µm and 50 µm in the upper and lower insets respectively. ............................................. 101

Figure 5.7: An SEM image of exfoliated boron nitride nanosheets (BNNSs) produced by a liquid exfoliation method. ............................................................................................................. 102

Figure 5.8: TEM images of exfoliated boron nitride nanosheets (BNNSs) with the corresponding electron diffraction pattern. An uneven edge of a BN sheet with a thickness of ~ 2.7 nm in the inset and the scale bar is 20 nm. .......................................................................................... 103

Figure 5.9: AFM images of boron nitride nanosheets (BNNSs) on SiO2/Si substrates in (a) and (b), with height profiles in (c) and (d) corresponding to the indicated lines in (a) and (b) respectively. (e) A 3D image of boron nitride nanosheets (BNNSs) on the SiO2/Si substrate (i.e. 10 x 10 µm). ....................................................................................................... 104

Figure 5.10: An optical image of individual hexagonal boron nitride (h-BN) flakes with a variation in shape and size on a glass slide as a substrate .............................................................. 105

Figure 5.11: An optical image of pure boron nitride nanosheets (BNNSs) film with BNNS rich regions indicated by arrows (i.e. using a 10x objective lens) ......................................................... 105

Figure 5.12: Raman spectrum of hexagonal boron nitride (h-BN), which collected from a large individual h-BN flake. The peak of Raman G band mode positions at 1366.15 cm⁻¹ with FWHM of 8.8 cm⁻¹ ........................................................................................................ 106

Figure 5.13: (a) Several Raman spectra of boron nitride nanosheets on SiO2/Si substrate. The G band peak position is located at ~1367.5 cm⁻¹. (b) Raman spectra taken from boron nitride nanosheets (BNNSs) film. ........................................................................ 107

Figure 5.14: Peak analysis of Raman spectrum collected from a boron nitride nanosheet (BNNS) on SiO2/Si substrate. The BN Raman peak was fitted by a Lorentzian peak function. .................. 108

Figure 5.15: SEM images of boron nitride nanotubes (BNNTs) taken from BNNTs buckypaper surface. The bundles of boron nitride nanotubes are in the inset and the scale bar is 2 µm. ........................................................................................................... 109

Figure 5.16: TEM images of boron nitride nanotubes (BNNTs) with contamination of BN nanoparticles. A multi-walled (3 to 4 walls) BN nanotube with outer diameter of ~ 4.6 nm
AND INNER DIAMETER OF ~ 2.2 NM IS IN THE UPPER INSET. BNNT BUNDLES ARE IN THE LOWER INSET. THE SCALE BARS ARE 10 NM AND 20 NM IN THE UPPER AND LOWER INSETS RESPECTIVELY. 

FIGURE 5.17: XRD PROFILES OF BORON NITRIDE NANOTUBES WITH COMPARING BETWEEN XRD PATTERN OF BN POWDER AND XRD PATTERN OF BNNTS. ................................................................. 110

FIGURE 5.18: AN OPTICAL IMAGE OF EXFOLIATED BORON NITRIDE NANOTUBES (BNNTs) ON A PMMA SUBSTRATE AFTER THE SHEAR-FORCE EXFOLIATION OF BNNT BUCKYPAPER. ........................................... 111

FIGURE 5.19: RAMAN SPECTRA OF BORON NITRIDE NANOTUBES BUCKYPAPER (BLACK LINE) COMPARED WITH BULK BORON NITRIDE (BN) (RED LINE). THE INSET SHOWS THE BLUE-SHIFT OF BNNTs RAMAN PEAK COMPARING TO THE BULK RAMAN PEAK. ........................................................................ 112

FIGURE 5.20: (A) RAMAN SPECTRA OF (I) BORON NITRIDE NANOTUBES (BNNTs) AND (II) SiO2/Si SUBSTRATE. (B) THE OBSERVED RAMAN PEAK OF BNNTs. (C) THE FITTED RAMAN PEAK OF BNNTs AND THE POSITION OF BNNTs RAMAN PEAK IS AT ~ 1368 cm⁻¹. (D) AN OPTICAL IMAGE OF BNNTs ON THE SiO2/Si SUBSTRATE AND THE RAMAN SPECTRUM COLLECTED FROM THE POINT WHERE THE BNNT ARROW INDICATES .......................................................................................................... 113

FIGURE 6.1: RAMAN SPECTRUM OF POLY(METHYL METHACRYLATE) (PMMA) SUBSTRATE. PMMA RAMAN PEAKS AROUND THE POSITION OF THE G BAND PEAK OF BN MATERIALS IN THE INSET. ......................... 116

FIGURE 6.2: RAMAN SPECTRA OF EXFOLIATED H-BN FLAKE ON A PMMA BEAM, WHERE THE BN RAMAN PEAKS POSITION WITH NO STRAIN AT 1365.7 cm⁻¹ (BLACK LINE) AND WITH 0.6% STRAIN AT 1362 cm⁻¹ (RED LINE)........................................................................................................................................ 116

FIGURE 6.3: PEAK FITTING FOR (A) THE UNDEFORMED RAMAN SPECTRUM AND (B) THE DEFORMED RAMAN SPECTRUM OF AN EXFOLIATED H-BN FLAKE ON THE PMMA SUBSTRATE. ........................................... 117

FIGURE 6.4: CHANGE OF BN RAMAN PEAKS POSITIONS WITH TENSILE STRAIN, WHERE AT EACH POINT OF STRAIN, UP TO THREE RAMAN MEASUREMENTS AT EACH POINTS ........................................................................ 118

FIGURE 6.5: THE AVERAGE OF PEAK POSITIONS OF BN G BAND MODE VS. STRAIN, WHERE THE UNSTRAINED BN PEAK POSITIONS AT 1366 cm⁻¹. THERE IS A DECREASE IN BN RAMAN SHIFTS AS TENSILE STRAIN IS INCREASED UP TO ~ 0.3%. THE ERROR BARS INDICATE THE STANDARD DEVIATION OF THE MEASUREMENTS .................................................................................................................. 119

FIGURE 6.6: A LINEAR FIT OF THE AVERAGE OF BN PEAK POSITIONS WITH A RANGE OF TENSILE STRAIN FROM ZERO TO ~ 0.3%, AND THE CHANGE RATE IN BN PEAK POSITIONS WITH STRAIN WAS FOUND TO BE ~ 4.2 cm⁻¹/%. ...................................................................................................................................... 119

FIGURE 6.7: CHANGE OF BN RAMAN PEAKS POSITIONS WITH TENSILE STRAIN, WHERE THERE ARE UP TO THREE MEASUREMENTS AT EACH POINT OF STRAIN. ........................................................................ 120
**Figure 6.8:** The average peak positions of BN G band mode vs. strain, where the unstrained BN peak positions at $\sim 1365.5 \text{ cm}^{-1}$, and there is a decrease in BN Raman shifts as strain is increased up to $\sim 0.3\%$. The error bars indicate the standard deviation of the measurements.

**Figure 6.9:** A linear fit of the average of BN peak positions with a range of strain from zero to 0.3\%, and the change rate in BN peak positions with strain was found to $-6.5 \text{ cm}^{-1}/\%$. ...

**Figure 6.10:** Raman intensity map for h-BN/glass composite samples. The position of BN peak is at $1366 \text{ cm}^{-1}$ and the area is $12 \text{ \mu m} \times 12 \text{ \mu m}$. The scale bar is for the intensity in count units from 1360 for a background noise (i.e. glass matrix and the PMMA substrate) to 5860 for the highest intensity.

**Figure 6.11:** Raman spectrum of the h-BN/glass composite specimen with the highest intensity in the Raman map.

**Figure 6.12:** An optical image for hexagonal boron nitride (h-BN)/glass (I) composites. This image for the top surface of the h-BN/ glass (I) composite disk.

**Figure 6.13:** Raman spectra of hexagonal boron nitride (h-BN) flakes in glass (I) matrix under tensile strain. The peaks are corresponding to Raman G band mode, and the dotted line indicates the position of unstrained G band peak at $\sim 1365.34 \text{ cm}^{-1}$ in Raman spectrum with black line. The legend shows the values of applied strain associated to each Raman spectrum.

**Figure 6.14:** The peak positions of G band mode of hexagonal boron nitride (h-BN) in the glass (I) matrix vs. strain, and a linear fit for the G band peak positions with strain. The shift rate of G band peak positions with strain was found to be $-7 \text{ cm}^{-1}/\%$. The error bars indicate the standard deviation of the measurements.

**Figure 6.15:** The peak positions of G band mode of hexagonal boron nitride (h-BN) in the glass (II) matrix vs. strain in (A), and a linear fit for the G band peak positions with (0 - 0.4\%) strain in (B). The shift rate of G band peak positions with strain was found to be $-2.8 \text{ cm}^{-1}/\%$. The error bars indicate the standard deviation of the measurements.

**Figure 6.16:** The unchanged G band peak positions with repeated Raman measurements for h-BN/glass (II) composites sample. The error bars indicate the standard deviation of the measurements.

**Figure 7.1:** An optical pictures for the 1wt% BNNSs/borosilicate composite. The arrows indicate boron nitride nanosheets in the glass matrix.
Figure 7.2: An optical image of the 2.5wt% BNNSs/borosilicate composite. The arrows indicate boron nitride nanosheets in the glass matrix.

Figure 7.3: Raman intensity map for 1wt% BNNSs/borosilicate nanocomposites.

Figure 7.4: Raman intensity map for 2.5wt% BNNSs/borosilicate nanocomposites.

Figure 7.5: Raman spectrum for the highest intensity in the Raman map of the 2.5wt% BNNSs/borosilicate nanocomposite sample. (i.e., from the bright point of red colour in Figure 7.4).

Figure 7.6: Raman spectra taken from BNNSs in (a) 1wt% BNNSs borosilicate nanocomposites with low intensity (left) and high intensity (right), and (b) 2.5wt% BNNSs borosilicate nanocomposites.

Figure 7.7: Peak fitting of Raman spectrum of BNNSs in the glass (II) matrix with no applying a tensile strain. The G band peak of BNNSs is located at ~1368.8 cm\(^{-1}\).

Figure 7.8: The Raman spectra of deformed BNNSs in BNNSs/glass (II) nanocomposites under tensile strain are in (a) and in (b) with smoothing by 2 points of an FFT filter.

Figure 7.9: The peak positions of G band mode of boron nitride nanosheets (BNNSs) in the glass (II) matrix vs. strain in (a), and a linear fit for the average G band peak positions with (0-0.2%) strain in (b). The shift rate of G band peak positions with strain was found to be –7.65 cm\(^{-1}\)/%. The error bars indicate the standard deviation of the measurements.

Figure 8.1: Raman intensity map for an area rich in boron nitride nanotubes (BNNTs) on the sample surface.

Figure 8.2: Raman spectra of deformed boron nitride nanotubes (BNNTs) under tensile strain. The dotted line is for the G band position of unstrained peak at ~1368.2 cm\(^{-1}\). The arrow indicates the increase in tensile strain.

Figure 8.3: A plot of change Raman peak positions of exfoliated boron nitride nanotubes (BNNTs) with tensile strain. Several Raman measurements are taken at each step of strain.

Figure 8.4: The average of G band peak positions of boron nitride nanotubes (BNNTs) vs. strain. A linear fit of the average of G band peak positions is made in a range of strain from zero to 0.13%. The shift rate of G band peak positions with strain was found to –25.7 cm\(^{-1}\)/%. The error bars indicate the standard deviation of the measurements.

Figure 8.5: Peak fitting of a deformed BNNT Raman spectrum with Lorentzian function. The position of Raman peak is located at 1373 cm\(^{-1}\) with FWHM of 21.8 cm\(^{-1}\).
FIGURE 8.6: THE RAMAN SPECTRA OF DEFORMED BNNTS UNDER TENSILE STRAIN ARE IN (A) AS COLLECTED AND IN (B) WITH SMOOTHING FUNCTION OF 2 POINTS OF AN FFT FILTER. .................................................................146

FIGURE 8.7: THE PEAK POSITIONS OF G BAND MODE OF BORON NITRIDE NANOTUBES (BNNTs) IN THE GLASS (II) MATRIX VS. STRAIN IN (A), AND A LINEAR FIT FOR THE G BAND PEAK POSITIONS WITH (0 - 0.13%) STRAIN IN (B). THE SHIFT RATE OF G BAND PEAK POSITIONS WITH STRAIN WAS FOUND TO BE – 23.6 cm⁻¹/%. THE ERROR BARS INDICATE THE STANDARD DEVIATION OF THE MEASUREMENTS.................................................................147
List of Tables

**Table 2.1:** Crystal information of hexagonal boron nitride (h-BN) and graphite [52, 59] ........ 29

**Table 2.2:** Shows a comparison between graphene and boron nitride (BN) in mechanical properties of 1-3 layers [192]. ................................................................. 54

**Table 2.3:** The Γ value of nanofillers with the most common geometries [219] ......................... 62

**Table 3.1:** Theoretical calculation (Thr) and experimental observation (Exp) of Raman active bands for boron nitride (BN) materials from the literature.

Note: The theoretical calculation [76, 78, 255-258] for Raman active bands for single walled boron nitride nanotubes (SWBNNTs) are not included here. ............ 74

**Table 4.1:** The compositions of materials for the matrix of h-BN/glass composites. ................. 92

**Table 7.1:** Summarisation of Raman peaks positions with averages for boron nitride nanosheets (BNNSs) film, and 1wt% and 2.5wt% BNNSs borosilicate composites ..................................................................................................................................... 135

**Table 7.2:** Calculation of residual strains in glass matrices of BNNSs nanocomposites .......... 140
To:
   The spirit of my father
   (1936-2014)

How deep is the word "my father", how cruel the moment of separation, but our consolation in the loss your remembrances still with us.
Deformation of Hexagonal Boron nitride

Abdulaziz Alharbi

Abstract

Boron nitride (BN) materials have unique properties, which has led to interest in them in the last few years. The deformation of boron nitride materials including hexagonal boron nitride, boron nitride nanosheets (BNNSs) and boron nitride nanotubes have been studied by Raman spectroscopy. Both mechanical and liquid exfoliations were employed to obtain boron nitride nanostructures. Boron nitride glass composites were synthesised and prepared in thin films to be deformed by bending test in-situ Raman spectroscopy.

Hexagonal boron nitride in the form of an individual flake and as flakes dispersed in glass matrices has been deformed and Raman measurement shows its response to strain. The shift rates were, -4.2 cm\(^{-1}\)/\%, -6.5 cm\(^{-1}\)/\% for exfoliated h-BN flake with thick and thin regions and -7.0 cm\(^{-1}\)/\%, -2.8 cm\(^{-1}\)/\% for the h-BN flakes in the h-BN/ glass (I) and glass (II) composites.

Boron nitride nanosheets (BNNSs) shows a G band Raman peak at 1367.5 cm\(^{-1}\), and the deformation process of BNNSs/ glass composites gives a shift rate of -7.65 cm\(^{-1}\)/\% for G band.

Boron nitride nanotubes (BNNTs) have a Raman peak with position at 1368 cm\(^{-1}\), and their deformation individually and in composites gives Raman band shift rates of -25.7 cm\(^{-1}\)/\% and -23.6 cm\(^{-1}\)/\%.

Glass matrices shows compressive stresses on boron nitride fillers and this was found as an upshift in the frequencies of G band peak of boron nitride materials. Grüneisen parameters of boron nitride (BN) were used to calculate the residual strains in glass matrices of BNNSs nanocomposites as well as to estimate the band shift rates which found to be in agreement with the experimental shift rate of bulk BN and BNNTs.

Key words: boron nitride materials, hexagonal boron nitride (h-BN), boron nitride nanosheets (BNNSs), boron nitride nanotubes (BNNTs), nanocomposites, Raman spectroscopy, deformation and glass composites.
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Chapter 1: Introduction

Boron nitride (BN) materials have been developed in the last few decades and have been found to be one of the most promising inorganic nanosystems [1]. The good properties of boron nitride (BN) materials are excellent mechanical strength [2], superior mechanical stiffness [1, 3], high thermal conductivity [4] and good lubrication [5]. Moreover, Boron nitride (BN) materials have a resistance against oxidation up to ~ 850 °C in air [6, 7], and because of this superior thermal stability, they have been chosen for high-temperatures applications, e.g. BN is an excellent barrier to protect metals at high temperatures from oxidation [8-10]. Furthermore, boron nitride (BN) nanosystems are considered to be insulators or semiconductors materials with wide band gaps in range of ~ 3-6 eV [11], where boron nitride nanosheets (BNNSSs) are acknowledged as the thinnest electrically insulating materials [2, 12-14], which make them excellent dielectric substrates suitable to improve the mobility of graphene and molybdenum disulfide (MoS$_2$) based devices [2, 15, 16].

Boron nitride (BN) nanostructures have also been used in optoelectronic devices such as ultraviolet-light emitters [12] and as nanofillers in nanocomposites [17-22]. In industry, boron nitride (BN) is widely used as well for cosmetics, microwave-transparent objects, anti-corrosion coatings and chemically-inert super hydrophobic films [23].

Boron nitride (BN) is a chemical compound, which is constructed from equal numbers of Boron (B) and Nitrogen (N) atoms. Boron nitrides (BN) can only be produced synthetically (i.e. not found in nature), except c-BN which has recently been discovered naturally [24]. In addition, BN materials have different crystalline structures similarly to Carbon (C) lattices: graphite-like hexagonal boron nitrides (h-BN), diamond-like cubic boron nitrides (c-BN) and wurtzite boron nitride (w-BN). Under standard conditions, however, hexagonal boron nitride (h-BN) is the most stable phase among the three structures [5].

The layered structure of hexagonal boron nitrides (h-BN) make it flexible in various nanostructural forms (i.e. like nanoplatelets, nanosheets and nanotubes) [25], which are attractive materials as nanofillers due to their low density ~2.1 g/cm$^3$, good mechanical properties (i.e. Young’s modulus ~0.9 TPa and fracture strength ~35 GPa) and other excellent thermal, electrical and chemical properties [26]. Thus, interest in hexagonal boron nitride (h-BN) has increased in last decade (i.e. See Figure 1.1). After the discovery of graphene in 2004 [27], which led to the 2010 Nobel Prize in Physics to Andre Geim and Kostya
Novoselov, this resulted in creation of a new class of materials with one dimension (i.e. the thickness) on the nanometer scale known as 2D materials [28]. In fact, since the isolation of single layer Graphene, the interest to study the structure and properties of graphene and other types of 2D materials (e.g. BN, MoS$_2$, WS$_2$…etc.) has increased greatly [29]. The two dimensional (2D) sheets of hexagonal boron nitride (h-BN) are analogues of graphene having in-plane atom arrangements in a honeycomb structure [30]. In addition, boron nitride nanotubes (BNNTs) are structural analogues of carbon nanotubes (CNTs), where boron (B) and nitrogen (N) atoms alternatively substitute carbon atoms in a graphitic-like sheet [31].

![Graph showing the increase in published documents on h-BN over years](image)

**Figure 1.1: Hexagonal boron nitride published documents (Data based on the Scopus database).**

Nanostructures of both carbon and boron nitride (BN) have been used to reinforce polymers and others nanocomposites [21, 22, 32-37]. Although, the applications of boron nitride nanostructures seem quite similar to that of corresponding carbon systems, boron nitride nanostructures have their own uniqueness. For instance, boron nitride nanostructures-polymer composites may appear in white colour or even transparent compared with the black colour of carbon-polymer composites [35]. In addition, the electrical insulation of polymers may be ruined by adding carbon nanostructures to matrices, while boron nitride nanostructures may even improve the polymers break down voltages [25].
In the composite applications, the ability to disperse the nanofillers homogeneously throughout the matrix while retaining the nanofillers for their efficient shapes gives the effective utilization of nanostructured materials. Moreover, one of the necessary conditions for improving the mechanical properties of composites is good interfacial bonding, which is surely required to achieve load transfer through the nanofiller-matrix interface [38].

Since Raman spectroscopy is useful to determine local stress [39], it has been applied to carbon-based materials for the evaluation of their mechanical properties by the observation of the shift of characteristic bands when the material is under strain, which can induce shifts in the vibrational frequencies [40]. Young and co-workers initially developed this technique for the deformation of carbon fibres [41], and later on to other materials carbon (i.e. nanotubes and graphene) [42-48], MoS$_2$ [49, 50] and WS$_2$ [51]. In this present study and perhaps for the first time, this technique has been applied to boron nitride (BN) materials. Therefore, this study may have important implications for the use of boron nitride materials as reinforcement in polymer and glass composites. As well as demonstrating that, it is possible to investigate the deformation of boron nitride materials in glass composites using Raman spectroscopy.

1.1 Aims and Thesis structure

This project is aimed to use Raman spectroscopy to study deformation of hexagonal boron nitride (h-BN) materials. It will include an investigation of the relationship between Raman band shift and mechanical properties in boron nitride nanostructures and their behaviour in nanocomposites. This Raman study is consisted of following the G band frequency during tensile deformation to assess the stress transfer between the matrix and BN filler in the composites.

This thesis is traditionally organised in different chapters as follows. Chapter 2 briefly reviews the development of boron nitride (BN) materials, where attention is paid to both bulk BN and BN nanostructures especially boron nitride nanosheets (BNNSs) and boron nitride nanotubes (BNNTs). This review covers many points of view including the structures, production methods, properties and applications.

Chapter 3 reviews the literature on the characterization of boron nitride (BN) materials using Raman spectroscopy, which is the main characterization method in this study. The principles of Raman scattering and the origins of the different Raman bands of boron nitride (BN) are
introduced briefly. The effect of strain-induced Raman band position shifts of BN materials is reviewed as well.

In chapter 4, the experimental methods of sample fabrication are described in detail including the procedure to deform BN materials with simultaneous Raman measurements. Also, the basic principles of characterisation tools are described with their use for BN materials.

Chapter 5 shows the characterisation of h-BN materials. Raman spectra of bulk single crystals, bulk BN powder, BNNSs and BNNTs are given as well as the characterisation of BN materials using different instruments including OM, SEM, TEM, AFM and XRD.

The effect of deformation on hexagonal boron nitride (h-BN) materials and their composites has been studied in chapters 6, 7 and 8.

In chapter 6, a deformation study of individual hexagonal boron nitride (h-BN) flake with regions of different thickness (i.e. thick and thin) is presented along with Raman measurements. Also, the deformations of h-BN crystals in two types of glass matrices of h-BN glass composites are studied as well.

In chapter 7, the deformation of boron nitride nanosheets (BNNSs) in glass nanocomposites are examined using Raman spectroscopy. The principle of strain induced shifts of the vibrational frequencies of Raman bands is investigated using compressive strain due to residual stress and tensile strain due to bending. Compressive strains are estimated using Grüneisen parameters.

In chapter 8, deformation of boron nitride nanotubes (BNNTs) is carried out using individual (exfoliated) BNNTs on a PMMA beam and BNNTs in glass matrix of BNNT/glass nanocomposites. Using Grüneisen parameters to estimate Raman band rate is provided as well.

Chapter 9 presents the conclusions of this study. Additionally, it features some of the future work that may be undertaken based upon this thesis, including some recommendation for researchers who would like to use Raman spectroscopy to study BN materials.
Chapter 2: Literature Review

2.1 Introduction
In this chapter, the atomic structure of hexagonal boron nitride (h-BN) and boron nitride nanostructures namely: boron nitride nanosheets (BNNSs) and boron nitride nanotubes (BNNTs) have been reviewed by comparing to the corresponding carbon system: graphite, graphene and carbon nanotubes (CNTs). Moreover, the synthesis of 3D, 2D and 1D boron nitride (i.e. h-BN, BN nanosheets and BN nanotubes respectively), their optical and mechanical properties and their used in nanocomposites are presented as follows:

Structures
a- Hexagonal boron nitride (h-BN)
b- Boron nitride nanosheets (BNNSs)
c- Boron nitride nanotubes (BNNTs)

Syntheses
a- Hexagonal boron nitride (h-BN)
b- Boron nitride nanosheets (BNNSs)
c- Boron nitride nanotubes (BNNTs)

Properties
a- Optical properties
b- Mechanical properties

Applications
a- Nanocomposites

2.2 Structures
Boron nitride (BN) is isostructural with carbon (C) systems and exists in various crystalline forms. In particular, the layered structural one is hexagonal boron nitride (h-BN), which is analogous to graphite. Moreover, boron nitride nanotubes (BNNTs) were synthesised just four years after the identification of carbon (C) nanotubes. The isolation of graphene from graphite led to 2D layered boron nitride nanosheets (BNNSs) being peeled off from h-BN crystals. The structures of hexagonal boron nitride (h-BN) and its nanomaterials, specifically boron nitride nanotubes and boron nitride nanosheets, will be discussed in this section.

2.2.1 Hexagonal boron nitride
Hexagonal boron nitride (h-BN) has a graphite-like layered structure, where boron (B) and nitrogen (N) atoms build in-plane blocks of honeycomb lattice arrangements with an
interlayer spacing of ~ 3.33 Å [52, 53]. Also, each boron (B) atom bonds to three atoms of nitrogen (N) in the plane and vice versa, and the length of these bonds is ~ 1.44 Å, where the angle between them is 120° [54]. In-plane boron and nitrogen atoms are strongly linked by sp² hybridized covalent bonds; while the planes in the structure are weakly bonded by van der Waals forces. (See Figure 2.1).

![Hexagonal boron nitride structure](image)

**Figure 2.1**: The layered structure of hexagonal boron nitride. Boron (B) and nitrogen (N) atoms connect in-plane with covalent bonds and out-of-plane with van der Waals bonds. The nearest neighbor distance between B and N is 0.1446 nm. The space between layers is 0.333 nm as the c-axis of the lattice is 0.6661 nm [55].

Compared to the graphite structure, hexagonal boron nitride (h-BN) has an AÅ stacking structure, with B atoms and N atoms on top of each other [56], whereas graphite has AB Bernal stacking, which has offset planes but with the same planar arrangement of atoms. This leads to just half of carbon (C) atoms having above and below direct neighbors [57]. (See Figure 2.2). It should be noted that other possible stacking of hexagonal boron nitride (h-BN) have been considered in elsewhere and more details are given in Ref.[58].
Table 2.1: Crystal information of hexagonal boron nitride (h-BN) and graphite [52, 59].

<table>
<thead>
<tr>
<th>Materials</th>
<th>Lattice</th>
<th>Bond length (Å)</th>
<th>Lattice parameters (Å)</th>
<th>Interlayer spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron nitride (BN)</td>
<td>hexagonal</td>
<td>1.44</td>
<td>$a$: 2.5 $c$: 6.66</td>
<td>3.33</td>
</tr>
<tr>
<td>Graphite</td>
<td>hexagonal</td>
<td>1.42</td>
<td>$a$: 2.46 $c$: 6.7</td>
<td>3.35</td>
</tr>
</tbody>
</table>

Values of lattice constants of hexagonal boron nitride (h-BN) structure are very close to those of graphite lattice and hence, the h-BN lattice is larger than graphene lattice by only 1.7% [54]. Thus, because of the structural analogy with graphite, hexagonal boron nitride (h-BN) has some of its common properties such as anisotropy along and perpendicular to the basal plane and very similar mechanical properties [5].

Figure 2.2: Structural stacking differences between graphite (left) and hexagonal boron nitride (right). The hexagons of neighbouring plans are shifted by a half hexagon in graphite (i.e. AB stacking), while they are superposed in hexagonal boron nitride (h-BN), where B and N atoms are in succession along the c axis (i.e. AA stacking) [60].

The electronic structure of h-BN is different from that of graphite; firstly, the $p_z$ orbitals of B atoms are vacant, while they are occupied by neighbouring electrons in N atoms. Therefore,
free electrons are not presented to overlap or for conduction. Thus, this gives an insulating character to boron nitride (BN) [56]. In contrast, unpaired \( \text{P}_z \) electrons on each atomic site join to form graphite which is a conductor due to the fourth valance electrons being paired with \( \pi \) bonds with other adjacent electrons of the plane. Secondly, there is a difference in electronegativity between boron and nitrogen atoms and this causes the \( \pi \) electrons to be localised around the nitrogen atoms with a partially-negative charge [53]. Hence, this gives partially ionic character to hexagonal boron nitride (h-BN), however, this is not the case in graphite [5]. Thirdly, the inter-layer electrostatic interaction may stabilise the A\(^{\text{II}}\) stacking of hexagonal boron nitride (h-BN), where boron atoms bearing a partial positive charge in one layer resides between the oppositely charged nitrogen atoms on the adjacent layers [53].

### 2.2.2 Boron nitride nanosheets (BNNSs)

Boron nitride nanosheets (BNNSs) are two-dimensional (2D) nanomaterials consisting typically of mono-, bi- or few-layers of hexagonal boron nitride (h-BN), where their thickness must be in the nanometer scale. Boron nitride nanosheets (BNNSs) can be obtained top-down from hexagonal boron nitride (h-BN) crystals (e.g. by mechanical cleavage method) or bottom-up from B and N precursors (e.g. the chemical vapour deposition (CVD) technique) [61].

A single layer of hexagonal boron nitride (h-BN), or a monolayer BNNS, consists of ring units of borazine (B\(_3\)N\(_3\)H\(_6\)) without the H atoms combined to form a honeycomb structure and it can be depicted as a monolayer graphene by substituting the carbon (C) atoms by alternating boron (B) and nitrogen (N) atoms [1, 62]. In addition, as in the bulk structure of hexagonal boron nitride (h-BN), within each boron nitride plane, the boron (B) and nitrogen (N) atoms are bound together by strong covalent bonds with ionic characteristics, whereas van der Waals forces hold the sheets together in the structure in direction parallel to the \( c \)-axis. The B-N bond length is 1.45 Å, while the distance between the centres of neighbouring borazine rings is 2.50 Å comparing to 2.46 Å in a graphene basal plane [62].

The edge of a boron nitride nanosheet (BNNS) can be either zigzag or armchair edge. The zigzag edges of boron nitride nanosheets (BNNSs) can be either boron (B) or nitrogen (N) edged, while the armchair edges are B-N pairs. (See Figure 2.3).

Moreover, Alem et al. [63] have demonstrated covalent interlayer B–N bonds are spontaneously formed at the edges of a BN bilayer using a combination of analytical scanning transmission electron microscopy and density functional theory. The interlayer
covalent bonds forming across the bilayered zigzag edge could lead to a “closed” edge termination. This could result in a structure analogous to a folded monolayer of boron nitride [64].

Different from the graphene monolayers, the boron nitride (BN) monolayers have rarely been observed due to the special B-N stacking characteristics and the difference in the electronegativity between boron (B) and nitrogen (N) atoms [64]. Figure 2.4 (a) and (b) illustrates the AA' stacking of boron nitride nanosheets (BNNSs), while AB stacking exhibits in graphene layers. However, Warner et al. [65] reported that AB stacking could be possible for bilayer regions of BN sheets, which were chemically exfoliated from h-BN as shown in Figure 2.4 (d). The AB stacking may not be intrinsic to the bulk hexagonal boron nitride (h-BN) but it may be only possible at the top and bottom of the layered structure where single BN sheets can slide easily along certain energetically-favourable directions [66].

![Figure 2.3: Schematic of 2D BN nanostructures, the distance between the centres of neighbouring hexagons is 2.50 Å and between two layers is 3.33 Å. The edge of a monolayer BNNS can be either zigzag (B- or N-edge) or armchair (BN pairs) [62].](image)

Moreover, the difference in electronegativity between boron B (2.04) and nitrogen N (3.04) atoms results in the B–N bonds being partially ionic, in contrast to the C–C bonds in graphitic structures [67]. This feature can lead to lip–lip interactions between neighbouring layers in boron nitride (BN) nanostructure (i.e. chemical bonds form as bridges between the atoms of adjacent layers) [64]. This phenomenon contributes to a metastable energy minimum by
decreasing the number of dangling bonds at the edges. Consequently, formation of multilayered boron nitride (BN) stabilises the whole structure [1], and the interlayer interactions make the exfoliation of h-BN into boron nitride nanosheets (BNNs) more difficult than peeling off graphene from graphite [68].

![Figure 2.4: (a) and (b) Models of the bi-layered h-BN and graphite sheets that display the difference in their stacking sequence respectively. (c) and (d) The atomic structural representation of AA’ and AB stacked BN bilayer with corresponding HRTEM image simulations respectively. The grey area indicates the size of the top BN sheet

2.2.3 Boron nitride nanotubes (BNNTs)

Boron nitride nanotubes (BNNTs) are the structural analogue of carbon nanotubes (CNT) in nature, when the carbon (C) atoms are substituted by alternating boron (B) and nitrogen (N) atoms. Boron nitride nanotubes (BNNTs) were theoretically predicted in 1994 [69] and multi-walled boron nitride nanotubes (MWBNNTs) were synthesised for the first time in 1995 [70], while single walled boron nitride nanotubes (SWBNNTs) were produced in 1996 [71].

Boron nitride nanotubes (BNNTs) can be defined as cylinders of concentric hexagonal boron nitride (h-BN) layers in range from one to many layers with diameters in the nanometres scale [1]. There are two models may help to describe the structure of multi-walled boron nitride nanotubes MWBNNTs): the Russian doll model, when hexagonal boron nitride (h-BN) sheets are arranged in separate concentric cylinders (i.e. a single walled BNNTs inside large ones), and the Parchment model, when a single sheet of hexagonal boron nitride (h-BN) is rolled around itself [72]. Considering the later model, rolling up a hexagonal boron nitride (h-BN) sheet along chosen chiral directions generates boron nitride nanotubes (BNNTs) of various chiralities with zigzag, chiral or armchair configurations [73]. In addition, boron nitride nanotubes (BNNTs) can be labelled with two indices \((n, m)\) that define uniquely the so-called chiral vector \(C_h\) (i.e.\(C_h = na_1 + ma_2\)) which defines the tube folding direction and
its direction is perpendicular to the tube axis. The angle between the chiral vector \( C_h \) and the lattice vectors \( a_1 \) and \( a_2 \) is known as the chiral angle \( \theta \). The value of chiral angle classifies boron nitride nanotubes as: zigzag \( (\theta = 0^\circ) \), armchair \( (\theta = 30^\circ) \) and chiral \( (0 < \theta < 30^\circ) \) [74]. Figure 2.5 illustrates the hexagonal boron nitride (h-BN) sheet with wrapping directions for zigzag and armchair configurations along with models of single-walled boron nitride nanotubes (SWBNNTs) structures as: (b) zigzag, (c) armchair, and (d) chiral [73].

Figure 2.5: A layer of hexagonal boron nitride (h-BN) with possible direction of wrapping for zigzag and armchair configurations (a). The structural models of single-walled boron nitride nanotubes (SWBNNTs) with (b) zigzag, (c) armchair, and (d) chiral configurations [73].

Moreover, Chirality indices \( (n, m) \) can be used to determine the diameter \( D \) and the chiral angle \( \theta \) of single-walled boron nitride nanotubes (SWBNNTs) [75, 76]:

\[
D = \frac{\sqrt{3}d_0}{\pi} \sqrt{n^2 + nm + m^2} \tag{2.1}
\]

\[
\tan \theta = \frac{\sqrt{3}m}{2n+m}, \quad 0 \leq \theta \leq 30^\circ \tag{2.2}
\]

where \( d_0 \) is the distance between neighbouring atoms in the hexagonal network (i.e. or bond length, which is 0.145 nm for hexagonal boron nitride (h-BN)).

Unlike carbon nanotubes (CNT), boron nitride nanotubes (BNNTs) possess a wave-like (i.e. rippled) surface [77], where boron (B) atoms rotate inwards and the nitrogen (N) atoms move outward. This leads to the formation of a negative outer N cylinder and a positive inner B cylinder. Due to charge transfer from B to N, the buckled tubular structure forms a dipolar
shell [1]. The buckling shell thickness is to a very good approximation inversely proportional to the tube diameter [78]. Figure 2.6 (c) illustrates a cross-section of the buckled geometry for a \((n, 0)\) zigzag tube with a single layer.

Menona and Srivastavac [79] found that the chiralities of the boron nitride nanotubes (BNNTs) can be determined by observing the morphologies of tube closing. Therefore, zigzag boron nitride tubes (BNNTs) may favour a flat end, while in armchair tubes the conical tube closure is more energetically favoured and chiral tubes may have the amorphous end.

**Figure 2.6:** (a) Side and top view of the flat tip of \((12, 0)\) BN nanotube. (b) Side and top view of the pencil-like (conical) tube closing of the \((5, 5)\) arm-chair tube [79]. (c) Buckling shell thickness \((r_N - r_B)\) in single-walled BN nanotubes as a function of tube diameter [78].

### 2.3 Syntheses

A variety of synthesis methods have been utilized for the fabrication of boron nitride materials. Most of the techniques for the preparation of carbon nanosystems are used in similar ways to synthesise the corresponding nanosystems of boron nitride (BN) with required modifications, especially for boron nitride nanosheets (BNNSs) and boron nitride nanotubes (BNNTs). Some of the most popular methods for growth of hexagonal boron nitride (h-BN), boron nitride nanosheets (BNNSs) and boron nitride nanotubes (BNNTs) will be reviewed in this section.
2.3.1 Hexagonal boron nitride (h-BN)

Boron nitride (BN) was first synthesised by Balmain et al. [80] in 1842 when they used the chemical reaction of molten boric acid (H$_3$BO$_3$) with potassium cyanide (KCN). However, stable BN materials in the form of powder were only produced in the early 1960s [1].

Several methods have been employed for the synthesis of hexagonal boron nitride (h-BN) such as the high-temperature synthesis route [81], self-propagation [82, 83] and direct combination of boron (B) with nitrogen (N$_2$). The last method depends on the reaction:

$$2B + N_2 \rightarrow 2BN$$

However, this process is not homogeneous even at high temperature [84].

In addition, hexagonal boron nitride (h-BN) can be produced with high purity through reaction involving the formation of elemento-organic boron nitride (BN) compounds e.g. boranes (B$_x$H$_y$) and borazines (B$_3$H$_6$N$_3$) by carbothermic decomposition processes [80].

The most popular commercial method of synthesizing hexagonal boron nitride (h-BN) powders is by heating boric acid (B(OH)$_3$) or boric oxide (B$_2$O$_3$) and an ammonia (NH$_3$), melamine (C$_3$H$_6$N$_6$) or urea ( NH$_2$CONH$_2$) mixture at 900 °C, followed by annealing at 1500 °C in nitrogen (N$_2$) atmosphere to increase the crystallinity of the powders [67]:

$$B(OH)_3/B_2O_3 + NH_3 \rightarrow BN + H_2O \quad \text{or} \quad B_2O_3 + NH_2CONH_2 \rightarrow 2BN + CO_2 + 2H_2O$$

In the industrial preparation of the layered-form, hexagonal boron nitride (h-BN), calcium hexaboride (CaB$_6$) can be used with boric oxide (B$_2$O$_3$) in presence of nitrogen (N$_2$):

$$3CaB_6 + B_2O_3 + 10N_2 \rightarrow 20BN + 3CaO$$

Additionally, high temperature heating (>1500 °C) is required to obtain hexagonal boron nitride (h-BN) from this reaction [82].

Pure single crystals of hexagonal boron nitride (h-BN) with size of ~ 1 mm can be synthesised by using a temperature gradient method under high pressure and high temperature (HPHT) [12, 85, 86]. During the growth process, purified source materials such as boron nitride (BN) or boron (B) powder are carefully treated with metal catalysis systems as solvents e.g. Ni-MO, Ni-Cr and Mg. The growth conditions of the pressure and the
temperature are 4.0–5.5 GPa and 1500–1750 °C respectively and the holding time for the growth varies from 20 to 80 hours [12].

![An optical image of hexagonal boron nitride (h-BN) single crystals. This is the final product of using a temperature gradient method with (HP/HT) technique and the solvent was Ni-Cr system [12].](image)

**Figure 2.7:** An optical image of hexagonal boron nitride (h-BN) single crystals. This is the final product of using a temperature gradient method with (HP/HT) technique and the solvent was Ni-Cr system [12].

### 2.3.2 Boron nitride nanosheets (BNNSs)

There are many methods that have been used to synthesise 2D boron nitride nanostructures. The majority of them are similar to the techniques applied for the preparation of graphene sheets with necessary modifications.

#### 2.3.2.1 Self-Assembly

Boron nitride nanomesh as a single-crystalline coating on Rhodium (Rh) substrate was the first production of a 2D BN nanostructure [87]. The experimental procedure consisted of exposing the atomically clean Rh (111) surface at 800 °C to borazine (B₃H₆N₃) vapour in a chamber under ultrahigh vacuum conditions, following by cooling to room temperature. However, the 2D BN film contained some holes due to the lattice mismatch of the BN film and Rh substrate.
2.3.2.2 Mechanical cleavage

This method is also known as mechanical exfoliation. In this technique, layers of hexagonal boron nitride are peeled off from single crystal h-BN by adhesive tape and attached to substrates e.g. SiO₂/Si. The initial use of this method was by Novoselov et al. to isolate monolayer graphene in 2004 [27]. Nanosheets obtained with this technique have a good combination of thickness and lateral size [64], which make them suitable for optoelectronics [88-90]. However, in contrast to the graphene case, mechanical cleavage technique has not been effective in rendering few-layer and monolayer boron nitride (BN). This might be due to the stronger lip-lip interaction between BN basal planes, where the formation of chemical bonds may occur as bridges between the atoms of adjacent layers [64]. In fact, to transfer the exfoliated layers to substrates successfully, the interaction between the surfaces on which the material has to be deposited after cleavage should be stronger than the interaction between the layers of sheets that have been exfoliated from the crystal structure [91].

Another approach to mechanical exfoliation is the utilization of shear forces instead of direct peeling forces [92]. The shear forces can have the same effect of exfoliation as that of peeling forces to break the weak van der waals bonding between adjacent BN layers and leave the in-plane strong covalent bonds. Boron nitride nanosheets (BNNSs) were produced from BN powder by using a wet ball milling process under nitrogen (N₂) gas atmosphere [92]. The milling agent in this process was benzyl benzoate (C₁₄H₁₂O₂) and it used to reduce the ball impact and milling contamination. (See Figure 2.8)

![Figure 2.8: SEM images of shear exfoliation in (a) and (c) by the shear force of milling balls with corresponding diagram mechanism in (b) and (d) for (a) and (c) images respectively [92].](image-url)
In another method, the concept of creating shear forces was applied via liquid to exfoliate boron nitride (BN) [93]. Boron nitride powder were suspended in N-methyl-2-pyrrolidinone and exfoliated inside a glass tube inclined by 45° with a rotating speed at 8000 rpm. (See Figure 2.9).

In this situation, shear occurs due to the interplay between centrifugal and gravitational forces. Boron nitride (BN) flakes are initially accelerated to the walls of the tube by the large centrifugal force. The liquid flow is upwards at the internal surface of the rotating tube and downwards close to the liquid surface. The suspension forms in a thin layer on the inner wall of the tube at the high rotating speed. When the BN layers are parallel to the rotation axis, shear forces can partially raise the layers. The shear induced displacement along the tube, results in layer slippage and exfoliation [93].

![Figure 2.9: Schematic for the microfluidic flow velocity (indicated by red arrows) for a section of the rotating tube at ω = 8000 rpm and θ = 45°, and the exfoliation process with slippage of BN layers on the inner surface of the tube [93].](image)

### 2.3.2.3 Chemical exfoliation

The general idea in the exfoliation process is to disperse the boron nitride (BN) in a solvent with an aid of sonication power [94], followed by centrifugation process to separate the supernatant dispersion from the residue, then filtration may be applied to collect the sediments, which consist of exfoliated boron nitride nanosheets (BNNSs).

In this approach, ultrasonic waves and the solvents are the two factors that play the main role to govern the exfoliation process. The ultrasonic waves create cavitation bubbles, which disrupt the layered structures. On the other hand, the solvent should be chosen to have surface energy that matches the energy per unit area of the BN, which is required to overcome the van der Waals forces [3], and its interaction with boron nitride (BN) should be stronger than the interaction between BN layers [1]. Moreover, Marsh et al. [95] suggested molecular weight of the solvent
may have a great impact on the exfoliation of hexagonal boron nitride (h-BN), due to the larger molecules ability to sterically separate the nanosheets, which prevent their recombination in the suspension. Therefore, larger solvent molecules serve to stabilize the individually-dispersed sheets more effectively than smaller solvent molecules [96].

Many solvents have been used in chemical exfoliation such as deionised water [22, 97], acetone [95], chloroform [98], methanol [95], ethanol [99], Isopropanol (IPA) [100], dimethylformamide (DMF) [3], methanesulfonic acid (MSA) [101], N-methyl-pyrrolidinone (NMP) [21, 102]. Hence, boron nitride nanosheets (BNNSs) with thicknesses in range 2 - 10 nm have been achieved in milligram levels by chemical exfoliation techniques [64].

The first production of mono- and few-layered nanosheets from single crystalline boron nitride (BN) by a chemical-solution-derived method was achieved in 2008 [103]. In this experiment, 0.2 mg of hexagonal boron nitride crystals were put in a 5 ml 1,2-dichloroethane solution of poly(m-phenyl-enevinylene-co-2,5-dictoxy-p-phenylenevinylene) (1.2 mg/10 ml), after that the solution sonicated for 1 hour to disperse and split up the BN crystals into few-layered of boron nitride. This method is similar to that used to prepare graphene nanoribbons [104]. Because of the strong interactions between the polar $N,N$-dimethylformamide (DMF) molecules and the BN particles’ surface, DMF as a strong polar solvent has also been employed in chemical exfoliation methods of boron nitride [3].

In another approach of chemical exfoliation, molten hydroxides were used to exfoliate boron nitride (BN) [105]. Potassium hydroxide (KOH) and sodium hydroxide (NaOH) were ground with boron nitride (BN) powder, then transferred to a polytetrafluoroethylene (PTFE)-lined stainless steel autoclave and heated up to 180 °C for 2 hours. As a result, boron nitride (BN) nanostructures were obtained in forms of nanosheets and nanoscrolls. (See Figure 2.10). Three sequences of exfoliation process are involved as follows: (1) self-curling of the sheets at the edges due to the adsorption of cations (Na' or K') on the outmost BN surface; (2) anions and cations entering the interlayer space and the adsorption of anions (OH-) on the positively curved surface which drives continuous curling of the BN layer; (3) direct peeling away from the parent materials, or cutting by the reaction of BN surface with hydroxides [105].

2.3.2.4 Other methods

Chemical vapour deposition (CVD) is one of the more popular techniques to synthesise boron nitride nanosheets (BNNSs). Large area boron nitride (BN) films consisting of 2–5 layers on a copper (Cu) foil were first reported in 2010 [106]. The copper (Cu) substrate was located in
the centre of a split tube furnace, and annealed at 600 °C for 20 min under an Ar–H₂ flow, then gradually heated up to 1000 °C. Ammonia borane (NH₃–BH₃) was firstly sublimated at 120–130 °C using a heating belt, then transferred to the high temperature reaction region for decomposition by the Ar–H₂ flow and held for 30–60 min to form the few-layered boron nitride (BN) films. Moreover, different substrates of transition metals have been successfully used to form boron nitride nanosheets (BNNSs) on their surfaces by CVD method, such as Nickel-Ni (111) [107, 108], Platinum-Pt (111) [109], Palladium-Pd (111 or 110) [110, 111], Iron-Fe (110) [112], Molybdenum-Mo (110) [113], Chromium-Cr (110) [114], Ruthenium-Ru (001) [115] and Rhodium-Rh (111) [87], (i.e. the numbers in brackets (hkl) indicate the most suitable surfaces where BN layers can be deposited).

Figure 2.10: SEM images (a) and (b) of folded BN nanosheets so-called nanoscrolls. (c) The exfoliation process of molten hydroxides [105].

Figure 2.11 (b) illustrates another method to produce boron nitride nanosheets (BNNSs), which is the chemical blowing technique [116]. Catalysts or substrates are not required in this technique, instead a moderate heating of ammonia borane (NH₃–BH₃) at atmospheric pressure is employed. The precursor is preheated at 80 °C, and then the temperature is increased to ~110 °C to begin the blowing process due to dehydrogenization, then to ~ 400 °C to dehydrogenate, where hydrogen is rapidly released from the soft swollen B–N–H compound. Further heating to 1300 °C for 3 hours is required for the crystallisation process of the material into the desired BN product. Ultrasonic stirring in ethanol for 1 minute and
centrifugation at 1000 rpm for 1 minute removed the bulky portions from the BN suspension and yielded few-layered polycrystalline boron nitride nanosheets (BNNSs).

Figure 2.11: (a) AFM image with a line-scan profile of a few-layered BN film with thickness of ~1 nm, which was grown by CVD method [106]. (b) A scheme of BN nanosheets synthesis by the chemical blowing method [116].

The substitution reaction method is an alternative method which has been used to synthesise nanosheets of boron nitride (BN) [117]. In this substitution reaction, graphene sheets are transferred to boron nitride sheets, where carbon atoms were replaced by boron and nitrogen atoms by the following chemical reaction:

\[
\text{B}_2\text{O}_3 \text{(gas)} + 3\text{C (sheets)} + \text{N}_2 \text{(gas)} \rightarrow 2\text{BN (sheets)} + 3\text{CO (gas)}
\]

In a series of experiments, boron trioxide (B\(_2\)O\(_3\)) in a powder form was placed in an open graphite crucible, covered firstly with molybdenum oxide (MoO\(_3\)) as a promoter, and after that with graphene sheets. The crucible was held in a flowing N\(_2\) atmosphere at 1650 °C for 30 minutes. After that, the product was collected from the bed of graphene sheets and heated in air at 650 °C for 30 minutes to remove the remaining carbon layers and obtain pure boron nitride (BN) sheets.

Finally, a high-energy electron irradiation technique can be used to fabricate freestanding monolayer boron nitride (BN) sheets by controlled electron irradiation through a layer-by-layer
sputtering processes inside a transmission electron microscope (TEM) [89, 118]. Boron nitride nanosheets (BNNSs) can be further thinned down to monolayers by intensive electron beam irradiation. The incident electron beam with a high intensity and a few nm in diameter is focused onto the specimen. By manual scanning of the electron beam on the specimen, the BN nanosheets are burnt layer-by-layer, until BN monolayers are obtained.

2.3.3 Boron nitride nanotubes (BNNTs)

Most methods of the fabrication of carbon nanotubes (CNT) have been modified to synthesise boron nitride nanotubes (BNNTs). Depending on the synthesis temperatures, these methods can be classified into two groups [1]: (a) high temperatures synthesis (>2000 °C) such as arc discharge and laser ablation methods, and (b) low temperatures synthesis (<2000 °C) such as chemical vapour deposition (CVD), ball milling and carbothermal methods. In this section, these methods of boron nitride nanotube (BNNT) production will be highlighted and described.

2.3.3.1 Arc discharge

The first fabrication of boron nitride nanotubes (BNNTs) was by arc-discharge between a boron nitride (BN)-packed tungsten (W) rod and a cooled copper (Cu) electrode [70]. The product was multiwall-boron nitride nanotubes (MWBNNTs) with inner diameters of the order of 1 to 3 nm and lengths up to 200 nm. This technique was improved by using graphite (i.e. as a cathode) and hafnium diboride HfB₂ (i.e. as an anode) as electrodes, and single-wall (SW) or double-wall (DW) boron nitride nanotubes (BNNTs) were synthesized [71, 119, 120]. In another approach, DWBNNTs were produced by arcing boron (B) electrodes with a small amount of nickel (Ni) and cobalt (Co) in a nitrogen (N₂) environment [121]. Since boron nitride (BN) is an insulating material, which makes it not suitable for electrodes, conductive boron compounds such as ZrB₂ and YB₆, were used instead [122, 123] with a nitrogen (N₂) atmosphere, which was used as a nitrogen source. Thus, the boron compounds can serve as catalysts during the growth of the nanotubes.

Boron nitride nanotubes (BNNTs), that were fabricated by arc-discharge possess, may have good crystallinity due to a high growth temperature (∼2700 °C) [77] but are produced with limited yields [31].

2.3.3.2 Laser ablation

This technique was firstly employed to synthesise multi-walled boron nitride nanotubes (MWBNNTs) in 1996 by Golberg et al. [124]. Single crystals of cubic or hexagonal boron
nitride (BN) targets were used as precursors. The target was heated up to 5000 °C by a CO$_2$ laser for a short time in a diamond anvil cell (DAC) under high pressures of nitrogen (N$_2$) gas. In the following experiment, single-walled boron nitride nanotubes (SWBNNTs) were synthesized by using a CO$_2$ continuous laser and rotating the hexagonal boron nitride (h-BN) target [125].

In another approach using the laser ablation method, catalysts of cobalt (Co) and nickel (Ni) were used with boron (B) as a target material to get longer tubes with single-walled or few-walled boron nitride nanotubes (BNNTs) [126, 127].

In 2009, a laser ablation method with a significant improvement in boron nitride nanotube (BNNT) synthesis was developed by utilizing the pressurized vapour/condenser (PVC) technique or the high temperature/high pressure (HTP) technique [128]. A high-powered laser of 1 kW (e.g. free electron laser or CO$_2$ laser) was used to vapourise the target (i.e. boron or boron nitride) inside a chamber, which was filled with high pressure of nitrogen (N$_2$) gas. A stream of hot boron vapour (~ 4000 °C) can be condensed into liquid boron droplets, which work as nucleation sites. The condenser, which is a cooled wire in the chamber, can be made from boron nitride (BN), boron (B), stainless steel, copper niobium (Cu-Nb) or tungsten (W). This approach has been used for the large scale growth of boron nitride nanotubes (BNNTs) with 2-5 walls at a production rate of ~120 mg/h. (See Figure 2.12).

Boron nitride nanotubes (BNNTs) which have prepared by laser ablation usually possess perfect crystallinity. However, the purity of the resultant product may be still not satisfactory, boron nitride nanotubes (BNNTs) can be found with BN cones, BN onions and amorphous boron flakes [77].

### 2.3.3.3 Carbothermal methods

This method is dependent on the idea of the structural similarities between carbon nanotubes (CNT) and boron nitride nanotubes (BNNTs). It is undertaken by turning carbon nanotubes (CNT) to boron nitride nanotubes (BNNTs) through a substitution reaction, where carbon (C) atoms are substituted by boron (B) and nitrogen (N) atoms [129]. Inside an induction furnace, boron trioxide (B$_2$O$_3$) powder is covered by carbon nanotubes (CNT) under a nitrogen (N$_2$) flow at 1500°C. Boron (B) and nitrogen (N) atoms fill the vacancies generated in the hexagonal structure, when carbon nanotubes (CNT) are oxidized by highly reactive boron trioxide (B$_2$O$_3$) vapour. In this technique the carbon nanotubes (CNT) perform as a template to produced boron nitride nanotubes (BNNTs). As a result, the product obtained is boron...
nitride nanotubes (BNNTs) doped with carbon atoms since the oxidation process cannot remove all the carbon (C) atoms from the tube lattice [77]. Thus, the carbon (C) content in the product can be reduced by using extra oxidising agent such as metal oxide (e.g. MoO₃) [130]. The morphology of starting carbon nanotubes (CNT) can be maintained in the boron nitride nanotubes (BNNTs). For instance, single-walled boron nitride nanotubes (SWBNNTs) [131] and aligned boron nitride nanotubes (BNNTs) ropes [132] are synthesised when corresponding morphologies of carbon nanotube (CNT) are used.

In an alternative approach, boron nitride nanotubes (BNNTs) with large diameters can be synthesised by using boron carbide (B₄C) and the carbothermal reduction of boron oxide with simultaneous nitriding at a temperature of 1100–1450 °C as in the following reaction [133]:

\[ \text{B}_2\text{O}_3 + 3\text{B}_4\text{C} + 7\text{N}_2 \rightarrow 14\text{BN} + 3\text{CO} \]

In addition, the carbothermal reduction of a mixture of activated carbon and boric acid (H₃BO₃) in the presence of ammonia (NH₃) at 1300 °C has been employed to produce boron nitride nanotubes (BNNTs) with an outer diameter of ~ 20 nm [134].

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**Figure 2.12:** (a) A 200 mg product of boron nitride nanotubes (BNNT) by the PVC method. (b) A PVC-grown BNNT yarn, 3 cm long and ~1 mm in diameter [128].
2.3.3.4 Chemical vapour deposition (CVD)

The initial growth of boron nitride nanotubes (BNNTs) by chemical vapour deposition (CVD) was reported in 2000 [135]. Borazine (B$_3$H$_6$N$_3$) was used as a precursor with nickel boride (Ni$_2$B) catalyst particles at a growth temperature of ~1100 °C. Two years later, Tang et al. [136] developed an effective chemical pathway to produce boron nitride (BN) precursor for the synthesis of boron nitride nanotubes (BNNTs). A mixture of boron (B) and magnesium oxide (MgO) was used to produce reactive boron oxide vapour which was transported by argon (Ar) into a reaction chamber at ~1100 °C under a flow of ammonia (NH$_3$). Further improvements to this boron oxide (BO)-CVD technique were performed by adding ferrous oxide (FeO) to the mixture of precursors [137] or by using lithium oxide (Li$_2$O) instead of magnesium oxide (MgO) [138]. This improvement is capable in producing pure boron nitride nanotubes (BNNTs) with average external diameters of ~10 nm and lengths of up to tens of µm [138]. This process was also very successful for producing boron nitride nanotubes (BNNTs) on the gram quantities in a laboratory environment [77]. Figure 2.13 (a) presents a scanning electron-microscope (SEM) image of highly-crystalline and purified BNNTs with a diameter of 40–50 nm and a length of ~10 µm.

![Figure 2.13: (a) SEM image of boron nitride nanotubes (BNNTs) synthesis by boron oxide (BO)-CVD method [35]. (b) The experimental schema for growth of boron nitride nanotubes (BNNTs) in tube](image-url)
furnace by growth vapour trapping (GVT) technique [139]. (c) Patterned boron nitride nanotubes (BNNTs) grown on substrates by using catalytic films [140].

In another approach with using the same chemical pathway, high-purity boron nitride nanotubes (BNNTs) have been produced in a conventional resistive tube furnace at 1200 °C [139]. The use of a closed-end quartz test tube to trap and confine the growth vapours is the key feature of this technique, which is called the catalytic CVD (CCVD)/growth vapour trapping (GVT) [139]. The growth of boron nitride nanotubes (BNNTs) by this approach can be controlled by the vapour-liquid-solid (VLS) process using catalytic films (e.g. MgO, Fe or Ni) coated on Si substrates [140]. An aluminium oxide (Al₂O₃) buffer layer is coated on the substrates before the catalytic films. This controlled approach gives a chance for the patterned growth of boron nitride nanotubes (BNNTs) to be achieved for the first time [140]. Hence, patterned growth of boron nitride nanotubes (BNNTs) not only participates in explanation of the catalysts role in the formation of boron nitride nanotubes (BNNTs), but it also opens an opportunity to fabricate boron nitride nanotube (BNNT) devices directly on substrates at controllable locations [7]. (See Figure 2.13 (b and c)).

2.3.3.5 The inductive thermal plasma method

The thermal plasma process was first used to synthesise boron nitride nanotubes (BNNTs) by using a DC plasma torch and a boron nitride (BN) sintered disk (i.e. 1.5 cm in diameter) at low pressure (~13.3 kPa) [141]. The DC plasma torch was generated using a power of 8 kW and Ar-H₂ (5 vol.%) as plasma gas. While the boron nitride (BN) disk was continuously vapourised by a DC plasma jet, multi-walled boron nitride nanotubes (MWBNNTs) were grown on the disk surface and from amorphous particles in the high temperature zone. Also, boron nitride nanotubes (BNNTs) were prepared at atmospheric pressure by a DC plasma jet using a power of 14 kW and Ar-N₂ (4.25 vol.%) as plasma gas [142]. Hexagonal boron nitride (h-BN) powder was mixed with nickel (Ni) and yttrium (Y) catalysts, and continuously injected into the plasma plume. Multi-walled boron nitride nanotubes (MWBNNTs) with a high-crystalline structure and diameter of 3 – 10 nm were grown from the metal catalysts.

Recently, the large-scale synthesis of boron nitride nanotubes (BNNTs) with high-crystalline structure and small diameter (~5 nm) was achieved by using an induction thermal plasma reactor [143]. In this experiment, the plasma was generated by using a fixed plate power of 50 kW and a constant pressure (93 kPa) of argon (Ar) gas, injected into the central region of the plasma torch. A further gas mixture of argon (Ar), nitrogen (N₂) and hydrogen (H₂) was
introduced around the plasma for further stabilization and chemical reactions. Pure hexagonal boron nitride (h-BN) powder was employed without a metal catalyst and directly injected into the plasma core by using a powder feeder with a feed rate of 0.5–1.0 g min\(^{-1}\) and using argon (Ar) carrier gas. Figure 2.14 shows the induction plasma system that was employed for the large-scale synthesis of boron nitride nanotubes (BNNTs) with a so-called hydrogen-assisted boron nitride nanotube synthesis (HABS). By this process, between 2- and 5-walled boron nitride nanotubes (BNNTs) were formed with a high production rate of 20 g h\(^{-1}\). (See Figure 2.14 (b, c and e)). The unique thermal flow inside the plasma reactor (i.e. a high cooling rate of \(\sim 10^5\) K/s) enhances the formation of small-diameter boron (B) droplets, which are effective precursors for small-diameter boron nitride nanotubes (BNNTs). Hydrogen (H\(_2\)) plays a catalytic role by inhibiting the formation of N\(_2\) from N radicals and promoting the creation of B–N–H intermediate species, which provide faster chemical pathways to the reformation of a h-BN-like phase. Also, hydrogen may increase the plasma power or enhance the heat transfer rate between the plasma and feedstock [144].

![Figure 2.14: Images of an induction plasma process for high production of boron nitride nanotubes (BNNTs). (a) Schematic of the three main parts of the induction plasma system: an induction plasma torch, a reaction chamber, a filtration chamber, and growth mechanism of BNNT from boron (B) droplets [144]. (b), (c) Photographs of as-grown BNNTs after an 11 h operation. In total, 192 g of BNNTs were synthesized in a single experiment. (d)–(f) SEM and TEM images of as-produced BNNTs. The walls of the BNNTs are defect-free, demonstrating their high structural quality and a bundle of BNNTs is illustrated with a scale bar of 20 nm [143].](image-url)
The high yield of boron nitride nanotubes (BNNTs) lead to fabrication of macroscopic boron nitride nanotube (BNNT) assemblies such as BNNT sheets and BNNT buckypaper. To fabricate freestanding boron nitride nanotube (BNNT) buckypaper, the nanotubes were dispersed in liquid (i.e. water or methanol) using a combination of stirring and horn and bath sonication to produce a fluffy dispersion. The dispersion was then vacuum-filtered through a 20 μm pore size polycarbonate membranes. The filtration process was done by using either standard laboratory filtration equipment to produce ~3.5 cm diameter circular buckypaper or a home-built vacuum table with custom size, rectangular funnels (up to 30 cm × 30 cm) to produce larger sheets of buckypaper [143].

Few months later, a similar inductive thermal plasma technique was employed for the synthesis of boron nitride nanotubes (BNNTs) with a high production rate [145]. However, hydrogen is not necessary for this approach. A plasma plume with a power between 40 to 50 kW was generated using pure nitrogen (N₂) as the plasma gas. Boron feedstock (i.e. amorphous boron (B) or hexagonal boron nitride (h-BN) powder) were injected at a rate of 100 to 1700 mg min⁻¹ using nitrogen (N₂) as the carrier gas into the plasma plume at pressures varying from 101 to 517 kPa. At high nitrogen (N₂) pressure, molten boron droplets formed within the plasma plume zone, which react with nitrogen (N₂) to form boron nitride nanotubes (BNNTs), yielding a growth rate of ~ 35 g per hour. The product material contained small diameter double-walled boron nitride nanotubes (DWBNNTs) with a diameter of ~4 nm and unreacted solidified boron particles surrounding by a shell of boron nitride (BN) [7].

![Figure 2.15: (a) a TEM image showing boron nitride nanotubes (BNNTs) grown from boron (B) nanoparticles [143]. (b) a TEM image for a bamboo-like structure of boron nitride nanotubes synthesised by ball milling method [146].](image)
2.3.3.6 Other methods

The high temperature ball milling process is one of other synthesis approaches for boron nitride nanotubes (BNNTs) [147]. Hexagonal boron nitride (h-BN) powder is first ball milled under nitrogen (N₂) atmosphere (i.e. pressure of 300 kPa) at room temperature using a vertical planetary ball mill in order to produce boron (B) nanoparticles. Thereafter, as-milled powder is heated under nitrogen (N₂) gas flow at different temperatures up to 1300°C for about 10 hours. Later, amorphous boron (B) powder (i.e. without or with the catalyst e.g. aluminium chloride (AlCl₃) and lithium oxide (Li₂O)) or boron oxide (B₂O₃) is used as the boron (B) nanoparticles precursor under a nitrogen (N₂) or ammonia (NH₃) atmosphere [148-152]. The time of milling process is varied from several to 150 hours and longer may be resulted in higher boron nitride nanotube (BNNT) yields.

This process has been further developed and refined using boron (B) ink, where the milled powder is mixed with ferric nitrate (Fe(NO₃)₃) and cobalt nitrate (Co(NO₃)₂) in ethanol [146, 153, 154]. After that, the solution is heated under N₂/NH₃ flow between 1000 °C and 1300 °C for several hours to produce boron nitride nanotubes (BNNTs). In addition, boron (B) ink could be coated on various substrates (e.g. SiO₂/Si) to enable boron nitride nanotubes (BNNTs) to be grown on their surfaces [154]. (See Figure 2.16).

![Figure 2.16: Schematic diagram showing the four steps involved in the B ink painting method. (a) Ball-milling of boron (B) powder in a NH₃ atmosphere to produce boron (B) nanoparticles. (b) Mixing milled B nanoparticles with metal nitrate in ethanol to form B ink. (c) Painting the B ink on the substrate. (d) Annealing of the painted substrate in a nitrogen-containing atmosphere to grow the boron nitride nanotubes (BNNTs) film.](image)

The majority of Boron nitride nanotubes (BNNTs) produced by ball milling and thermal annealing, have large diameters ranging from ~50 nm to 200 nm with a bamboo-like structure (See Figure 2.15 (b)), possibly due to the contamination with metal particles from the steel
milling balls. However, the boron (B) ink approach seems to overcome the bamboo-like issue [7, 144].

An auto-clave method has also been used to grow boron nitride nanotubes (BNNTs) [155-158]. In one of the experiment in this technique, a mixture of Mg(BO$_2$)$_2$·H$_2$O, NH$_4$Cl, NaN$_3$ and Mg powder was put in an autoclave and heated at 600 °C for 20–60 h [158]. Boron nitride nanotubes (BNNTs) with diameters mainly 30–300 nm and lengths up to ~5 μm were obtained. In other experiments, iron (Fe) or cobalt (Co) could be used as catalysts with a boron (B) source in the presence of nitrogen (N$_2$) for growth of boron nitride nanotubes (BNNTs) [155, 157].

2.4 Properties

Hexagonal boron nitride (h-BN) has many interesting properties such as low density, electrical insulation, high thermal stability and conductivity, excellent inertness and a low friction coefficient [64]. Boron nitride nanomaterials like nanosheets and nanotubes, also, possess these advantageous properties from hexagonal boron nitride (h-BN) [159], which encourages their usage in various applications. For example, due to the high thermal stability of boron nitride (BN) nanostructures, they are much more suitable to work under oxidation environments and can be used as high-performance oxidation-resistant coatings [6, 160]. In another example, boron nitride (BN) nanomaterials have been employed as substrates to improve the dielectric properties for graphene devices due to their insulating properties [161]. In this section, the optical properties and mechanical properties of boron nitride (BN) materials will be reviewed.

2.4.1 Optical properties

Boron nitride (BN) materials have a wide band gap, so the boron nitride (BN) structures usually possess a white appearance and have a tendency to be transparent as they become much thinner [25, 64]. Boron nitride nanostructures do not exhibit any optical absorption in the visible region of the electromagnetic spectrum 390 - 700 nm. However, they show an absorption peak in the ultraviolet (UV) range at ~210 - 220 nm [162, 163] as shown in Figure 2.17 (b), which make boron nitride nanostructures, either nanotubes or nanosheets, a unique choice for the fabrication of transparent polymer films to block ultraviolet light [25].

Boron nitride materials have almost zero opacity (i.e. they do not absorb visible light) [88]. Gorbachev et al. [88] studied the contrast of atomically-thin boron nitride BN. They found
monolayer boron nitride (BN) exhibits less than ~1.5% contrast on silicon (Si) wafer with ~300 nm of silicon dioxide (SiO$_2$) in thickness when the white-light is used. By using a ~80 nm SiO$_2$ layer, the contrast is enhanced to ~2.5% per layer in white-light and to ~3% with green filter. In addition, Golla et al. [164] reported an optical reflectivity contrast method to determine the optical thickness of 1-80 hexagonal boron nitride (h-BN) layers by using a multilayer interference model. Considering three layers h-BN/SiO$_2$/Si, where SiO$_2$ layer has a thickness of 282 nm, the negative contrast varied linearly with the thickness of the hexagonal boron nitride (h-BN) from 1-80 layers when 516 nm wavelength light was used.

**Figure 2.17:** (a) The thermogravimetry (TGA) for BNNTs and CNT in air, which shows the high thermal stability of BNNTs up to ~1000 °C [165, 166]. (b) The ultraviolet–visible absorption spectrum with a peak at ~203 nm for boron nitride materials [163].

### 2.4.2 Mechanical properties

The mechanical properties of boron nitride nanomaterials are slightly inferior to those of their corresponding carbon systems [77]. The elastic properties of boron nitride (BN) nanostructures have been investigated in many works both theoretically and experimentally [106, 167-185]. The Young’s modulus of boron nitride nanotubes (BNNTs) was calculated to be between 0.837 TPa and 0.912 TPa, close to the value for carbon nanotubes (CNT) (i.e. 1.22 - 1.26 TPa) [167], while it was found for monolayer boron nitride to be in range of 0.716 -0.977 TPa, smaller than the calculated Young’s modulus of graphene (i.e. 1.05 - 1.25 TPa) [186, 187].

For boron nitride nanotubes (BNNTs), however, the experimental values of Young’s modulus were variable and they may depend on the synthesis processes. From the thermal vibration amplitude of a cantilevered BN nanotube observed in a transmission electron microscope
(TEM), Chopra and Zettl [170] reported that boron nitride nanotubes (BNNTs) synthesised by arc-discharge method have an axial Young’s modulus of 1.22 TPa, which is higher than theoretical values. On the other hand, for boron nitride nanotubes (BNNTs) synthesised by chemical vapour deposition (CVD), the elastic modulus values were found to be 0.722 TPa [168] and in rage of 0.5 – 0.6 TPa [169], when an electric-field-induced resonance method inside a TEM and a TEM-AFM piezodriven holder equipped with a force sensor were used respectively.

Figure 2.18: (a) Optical contrast for mono- and bi-layer boron nitride on SiO$_2$ layer with 290 nm in thickness [88]. (b) Boron nitride flake with monolayer regions on SiO$_2$ layer with a thickness of 90 nm [88]. (c) The optical contrast as function of the wavelength and the thickness of hexagonal boron nitride (h-BN) from 1-80 layers on a 282 nm SiO$_2$ layer [164]. The line indicates the change in contrast along the thickness from 1 to 80 layers of boron nitride (BN) with 516 nm wavelength.

Plastic deformation of boron nitride nanotubes (BNNTs) was studied theoretically and revealed an unexpected weakness of zigzag BNNTs, where they have small elastic limits against bond rotation [188]. This defect leads to bond breaking, which affects their elastic response. However, armchair boron nitride nanotubes (BNNTs) have plastic limits
comparable to carbon nanotubes (CNT) with similar wrapping angles. In one experiment, individual multi-walled boron nitride nanotubes (MWBNNTs) were deformed between two gold leads inside a TEM with a high resolution [189]. The nanotubes were found to be flexible and elastic and restored their perfect shapes after the load was released.

Moreover, at high temperatures or after long deformation times, boron nitride nanotubes (BNNTs) were predicted to be more thermomechanically stable than carbon nanotubes (CNT) due to their higher formation energies [25], whereas at room or moderate deformation temperature carbon nanotubes (CNT) should be stronger [31].

For boron nitride nanosheets (BNNSs), there are a few experimental reports of investigations of the mechanical properties of layered boron nitride (BN) with different thicknesses. Those thicknesses were 25 - 300 nm, 1 - 2 nm and 1 - 3 layers of BNNSs.

An experimental study was carried out to investigate the bending modulus of boron nitride nanosheets (BNNSs) [190], which were synthesised by the exfoliation method with a thickness of 25 - 300 nm and lateral size of 1.2 – 3 μm. Three-point bending tests inside an atomic force microscopy (AFM) were used, where the boron nitride nanosheets (BNNSs) were suspended on a trench SiO₂ substrate and clamped with metal films. An increase in bending moduli was found with a decrease in sheets thickness, and its value nearly approached the bulk hexagonal boron nitride (h-BN) value of 31.2 GPa, when the thickness of the boron nitride nanosheets (BNNSs) was below ~50 nm.

In another experiment, boron nitride nanosheets (BNNSs) were synthesised by chemical vapor deposition (CVD) with thickness of 1-2 nm, and transferred to a Si substrate containing circular holes of ~1 μm diameter [106]. By using AFM nanoindentation measurements with diamond tips, 2D elastic constant (E²D) was calculated to be in range 220 – 510 Nm⁻¹, and the fracture point for boron nitride nanosheets (BNNSs) was at deflection of ~70 nm when a ~220 nN force was applied as shown in Figure 2.19 (b).

In 2008, the Young’s modulus of monolayer graphene was measured to be 1TPa [191], whereas the mechanical properties of boron nitride monolayer were only recently examined. They were experimentally measured by using nanoindentation test inside an AFM for the first time [192]. Boron nitride nanosheets (BNNSs) were exfoliated from single crystal hexagonal boron nitride (h-BN) and transferred to SiO₂/Si substrate with wells of 1.3 μm in diameter. The Young’s modulus of 0.865 TPa and fracture strength of 70.5 GPa were measured for
monolayer boron nitride. Table 2.2 summarises the mechanical properties of monolayer (1L), bilayer (2L) and trilayer (3L) of graphene and boron nitride (BN).

In Figure 2.20 (a-d), boron nitride nanosheets (BNNSs) have mechanical stiffness slightly lower than those of graphene with the same number of layers. Interestingly, few layers of boron nitride nanosheets (BNNSs) have strengths similar to a monolayer of boron nitride (BN), whereas the strength of graphene (G) decreases with an increase in number of layers as in Figure 2.20 (e-f). This difference could be caused by the distinct interlayer interactions in these two nanostructured materials under large in-plane strain and out-of-plane compression [192].

![Image](image_url)

**Figure 2.19:** (a) Schematic of AFM nanoindentation on suspended BN nanosheets [106]. (b) Force vs. indentation curves of two films of BN [106]. (c) Schematic of AFM bending test for a clamped BN film [190]. (d) Measured-bending modulus vs. thickness of BN nanosheets, where the dashed line indicates the theoretical value of bulk hexagonal boron nitride (h-BN) [190].

Table 2.2: shows a comparison between graphene and boron nitride (BN) in mechanical properties of 1-3 layers [192].

<table>
<thead>
<tr>
<th>Mechanical property</th>
<th>Graphene</th>
<th>Boron nitride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Breaking strength, (GPa)</td>
<td>1L</td>
<td>2L</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>107</td>
</tr>
<tr>
<td>2D strength, (Nm⁻¹)</td>
<td>41.9</td>
<td>72.1</td>
</tr>
<tr>
<td>2D Young’s modulus, E²D (Nm⁻¹)</td>
<td>342</td>
<td>645</td>
</tr>
<tr>
<td>Young’s modulus, E (TPa)</td>
<td>1.026</td>
<td>-</td>
</tr>
</tbody>
</table>


Figure 2.20: Mechanical properties of few layered graphene and boron nitride [192]. Load vs. displacement curves for 1-3L (a) graphene and (b) boron nitride (BN). Changing 2D Young’s modulus ($E^{2D}$) and Young’s modulus ($E$) in (c) and (d) respectively with layer numbers of graphene (G) and boron nitride (BN). (e) Fracture load and (f) breaking strength as functions of layers numbers of graphene (G) and boron nitride (BN). The dashed lines in (c) and (e) are based on the multiplication of the values of monolayers by the number of layers of graphene and boron nitride, while in (d) and (f), they indicate the values of monolayers of graphene and boron nitride (BN).
Boron nitride (BN) nanostructures (i.e. nanosheets or nanotubes) are therefore one of the strongest insulating materials, and along with their high thermal stability. This makes them ideal candidates for mechanical reinforcement applications, e.g. composites of polymers, glass, ceramics or metals.

2.5 Applications

The unique properties of boron nitride (BN) materials lead them to be used in many applications. For instance, the wide band gap of hexagonal boron nitride (h-BN) materials make them suitable to be utilized as substrate and gate insulator to achieve high carrier mobility in layered channel materials, especially graphene [161]. Also, the insulating features of boron nitride nanostructures possess an advantage to be used for preparation of electrically-insulating nanocables, which makes them have potential use for nanoscale electronic devices [193, 194].

Boron nitride nanomaterials have an effective role in the process of oxygen reduction reactions (ORR), which is very important for fuel cells, Li-O₂ batteries and sensors application [195-199]. Moreover, adsorption properties of porous boron nitride materials, to remove a wide range of pollutants such as oils, organic solvents, dyes and metal ions from water, enable water cleaning by boron nitride (BN) materials [200, 201]. Furthermore, boron nitride nanomaterials can be used in nanomedical fields (i.e. they have good biocompatibility), for scanning probe microscopy as ultrathin stiff tips and in field emission applications [159, 202, 203].

In addition, the thermal conductivity of poly(vinyl formal) (PVF) polymer was improved by ~ 160 % with only a 1 wt% boron nitride nanotubes (BNNTs) loading fraction [204]. Hence, boron nitride nanomaterials are potentially used as nanofiller in composite applications. Utilising boron nitride (BN) nanomaterials as nanofillers for the mechanical reinforcement of nanocomposites materials will be discussed in this section.

2.5.1 Nanocomposites

Nanostructured Boron nitrides (BN) are favourable for use in nanocomposites for mechanical applications due to their good mechanical properties, along with their excellent chemical inertness and high thermal stability [7]. Boron nitride (BN) nanotubes and nanosheets have been employed as nanofillers into polymers, ceramics and metals matrices of composites. For example, the Young’s modulus of poly(methyl methacrylate) (PMMA) polymer films was
increased by 22 % and their strength by 11 % with adding only 0.3 wt% of boron nitride nanosheets (BNNSs) into the polymer matrix [3], whereas just 0.1 wt% loading fraction of BNNSs into poly(vinyl alcohol) (PVA) polymer matrix enhanced the elastic modulus and the strength by 20 % and 15 % respectively [205], and when the loading fraction was increased to 0.12 vol% (~0.2 wt%), the Young’s modulus improved by 40 % [22]. Moreover, by using 1 wt% loading fraction of boron nitride nanotubes (BNNTs), the elastic modulus and the strength of polystyrene (PS) polymer matrix increased by 21 % and 22 % respectively [35], while their values for polycarbonate (PC) polymer matrix were enhanced by just 13 % and 5% respectively [206]. On the other hand, boron nitride nanosheets (BNNSs) can improve the mechanical properties of PC polymeric composites by 22 % for elastic modulus and 35 % for the strength, when a loading fraction of 2 wt% is used [207].

It may worth mentioning that with an increase in the loading fraction of boron nitride nanofillers into the polymer matrices, the elastic modulus is continuously increased, whereas the trend of tensile strength is complicated and not clear [5]. Although, unmodified boron nitride (BN) nanostructures have improved the mechanical properties of polymers matrices, BN nanomaterials can be covalently functionalised with chemical groups such as hydroxyl (-OH) and alkyl (-R), and this has revealed a considerable reinforcement of polymer matrices [5]. By using a 1 wt% loading fraction, the elastic modulus of poly(vinyl butyral) (PVB) polymer matrix was improved by 25 % with unfunctionalised boron nitride nanotubes (BNNTs) and by 36.5 % with functionalised (-OH) BNNTs, while the strength was enhanced by 7 % with unfunctionalised BNNTs and by 32 % with OH-BNNTs [206]. Also, poly(vinyl alcohol) (PVA) polymer matrix was mechanically enhanced with 0.1 wt% loading fraction of boron nitride nanosheets (BNNSs), where the elastic modulus increased by 20 % with unfunctionalised BNNSs and by 186 % with OH-BNNSs, while the strength improved from 15 % with unfunctionalised BNNSs to 66 % with OH-BNNSs [205]. Many other polymer matrices have shown elastic modulus and tensile strength improvements when used in boron nitride nanocomposites. They include polylactide–polycaprolactone copolymer (PLC) [34], polyaniline (PANI) [208], polypropylene (PP) [209], epoxy [26], thermoplastic polyurethane (TPU) [210], polyethylene [211] and poly(ethylene vinyl alcohol) (PEVA) [212].

In ceramic composites, boron nitride (BN) nanomaterials are often used as nanofillers to improve the fracture toughness of ceramic matrices. An improvement of 24.4 % in fracture toughness of ZrB$_2$-SiC composites was achieved with 1 wt% loading fraction of a mixture of 1D (nanotubes) and 2D (nanoplatelets) boron nitride (BN) nanomaterials [213]. In addition,
improvements of 90% in the fracture strength and 35% in fracture toughness were obtained by introducing 4 wt% boron nitride nanotubes (BNNTs) into barium calcium alumina silicate (BCAS) glass composites [20]. Moreover, borosilicate glass matrices have been reinforced by 5 wt% concentration of boron nitride nanosheets (BNNSs) and boron nitride nanotubes (BNNTs) and improvements in fracture toughness by 45% with BNNSs and by 30% with BNNTs were achieved [214, 215]. Furthermore, boron nitride nanoplates (BNNPs) with a thickness of 30 nm enhanced the fracture toughness and the strength of the ceramic matrix of the BNNP/Si3N4 nanocomposite by 24.7% and 9.4% respectively with 2 vol% of BNNPs [216].

For metal matrix composites, aluminium (Al) matrices have been reinforced by 5 wt% concentration of boron nitride nanotubes (BNNTs), and the tensile strength of aluminium (Al) matrices was enhanced by a factor of 2 higher than that of pure aluminium (Al) [217]. Also, lightweight aluminium ribbons have been reinforced with 3 wt% BNNTs loading and the tensile strength and the Young’s modulus were found to be more than double their values for the pure metal [218].

2.5.1.1 Filler geometry

Generally, nanofillers into different matrices of nanocomposites can be divided according to their geometry into three categories [219]:

1. Nanoparticles when the three dimensions of particulates are in the nanometre scale and they are referred as isodimensional nanoparticles or nanocrystals such as boron nitride nanoplates (BNNPs)
2. Nanotubes when two dimensions are in the nm scale while the third is larger to form elongated structures and they are termed as nanotubes, nanofibres or whiskers (e.g. boron nitride nanotubes (BNNTs)).
3. Nanolayers when only one dimension is in order of nm scale and they are usually represented as nanosheets with thickness of one to few nanometers (e.g. boron nitride nanosheets (BNNSs)).

Nanostructured boron nitrides (BN) have attractive features due to their high aspect ratio as well as with their high mechanical strength and thermal conductivity [25]. So, the advantages of nano-sized boron nitride (BN) compared with traditional boron nitride (BN) (i.e. micro-sized BN) originate from their maximally exposed the basal atomic lattice plane that leads to the high performance property of h-BN as shown in Figure 2.22.
Figure 2.21: (a) Stress–strain curves for pure poly(vinyl alcohol) (PVA) polymer, unmodified BNNSs-PVA nanocomposites and functionalised OH-BNNSs-PVA nanocomposites [205]. (b) Stress vs. strain curves of pure aluminium (Al) and Al-BNNTs nanocomposites with 0.5 wt%, 1 wt% and 3 wt% concentrations of BNNTs at room temperature [218]. (c) Improvements of fracture toughness and flexural strength of BNNSs-BS glass composites with different concentration of BNNSs [214].

In nanocomposites, there is a large amount of interfacial contact between the matrix phase and the nanofiller phase, which leads to achieving enhancement in the mechanical properties with lower volume fraction of nanofillers compared to conventional composites [220]. Thus, using nanofillers for reinforcements has the following benefits over traditional fillers [221]:

1. Large number density of particles per unit volume ($10^6–10^8$ particles/μm$^3$).
2. Low-percolation threshold (~0.1–2 vol.%).
3. Short distances between particles (10–50nm at ~1–8 vol.%).
4. Extensive interfacial area per volume of particles ($10^3–10^4$ m$^2$/ml).
Figure 2.22: Schematic of high performance of nanostructured boron nitride compared with traditional BN particles [25]. It would have poor enhancements of mechanical properties along c axis of BN particles (a), while good enhancements of mechanical properties can be achieved along the axis of BNNTs (b) or the basal planes of BNNSs (c).
Moreover, nanofillers with their high aspect ratio, whether nanotubes (length/diameter) or nanoplates (thickness/diameter), generate one to three orders of magnitude more internal interfacial area per particle than classic fillers [221]. (See Figure 2.23)

Figure 2.23: The geometry of (a) nanotubes and (b) nanoplatelets, where d and t should be in order of nanometers to achieve high aspect ratios [222].

The key to the mechanical enhancement of nanocomposites properties is the interaction between the nanofillers and the host matrix, and this will be affected by many factors such as the filler volume fraction, dispersion degree, geometry and orientation of the filler [219]. Figure 2.24 shows schematic of different orientations states of reinforced nanocomposites. If only the geometry (i.e. the aspect ratio) and orientation of the filler are considered, the effective surface area per unit volume of the filler, $\bar{\gamma}$, can be defined as:

$$\bar{\gamma} = \frac{\bar{A}}{V} \quad (2.3)$$

where $V$ is volume of the filler and $\bar{A}$ is the effective surface area of the filler, which represents the portion of surfaces that is normal to the direction of major axis. For example, the value of $\bar{\gamma}$ for fillers with the shape of a sphere, disk, and cylinder and orientated along the major axis is $3/2t$, $2/t$, and $4/t$, respectively. (See Table 2.3).

One of the most important issue in the fibre reinforcement is the stress transfer process from the matrix (low modulus) to reinforcing fibre (high modulus) [5, 223]. In composites with high aspect ratios and long aligned fibres, the majority of the load will be taken by the high modulus fibre in the axial deformation, where the fibre strain is considered to be same as that of the matrix. On the other hand, in the case of short fibres, there is a complexity where a shear stress is present at the fibre-matrix interface and the stress will be built up from the ends of the fibre [29, 223].
Figure 2.24: Schematic of reinforced nanocomposites by a) aligned fibre, b) randomly oriented fibre, c) aligned nanoplatelets and d) randomly oriented nanoplatelets [222].

Table 2.3: The $\gamma$ value of nanofillers with the most common geometries [219].

<table>
<thead>
<tr>
<th>Name</th>
<th>Shape</th>
<th>$\gamma$</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere</td>
<td><img src="https://via.placeholder.com/150" alt="Sphere" /></td>
<td>$\frac{6}{t}$</td>
<td>$t$-diameter</td>
</tr>
<tr>
<td>Cylinder</td>
<td><img src="https://via.placeholder.com/150" alt="Cylinder" /></td>
<td>$\frac{2}{t} + \frac{1}{a} \approx \frac{4}{t}$</td>
<td>$t$-diameter of cross section area, $a$-length</td>
</tr>
<tr>
<td>Disk-like (platelet)</td>
<td><img src="https://via.placeholder.com/150" alt="Disk-like" /></td>
<td>$\frac{2}{t} + \frac{1}{a} \approx \frac{2}{t}$</td>
<td>$t$-thickness, $a$-radius</td>
</tr>
<tr>
<td>Rectangular (platelet)</td>
<td><img src="https://via.placeholder.com/150" alt="Rectangular" /></td>
<td>$\frac{1}{t} + \frac{1}{a} + \frac{1}{b} \approx \frac{2}{t}$</td>
<td>$t$-thickness, $a$ and $b$ length and width</td>
</tr>
</tbody>
</table>
2.5.1.2 Micromechanical models for estimating the elastic modulus of a composite

There are many micromechanical models, which have been used to predict the Young’s modulus of nanocomposites. The most popular models for nanofibres can be summarised as follows:

**Upper and lower bounds or V-R model (Voigt and Reuss model)**

There are upper and lower bounds (i.e. upper bound predicted by Voigt [224] while lower bound derived by Reuss [225]) for the Young’s modulus of nanocomposites rather than single values. These bounds can be determined when the fibre and the polymer matrix are subjected to either uniform strain or uniform stress. If a uniform strain in the longitudinal direction is applied (i.e. the parallel coupling case) the Young’s modulus, \( E_c \), of the composite is giving by “the rule of mixtures” as:

\[
E_c = \phi E_f + (1 - \phi) E_m \tag{2.4}
\]

where \( \phi \) is the volume fraction of the fibres and \( E_f \) and \( E_m \) are the modulus of the fibre and matrix respectively. In case of applying uniform stress (i.e. series coupling) in the transverse direction, the modulus, \( E_c \), predicted using “the inverse rule of mixtures” is:

\[
\frac{1}{E_c} = \frac{\phi}{E_f} + \frac{(1-\phi)}{E_m} \tag{2.5}
\]

**Halpin-Tsai model (H-T model)**

For aligned reinforcement of composites, Halpin and Tsai [226-229] developed a micromechanics method to predict the Young’s modulus based on Hermans’ [230] and Hill’s [231] work. In this model, geometry of the fibre is taken into account. The elastic modulus of the composite is given by:

\[
E_c^L = \frac{1+2\left(\frac{l}{d}\right)\eta_L}{1-\phi\eta_L} E_m \tag{2.6}
\]

\[
E_c^T = \frac{1+2\eta_T}{1-\phi\eta_T} E_m \tag{2.7}
\]

where \( L \) and \( T \) superscripts refer to the longitudinal and transverse directions, respectively, \( l \) and \( d \) are the length and diameter of the fibre (i.e. \( d \) can be replaced by the thickness \( t \) in case of platelets) and \( \eta_L \) and \( \eta_T \) are given by:

\[
\eta_L = \frac{E_f - E_m}{E_f + 2\left(\frac{l}{d}\right)E_m} \tag{2.8}
\]
\[
\eta_T = \frac{E_f - E_m}{E_f + 2E_m}
\]  

(2.9)

**Shear lag model**

![Schematic diagrams of the basis of the shear lag model showing: (a) unstressed system and (b) a deformation pattern for a discontinuous flake in a polymer matrix [48].](image)

One of the most often used approaches of micromechanics model for fibre-reinforced composites is the shear lag model [232]. Cox [233] used a model of composite as a single fibre with length \( l \) and radius \( r_f \), which is encased in a concentric cylindrical shell with radius \( R \) of matrix. He derived the modulus in the longitudinal direction as:

\[
E'_c = \eta_L \phi E_f + (1 - \phi) E_m
\]

(2.10)

where \( \eta_L \) is a factor of length-dependent efficiency as:

\[
\eta_L = 1 - \frac{\tanh(\beta l)}{\beta l}
\]

(2.11)

with

\[
\beta^2 = \frac{4\mu_m}{r_f^2 E_f \ln(\frac{R}{\phi})}
\]

(2.12)

where \( K_R \) is a constant, which depends on the fibre packing arrangements.

2D materials such as graphene and boron nitride nanosheets can be considered as platelets, and when they are used for reinforcement of composites, they can be considered as a 2D version of fibre reinforcement [29]. All micromechanical models of fibres reinforcements can be modified to be suitable for nanoplatelets [222].
Gong et al. [48] studied the mechanics of reinforcement of polymers by graphene platelets, where a single graphene monolayer flake (bilayer or few-layer graphene may be used as well) is placed in between two thin layers of transparent polymer on a beam of poly (methyl methacrylate) (PMMA) (See Figure 2.26). By using the sensitive 2D Raman band of graphene to follow strain [45, 234-238], stress transfer from polymer matrix to graphene flake can be followed by determining the variation of local strain across graphene flake [48]. From shear lag analysis, the variation of strain in the graphene monolayer was predicted by Gong et al. [48] as:

$$e_f = e_m \left[ 1 - \frac{\cosh(ns^2 x)}{\cosh(ns^2 l)} \right], \text{and} \quad n = \sqrt{\frac{G_m}{E_g} \left( \frac{t}{T} \right)}$$

where $e_f$ is the strain in the graphene monolayer, $e_m$ is the matrix strain, $x$ is the position, $l$ is the length of graphene monolayer in the x direction, $s$ is the aspect ratio of graphene, $n$ is widely accepted to be interfacial stress transfer efficiency, $G_m$ is matrix shear modulus, $E_g$ is Young’s modulus of the graphene monolayer, $t$ is thickness of graphene monolayer and $T$ is the total resin thickness.

At low strains, the strain will build up from the edges of the flake to becoming equal to the applied matrix strain across the middle of the flake [223] as shown in Figure 2.26, and this strain behaviour is analogous to that was found in fibre composites.

![Image of graphene nanocomposites](image)

**Figure 2.26:** (a) A model of single monolayer graphene nanocomposites (not to scale) and (b) The strain distribution in the graphene monolayer at 0.4% strain and calculated curves with different values of $ns$ [29].
2.5.1.3 *Mechanisms of mechanical enhancement in nanocomposites*

Since the boron nitride (BN) fillers and the employed host matrices interact via weak van der Waals forces or π-π interactions, it is important to chemically modify the BN nanofillers with appropriate functional groups to enhance such interactions or introduce other strong interactions [5]. Moreover, for the boron nitride (BN) materials, the basal plane is molecularly smooth and has no surface functional groups available for chemical bonding or interactions [239]. In contrast, the edge planes have functional groups such as hydroxyl (-OH) and amino (-NH₂) groups, and these functional groups allow the boron nitride (BN) fillers to chemically bond with other molecules, which gives enhancements to mechanical properties of boron nitride (BN) nanocomposites.

To understand the mechanism of mechanical enhancement in nanocomposites, there is a transition region or an interphase existing between the nanofiller and the matrix, and in this interphase, mechanical properties change from the properties of the filler to that of the matrix [219]. In silica nanoparticle/polymer composites, Boutaleb et al. [240] studied the interphase influence on the overall behaviour of nanocomposites and their results show the interphase is controlling the overall nanocomposite behaviour. Yet, the interphase, which coats the spherical nanoparticles of silicates, is represented as a third phase in the polymer composite. (See Figure 2.27).

![Figure 2.27: Polymer matrix of nanocomposites with randomly dispersed nanoparticles (left) and a nanoparticle is coated by interphase (right) [240].](image-url)
Saber-Samandari and Khatibi [241] developed a model to estimate the elastic modulus of interphase, $E(r)$, at any point, $r$, in the nanocomposite as:

$$E_i(r) = \frac{E_m r_i}{r} + \left( E_f - \frac{E_m r_i}{r_f} \right) \left( \frac{r_i - r}{r_i - r_f} \right)^{n/2}$$  \hspace{1cm} (2.14)

where $E_m$ and $E_f$ are elastic modulus of matrix and filler respectively, $r_f$ and $r_i$ are the filler and interphase radii respectively, and $n$ is the enhancement factor, which depends on the chemistry and surface treatment of the filler particles.
Chapter 3: Raman bands characterisation of hexagonal boron nitride (h-BN) materials

3.1 Introduction

The Raman effect was discovered by the Indian physicist Chandrasekhara Venkata Raman in 1928 [242] and it led to the award of the Nobel Prize in 1930. When monochromatic light (e.g. laser radiation) is encountered at a sample of a material, there is a probability that a photon scattering process occurs due to the interaction between incident photons and the quantised lattice vibrations, which are called phonons. If the scattering is elastic, the incident photon and scattered photon have the same frequency and this process is called Rayleigh scattering. On the other hand, in inelastic scattering, the frequency of scattered photons will be changed to be either up-shifted or down-shifted in energy and this process is called Raman scattering.

![Figure 3.1: The energy level diagram of scattering process types [243], $E_0$ is the ground state of the molecule, incident photons (up green arrows) and Rayleigh scattering photons (down green arrow) have the same frequencies $\nu_0$, while scattered photons in Stokes (red arrow) and Anti-Stokes (blue arrow) scattering are down-shifted and up-shifted of frequencies respectively.](image)

68
In Raman scattering the lines or bands at frequencies less than the frequency of incident photons are referred to as so-called Stokes scattering and those at frequencies greater than the frequency of the incident photons are referred to as so-called anti-Stokes scattering.

The Raman change in frequencies is associated with transitions between electronic, vibrational and rotational states of energy in the molecular system [244]. Hence, the molecule will be excited from its ground state by incident photons to excited electronic state or virtual states (i.e. vibrational or rotational energy levels), thereafter, the molecule will relax to an energy state that differs from the original state by emission of scattered photons. These scattered photons have different polarisation characteristics from those of the incident photons [244]. The change in polarisability of the molecule with respect to its vibration is governed by whether the molecular vibration is Raman active or not and this statement is the basis of the selections rules for Raman scattering [242].

![Image](image.png)

**Figure 3.2:** The induced dipole moment, $P$, by incident oscillating electric field, $E$, of laser radiation. Scattering waves in two direction are shown as well (i.e. back scattering ($180^\circ$) or right angle ($90^\circ$)) [242].

### 3.2 Theory of the Raman effect

The incident oscillating electric field ($E$) of an electromagnetic wave interacts with the electron cloud of the molecule to result in a periodic separation of charge with a frequency the same as the frequency ($\nu$) of the incident electric field ($E$). This leads to inducing an oscillating dipole moment ($P$), which is manifest as a source of electromagnetic radiation for scattered photons.
The strength of the induced dipole moment \( (P) \) is governed by the strength of the electric field \( (E) \) of incident photons and the polarizability \( (\alpha) \) which is a property of the matter that depends on the atom locations and the nature of the bonds in the molecular structure. Thus,

\[
P = \alpha E
\]  
(3.1)

where the electric field \( (E) \) can be expressed as:

\[
E = E_0 \cos(2\pi v_0 t)
\]  
(3.2)

The time-dependent induced dipole moment is given by substituting Equation (3.2) into (3.1) as:

\[
P = \alpha E_0 \cos(2\pi v_0 t)
\]  
(3.3)

The polarizability \( (\alpha) \) is a function of the instantaneous position of constituent atoms since it depends on the relative location of individual atoms in the molecular structure. The individual atoms, in addition, are confined to specific vibrational modes for any molecular bond, in which the vibrational energy \( (E_{vib}) \) levels are quantized in a way similar to electronic energies [245]. The vibrational energy \( (E_{vib}) \) of a particular mode is given by:

\[
E_{vib} = \left( j + \frac{1}{2} \right) \hbar v_{vib}, \quad j = 0, 1, 2 \ldots
\]  
(3.4)

where \( j \) is the quantum number of vibrations, \( \hbar \) is Planck’s constant and \( (v_{vib}) \) is the frequency of the vibrational mode. The displacement \( Q_j \) about the equilibrium position of atoms due to the particular vibrational mode \( j \) can be expressed as:

\[
Q_j = Q_j^0 \cos(2\pi v_{vib} t)
\]  
(3.5)

where \( Q_j^0 \) is the maximum displacement at the equilibrium position. The polarizability \( \alpha \) will be modulated by the molecular vibration as a Taylor series expansion:

\[
\alpha = \alpha^0 + \frac{\partial \alpha}{\partial Q_j} Q_j + \cdots
\]  
(3.6)

where \( \alpha^0 \) is the polarisability of the molecular mode at the equilibrium position. By substituting Equation (3.5) into (3.6), the polarisability for such small displacement may be given as:

\[
\alpha = \alpha^0 + \frac{\partial \alpha}{\partial Q_j} Q_j^0 \cos(2\pi v_{vib} t)
\]  
(3.7)
Finally, by substituting Equation (3.7) into (3.3) and using $\cos \alpha \cos \beta = \frac{1}{2} \left[ \cos(\alpha + \beta) + \cos(\alpha - \beta) \right]$, the induced dipole moment is given by:

$$P = |E_0| \cos(2\pi \nu t) + \frac{q |E_0|}{2} \sum \left[ \cos[2\pi(\nu + \nu_{\text{vib}})t] + \cos[2\pi(\nu - \nu_{\text{vib}})t] \right] \quad (3.8)$$

From Equation (3.8), photons will be scattered at three frequencies, namely $\nu_0$ and $(\nu_0 \pm \nu_{\text{vib}})$, which are related to the same three frequencies of the induced dipole moments. The first term is Rayleigh scattering, which is at the same frequency $\nu_0$ as the incident photons, while the latter two frequencies $(\nu_0 \pm \nu_{\text{vib}})$ are Raman scattering, where Stokes scattering occurs at $(\nu_0 - \nu_{\text{vib}})$ with a down-shifted frequency and anti-Stokes scattering occurs at $(\nu_0 + \nu_{\text{vib}})$ with an up-shifted frequency. On the other hand, the term $\left( \frac{\partial \alpha}{\partial Q_j} \right)$ must be non-zero for Raman scattering to occur, which means that the vibrational displacement of atoms corresponding to a particular vibrational mode must result in a change of polarisability and this applies as a selection rule for Raman scattering.

![Diagram](image)

**Figure 3.3**: The hexagonal structure and the first Brillouin zone of monolayer hexagonal boron nitride (h-BN). (a) The real lattice unit vectors $a_1$ and $a_2$ in the primitive cell. (b) The reciprocal lattice vectors $b_1$ and $b_2$ in 2D Brillouin zone [246].
3.3 Raman active bands of (h-BN) materials

Boron nitride (BN) materials have spectroscopic signatures such as Raman and infrared (IR) characteristic peaks related to their vibrations modes. We must first recall the structure of hexagonal boron nitride (h-BN) from section 2.2.1, which has a $D_6^h$ (P63/mmc) space group symmetry [247, 248]. Figure 3.3 illustrates the hexagonal structure of a monolayer h-BN and the first Brillouin zone (BZ), where $a_1$ and $a_2$ are the real lattice unit vectors in the primitive cell and $b_1$ and $b_2$ are the reciprocal lattice vectors in the 2D Brillouin zone [246].

The symmetry transformations of the optical phonons at the Brillouin zone centre (Г) can be classified as:

$$\Gamma = 2E_{2g} + 2B_{1g} + A_{2u} + E_{1u}$$  \hspace{1cm} (3.9)

The $E_{2g}$ modes are Raman-active, the $A_{2u}$ and $E_{1u}$ modes are IR-active and the $B_{1g}$ modes are optically silent [64, 247, 249-251]. The two Raman-active $E_{2g}$ modes are due to in-plane atomic displacements. $E_{2g_1}$ is a low frequency mode and it is characterized by whole planes sliding against each other, while $E_{2g_2}$ is a high frequency mode and is due to boron (B) and nitrogen (N) atoms moving against each other within a plane. Figure 3.4 shows the Raman spectrum of hexagonal boron nitride (h-BN) including the low frequency mode $E_{2g_1}$ with anti-Stokes (AS) and Stokes (S) peaks, and a Stokes peak of the high frequency mode $E_{2g_2}$ or so-called the G band mode [252].

The low frequency mode $E_{2g_1}$ has a low intensity and an experimental peak position in the range of 49–52.5 cm$^{-1}$. It has been less observed because its low frequency is close to the high Rayleigh background and it may be difficult to observe due to the frequency cut-off of the notch filter in Raman spectrometers [252].

In contrast, the high frequency mode $E_{2g_2}$ has a high intensity and an experimental peak position at $\sim 1366 \pm 1$ cm$^{-1}$ in common for the bulk hexagonal boron nitride (h-BN). Compared to the bulk h-BN Raman peak position, boron nitride (BN) nanostructures exhibit different Raman peak positions with red-shifts or blue-shifts depending on the layer number of boron nitride nanosheets (BNNSs) [2, 6, 88, 162] and tube diameters and chiralities in boron nitride nanotubes (BNNTs) [78]. Gorbachev et al. [88] reported the Raman G band of a monolayer boron nitride (BN) is upshifted by 4 cm$^{-1}$, while downshifts were observed for
few-layer BN (e.g. bilayer by 2 cm\(^{-1}\)) compared to the Raman G band of the bulk h-BN as shown in Figure 3.5 (a). However, other researchers reported only upshifts for the Raman G band of monolayer and few layer boron nitrides (BN) [2, 6, 162, 253] as in Table 3.1 and Figure 3.5 (b). Therefore, it seems that the Raman G band of boron nitride (BN) is located at 1371 ± 1 cm\(^{-1}\) for the monolayer and slightly downshifted with increasing of layer number until it reaches the bulk G band position. Since there is hardening of the \(E_{2g}\) phonon mode due a slightly shorter B–N bond in the monolayer [88], the red shift may be explained by the interactions of the neighbouring layers in few-layered nanosheets could lead to a small elongation of the B–N bonds and consequently a softening of the phonons [254].

![Raman spectrum of hexagonal boron nitride (h-BN)](image)

Figure 3.4: Raman spectrum of hexagonal boron nitride (h-BN). This spectrum exhibits the low frequency lines at ~52.5 cm\(^{-1}\) (anti-Stokes) and 52.5 cm\(^{-1}\) (Stokes) with a width of ~ 1.1 cm\(^{-1}\) and a high frequency line at 1366 cm\(^{-1}\) (Stokes) with a full width at half maximum (FWHM) of ~ 8 cm\(^{-1}\). The insets show the in-plan displacements of B and N atoms that correspond to the two Raman-active \(E_{2g}\) modes [252].
Table 3.1: Theoretical calculation (Thr) and experimental observation (Exp) of Raman active bands for born nitride (BN) materials in the literature. Note: the theoretical calculation [76, 78, 255-258] for Raman active bands for single walled boron nitride nanotubes (SWBNNTs) are not included here.

<table>
<thead>
<tr>
<th>Raman active bands (cm⁻¹):</th>
<th>Bulk hexagonal boron nitride (h-BN)</th>
<th>Boron nitride nanosheets (BNNSs)</th>
<th>Boron nitride nanotubes (BNNTs)</th>
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<tr>
<td></td>
<td>$E_{2g_1}$</td>
<td>$E_{2g_2}$</td>
<td>$E_{2g_2}$</td>
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<td>Michel et al. (Thr)[249]</td>
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<td>-</td>
</tr>
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<td>Serrano et al. (Thr)[260]</td>
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<td>-</td>
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<tr>
<td>Hoffman et al. (Exp)[261]</td>
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<td>1367</td>
<td>-</td>
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<tr>
<td>Reich et al. (Thr)[250]</td>
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<td>1364</td>
<td>-</td>
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<tr>
<td>Geick et al. (Exp)[56]</td>
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<td>1370</td>
<td>-</td>
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<tr>
<td>Nemanich et al. (Exp)[248]</td>
<td>51.8</td>
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<td>-</td>
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<td>Coa et al. (Exp)[262]</td>
<td>-</td>
<td>1370</td>
<td>-</td>
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<td>-</td>
<td>1366</td>
<td>1370</td>
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<td>Li et al. (Exp)[6]</td>
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<td>1366.2</td>
<td>1370.5</td>
</tr>
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<td>1369.6</td>
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<td>-</td>
<td>1371</td>
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<tr>
<td>Yeh et al. (Exp)[276]</td>
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<td>Evans et al. (Exp)[282]</td>
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<td>Popov (Thr)[76]</td>
<td>43</td>
<td>1366</td>
<td>-</td>
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<td>Song et al. (Thr)[106]</td>
<td>-</td>
<td>1370</td>
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<tr>
<td>Falin et al. (Exp)[192]</td>
<td>-</td>
<td>1366.5</td>
<td>-</td>
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</tbody>
</table>

Single walled- (SW), Double walled- (DW) and Multi-walled (MW) NTs, & Bamboo like-structure (BS) and Cylindrical like-structure (CS)
In addition, Cai et al. [2] carried out theoretical calculations to simulate the Raman spectra of BN monolayer and few layered BN nanosheets. They predicted the Raman G band modes of freestanding 1L, 2L, 3L nanosheets and bulk BN were at 1348.5, 1343.3, 1347.6 and 1343.7 cm\(^{-1}\), respectively as shown in Figure 3.5 (c). These values are however clearly lower than experimental values, and such differences can be noticed in Table 3. for the bulk h-BN, so this approach may need further investigation.

Gorbachev et al. [88] and Cai et al. [2] found the intensity of Raman G band of boron nitride (BN) is proportional to the layer number as seen in Figure 3.5 (d). As the number of BN layers decreases from several layers to monolayer, the intensity decreases and the G band peak becomes weaker. Moreover, the intensity of G band peak for boron nitride (BN) monolayer is smaller than G band peak of graphene by ~ 50 times under the same measurement conditions [88].

Figure 3.5: Raman spectra of 1-3 layer boron nitride (BN) nanosheets and bulk h-BN based on experiments in (a) [88] and (b) [6], and on theoretical calculations in (c) [2]. (d) The change in the G band intensity of Boron nitride (BN) with the number of layers (N) and the inset shows the phonon mode responsible for the Raman peak [88].
From Table 3.1, the observed Raman frequencies of the in-plane stretching optical phonons of the G band are located in the range of 1354 – 1370 cm\(^{-1}\) for multi-walled boron nitride nanotubes (MWBNNTs) and at 1370 cm\(^{-1}\) for single-walled boron nitride nanotubes (SWBNNTs). However, the radial breathing modes (RBM) of boron nitride nanotubes (BNNTs) are difficult to observe due to their low frequency. Popov [76] calculated the dependence of the frequency of the radial breathing mode (RBM) in (cm\(^{-1}\)) on tubes radius \(R\) in (Å) as:

\[
\omega_{(RBM)} = \frac{851}{R}
\]  

(3.10)

Figure 3.6 (a) shows the RBM frequencies for tubes with radii between 5 and 25 Å. Therefore, because of the frequency cut-off of the notch filter in Raman spectrometer, which is usually about 100 cm\(^{-1}\), one may expect to observe the RBM peaks if the diameter of boron nitride nanotubes (BNNTs) is less than 1 nm.

In addition, Popov [76] stated that the frequencies of the Raman G band mode of the boron nitride nanotubes (BNNTs) are the radius dependent and with the increase of the radius, the G band modes of BNNTs tend asymptotically to the G band frequency of the boron nitride (BN) sheet. Moreover, Arenal et al. [266], also showed the high-frequency A mode converges toward the \(E_{2g}\) frequency of a single sheet of hexagonal boron nitride (h-BN) with increasing the diameter of single walled boron nitride nanotubes (SWBNNTs) and their calculation of the Raman optical A mode frequencies for different zigzag BNNTs is presented in Figure 3.6 (b). The calculated frequencies of Raman A modes for zigzag BNNTs in cm\(^{-1}\) as a function of the diameter \(D\) in Å is:

\[
\omega_{(D)} = \omega_{\text{sheet}} - \frac{1268.3}{D^{2.29}}
\]  

(3.11)

The Raman G band modes in boron nitride nanotubes (BNNTs) may be considered as a composite signal due to the tangential \(A_g\) and longitudinal \(E_{2g}\) modes for armchair tubes, while in the case of zigzag and chiral tubes the corresponding assignment is \(A_1\) and \(E_g\) modes [266]. Figure 3.7 illustrates the calculated Raman spectra of single-walled boron nitride nanotubes (SWBNNTs) with (9,0), (13,0), (16,0) zigzag and (10,10) armchair chiralities, and sketches of the high frequency A modes in zigzag BNNTs.

Moreover, the softening/hardening of the frequencies of the G band modes is entirely a curvature effect, which causes bond weakening in boron nitride nanotubes (BNNTs) with
small diameters. So, red-shifts are expected to be observed in the frequencies of the G band modes [76, 78].

Figure 3.6: (a) The frequency of the radial breathing mode (RBM) vs. tube radius in range between 5 and 25 Å [76]. (b) Calculated frequencies of the Raman optical A1 mode for different (n,0) zigzag BNNTs, where the dashed lines shows the frequencies of h-BN sheet, BNNTs and bulk h-BN [266].

Figure 3.7: (a) The calculated Raman intensities for three different zigzag BNNTs and the (10,10) armchair BNNT [283]. Sketch of high frequency A modes in a zigzag BNNT [78]: (b) radial buckling (R) mode, (c) bond-stretching or longitudinal (L) mode and (d) bond-bending or tangential (T) mode.
In contrast to carbon nanotubes (CNT) which can be either metallic/semiconducting depending on the chirality of the tube, boron nitride nanotubes (BNNTs) are always semiconducting with a wide band gap of about 5.5 eV and this band gap is independent of the tube diameter, chirality, and whether the nanotube is single walled, multiwalled, or packed into bundles [69]. Therefore, due to the wide band gap not only in BNNTs, the boron nitride (BN) materials have Raman intensities in the visible light frequencies much weaker than those of carbon systems, since the Raman scattering is non-resonant [78]. In addition, the intensity of most of the boron nitride nanotubes (BNNTs) modes may be very weak and decreases with increasing the tube length due to the reduced symmetry. This could be the reason for just observing the G band mode of boron nitride nanotubes (BNNTs). (See Table 3.1).

### 3.4 Strain effects on the Raman band modes of BN materials

Raman peak frequencies would shift to higher and lower frequencies under compressive and tensile strains respectively [64, 284], since strain modifies the crystal phonons, with tensile strain usually resulting in mode softening and the opposite for compressive strain. The rate of these changes is summarized in the Grüneisen parameters [236]. The magnitude of the shift of phonon frequencies with strain is proportional to the Grüneisen parameter ($\gamma$), if this is considered to the G band mode, which is the main Raman peak for boron nitride materials, the relation could be written as [2]:

$$\Delta \omega_G = -2 \gamma \omega_G^0 \epsilon$$  \hspace{1cm} (3.12)

where $\Delta \omega_G$ is frequency shift of G band mode, $\gamma$ is Grüneisen parameter of boron nitride (BN) and $\omega_G^0$ is the unstrained frequency of G band mode.

There are two methods, which have been adopted to apply strain to the boron nitride (BN) materials: a high pressure technique in a diamond anvil cell (DAC) and a heat treatment technique [285]. Using the high pressure method, Kuzuba et al. [284] studied hexagonal boron nitride (h-BN) powder pressurised in a diamond anvil cell (DAC) in range of 1 bar to 110 kbar at room temperature. They found the Raman frequencies of the h-BN modes (i.e. shear rigid layers (SRL) or the low frequency mode, and the intralayer (G band) or high frequency mode) were shifted to higher frequencies as the pressure increased. The mean shifts of the low frequency (SRL) and the intralayer (G band) modes were 0.5 cm$^{-1}$/kbar (i.e. 5 cm$^{-1}$/GPa) and 0.4 cm$^{-1}$/kbar (i.e. 4 cm$^{-1}$/GPa) respectively.
Figure 3.8: (a) Phonons energy (frequency) of the shear type and G band modes of hexagonal boron nitride (h-BN) vs. pressure [284]. Raman G band peak frequency as a function of pressure are (b) for MWBNNTs and (c) for h-BN and the phase transition from h-BN to w-BN was noticed at $\sim$ 13 GPa in (c), where filled and open circles correspond to increasing and decreasing the pressure respectively [270].

In addition, Saha et al. [270] applied the same experimental technique of high pressure upto $\sim$ 12 GPa on hexagonal boron nitride (h-BN) and multi-walled boron nitride nanotubes (MWBNNTs) with diameters of 20-60 nm. They found that the frequency shift rates of G band mode with increasing the pressure for h-BN and MWBNNTs were 4.3 cm$^{-1}$/GPa and 4.2 cm$^{-1}$/GPa respectively, and there is a phase transition of boron nitride (BN) from hexagonal to wurtzite phase at $\sim$13 GPa as shown in Figure 3.8 (c).

In the other method, the thermal effect was used to induce strain based on the difference in thermal expansion coefficients between boron nitride (BN) materials and a substrate. Stenger et al. [252] reported atomically-thin hexagonal boron nitride (h-BN) flakes on a silicon (Si) substrate with a silica (SiO$_2$) layer of 90-300 nm in thickness, were heated up from 300 K to 680 K in a Linkam oven. When the h-BN flakes follow the thermal expansion of the substrate with increasing the temperature, the frequencies of the two Raman band modes were downshifted under this heating effect (i.e. tensile strain). The mean shifts of the Raman low and high frequencies of h-BN modes were found to be $-0.006$ cm$^{-1}$/K and $-0.023$ cm$^{-1}$/K.
respectively as in Figure 3.9 (a). Moreover, Lu et al. [263] carried out the heating treatment method on hexagonal boron nitride (h-BN) and bamboo-like multi-walled boron nitride nanotubes (MWBNNTs) with diameters ranging from tens to hundreds of nanometers. Comparing to that of hexagonal boron nitride (h-BN) at the same temperature, they found the Raman peak of the E\textsubscript{2g} mode of BNNTs to be downshifted with increasing temperature from 400 K to 800 K due to the elongation of the B–N bond in BNNTs structures. The mean shifts in frequencies of the G band modes were -0.01 cm\textsuperscript{-1}/K for BNNTs and -0.014 cm\textsuperscript{-1}/K for h-BN. In addition, Arutyunyan et al. [286] found a mean frequency shift of Raman G band mode of single walled boron nitride nanotubes (SWBNNTs) with increasing temperature to be -0.027 cm\textsuperscript{-1}/K.

Figure 3.9: (a) Raman peak frequencies as a function of temperature for the shear type and G band modes of hexagonal boron nitride (h-BN) [252]. (b) The frequency shift of E\textsubscript{2g} mode for multi walled boron nitride nanotubes (MWBNNTs) as function of temperature [263]. (c) Raman peak position of G band mode for 1-3L boron nitride (BN) before and after heat treatment, where Raman peaks upshifted to higher frequencies after heating effect due to biaxial compressive strain in the nanosheets during the cooling down stage [2].

In contrast, the heating effect causes the upshifted G band mode of boron nitride nanosheets (BNNSs) due to strain induced by the substrate (i.e. roughness). Cai et al. [2] experimentally modified the level of strain in atomically thin boron nitride (BN) (i.e. 1-3L) on SiO\textsubscript{2}/Si
substrate via heat treatment, which can further increase the corrugation between BN and SiO$_2$ layers and hence strain in atomically thin BN layers. Boron nitride nanosheets (BNNSs) were heated up to 400 °C in argon (Ar) gas for 1 h, and the Raman G band frequencies of the 1–3L BN were upshifted after the heat treatment due to increasing the biaxial compressive strain in the nanosheets, while SiO$_2$ contracted during the cooling down stage. Figure 3.9 (c) shows the corresponding Raman G band peaks of 1-3L BN before and after the heat treatment with upshifts of 3 cm$^{-1}$, 2.7 cm$^{-1}$ and 2.2 cm$^{-1}$ respectively.
Chapter 4: Materials and Experimental Techniques

4.1 Materials

1. Hexagonal boron nitride, h-BN, as single crystals with ~ 1mm long flake and purity of 99.99% from HQ Graphene.
2. Boron nitride, BN, in powder form (i.e. single crystal platelet), from Momentive, with particle size of ~ 45 µm, surface area 0.6 m²/g and density 0.7 g/cm³.
3. Silicon dioxide, SiO₂, in powder form, from Sigma-Aldrich, with purity ≥99.995% and density 2.6 g/mL at 25 °C.
4. Aluminium oxide, Al₂O₃, in powder form, from Sigma-Aldrich, with purity ≥98%.
5. Sodium carbonate, Na₂CO₃, in powder form, from Sigma-Aldrich, with purity ≥99.0% and melting point at 851 °C.
6. Potassium carbonate, K₂CO₃, in powder form, from Sigma-Aldrich, with purity ≥99.0% and melting point at 891 °C.
7. Boron trioxide, B₂O₃, in powder form, from Sigma-Aldrich, with purity 99.98% and melting point at 450 °C.
8. Lead oxide, PbO, in powder form, from Sigma-Aldrich, with purity ≥99.0% and melting point at 886 °C.
9. Three samples, boron nitride nanosheets (BNNS) pure film, 1 wt% and 2.5 wt% BNNS borosilicate composites, were received from the Materials Research Institute, Queen Mary University of London to study by Raman spectroscopy. Boron nitride nanosheets BNNSs was prepared by liquid exfoliation method and the composites were fabricated by using spark plasma sintering (SPS) [214].
10. Boron nitride nanotubes (BNNTs) in a circular form of buckypaper with ~ 3.5 cm in diameters and 50 – 80 µm in thickness from National Research Council Canada [143].

4.2 Characterisation techniques of the boron nitride materials

4.2.1 Optical Microscopy
Optical microscopy is very useful tool for identifying the number of layers in nanomaterials systems. For example, the optical contrast has been employed to identify the number of
graphene layers on various substrates [287-289]. However, the situation is different in the case of boron nitride (BN) materials and it is much harder to find boron nitride than graphene monolayers by optical microscopy since BN materials have a wide band gap [88, 164]. The number of BN layers could be obtained by optical microscopy with special requirements such as using SiO₂/Si substrate with 80 nm thickness of SiO₂ layer and optical filters (e.g. green filter) [88]. (See section 2.4.1 of optical properties of boron nitride).

In this project, Axio Imager Pol optical microscopy was used, and optical images have been taken by AxioCam ICc5 ZEISS camera with 10×, 20×, 50× and 100× objective lenses. Figure 4.1 illustrates the optical microscope with the camera and the parts of the microscope with one of the possible light path. Moreover, all Raman spectrometer systems are equipped with optical microscopes, which may be used to take optical images as well as its utilization to focus the laser beam.

![Figure 4.1: The Axio Imager Pol optical microscope with the AxioCam ICc5 ZEISS camera and the parts of the microscope with one of the possible light path [290].](image-url)
4.2.2 Electron Microscopy (SEM and TEM)
In addition to optical microscopy (OM), electron microscopy (EM) techniques (i.e. scanning electron microscopy (SEM) and transmission electron microscopy (TEM)) were employed for analysis of boron nitride (BN) materials structures. Previously, SEM and TEM with high resolution have been used for boron nitride (BN) nanomaterials to investigate the local atomic arrangement, atomic packing, number of layers and elemental identification …etc. [63, 116, 266, 291, 292].

As in the optical microscopy where a light beam is used to generate the sample images, a beam of electrons is used with a set of magnetic lenses in a vacuum system to create the structural image of the sample in the electron microscopy (EM) [293]. Figure 4.2 shows a comparison between optical and electron microscopes, and due to the short electron wavelength, EM has superior resolution compared to optical microscopy.

The field emission gun (FEG) is typically used to generate a beam of electrons depending on the quantum tunnelling effect, where electrons in the conduction band of the surface of a metal can cross the surface potential barrier when a very high electric field is applied, in order of $\sim 10^{10}$ V/m [294]. Figure 4.3 (a) shows the biasing circuit for a thermal field-emission electron gun. Moreover, magnetic lenses play the most important in the electron microscopy role to control, deflect and focus the electronic beam to form the image.

The TEM specimen must be very thin to allow the electrons beam to penetrate it, while in the SEM, the specimen could be thick and when it scanned by electron beam, it displays many types of interaction effects such as electron scattering (elastic and inelastic scattered), Auger electron emission, photon emission (x-ray and optics) and electron absorption. Each of these effects can be used to provide suitable measurements by amplified the output of the selected detector into an electrical signal processes. (See Figure 4.3 (b)).

In this project, Titan ChemiS TEM system, Philips XL30 FEGSEM and Quanta SEM system were used to obtain images of boron nitride (BN) materials sample. Because hexagonal boron nitride (h-BN) is an electrical insulator, charging of the BN materials was a major problem which could distort the SEM image. To minimize these charging effects, samples were coated with a thin metal layer ($\sim 10$ nm of Pd) before SEM analysis.
Figure 4.2: Differences between Light Microscope and Transmission and Scanning Electron Microscopes (i.e. TEM and SEM) [295].

Figure 4.3: (a) The biasing circuit for a thermal field-emission electron gun [296]. (b) types of interaction between electron beam and the specimen in the scanning electron microscopy (SEM).
4.2.3 Raman Spectroscopy
Raman spectroscopy is the main instrument used in this project and its principle is already presented in chapter 3. Raman spectra were collected using Renishaw 1000/2000 Raman spectrometer systems with Olympus BH-2 microscope and by Horiba LabRAM HR Evolution Raman spectrometer, both with a backscattering geometry. A schematic diagram of the Renishaw Raman instrument is shown in Figure 4.4. Different laser sources with wavelength $\lambda = 488$, 514.5, 633 or 785 nm were used and the spot size of the laser beams on the samples was about 1-2 µm when 50x objective lens was used. The exposure times were 60 s or 30 s with 20, 10, 5 or 3 accumulations. The polarization of incident laser beams was always parallel to the x-axis, or parallel to strain axis when the four-point bending setups were used.

![Figure 4.4: Schematic diagram of the Renishaw Raman spectrometer, the laser source is not shown here.](image)

4.2.4 Atomic Force Microscopy (AFM)
Atomic Force Microscopy (AFM) is not only a useful tool to investigate the structure of thin boron nitride (BN) materials but also, it can be used to estimate the layer number of boron nitride flakes, where the step height of a BN monolayer considered to be ~ 0.4 nm [88, 297]. In addition, mechanical properties of boron nitride nanomaterials were measured using the atomic force microscope (AFM) [106, 190, 192] (See section 2.4.2).

The AFM consists of a cantilever with a tip. When the tip is brought close proximity to a sample surface, a force between the tip and the sample leads to a deflection of the cantilever according to Hooke's law, and this deflection is measured by using a laser spot reflected from
the top of the cantilever as shown in Figure 4.5 [298]. The tip is then scanned across the sample surface and the vertical displacement is recorded. The resulting map of (x,y) surface represents the topography of the sample.

Figure 4.5: Schematic diagram showing the principle working of the atomic force microscopy (AFM) [298].

In this project, atomic force microscope (AFM) images were obtained from the surfaces of boron nitride nanosheets (BNNSs) by using a Bruker Dimension 3100 AFM in the tapping mode with Bruker TESPA probes.

4.2.5 X-ray diffraction (XRD)
X-ray diffraction (XRD) technique is one of the best known methods to determine the structure of crystalline materials. This technique relies on Bragg’s law for diffraction of x-rays, where atomic plans (i.e. layers) in the crystals act as reflecting plans when the X-rays passing through a crystalline material [299]. X-ray diffraction results from the scattering interaction between X-ray photons and electrons of atoms and the arising of the intensity in the XRD pattern comes from the reflections of separate X-ray waves by electron density of atoms in parallel plans [300]. In fact, constructive interface between scattered waves occurs when the path difference between two reflected rays from successive plans differs by a whole.
number of wavelengths otherwise destructive interface will occur. This condition is described by Bragg’s law as:

\[ n\lambda = 2d \sin \theta \quad \text{and} \quad n = 1, 2, 3 \ldots \]  

(4.1)

where \( n \) is diffraction order, \( \lambda \) is wavelength of incident X-ray beam, \( d \) is interlayer spacing between a set of lattice planes and \( \theta \) is the angle between the incident wave and the lattice plane.

![Figure 4.6: schematic drawing for the principal of X-ray diffraction techniques [300] with illustration of the in phase reflection of waves 1 and 2 from two parallel atomic planes in a crystal structure. The difference in path between wave 1 and wave 2 is CB+BD, or \( 2d \sin \theta \).](image)

Lattice planes are indicated by Miller indices \((hkl)\), so, d-spacing for \((hkl)\) planes is given as:

\[ d_{hkl} = \frac{\lambda}{2 \sin \theta_{hkl}} \]  

(4.2)

For hexagonal lattice, the relation between d-spacing and lattice parameters is given by:

\[ \frac{1}{d_{hkl}^2} = \left[ \frac{4}{3} \left( \frac{h^2 + k^2 + hl}{a^2} \right) + \frac{l^2}{c^2} \right] \]  

(4.3)

where \( a \) and \( c \) are the hexagonal lattice parameters.

In this study, XRD patterns were collected using a Shimadzu-Lab XRD-6100 X-ray diffractometer with X-ray tube of CuK\(_{\alpha1}\) (i.e \( \lambda = 1.54 \) Å) running by voltage of 40 kV and current of 30 mA. The scan range of \( 2\theta \) is 20° – 90° with a step size of 0.2°. XRD patterns were measured for BN powder and BNNT buckypaper. The specimen of BNNT buckypaper was placed on glass substrate for XRD.
4.3 Sample fabrication

4.3.1 Mechanical cleavage
In this technique, a surface of about ~ 20 cm length of Scotch tape was coated with exfoliated hexagonal boron nitride (h-BN) flakes.

Two pieces of the tape with length of ~ 15 cm were used, where one of them was fixed on a table surface, and the sticking surface of this tape facing upwards. Then, by using a tweezer, a h-BN crystal was placed in the middle side of the fixed piece of the tape. To cleave the h-BN crystal, the other piece of the tape was used, and the sticking surfaces of the two tape pieces faced each other, where the side of the top piece faced the opposite corresponding side of the fixed tape. For example, from a horizontal view, the upper side of the top piece faced the lower side of the fixed tape. When the top tape was pulled off, the primary h-BN crystal cleaved into two h-BN crystals, one placed on the fixed tape and the other one on the top piece. After that, the two cleaved h-BN crystals were positioned next to each other along the width of fixed tape, and by repeating cleaved process, two lines of cleaved h-BN crystals over the middle of the two tape pieces were obtained.

![Figure 4.7: Schematic representation of the standard procedure of mechanical cleavage technique for hexagonal boron nitride (h-BN) crystals [54].](image)

Thereafter, by placing the side to its corresponding side of the two tape pieces, the two lines of cleaved h-BN crystals were shifted in order to obtain two lines of cleaved crystals in each fixed and top pieces of the tape, when the top tape was pulled off. By repeating this process for a few times, about 10 cm length surfaces of the fixed and top tapes were coated by the cleaved h-BN crystals to end with a total surface of 20 cm in length coated by thin cleaved h-BN flakes as shown in Figure 4.8.

In addition, the mechanical exfoliation via shear forces was applied to the buckypaper of boron nitride nanotubes (BNNTs) with original thickness in range of ~ 50 - 80 µm. The
BNNT buckypaper was sheared to reduce its thickness by spreading over a large area. A small piece cut from the BNNT buckypaper, and placed on the middle of a PMMA beam. Then, another PMMA beam was placed on top of the former one, where the BNNTs were sandwiched in between the two PMMA beams. To start the exfoliation process, the two PMMA beams need to move against each other by applying shear forces with maintain the surfaces of the two beams in touching state during the process. By repeating this process for few times, the surfaces of the two beams were coated by BNNTs, when the top PMMA beam was taken off. A thin layer of BNNTs can be transferred to a clean PMMA beam for Raman measurement by just applying this beam on top of one of those beams with coated BNNTs.

Figure 4.8: A single crystal of h-BN was coated on the surface of Scotch tape by repeated mechanical cleavage technique.

Figure 4.9: Schematic diagram for exfoliation process of the boron nitride nanotubes (BNNTs).
### 4.3.2 Liquid Exfoliation

Liquid exfoliation method was used to synthesise boron nitride nanosheets (BNNSs) from hexagonal boron nitride (h-BN) polycrystals (i.e. from Momentive with particle size of ~ 45 µm). A mixture of deionised water and ethanol was used as a solvent for liquid-phase exfoliation of boron nitride (BN) powder. 100 - 200 mg of BN powder was added to ~ 100 ml of the solvent. Then, the mixture of BN and the solvent was subjected to a sonication tip with a pulsed mode for about 1 h, where the amplitude is in range of ~ 10 - 50 and the time was set as 10 s ON and 10 s OFF. To control the sample temperature, an ice bath was used during the sonication process. Thereafter, the samples were placed in sonication bath for ~ 24 h in a low power, followed by centrifugation for ~3 h with speed of 5000 rpm at room temperature. The supernatant was collected from the centrifuged dispersions, and the solutions obtained were used for AFM, TEM and SEM as well as for the preparation of composites.

In addition, boron nitride nanotubes (BNNTs) were dispersed in ethanol, which were used as solvents. A magnetic stirring technique was used for 10 - 15 min at temperatures of ~ 50 – 60 °C, followed by a sonication bath in a low power for 20 - 30 min. The solution obtained was used for TEM as well as for the preparation of composites.

![Image of dispersed solutions](image.png)

**Figure 4.10: Three samples of dispersed solutions for boron nitride nanostructures, boron nitride nanosheets (BNNSs) and boron nitride nanotubes (BNNTs).**
4.3.3 Glass matrices and BN/glass composites

For boron nitride (BN)/glass composites, two glass matrices were prepared by using the composition of materials: SiO$_2$, Al$_2$O$_3$, Na$_2$O, K$_2$O, PbO and B$_2$O$_3$ as in Table 4.1. The quantities of Na$_2$O and K$_2$O were calculated according to the following reactions:

\[ \text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{O} + \text{CO}_2 \quad \text{and} \quad \text{K}_2\text{CO}_3 \rightarrow \text{K}_2\text{O} + \text{CO}_2 \]

Table 4.1: The compositions of materials for the matrix of h-BN/glass composites.

<table>
<thead>
<tr>
<th>Glass identification (wt%)</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>B$_2$O$_3$</th>
<th>PbO</th>
<th>Working point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead glass (I)</td>
<td>55</td>
<td>1</td>
<td>8</td>
<td>14</td>
<td>-</td>
<td>22</td>
<td>~ 950</td>
</tr>
<tr>
<td>Lead glass (II)</td>
<td>3</td>
<td>11</td>
<td>-</td>
<td>-</td>
<td>12</td>
<td>74</td>
<td>~ 650</td>
</tr>
</tbody>
</table>

For the glass matrices, the raw materials were mixed for 24 hours in a planetary ball milling using plastic bottles with alcohol (Propanol) as medium and zirconia balls. Then, the slurries were dried in an oven at 85°C for 24 hours. After that, the mixtures were placed in alumina crucibles inside an electric furnace. The mixtures of glass (I) and glass (II) heated rapidly and separately up to 1000 °C and 700 °C respectively for 1.5 h, for melting. Once the melting was complete, the crucible was removed from the furnace and the molten glass was poured into cold distilled water. It was then dried and ground in a mortar.

For the BN/glass composites, hexagonal boron nitride (h-BN) powder, boron nitride nanosheets (BNNSs) and boron nitride nanotubes (BNNTs) were used as fillers to prepare the glass based composites (i.e. four types of BN glass composites) as (1) h-BN/glass (I) composite, (2) h-BN/glass (II) composite, (3) BNNS/glass (II) composite and (4) BNNT/glass (II) composite.

To prepare the h-BN/glass (I) composite, hexagonal boron nitride (h-BN) powder was added to the glass matrix (I) and mixed for 24 hours in a planetary ball milling using plastic bottle with alcohol (Propanol) as medium and zirconia balls, then, dried in an oven at 85°C for 24 hours. Thereafter, the mixture was pressed in a disk shape before it placed in the furnace for sintering and heated up to 600 °C for 1h at a rate of 5 °C/min from room temperature and cooled down to room temperature with the same rate. Figure 4.11 illustrates a diagram for preparation procedures of glass matrices and BN/glass composites.
Figure 4.11: A diagram of the experimental procedure for fabrication of BN/glass composites.
To prepare BN/glass (II) composites, hexagonal boron nitride (h-BN) powder, boron nitride nanosheets (BNNSs) and boron nitride nanotubes (BNNTs) were added separately to the glass (II) powder and mix with ethanol as medium, and then placed in sonication bath for 15 min in a low power. Then, the samples transferred to the magnetic stirring device and mixed for 24 h at ~ 60 ºC. After that, they were dried in an oven at 80 ºC for 48 h. Then, each mixture was pressed into a disk shape before it being placed in the furnace for sintering, then heated up to 400 - 450 ºC for 0.5 h with rate of 5 ºC/min from room temperature and cooled down to room temperature at the same rate.

### 4.4 Experimental Procedure for the Deformation of BN materials

For deformation analysis, exfoliated hexagonal boron nitride (h-BN) flake was obtained by mechanical cleavage method, and transferred to a PMMA beam as shown in Figure 4.12.

![Image of exfoliated h-BN flake on PMMA beam](image)

**Figure 4.12:** An optical image of exfoliated h-BN flake with two regions (i.e. thick (Δ) and thin (□)) on a PMMA beam with a strain gauge, which attached parallel to the beam axis. Arrows indicate the direction of tensile strain in the deformation experiments.

Moreover, boron nitride nanotubes (BNNTs) were exfoliated via shear forces from the buckypaper, and transferred to a PMMA beam as well. Furthermore, boron nitride (BN)/glass composites samples were disk shape. Each sample disk was attached to a PMMA beam as in Figure 4.13. Then, the disks were carefully polished down with checking after each step of the polishing process by optical microscope to end with a thin film of BN/glass composites on the surface of the beam.
Figure 4.13: A boron nitride (BN)/ glass composite disk, when it was attached to the PMMA beam before the polishing process.

In addition, strain gauges were attached to the surface of the PMMA beams and to be parallel to the beam axis as in Figure 4.12. By connecting the strain gauge to a multimeter, the applied strain ($\varepsilon$) could be calculated as:

$$\varepsilon = \frac{\Delta R}{S_G R^*} \quad \text{and} \quad \Delta R = R_1 - R^*$$  \hspace{1cm} (4.4)

where $R^*$ is the strain gauge resistance without loading, $R_1$ is the strain resistance with loading and $S_G$ is the strain factor.

The deformation processes for boron nitride (BN) samples were carried out by employing a four-point bending rig, which consists of four bars as in Figure 4.14. Two bars are fixed whereas the other two bars can be adjusted up and down by turning the load screw, and the rise of the bending force is derived from opposite movements of the two pair bars.

By placing the four-point bending rig with BN specimens on the PMMA beams in the Raman spectroscopy instruments, Raman spectra were collected at each step of loading when the BN specimens under tensile strain, and the strain gauge resistances were recorded as well. The Raman spectra of BN samples were curve-fitted by OriginPro 8.1 software with using a Lorentzian function to determine the information of the Raman bands. The shifts in the position of Raman G band peak for boron nitride (BN) samples were then plotted as a function of applied strain.
Figure 4.14: shows the setup of four-point bending rig where the BN specimen was placed between the fixed and adjusted bars in tension case and the up and down arrows indicates the opposite movements of the bars.

It should be notice that the PMMA beams must be cleaned before the BN specimens are placed. This is due to raising the adhesion between the BN samples and the surface of the PMMA beams as the contaminations may prevent such interaction between the surfaces of the sample and the beam.

One may suggest that to clean the PMMA beams, PMMA beams clean manually from any small residual pieces due to cutting process. Ethanol could be used as a medium when the PMMA beams were placed in the sonication bath with high power for 10 – 15 min. Then, dry the beams in an oven at 60°C – 70°C for 1 h.
Chapter 5: Characterisation of Hexagonal Boron nitride (h-BN) materials

5.1 Introduction
In this chapter, there are three forms of hexagonal boron nitride (h-BN), which have been used in this project. Single crystal of h-BN, boron nitride powder and boron nitride nanotube buckypaper are characterised by different research tools such as optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), X-ray diffraction (XRD) and Raman spectroscopy.

5.2 Single crystal of hexagonal boron nitride (h-BN) and exfoliated h-BN flakes
Single crystals of hexagonal boron nitride (h-BN) were used in process of mechanical cleavage to obtain atomically thin boron nitride flakes. Then, BN flakes were transferred to SiO$_2$/Si or PMMA substrates for characterisation.

5.2.1 Optical microscopy
Optical images of a single crystal of hexagonal boron nitride (h-BN) are shown in Figure 5.1 (a) and (b). The BN crystals have a lateral size in range of a couple millimetres.

![Figure 5.1: Optical images of a single crystal of hexagonal boron nitride (h-BN). (a) The top view of the BN single crystal and (b) its edge.](a) The optical contrast of BN materials increases proportionally as the number of layers increases [88]. Therefore, when white light is used, thin BN flakes tend to be transparent whereas thick BN flakes appear in white colour. (See Figure 5.2 and Figure 5.3).
A hexagonal boron nitride (h-BN) flake was exfoliated from the BN single crystal and successfully deposited on the surface of PMMA beam. Two regions of the exfoliated h-BN flake were chosen for Raman measurements under tensile strain. These two regions are indicated in Figure 5.2 (c).

Figure 5.3 shows an optical image of hexagonal boron nitride flakes with different thick and thin regions on different substrates (i.e. SiO$_2$/Si in (a) and PMMA beam in (b)). Furthermore optical microscopes are fitted with useful features such as bright and dark fields of illumination. Despite of bright-field illumination benefits, dark-field illumination was more effective to identify the thin regions boundary of hexagonal boron nitride (h-BN) flakes as shown in Figure 5.3 (c and d).

**Figure 5.2**: Optical images of h-BN flakes. (a) Thin BN flakes, (b) thin and thick BN flakes and (c) a long BN flake with thin and thick regions. They were exfoliated from a signals crystal of hexagonal boron nitride and transferred to PMMA beams as substrates and the BN flakes have different thickness, where thick flakes appear in white colour while thin flake tend to be transparent.
Figure 5.3: Optical micrographs of hexagonal boron nitride (h-BN) flakes on SiO2/Si substrate in (a) which illustrates the white appearance in thick region and transparency in thin region, and on a PMMA beam in (b). (c) and (d) are a h-BN flake with bright and dark fields of illumination respectively.

5.2.2 Raman spectroscopy
A typical Raman spectrum in range of 200-2000 cm\(^{-1}\) for bulk h-BN from the single crystal is shown in Figure 5.4, where the Raman peak is related to E\(_{2g}\) phonon mode and it occurs at 1366.6 cm\(^{-1}\) with full width at high maximum (FWHM) of 8.1 cm\(^{-1}\).

Figure 5.4: A typical Raman spectrum of hexagonal boron nitride (h-BN) in range of 200-2000 cm\(^{-1}\), and the G band peak at position of 1366.6 cm\(^{-1}\) with full width at high maximum (FWHM) of 8.1 cm\(^{-1}\).
5.3 Boron nitride (BN) powder and exfoliated BN sheets

Boron nitride (BN) powder has a particle size of ~ 45 µm in average and a hexagonal structure of single crystal platelets. Also, boron nitride sheets were exfoliated from BN powder by liquid exfoliation process. Both BN powder and BN sheets were used as fillers in a glass matrix of BN/glass composites. Characterisation of BN powder and BN sheets are presented in this section.

5.3.1 X-ray diffraction (XRD)

The X-ray diffraction (XRD) technique shows that the BN powder has a hexagonal BN structure (JPDCS No. 45–895) [301]. The resulting XRD pattern including peaks for hexagonal boron nitride is shown in Figure 5.5. This XRD pattern is dominated by a (002) peak, which related to X-ray photon reflections by the basal plans in the hexagonal crystal lattice of boron nitride.

![XRD pattern of boron nitride (BN) powder](image)

*Figure 5.5: An XRD pattern of boron nitride (BN) powder. The scattering angle (2θ) is plotted in degrees from 20° to 90°. The (002) peak is located at 26.5° in the XRD pattern.*

From Equation (4.2) and Equation (4.3), the lattice parameters have been calculated to be $a = 2.5 \, \text{Å}$ and $c = 6.7 \, \text{Å}$ with interlayer spacing of $d = 3.3 \, \text{Å}$. These lattice parameters are in good agreement with those in the Table 2.1.
5.3.2 Scanning electron microscopy (SEM)

The morphologies of the original BN powder and exfoliated BN sheets were studied using SEM. As shown in Figure 5.6, SEM images show BN powder structure with a particle size of ~ 45 µm in average and some of BN flakes are stacked together. BN flakes have a thickness in range of ~ 2 - 4 µm as in the lower inset. Moreover, a twined structure has been noticed in the BN powder sample and this phenomenon has been also observed in the carbon systems [302, 303]. However, lower lattice symmetry and binary composition of h-BN make the situation to be quite different than that of carbon system [304]. First, determination of edge energy for h-BN islands is complicated due to the lack of inversion symmetry in h-BN, which leads to a richer variety of its edges. Second, the chemical potential balance between B and N adds extra degree of freedom to h-BN growth. Third, the possibilities for atom accretion sequences in the h-BN lattice growth are broadened due to having two chemical constituents.

![SEM image of hexagonal boron nitride (h-BN) powder with particle size of ~ 45µm. The edge of h-BN flake with thickness of ~ 3 µm in the lower inset. The arrows show the twined structure of h-BN as well as in the upper inset with an angle of ~ 58°. The scale bars are 20 µm and 50 µm in the upper and lower insets respectively.](image-url)
The grain boundaries of twined BN structure are demonstrated by arrows in Figure 5.6 and as example for twin BN crystals with an angle between them of ~ 58° is shown in the upper inset.

After the exfoliation process, crystals much thinner and smaller than their precursor BN nanosheets (BNNSs) were observed in Figure 5.7. One may see the lateral size of BNNSs varies but it may be in range of ~ 2 - 6 µm. Hence, the sonication process is able to peel off BNNSs from BN particles due to interactions between BN particle surfaces and solvent molecules. It should be noticed that atomically thin nanosheets tend to corrugate or ripple, and this has been observed in graphene [305, 306]. In Figure 5.7, an SEM image of Boron nitride nanosheets (BNNSs) shows some flakes with wrinkles.

Compared to unexfoliated particles, not only the particle thicknesses are reduced, but also the lateral sizes of BN sheets become smaller. This indicates that the sonication process can peel off a BN nanosheet from some defective areas of precursor BN particles [3].

![Figure 5.7: An SEM image of exfoliated boron nitride nanosheets (BNNSs) produced by a liquid exfoliation method.](image)
5.3.3 Transmission electron microscopy (TEM)

TEM images of exfoliated boron nitride nanosheets (BNNSs) with corresponding electron diffraction pattern are shown in Figure 5.8. The overlapping BN sheets are observed with small lateral size and uneven edges, which may result from hard sonication conditions. The edge of a BN sheet was investigated and was less than 3 nm thick or fewer than 10 in layer number as shown in the inset.

![TEM image of exfoliated boron nitride nanosheets (BNNSs) with corresponding electron diffraction pattern. An uneven edge of a BN sheet with a thickness of ~ 2.7 nm in the inset and the scale bar is 20 nm.](image)

5.3.4 Atomic force microscopy (AFM)

AFM images with corresponding thickness profiles on SiO₂/Si wafer for boron nitride nanosheets (BNNSs) are shown in Figure 5.9 (a) and (b). From height profiles in Figure 5.9 (c) and (d), the thickness of BNNSs was in range of 3 - 5 nm, corresponding to ~ 7 – 12 atomic layers. Although, the layer numbers can be estimated from the step height information, it should be noted that the underlying contamination between the BNNSs and the SiO₂ substrate can often increase the thickness of the BN nanosheets [62]. Typically,
monolayers of BNNSs on top of an oxidised Si wafer after mechanical exfoliation have a step height of \( \sim 0.4 \text{ nm} \) \[88\]. However, for liquid-exfoliated nanosheets, the trapped solvent molecules between the monolayer BNNS and the underlying substrate might make its AFM step height close to \( \sim 1 \text{ nm} \) \[62\]. Therefore, the layer number estimation from AFM step height measurements should take into account the methods for obtaining the BNNSs and preferably should be confirmed with other techniques such as TEM. Additionally, thin BN nanosheets confirmed in an AFM image with a 3D view are illustrated in Figure 5.9 (e).

Figure 5.9: AFM images of boron nitride nanosheets (BNNSs) on SiO\(_2\)/Si substrates in (a) and (b), with height profiles in (c) and (d) corresponding to the indicated lines in (a) and (b) respectively. (e) A 3D image of boron nitride nanosheets (BNNSs) on the SiO\(_2\)/Si substrate (i.e. 10 x 10 \( \mu \text{m} \)).

### 5.3.5 Optical microscopy

Individual hexagonal boron nitride (h-BN) flakes obtained from BN powder on a glass slide are shown optically in Figure 5.10. These h-BN flakes demonstrate the platelet shape of the flakes in the BN powder sample with a variety of flake sizes. Some of the h-BN flakes may have a lateral size of \( \sim 60 \mu \text{m} \), although the average of particle size in BN powder is 45 \( \mu \text{m} \) as shown in SEM images.

Figure 5.11 illustrates an optical view for a film of boron nitride nanosheets (BNNSs) prepared by liquid exfoliation technique as coated on a paper filter.
Figure 5.10: An optical image of individual hexagonal boron nitride (h-BN) flakes with a variation in shape and size on a glass slide as a substrate.

Figure 5.11: An optical image of pure boron nitride nanosheets (BNNSs) film with BNNS rich regions indicated by arrows (i.e. using a 10x objective lens).
5.3.6 Raman spectroscopy

From the largest h-BN flake in Figure 5.10, Raman spectrum was collected and the G band peak positions is at 1366.15 cm\(^{-1}\) with full width at high maximum (FWHM) of 8.8 cm\(^{-1}\) as shown in Figure 5.12. One can see the similarity between this spectrum and that one collected from single crystal h-BN as seen in Figure 5.4.

In Figure 5.13, several Raman spectra of boron nitride nanosheets (BNNSs) were collected from (a) BNNSs on a SiO\(_2\)/Si substrate showing a G band peak position at ~ 1367.5 cm\(^{-1}\) and (b) BNNS film on a paper-filter substrate showing a G band peak position at ~ 1365.1 cm\(^{-1}\). The Raman spectra of BNNS film were collected from different points in the same sample whereas Raman spectra of BNNSs were obtained from the same point with multi-measurements.

The G band peak of boron nitride can be fitted using a Lorentzian peak function. Raman peak analysis for BNNS is shown in Figure 5.14, where the BN peak located at 1367.6 cm\(^{-1}\) with FWHM of 16.1 cm\(^{-1}\). G band peak position is upshifted comparing to the bulk peak position, and this could be due to different degree of corrugation.

![Raman spectrum](image)

*Figure 5.12: Raman spectrum of hexagonal boron nitride (h-BN), which collected from a large individual h-BN flake. The peak of Raman G band mode positions at 1366.15 cm\(^{-1}\) with FWHM of 8.8 cm\(^{-1}\).*

106
Figure 5.13: (a) Several Raman spectra of boron nitride nanosheets on SiO$_2$/Si substrate. The G band peak position is located at ~1367.5 cm$^{-1}$. (b) Raman spectra taken from boron nitride nanosheets (BNNSs) film.
5.4 Boron nitride nanotube buckypaper and exfoliated BNNTs

Boron nitride nanotubes (BNNTs) were received as circular sheets with 3.5 cm in diameter and ~ 60 μm thick, known as BNNT buckypaper. Its thickness prevents a use of BNNT buckypaper in deformation experiments. So, boron nitride nanotubes were obtained from BNNT buckypaper using (i) a dry shear-force exfoliation to reduce its thickness or (ii) in droplets from a dispersion of BNNT in ethanol using an ultrasonic bath and magnetic stirring. Thus, characterisation of BNNT buckypaper and exfoliated BNNTs are presented in this section.

5.4.1 Scanning electron microscopy (SEM)

Boron nitride nanotubes (BNNTs) were in form of buckypapers. Low-magnification and high-magnification SEM images of a BNNT buckypaper surface are shown in Figure 5.15. Also, the inset shows the boron nitride nanotubes (BNNTs) are formed in bundles and small
bundles may join together to build a large bundle. One can see that BNNT bundles have relatively long lengths in range of tens of micrometers.

Figure 5.15: SEM images of boron nitride nanotubes (BNNTs) taken from BNNTs buckypaper surface. The bundles of boron nitride nanotubes are in the inset and the scale bar is 2 µm.

5.4.2 Transmission electron microscopy (TEM)

TEM images of boron nitride nanotubes (BNNTs) are shown in Figure 5.16, where BNNTs were dispersed in ethanol, and droplets placed on a TEM carbon grid. Impurities of BN nanoparticles can be observed in the BNNT sample.

The upper inset shows an individual boron nitride nanotube (BNNT) with 3 – 4 walls, where the line indicates its outer diameter of ~ 4.6 nm and the inner diameter is ~ 2.2 nm.

In addition, from TEM images, BNNTs have a multi-walled structure as it can be seen in the upper inset. BNNTs are also assembled in bundles of a few nanotubes and the bundles structure of boron nitride nanotubes (BNNTs) can be seen in the lower inset.
Figure 5.16: TEM images of boron nitride nanotubes (BNNTs) with contamination of BN nanoparticles. A multi-walled (3 to 4 walls) BN nanotube with outer diameter of ~ 4.6 nm and inner diameter of ~ 2.2 nm is in the upper inset. BNNT bundles are in the lower inset. The scale bars are 10 nm and 20 nm in the upper and lower insets respectively.

5.4.3 X-ray diffraction (XRD)

The crystalline structure of the BNNTs was investigated by XRD, where BNNT buckypaper placed on glass slide before XRD pattern is obtained. The XRD profile of BNNT sample aside to the XRD profile of BN powder sample are shown in Figure 5.17. The main peaks corresponding to the crystalline phase of the hexagonal boron nitride (h-BN) have been observed in the XRD pattern of BNNTs. This confirmed that BNNTs have the hexagonal crystalline structure of boron nitride.

One can see other peaks in XRD pattern of BNNTs, which are not belonging to the hexagonal phase of boron nitride. Those peaks may come from the pure boron or its compounds like B$_2$O$_3$ as boron is usually used in the process of BNNT synthesis [141, 307]. It should be noticed that the XRD profiles are plotted as collected, so, the higher signal noise in the XDR pattern of BNNTs comes from using the glass substrate.
5.4.4 Optical microscopy

Boron nitride nanotubes (BNNTs) were exfoliated from BNNT buckypaper using mechanical exfoliation via shear forces, and deposited on a PMMA beam. Figure 5.18 illustrates an optical image for exfoliated boron nitride nanotubes (BNNTs) on the PMMA substrate. Deformation of these BNNTs under tensile strain is reported in chapter 8.

Figure 5.17: XRD profiles of boron nitride nanotubes with comparing between XRD pattern of BN powder and XRD pattern of BNNTs.

Figure 5.18: An optical image of exfoliated boron nitride nanotubes (BNNTs) on a PMMA substrate after the shear-force exfoliation of BNNT buckypaper.
5.4.5 Raman spectroscopy

Raman spectrum in range of 100 - 3200 cm\(^{-1}\) was collected from the BNNT buckypaper and the G band peak is clearly observed. Figure 5.19 shows the Raman spectrum of BNNTs aside to the Raman spectrum of bulk BN powder sample. One can see the G band peak of BNNTs is blue-shifted with comparison to bulk G band peak of boron nitride (BN) as in the inset.

Boron nitride nanotubes (BNNTs) on a SiO\(_2\)/Si substrate were examined by Raman spectroscopy as seen in Figure 5.20. Raman spectra were collected in range of 100-2000 cm\(^{-1}\) from (i) the SiO\(_2\)/Si substrate and (ii) a rich area of BNNTs. By comparing the two Raman spectra, only the G band peak has been observed for boron nitride nanotubes (BNNTs) as it can be seen in Figure 5.20 (a) and (b). Figure 5.20 (c) shows the peak fitting for the observed Raman peak of BNNTs and it is located at 1368 cm\(^{-1}\). An optical graph of boron nitride nanotubes (BNNTs) on the substrate was taken and presented in Figure 5.20 (d), where the arrow indicates the rich area of the BNNTs.

![Figure 5.19: Raman spectra of boron nitride nanotubes buckypaper (black line) compared with bulk boron nitride (BN) (red line). The inset shows the blue-shift of BNNTs Raman peak comparing to the bulk Raman peak.](image)

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112
Figure 5.20: (a) Raman spectra of (i) boron nitride nanotubes (BNNTs) and (ii) SiO$_2$/Si substrate. (b) The observed Raman peak of BNNTs. (c) The fitted Raman peak of BNNTs and the position of BNNTs Raman peak is at ~ 1368 cm$^{-1}$. (d) An optical image of BNNTs on the SiO$_2$/Si substrate and the Raman spectrum collected from the point where the BNNT arrow indicates.

The upshift of the Raman peak of boron nitride nanotubes compared to that of bulk boron nitride (at ~ 1365 cm$^{-1}$) has been also observed for single-walled BNNTs (~ 1370 cm$^{-1}$) [266] and multi-walled BNNTs (~ 1368.1 cm$^{-1}$) [269]. The G Raman band of boron nitride nanotubes is considered to be a composite signal of BNNT phonon modes due to the A$_g$ and E$_{2g}$ modes for armchair nanotubes or A$_1$ and E$_g$ modes for zigzag and chiral nanotubes [266]. Arenal et al. [266] considered the G band mode of single-walled BNNTs is intrinsic and blue-shifted compared to the h-BN E$_{2g}$ mode at 1365 cm$^{-1}$, because of the interaction of the neighbouring sheets in h-BN, where the interaction leads to a small elongation of the B-N bond length and consequently a softening of the phonon modes.

5.5 Summary

The single crystals of hexagonal boron nitride (h-BN) were used as a precursor for exfoliated h-BN flake with two regions (thick and thin), which was obtained using the mechanical cleavage method.
Boron nitride (BN) powder shows a high crystalline structure with a hexagonal lattice in the XRD pattern and Raman spectrum. The average of particle size is ~ 45 µm and the particles have a thickness of ~ 4 µm. Twin crystals were observed in the SEM images. BN powder was a precursor for boron nitride nanosheets (BNNSs). The BNNSs were obtained using the liquid exfoliation method. BNNSs have a lateral size of ~ 6 µm and thickness of ~ 4 nm corresponding to ~ 10 BN layers.

Boron nitride nanotube (BNNT) buckypaper was a precursor for exfoliated BNNTs. SEM and TEM show BNNTs are arranged in long bundles of nanotubes with small diameter (~ 5 nm) and ~ 4 walls.

Raman spectra show a peak of G band mode, which associated to the vibration mode of $E_{2g}$ phonons. The Raman peak frequency was observed for bulk BN at 1366 cm$^{-1}$, BNNSs at 1367 cm$^{-1}$ and BNNTS at 1368 cm$^{-1}$. 
Chapter 6: Deformation of Hexagonal Boron Nitride (h-BN)

6.1 Introduction

In this chapter, bulk boron nitride materials as single crystals of h-BN and BN powder were used to synthesise one specimen of an exfoliated h-BN flake with two regions (i.e. thick (Δ) and thin (□)) and two samples of h-BN/glass composites were deformed under tensile strain with in-situ Raman spectroscopy.

The exfoliated h-BN flake was obtained using mechanical cleavage of a single crystal of hexagonal boron nitride as demonstrated in Figure 5.2 (c). The thick (Δ) and thin (□) regions of exfoliated h-BN flake with deformation direction and experimental arrangement are illustrated in section 4.4.

Moreover, in the h-BN/glass composites, as-received BN powder was dispersed in glass (I) and glass (II) matrices using ball milling and magnetic stirring respectively. More details about fabrication of these samples are in section 4.3.3.

6.2 Exfoliated h-BN flakes

Raman spectrum of poly(methyl methacrylate) (PMMA) substrate is shown in Figure 6.1 as the exfoliation h-BN flake was placed on the surface of PMMA beam. The inset shows no PMMA peaks on the position of BN Raman peak and the two peaks of PMMA, where the BN Raman peak will appear in between them. Thus, Raman spectra were collected from the h-BN flake with no applied strain and under tensile strain. Figure 6.2 shows the Raman spectra of the h-BN flake without loading and under tensile strain of 0.6 %.

Figure 6.3 shows beak fitting for undeformed Raman spectrum and deformed Raman spectrum of exfoliated h-BN flake on the PMMA substrate. The BN Raman peak appears between the two peaks of PMMA beam. The position of G band peak was at 1365.7 cm\(^{-1}\) in the undeformed Raman spectrum, and at 1362 cm\(^{-1}\) in the deformed Raman spectrum of exfoliated h-BN flake at 0.6 % strain.

Raman measurements show the response of exfoliated h-BN flake to tensile strain, where the G band peak of BN is shifted to a lower frequency by 3.7 cm\(^{-1}\). Also, the Raman position of the two PMMA peaks shows a small change in frequencies.
Figure 6.1: Raman spectrum of poly(methyl methacrylate) (PMMA) substrate. PMMA Raman peaks around the position of the G band peak of BN materials in the inset.

Figure 6.2: Raman spectra of exfoliated h-BN flake on a PMMA beam, where the BN Raman peaks position with no strain at 1365.7 cm\(^{-1}\) (black line) and with 0.6% strain at 1362 cm\(^{-1}\) (red line).
Figure 6.3: Peak fitting for (a) the undeformed Raman spectrum and (b) the deformed Raman spectrum of an exfoliated h-BN flake on the PMMA substrate.
6.2.1 Thick region (\(\Delta\)) of the exfoliated h-BN flake

Raman spectra were collected from the thick region (\(\Delta\)) of the exfoliated h-BN flake, and the Raman shift of G band peaks was plotted as a function of strain in Figure 6.4. Up to three Raman measurements were taken at each step of tensile strain. By taking the average of the Raman measurements at each strain points, the average of G band peak positions versus strain is shown in Figure 6.5, where the error bars indicate the standard deviation of the measurements.

The unstrained Raman peak is located at \(~ 1366\ \text{cm}^{-1}\), which is close to bulk Raman peak position of the h-BN single crystal (See Figure 5.4). Afterwards, as the tensile strain was gradually increased, the Raman peak positions redshifted linearly (i.e. to lower frequencies) up to \(~ 0.3\ \%\) tensile strain with a shift rate of \(-4.2\ \text{cm}^{-1}/\%\) as shown in Figure 6.6.

One can notice the slippage behaviour of the hexagonal boron nitride (h-BN) flake in the thick region could be seen above a tensile strain of 0.3\% as shown in Figure 6.4.

![Figure 6.4: Change of BN Raman peaks positions with tensile strain, where at each point of strain, up to three Raman measurements at each points.](image-url)
Figure 6.5: The average of peak positions of BN G band mode vs. strain, where the unstrained BN peak positions at 1366 cm$^{-1}$. There is a decrease in BN Raman shifts as tensile strain is increased up to $\sim 0.3\%$. The error bars indicate the standard deviation of the measurements.

Figure 6.6: A linear fit of the average of BN peak positions with a range of tensile strain from zero to $\sim 0.3\%$, and the change rate in BN peak positions with strain was found to be $-4.2$ cm$^{-1}$/%.
6.2.2 Thin region (□) of the exfoliated h-BN flake

Raman spectra were collected from the thin region (□) of the exfoliated h-BN flake, and the Raman shift of G band peaks was plotted as a function of strain in Figure 6.7. Up to three Raman spectra were obtained at each step of tensile strain. By taking the average of the Raman measurements at each strain points, the average of G band peak positions versus strain is shown in Figure 6.8, where the error bars indicate the standard deviation of the measurements.

The unstrained Raman peak was located in average at ~ 1365.5 cm\(^{-1}\), which is less than that of bulk Raman peak position of the h-BN single crystal by ~ 1 cm\(^{-1}\) (See Figure 5.4). Thereafter, as the tensile strain is increased, the Raman peak positions are linearly redshifted (i.e. to lower frequencies) up to ~ 0.3 % strain with a shift rate of ~ 6.5 cm\(^{-1}\)/% as shown in Figure 6.9.

![Figure 6.7: Change of BN Raman peaks positions with tensile strain, where there are up to three measurements at each point of strain.](image)
Figure 6.8: The average peak positions of BN G band mode vs. strain, where the unstrained BN peak positions at ~ 1365.5 cm\(^{-1}\), and there is a decrease in BN Raman shifts as strain is increased up to ~ 0.3%. The error bars indicate the standard deviation of the measurements.

Figure 6.9: A linear fit of the average of BN peak positions with a range of strain from zero to 0.3%, and the change rate in BN peak positions with strain was found to – 6.5 cm\(^{-1}\)/%. 

121
6.3 h-BN/ glass based composites

In this section, BN powder particles were dispersed into two types of glass matrix (i.e. glass (I) and glass (II)) to synthesise h-BN/ glass (I) composites and h-BN/ glass (II) composites samples. The h-BN/glass composites formed in disk shapes and attached to PMMA beams as thin films (See section 4.3.3). These samples were deformed under tensile strain in-situ Raman spectroscopy. Raman spectrum of PMMA substrate is previously provided in Figure 6.1.

Raman peak intensity indicates information about concentration and distribution of different phases in a material [308]. In the Raman intensity map, numerous Raman spectra are collected from different location of the sample surface and the intensity data set made of I (x,y,υ), where x and y are the map image coordinates and υ is the wave number [309]. Thus, Raman intensity map for h-BN/glass composite samples is shown in Figure 6.10, where the red colour indicates the highest intensity of BN G band mode as in the scale bar. The Raman spectrum picked from the red area of the Raman map is shown in Figure 6.11. A clear Raman peak of BN G band mode is observed with some other peaks from PMMA substrate as the h-BN/glass composite specimen forms in a thin film on a PMMA beam.

Figure 6.10: Raman intensity map for h-BN/glass composite samples. The position of BN peak is at 1366 cm⁻¹ and the area is 12 µm x 12 µm. The scale bar is for the intensity in count unites from 1360 for a background noise (i.e. glass matrix and the PMMA substrate) to 5860 for the highest intensity.
Hexagonal boron nitride (h-BN) powder was used to synthesise h-BN/glass (I) composite sample and dispersed in the glass (I) matrix as shown in Figure 6.12, where the optical image was taken from the top surface of the h-BN/glass (I) composite disk. From optical contrast, one can see that the h-BN flakes were exfoliated during the mixing process by ball milling. In addition, the h-BN flakes are parallel to the disk surface of h-BN/glass composite.

Hexagonal boron nitride (h-BN) flakes in the glass (I) matrix were deformed under tensile strain. Raman spectra were collected at each step of strain and plotted in Figure 6.13. The peak positions of G band changes as function of strain as shown in Figure 6.14. The data was linearly fitted, and the shift rate was found to be -7.0 cm⁻¹/%. Moreover, the maximum redshift in the frequency of G band peak was observed with ~ 0.2% tensile strain. However, unstrained G band peak of h-BN flakes recorded Raman shift slightly less than that of individual h-BN flake by 0.8 cm⁻¹.
Figure 6.12: An optical image for hexagonal boron nitride (h-BN)/glass (I) composites. This image for the top surface of the h-BN/ glass (I) composite disk.

Figure 6.13: Raman spectra of hexagonal boron nitride (h-BN) flakes in glass (I) matrix under tensile strain. The peaks are corresponding to Raman G band mode, and the dotted line indicates
the position of unstrained G band peak at \( \sim 1365.34 \text{ cm}^{-1} \) in Raman spectrum with black line. The legend shows the values of applied strain associated to each Raman spectrum.

![Raman spectrum graph](image)

**Figure 6.14:** The peak positions of G band mode of hexagonal boron nitride (h-BN) in the glass (I) matrix vs. strain, and a linear fit for the G band peak positions with strain. The shift rate of G band peak positions with strain was found to be \(-7 \text{ cm}^{-1}/\%\). The error bars indicate the standard deviation of the measurements.

### 6.3.2 h-BN/glass (II) composites

In addition to the glass (I) matrix, hexagonal boron nitride (h-BN) powder was used to synthesise h-BN/glass (II) composite sample as well. Raman spectra were collected from the h-BN/glass (II) composite sample during the deformation process under tensile strain.

Figure 6.15 shows the positions of G band peak as function of strain (a), where there are several Raman measurements at each strain points, and the averages of Raman measurements were linearly fitted in strain range from zero to 0.4\% as in (b).

The unstrained peak of G band peak is blue-shifted comparing to the individual h-BN flake Raman peak. The Raman shift rate was found to be \(-2.8 \text{ cm}^{-1}/\%\). Moreover, the Raman measurements were repeated for the same sample, and the G band peaks show no change in their position with increasing tensile strain as in Figure 6.16.
Figure 6.15: The peak positions of G band mode of hexagonal boron nitride (h-BN) in the glass (II) matrix vs. strain in (a), and a linear fit for the G band peak positions with (0 - 0.4%) strain in (b). The shift rate of G band peak positions with strain was found to be $-2.8 \text{ cm}^{-1}/\%$. The error bars indicate the standard deviation of the measurements.

Figure 6.16: The unchanged G band peak positions with repeated Raman measurements for h-BN/glass (II) composites sample. The error bars indicate the standard deviation of the measurements.

6.4 Discussion

To explain the observed shifts in G band mode peaks of hexagonal boron nitride (h-BN) materials, one may invoke strain that induced phonon shifts of G band Raman peaks of h-BN materials [284]. This may be supported by the observations of strain-induced shifts of Raman peaks for similar materials such as carbon materials [41-48], MoS$_2$ [49, 50] and WS$_2$ [51].
6.4.1 Exfoliated h-BN flake

The flake of hexagonal boron nitride (h-BN) used in this study was mechanically exfoliated from a high quality h-BN single crystal as the Raman spectrum shows a peak at 1366.6 cm\(^{-1}\) and FWHM of Raman peak of 8.1 cm\(^{-1}\), which reflects the quality of crystals [310]. (See Figure 5.4). The main peak position is similar to reported result in Table 3.1 for \(E_{2g2}\) phonon mode. The Raman spectrometers have notch filters with a cut-off frequency of \(~100\) cm\(^{-1}\), consequently, the low frequency mode of boron nitride materials cannot be detected in this study.

In Figure 6.2, Raman spectra show the deformation of exfoliated h-BN flake under tension. The BN G band peaks are fitted in Figure 6.3 and showed a redshift of \(~3.7\) cm\(^{-1}\) in the G band peak position of h-BN when the h-BN flake was on a PMMA beam was stretched by \(~0.6\) % strain using a bending technique.

The stress transferred from the polymer matrix to the h-BN flake when tensile strain is applied. As a result, the B–N bonds elongate and consequently softening of the \(E_{2g}\) phonons [254]. Also, it can be seen from Figure 6.5 and Figure 6.8 that, there is a stress-induced shift of the G band peak for both thick and thin regions of the h-BN flake. There is a linear shift of the G band frequencies up to \(~0.3\) % strain, and the slope of the linear shifts are \(-4.2\) cm\(^{-1}\)/% for thick region and \(-6.5\) cm\(^{-1}\)/% for thin region.

The level of adhesion between the hexagonal boron nitride (h-BN) flake and the surface of PMMA beam plays the main role in stress transfer from the polymer to the h-BN flake. Further loading up to 0.6% strain affect the interfacial phase between the flake and the polymer and a slippage of the flake was observed during the tensile deformation. This behaviour was observed as well in graphene/PMMA nanocomposites at 0.4% strain [48].

It was found for graphene nanocomposites that the strain builds up from the edges of the flake to becoming equal to the applied matrix strain across the middle of the flake [223]. Therefore, both thick and thin regions of h-BN flake were chosen to be as close as possible to the middle. Moreover, it was found that the band shift rate tends to decrease with an increase in the number of layers, indicating poor stress transfer between the inner graphene layers [32]. If this is the case in h-BN flake, this explain the difference in shift rate of G band peaks between thick and thin regions of exfoliated h-BN flake, where the thin region of the flake has higher shift rate than the thick one by \(2.3\) cm\(^{-1}\).
6.4.2 H-BN/glass based composites

In Figure 5.6, hexagonal boron nitride (h-BN) in form of powder with particle size of ~45µm and thickness of ~2-4 µm used to produce h-BN/glass based composites. The Raman spectrum in Figure 5.12 shows a G band peak at 1366.15 cm⁻¹ with FWHM of 8.8 cm⁻¹, which indicates high quality of h-BN powder.

Hexagonal boron nitride (h-BN) powder was mixed with glass (I) matrix by a ball milling technique. Thus, BN powder particles exfoliated and dispersed in the glass matrix. (See Figure 6.12). The shear forces applied by ball milling exfoliated BN layers via breaking the weak van der waals bonding between adjacent BN layers and leave the in-plane strongly covalent bonds [92].

One can see that the frequencies of G band peak are redshifted, when h-BN flakes in the glass matrices subjected to tensile strain in Figure 6.14 and Figure 6.15. The shift rate was vary between the responds of h-BN flakes in glass (I) and in glass (II) matrices, where the shift rates were -7.0 cm⁻¹%/ and -2.8 cm⁻¹%/ respectively. This may be due to poor stress transfer through the BN layers [32], and it may depend on the sample preparation process.

Raman shift rate of G band mode can be expressed as [236]:

\[
\frac{\partial \omega_G}{\partial \varepsilon} = -2 \gamma \omega_G^\circ
\]

(6.1)

where \(\Delta \omega_G\) is frequency shift of G band mode, \(\omega_G^\circ\) is the unstrained frequency of G band mode ( 1366 cm⁻¹) and \(\gamma\) is Grüneisen parameter of BN. Kern et al. [311] calculated a Grüneisen parameter of 0.1 for the hexagonal phase of bulk BN. So, the shift rate can be estimated for bulk BN to be -2.7 cm⁻¹%/ and -2.8 cm⁻¹%/ respectively. This value of shift rate is in agreement with that found for h-BN flakes in glass (II) matrix. Because of the sample preparation process, which causes some h-BN flakes to exfoliate in glass (I) matrix but this is not the case for h-BN flakes in glass (II) matrix.

In glasses and ceramics, there are thermal residual stresses, which arise upon cooling as a result of elastic and thermal mismatch between precipitates and glassy matrix [312]. So, boron nitride (BN) materials may face compressive stresses in the glass matrices of composites.
In Figure 6.15, the unstrained G band peaks of h-BN flakes in glass (II) matrix show a blue-shift comparing to the peak position of individual h-BN flake (i.e. ~1366.15 cm\(^{-1}\)). These upshifts could be resulted from thermal mismatch between h-BN flakes and the glass matrix [312], and consequently, the glass matrix applied some of compressive stress on h-BN flakes causes a hardening of the \(E_{2g}\) phonon mode. The compressive stress applied by the glass matrix on BN nanosheets will be studied in the next chapter (7).

Repeated measurement of deformation for h-BN/glass (II) composite sample indicates that the interfacial phase is breaks during the bending with poor stress transfer as the G band peak positions do not change with increasing the strain as it can be seen in Figure 6.16.

### 6.5 Summary

Single crystals of hexagonal boron nitride (h-BN) and h-BN powder were used as raw materials to obtain an individual h-BN flake and synthesise h-BN glass composites respectively. The individual h-BN flake was exfoliated using mechanical cleavage technique and it is called exfoliated h-BN flake. H-BN powder was dispersed in two glass matrices to fabricate h-BN/ glass (I) composites and h-BN/ glass (II) composites.

Raman spectra of deformation of exfoliated h-BN flake under tension show downshift of G band frequencies with increasing the tensile strain. Up to 0.3% strain, the shift rates of thick and thin regions of h-BN flake were found to be -4.2 cm\(^{-1}\)/% and -6.5 cm\(^{-1}\)/% respectively. Above 0.3% strain, the interfacial phase was broken down and slippage behaviour was observed in the deformation measurements of the thick region.

The mechanical response of deformed h-BN crystals in glass composites is examined using Raman spectroscopy. Raman measurements of deformed h-BN crystals in glass (I) and in glass (II) matrices of the composites show stresses transferred to h-BN crystals and cause redshifts in G band frequencies with increasing the tensile strain. The shift rates of h-BN G band were found to be -7.0 cm\(^{-1}\)/% and -2.8 cm\(^{-1}\)/% for h-BN crystals in glass (I) and in glass (II) matrices respectively. The unstrained G band peak of h-BN crystals in glass (II) matrix is shifted to higher frequency due to the residual stress.
Chapter 7: Deformation of Boron nitride nanosheets (BNNS) glass-based nanocomposites

7.1 Introduction

The residual stress developing through processing of glass matrices and operating conditions (i.e. heating and cooling) cannot be neglected, where cooling through the curing cycle it leads to a volumetric shrinkage of the glass matrix [313]. The mechanical behaviour of boron nitride nanosheets (BNNSs) and their response to the residual stresses have been investigated in this study using Raman spectroscopy.

Two types of glass matrices, borosilicate glass and lead glass (II), were used to synthesise BNNSs/ glass-based nanocomposites. Raman spectra were collected from BNNSs near to the sample surface of the nanocomposites and from BNNSs produced using the liquid exfoliation method. The position of G band peaks of BNNSs in the glass matrix was compared to that of pure BNNSs.

In addition, a specimen of BNNSs/glass (II) nanocomposite was deformed under tension and band shifts followed using in-situ Raman spectroscopy.

7.2 BNNSs/ borosilicate nanocomposites

Two samples of boron nitride nanosheets (BNNSs)/ borosilicate nanocomposites were studied as well as a boron nitride nanosheets (BNNSs) film was as a reference for Raman spectroscopic measurements. Boron nitride nanosheets (BNNSs) were used to synthesise BNNSs/borosilicate nanocomposites with loading of 1wt% and 2.5wt% of BNNSs. Figure 5.11 illustrates an optical image of the boron nitride nanosheets (BNNSs) pure film focussed near to the surface and the concentration of boron nitride nanosheets (BNNSs) may be different from area to another in the film due to BNNSs were overlapping [214].

Figure 7.1 and Figure 7.2 show optical images of the 1wt% and 2.5wt% BNNSs borosilicate nanocomposites samples, respectively with the dispersion of boron nitride nanosheets in the glass matrices. The arrows indicate the BNNSs in the nanocomposite sample.

Raman intensity maps for both 1wt% and 2.5wt% of BNNSs/borosilicate nanocomposites are shown in Figure 7.3 and Figure 7.4 respectively as well as with the related optical images.
Figure 7.1: An optical picture for the 1wt% BNNSs/borosilicate composite. The arrows indicate boron nitride nanosheets in the glass matrix.

Figure 7.2: An optical image of the 2.5wt% BNNSs/borosilicate composite. The arrows indicate boron nitride nanosheets in the glass matrix.
Figure 7. 3: Raman intensity map for 1wt% BNNSs/borosilicate nanocomposites.
Figure 7.4: Raman intensity map for 2.5wt% BNNSs/borosilicate nanocomposites.

Raman maps are a useful tool to identify BN sheets that suitable for Raman measurements in the glass composites. One can see the Raman BN images, and understand how the data can be analysed to obtain useful information. Many BN flakes appear in the optical images whereas only some points with reasonable intensities are shown in the BN Raman maps.
Raman spectra show high intensity of G band mode for BNNSs that are close to the sample surface. However, the intensity decreases as the BNNSs become deeper due to focal depth limit of the laser beam. For example, Figure 7.5 shows the Raman spectrum for the highest intensity region in the Raman map of 2.5wt% BNNSs/borosilicate nanocomposite sample. BNNSs/ borosilicate nanocomposite samples were examined by Raman spectroscopy and several Raman spectra were collected from different BNNSs in the glass matrices as shown in Figure 7.6. Raman spectra shown in Figure 7.6 (a) were taken from different BNNSs with high and low intensity of G Raman peak of BNNSs in 1wt% BNNSs nanocomposites, while those in Figure 7.6 (b) correspond to BNNSs in 2.5 wt% BNNSs nanocomposites samples.

Peak positions of Raman spectra were analysed and summarised in Table 7.1. G band peak of pure boron nitride nanosheets (BNNSs) was located at ~ 1365.0 ± 0.1 cm⁻¹. The average of G band peak positions for BNNSs were found to be at 1366.3 ± 1.6 cm⁻¹ and at 1366.8 ± 1.5 cm⁻¹ in borosilicate matrices with 1 wt% and 2.5 wt% BNNSs respectively. Raman peak positions were slightly upshifted by 1.3 cm⁻¹ and 1.8 cm⁻¹ in 1 wt% and 2.5 wt% BNNSs borosilicate nanocomposites respectively with respect to its position in pure BNNSs film due to residual stresses.
Figure 7.6: Raman spectra taken from BNNSs in (a) 1wt% BNNSs borosilicate nanocomposites with low intensity (left) and high intensity (right), and (b) 2.5wt% BNNSs borosilicate nanocomposites.

Table 7.1: summarisation of Raman peaks positions with averages for boron nitride nanosheets (BNNSs) film, and 1wt% and 2.5wt% BNNSs borosilicate composites

<table>
<thead>
<tr>
<th>Measurements No.</th>
<th>BNNSs film</th>
<th>BNNSs/borosilicate composites</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 wt% BNNSs</td>
</tr>
<tr>
<td>1</td>
<td>1364.86</td>
<td>1366.54</td>
</tr>
<tr>
<td>2</td>
<td>1364.93</td>
<td>1366.61</td>
</tr>
<tr>
<td>3</td>
<td>1365.13</td>
<td>1368.57</td>
</tr>
<tr>
<td>4</td>
<td>1365.12</td>
<td>1364.79</td>
</tr>
<tr>
<td>5</td>
<td>1365.04</td>
<td>1365.36</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>1364.86</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>1365.13</td>
</tr>
<tr>
<td>8</td>
<td>-</td>
<td>1369.43</td>
</tr>
<tr>
<td>9</td>
<td>-</td>
<td>1366.49</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>1365.23</td>
</tr>
<tr>
<td>Average</td>
<td>1365.0±0.1</td>
<td>1366.3±1.6</td>
</tr>
</tbody>
</table>
It is important to notice that the peak position of G band mode of BNNSs in the glass (II) matrix is shifted to higher frequency comparing to Raman peaks position of pure BNNSs (See Figure 5.13 (a)). A blue-shift of ~ 1.3 cm\(^{-1}\) was observed in the G band position of BNNSs in the glass (II) matrix due to residual stresses. Figure 7.7 shows peak fitting of Raman spectrum of BNNSs in the glass (II) matrix, where no tensile strain is applied.

![Figure 7.7: Peak fitting of Raman spectrum of BNNSs in the glass (II) matrix with no applying a tensile strain. The G band peak of BNNSs is located at ~ 1368.8 cm\(^{-1}\).](image)

**7.3 BNNSs/ glass (II) nanocomposites**

Boron nitride nanosheets (BNNSs) were dispersed in the glass (II) matrix to synthesise BNNSs/glass (II) nanocomposites. The as-prepared BNNSs have a lateral size of 2-6 µm and thickness in range of 2-5 nm as reported in section 5.3.

One specimen of the BNNSs/glass (II) nanocomposites was fixed to a PMMA beam as a thin film and deformed under tensile strain using in-situ Raman spectroscopy. In Figure 7.8, Raman spectra of deformed BNNSs in the glass (II) matrix under tensile strain are presented in (a) as collected and in (b) with smoothed functions by 2 points of an FFT filter.
Figure 7.8: The Raman spectra of deformed BNNSs in BNNSs/glass (II) nanocomposites under tensile strain are in (a) and in (b) with smoothing by 2 points of an FFT filter.
The positions of G band peak as a function of strain are shown in Figure 7.9 (a), where there are several Raman measurements at each strain points. Change in the average position of Raman measurements with tensile strain is shown in Figure 7.9 (b) and fitted linearly in the strain range from zero to 0.2%. The Raman shift rate was found to be $-7.65 \text{ cm}^{-1}/\%$.

![Figure 7.9](image.png)

**Figure 7.9:** The peak positions of G band mode of boron nitride nanosheets (BNNSs) in the glass (II) matrix vs. strain in (a), and a linear fit for the average G band peak positions with (0-0.2%) strain in (b). The shift rate of G band peak positions with strain was found to be $-7.65 \text{ cm}^{-1}/\%$. The error bars indicate the standard deviation of the measurements.
7.4 Discussion

7.4.1 Residual strains

The upshift in the G band mode frequency of BNNSs in the glass matrix of nanocomposites was observed before deformation comparing to G band frequency of pure BNNSs. This can be caused by oxygen doping as the fabrication of BNNSs glass nanocomposites required heat treatments. However, BN materials have a high oxidation resistant up to ~ 850 °C in air [6] and the temperature of less than ~ 600 °C was used to synthesise the BNNSs nanocomposite samples.

Moreover, Li et al. [6] reported that the start-up temperature of oxidation for 4 BN layer nanosheets is 870 °C, while BNNSs used in the nanocomposites have around 10 BN layers.

In addition, the local temperature increase caused by the laser leads to a redshift of G band mode; even though the laser was set to work with low power during the Raman experiments. In fact, the observed frequency of G band mode of BNNSs was blue-shifted.

The possible explanation for the blue-shift of G band mode of BNNSs can be due to mismatch of thermal expansion between BNNSs and the glass matrix. The coefficient of thermal expansion of BN is negative (-2.9x10^-6/K at 293 K along a-axis) and during cooling, the BNNSs expanded while the glass matrix shrank, which generates a compression stress around the BNNSs in the nanocomposite [214]. Also, it is known a Raman peak frequency would shift to higher frequencies under compressive stresses [284].

Similarly to the h-BN/glass (II) composites in chapter 6, the residual stress affected the G band Raman peak of boron nitride nanosheets (BNNSs) in borosilicate glass and glass (II) matrices. Raman peak positions were slightly upshifted by 1.3 cm^-1 and 1.8 cm^-1 in 1wt% and 2.5wt% BNNSs borosilicate nanocomposites respectively with respect to its position in pure BNNSs film. Also, the position of unstrained G band peaks shifted to higher frequencies for boron nitride nanosheets (BNNSs) in glass (II) matrix as it can be seen in Figure 7.9 (a) comparing to its position of Raman peak of pure BNNSs.

The compressive stresses around BNNSs contribute to improve the fracture toughness of glass matrix in the nanocomposites [214, 314]. So, an estimate of internal stresses generated around BNNSs surface could contribute to the understanding the toughening mechanisms in
nanocomposites, as the key factor that determines the Raman frequency of BNNSs is the strain.

The Raman upshift of BNNS G band mode can be used to determine the strain as [236]:

\[
\varepsilon = -\frac{\Delta \omega_G}{2\gamma \omega_G^0}
\]

where \(\Delta \omega_G\) is the shift of G band frequency, \(\gamma\) is the Grüneisen parameter of BNNSs, \(\omega_G^0\) is the unstrained G band frequency of BNNNSs.

Cai et al. [2] performed theoretical calculations to estimate the Grüneisen parameters (\(\gamma\)) of BNNSs using \textit{ab initio} DFT, and they found its value to be 0.64 deduced from the phonon-dispersion relations. Using this value of the Grüneisen parameter and the G band frequency of pure BNNSs (1365 cm\(^{-1}\)), the residual strains calculated based on the average upshift of the BNNS G bands in the glass matrices of nanocomposites as presented in Table 7.2.

Table 7.2: Calculation of residual strains in glass matrices of BNNSs nanocomposites.

<table>
<thead>
<tr>
<th>BNNSs in</th>
<th>(\omega_G) (cm(^{-1}))</th>
<th>(\Delta \omega_G) (cm(^{-1}))</th>
<th>(\varepsilon) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Borosilicate (1wt%)</td>
<td>1366.3</td>
<td>1.3</td>
<td>0.07</td>
</tr>
<tr>
<td>Borosilicate (2.5wt%)</td>
<td>1366.8</td>
<td>1.8</td>
<td>0.10</td>
</tr>
<tr>
<td>Lead glass (II)</td>
<td>1368.7</td>
<td>3.7</td>
<td>0.21</td>
</tr>
</tbody>
</table>

The mismatch of thermal expansion coefficient between BNNSs and glass matrices has a significant impact as residual compressive stresses on BNNSs, since the blueshifts have been observed in the unstrained G bands of BNNSs. Raman shift of G band mode shows frequencies correlated to thermal expansion coefficient of glass matrices. Hence, a small Raman upshift was observed for BNNSs in borosilicate glass with a low thermal expansion coefficient (3.3x10\(^{-6}\)/K) [214] (i.e. low compressive strain), whereas lead glass (II) with a high thermal expansion coefficient (7.5-11x10\(^{-6}\)/K) [315, 316] (i.e. high compressive strain) affects the G band frequency of BNNSs with a significant blueshift.

7.4.2 Raman band shift during deformation

The Raman spectra show clearly a redshift change in G band frequency as the tensile strain increased. The position of G band peak for deformed boron nitride nanosheets (BNNSs) in glass (II) matrix as a function of strain are plotted in Figure 7.9 (a). The linear shift was fitted and the shift rate found to be -7.65 cm\(^{-1}/\%\) as shown in Figure 7.9 (b). Loading over 0.2%
strain may cause the interfacial phase break down during the bending process of the BNNSs as the debonding or loss of stress transfer to BNNSs can be seen in Figure 7.9.

7.5 Summary

Boron nitride nanosheets (BNNSs) were exfoliated from h-BN powder and used to synthesise the BNNS glass based nanocomposites. BNNSs in the glass matrices were studied using Raman spectroscopy to investigate the mechanical response of BNNSs in the glass matrices.

Raman measurements show the response of BNNSs to compressive and tensile stresses. The G band peak is shifted to higher frequency with compressive stress applied by shrinkage of glass matrices, and to lower frequency with tensile stress during bending process.

Under tension, Raman peak of G band mode of BNNSs show a shift rate of – 7.65 cm\(^{-1}/%\), when tensile strain was increased up to 0.2% strain. The debonding of BNNSs was an evidence of interfacial failure above 0.2% strain.
Chapter 8: Deformation of Boron nitride nanotubes (BNNTs)

8.1 Introduction

Boron nitride nanotubes (BNNTs) have been used in the nanocomposite production, and the improvements of mechanical performances have been achieved in these nanocomposites [20, 34-36, 217, 317]. This demonstrates that the effectiveness of BNNT has been proved in reinforcing-composite applications [19, 318].

Boron nitride nanotube (BNNT) buckypaper was used as a precursor. A specimen of BNNTs was obtained as a thin layer coated on the surface of PMMA beam using shear exfoliation of BNNT buckypaper, to give so-called exfoliated BNNTs. Also, dispersed BNNTs in ethanol were used to synthesise BNNT/glass (II) nanocomposites. Deformation of the exfoliated BNNTs on a PMMA beam and BNNTs in the glass (II) matrix under tension were performed using in-situ Raman spectroscopy as well as Raman maps were used to identify the BNNTs in the samples, as can be seen in Figure 8.1.

![Raman intensity map for an area rich in boron nitride nanotubes (BNNTs) on the sample surface.](image)
8.2 exfoliated boron nitride nanotubes (BNNTs)

Exfoliated boron nitride nanotubes (BNNTs) were deformed under tension. During the deformation experiment of the exfoliated BNNTs, several Raman measurements were collected at each point of strain. The Raman spectra collected are plotted as shown in Figure 8.2. The redshift is observed as the Raman position of G band peaks shifting to lower frequencies with increasing tensile strain.

In Figure 8.3, Raman measurements of G band peak positions as a function of strain are presented. Also, the average of Raman measurements at each point of strain is plotted as a function of strain and shown in Figure 8.4. They are fitted linearly up to 0.13% strain and the shift rate was found to be \(-25.7\ \text{cm}^{-1}/\%\). As the tensile strain was increased up to \(-0.13\ %\) strain, the frequencies of G band peaks are downshifted. Above 0.13% strain, the frequencies of G band peaks almost remain steady around 1364.6 cm\(^{-1}\) with increasing strain (See Figure 8.4).

The unstrained positions of G band peaks were in range of \(~1367-1369.7\ \text{cm}^{-1}\) with in average of 1368.2 cm\(^{-1}\), which is shifted to higher frequencies compared to the corresponding position of the bulk boron nitride (BN) peak at \(~1366\ \text{cm}^{-1}\) as demonstrated in chapter 5.

Figure 8.2: Raman spectra of deformed boron nitride nanotubes (BNNTs) under tensile strain. The dotted line is for the G band position of unstrained peak at \(~1368.2\ \text{cm}^{-1}\). The arrow indicates the increase in tensile strain.
Figure 8.3: A plot of change Raman peak positions of exfoliated boron nitride nanotubes (BNNTs) with tensile strain. Several Raman measurements are taken at each step of strain.

Figure 8.4: The average of G band peak positions of boron nitride nanotubes (BNNTs) vs. strain. A linear fit of the average of G band peak positions is made in a range of strain from zero to 0.13%. The shift rate of G band peak positions with strain was found to $-25.7 \text{ cm}^{-1}/\%$. The error bars indicate the standard deviation of the measurements.
8.3 BNNT/glass (II) nanocomposites

The Boron nitride nanotubes (BNNTs) dispersed in ethanol were used to produce boron nitride nanotubes (BNNTs)/glass (II) nanocomposites. A specimen in the form of a thin film on a PMMA beam of BNNTs/glass (II) nanocomposites was deformed under tension. Several Raman measurements at each strain steps were taken. Figure 8.5 shows a deformed Raman spectrum of BNNTs in glass (II) matrix with peak fitting using Lorentzian peak function. Raman spectra for BNNT deformation in the glass (II) matrix are illustrated in Figure 8.6 (a) as collected and in (b) with a smoothing function by 2 points of an FFT filter.

The position of G band peaks as a function of strain is shown in Figure 8.7 (a). The change of Raman measurement averages with strain were plotted in Figure 8.7 (b) and fitted linearly in strain range from zero to 0.13%. The Raman shift rate was found to be \(-23.6\) cm\(^{-1}\)/%.

The unstrained peak of G band peak is blue-shifted comparing to Raman peak position of BNNTs on the SiO\(_2\)/Si substrate. As demonstrated in chapter 7, the compressive stresses applied by glass (II) matrix on BN fillers in the composites cause the G band peak to shift to higher frequency compared to unstrained peak of the G band mode.

![Figure 8.5: Peak fitting of a deformed BNNT Raman spectrum with Lorentzian function. The position of Raman peak is located at 1373 cm\(^{-1}\) with FWHM of 21.8 cm\(^{-1}\).](image)
Figure 8.6: The Raman spectra of deformed BNNTs under tensile strain are in (a) as collected and in (b) with smoothing function of 2 points of an FFT filter.
Figure 8.7: The peak positions of G band mode of boron nitride nanotubes (BNNTs) in the glass (II) matrix vs. strain in (a), and a linear fit for the G band peak positions with (0 - 0.13%) strain in (b). The shift rate of G band peak positions with strain was found to be $-23.6 \text{ cm}^{-1}/\%$. The error bars indicate the standard deviation of the measurements.
8.4 Discussion

Boron nitride nanotubes (BNNTs) could be individual tubes or bundles, where they are packed together through van der Waals inter-tubes interactions [255]. In chapter 5, SEM and TEM images show BNNTs are packed in long bundles with some impurities of nanoparticles. The effect of contaminants is important, since it can hide the spectroscopic response of BNNTs [266] or the signal may also include contributions from similar-size hexagonally structured nanoparticles [269].

Raman spectra of deformed BNNTs show the rise of G band redshift with increasing tensile strain. Also, the unstrained peak position was in range of ~1367-1369.7 cm\(^{-1}\), which is in agreement with the observed values of multi-walled boron nitride nanotubes (BNNTs) in Table 3.1. There is a linear shift in the G band mode frequency up to 0.13% tensile strain, and the shift rate is -25.7 cm\(^{-1}\)/%. The position of G band peak of undeformed BNNTs was found to be at 1368 cm\(^{-1}\) as demonstrated in chapter 5. However, the unstrained Raman peaks for boron nitride nanotubes (BNNTs) in glass (II) matrix show significant upshifted in their frequency due to residual stresses similar to the behaviour of h-BN and BNNSs in glass (II) matrix with compressive strains. Deformation experiment of BNNTs in glass (II) matrix reveals a linear shift with a rate of -23.6 cm\(^{-1}\)/% for G band frequency with tensile strain.

Stress transfer from the composite matrices to the nanotubes is demonstrated from the high shift rate, where strain-induced G band shift; as a result, the BNNTs contribute to reinforcing the matrices.

To understand the mechanical behaviour of deformed BNNTs, the elongation of the B–N bond in the structure of boron nitride (BN) materials, induced by tensile strain is soften the E\(_{2g}\) phonon mode, and consequently redshifted the G band frequencies [263]. However, the downshift of G band frequencies could be due to anharmonic effects [266, 285]. The temperature increase means that the anharmonicity in the vibrational potential should be considered, which results in a softening and asymmetrical broadening of the E\(_{2g}\) phonons [263]. Therefore, a laser beam with high power increased the local temperature, consequently, soften E phonons mode due to anharmonic effects. Because of this, the laser source was used with low power to avoid sample heating.
The high shift rate of G band mode of boron nitride nanotubes (BNNTs) may reveal strong interfacial binding between BNNTs and the PMMA polymer due to surface polarization of BNNTs since the B-N bond is slightly ionic, which gives rise to strong electrostatic interaction between them [25]. Thus, the partially ionic nature of BNNTs makes both electrostatic and van der Waals interactions exist in the BN system.

In addition, the radial buckling is defined as [319]:

$$\beta = r_N - r_B$$  \hspace{1cm} (8.1)

where $r_N$ and $r_B$ are the mean radii of the cylinders formed by nitrogen and boron atoms of the BNNT, respectively.

The buckling gives an increased surface area of BNNT cylinders to interact with the composite matrix. However, the radial buckling of the BNNTs will be reduced when tensile load is increased and this makes the surfaces of BNNTs tend to have smoother cylindrical surfaces [320].

Raman shift rate of G band mode with strain units can be expressed as [236]:

$$\frac{\partial \omega_G}{\partial \varepsilon} = -2 \gamma \omega_G^\circ$$  \hspace{1cm} (8.2)

where $\Delta \omega_G$ is frequency shift of G band mode, $\omega_G^\circ$ is the unstrained frequency of G band mode (1368 cm$^{-1}$) and $\gamma$ is Grüneisen parameter of boron nitride (BN). Grüneisen parameter was calculated to be 0.89 for a boron nitride (BN) sheet [321]. As BNNTs have a small number of BN layers (~ 4 walls) with a small diameter (~ 5 nm), this value of Grüneisen parameter could be used to estimate the shift rate of BNNT G band.

Thus, the calculated shift rate would be -24.4 cm$^{-1}$/%, and this value is basically in agreement with that obtained from BNNT deformation under tension.

During the deformation process, direct evidence of stress transfer to BNNTs is demonstrated by the high Raman shift rate of BNNTs which could be due to boron nitride nanotubes (BNNTs) have a small diameter and long length mean by high aspect ratio, which gives them the better characteristic to enhance the mechanical properties of the composites according to Halpin-Tsai model in longitudinal direction and shear lag model as it can be realised from
Equations (2.6) and (2.10) respectively. Hence, BNNTs have an advantage to be one of the best candidates to reinforce polymeric and glassy matrices in composites application.

8.5 Summary

Boron nitride nanotubes (BNNTs) that were used for the deformation experiments were obtained from BNNT buckypaper. BNNTs were deformed as (i) a thin layer (i.e. exfoliated BNNTs) on PMMA substrate and (ii) in a specimen of BNNTs/glass (II) nanocomposites.

Raman measurements show high band shift of G peak of exfoliated BNNTs and BNNTs in the glass (II) matrix and the shift rate are \(-25.7 \text{ cm}^{-1/\%}\) and \(-23.6 \text{ cm}^{-1/\%}\) respectively. The excellent response of BNNTs to tensile strain applied to composite matrices indicates the worthy contribution of BNNTs to improve the mechanical properties of nanocomposites.

The effect of residual stress of glass (II) matrix was observed on the position of unstrained G band peak of BNNTs, where the G band position is shifted to higher frequency, showing high residual compressive stress.
Chapter 9: Conclusions and Future work

9.1 Conclusions

This thesis has paved the way for Raman studies of boron nitride material deformation using a bending technique. The deformation effects upon boron nitride (BN) materials including hexagonal boron nitride (h-BN), boron nitride nanosheets (BNNSs) and boron nitride nanotubes (BNNTs) have been studied as well as the investigation of their behaviour in glass composites using in-situ Raman spectroscopy. The typical Raman spectrum of boron nitride (BN) materials has a single peak due to $E_{2g}$ stretching phonon mode. The frequency response of this phonon mode to strain was the key to assess stress transfer from the matrix to BN filler in the composites.

Mechanical cleavage and liquid exfoliation were employed on single crystals of h-BN and BN powder to obtain atomically thin boron nitride (BN) samples e.g. an exfoliated h-BN flake and boron nitride nanosheets (BNNSs). Boron nitride nanotubes (BNNTs) were in form of buckypaper, and they were prepared as exfoliated BNNTs to form a thin layer on a PMMA beam or dispersed in ethanol. Using a shear force exfoliation technique to get exfoliated BNNTs is novel and it can be expanded to the exfoliation of single crystal h-BN, instead of using the tape, to avoid the residual glue on the specimens.

The exfoliated h-BN flake had two main regions classified as thick and thin regions. The exfoliated h-BN flake was deformed under tension using bending technique. The tensile deformation of the h-BN flake gives shift rates of $-4.2 \ \text{cm}^{-1}/\%$ and $-6.5 \ \text{cm}^{-1}/\%$ for thick and thin regions respectively. In addition, hexagonal boron nitride (h-BN) powder was used to produce two types of glass composites i.e. glass (I) and glass (II) matrices. The deformation of these composites was carried out and Raman spectra were collected at each strain step. The shift rates varied between the composite samples, and they were found to be $-7.0 \ \text{cm}^{-1}/\%$ for h-BN flakes in glass (I) matrix and $-2.8 \ \text{cm}^{-1}/\%$ for h-BN flakes in glass (II) matrix, due to ball milling exfoliation of the h-BN flakes in glass (I). The unstrained G band peak of h-BN flakes in glass (II) is blueshifted due to residual stress.

Boron nitride nanosheets (BNNSs) were obtained using a liquid exfoliation method, and they used to form BNNSs/borosilicate nanocomposites and BNNSs/glass (II) nanocomposites. The effect of residual stresses in glass matrices on BNNSs has been demonstrated with an
estimation of the residual strains. The deformation was undertaken on BNNSs/glass (II) composites under tension, and gives a shift rate of -7.65 cm\(^{-1}\)/\%. 

Boron nitride nanotubes (BNNTs) were deformed as well using the same technique of bending. The Raman spectra were collected as the strain increased. The shift rate was found to be -25.7 cm\(^{-1}\)/\%. Boron nitride nanotubes (BNNTs) were used to form BNNTs/glass (II) composites. The deformation of the BNNTs gives a shift rate of -23.6 cm\(^{-1}\)/\%.

The Raman shift rates of bulk h-BN and boron nitride nanotubes (BNNTs) are calculated using the Grüneisen parameter and found to be in agreement with the experimental values. 

Borosilicate and glass (II) matrices applied compressive stresses on boron nitride fillers and this was observed as upshifts in the Raman frequency of the G band peaks of boron nitride materials. This enabled the residual strains to be calculated with the use of Grüneisen parameters.

Despite of the small limit of tensile strain due to interfacial failure in glass matrices, evidence of stress transfer between the matrix and the BN has been observed from the stress induced shifts of the G Raman band and the BN band rates have been achieved.

### 9.2 Recommendations and Further work

Boron nitride (BN) materials have a weak Raman peak especially when the numbers of layers are reduced, but using a laser source with high power to enhance the intensity of G band peak is risky and may induce sample heating and cause redshift of G band mode. By using laser source with low power, increasing the exposure time and accumulations were found effective with boron nitride materials.

From a mechanical view, this project is just start the deformation of boron nitride (BN) materials using a bending technique in-situ Raman spectroscopy and perhaps most of the studies which have been carried out on carbon materials could be applied to BN materials as well.

Many solvents have been used to obtain atomically thin BN sheets. In this study, ethanol was used to exfoliate the BN powder using a liquid exfoliation technique with hard sonication conditions. So, using other solvents such as dimethylformamide (DMF) [3], methanesulfonic acid (MSA) [101], N-methyl-pyrrolidinone (NMP) [21, 102] may improve the lateral size of as-produced BNNSs when the less hard sonication conditions are needed. This may
contribute to enhance the mechanical properties of the nanocomposites, and would be reflected obviously on the BNNSs response to strain by a higher Raman shift rate.

The Raman spectrum of boron nitride nanotubes (BNNTs) compared to the bulk BN materials shows upshift and broadening of $E_{2g}$ mode. From Table 3.1, since it has been observed both an upshift and downshift of the G band of BNNTs compared to the bulk peak, it may be one of challenges of BN materials that needs to be explored. In addition, the Raman signature of RBMs should be explored for boron nitride nanotubes (BNNTs) since there are rabid improvements in the BNNT production and BNNTs with a small diameter have been produced.

The shear force exfoliation technique of BNNTs allows a thin layer of BNNTs to be obtained, and this makes them suitable for a deformation study using Raman spectroscopy. This technique may have the advantage of no tape adhesion residue on the sample compared with using a tape cleavage. In addition, this technique can be expanded to exfoliate the single crystals of h-BN.

Deformation experiments of exfoliated h-BN flake and exfoliated BNNTs could be replicated using a coating layer of PMMA polymer on top the BN samples to enhance the adhesion of boron nitride flakes to the beam, so, further loading can be achieved.

One of the main challenges of BN materials is the deformation of monolayer boron nitride, which has not been examined yet by bending tests due to its weak Raman signal. This may eventually be possible using a UV laser source (i.e. BN has a wide band gaps $\sim 6$ eV [11]), so the resonance can be obtained, similar to monolayer graphene.

Raman spectra show significant upshift of BNNT G band mode, since the lead glass (II) applied a compressive stress on BNNT fillers in the nanocomposites. The effect of strain on the band gap of BNNTs could be interesting to study as the radial compression can greatly reduce the resistance and band gap of BNNTs, changing them from insulators to semiconductors [322].
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