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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**NOVEL COMPOSITE ARCHITECTURES BASED ON LOW
DIMENSIONAL C/BN WITH ENHANCED MECHANICAL AND
THERMAL RESPONSES FOR SPORTS APPLICATIONS**

JING LIN

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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THERMAL RESPONSES FOR SPORTS APPLICATIONS**

JING LIN

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2018

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research
and has not been submitted for a higher degree to any other University or Institution.

18 December 2018

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Date

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Jing Lin

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

18 December 2018

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Date

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Alfred Tok Iing Yoong

Authorship Attribution Statement

This thesis contains materials from 6 papers published in following peer-reviewed journals where I was the first author.

Chapter 4 is published as L. Jing, R. Y. Tay, H. L. Li, S. H. Tsang, J. F. Huang, D. L. Tan, B. W. Zhang, E. H. T. Teo,* A. I. Y. Tok*. Coaxial Carbon@ Boron Nitride Nanotube Arrays with Enhanced Thermal Stability and Compressive Mechanical Properties. *Nanoscale* **2016**, 8, 11114–11122. DOI: 10.1039/c6nr01199c.

The contributions of the co-authors are as follows:

- Prof. Edwin Teo Hang Tong and Prof. Alfred Tok Iing Yoong proposed the initial research direction and guided the project.
- I, Dr. Li Hongling and Dr. Roland Tay Yingjie conceived the idea and designed the experiment, synthesized the materials, conducted the characterizations, tested the mechanical performances, analyzed the data and drafted the manuscript.
- Dr. Tsang Siu Hon helped revise the manuscript.
- Dr. Huang Jingfeng, Dr. Tan Dunlin and Mr. Zhang Bowei assisted in the TEM characterization.

Chapter 5 is published as L. Jing,[¶] M. K. Samani,[¶] B. Liu[¶] ([¶] co-first author), H. L. Li, R. Y. Tay, S. H. Tsang, O. Cometto, A. Nylander, J. Liu, E. H. T. Teo,* A. I. Y. Tok*. Thermal Conductivity Enhancement of Coaxial Carbon@Boron Nitride Nanotube Arrays. *ACS Applied Materials & Interfaces* **2017**, 9, 14555–14560. DOI: 10.1021/acsami.7b02154.

The contributions of the co-authors are as follows:

- Prof. Edwin Teo Hang Tong and Prof. Alfred Tok Iing Yoong proposed the initial research direction and guided the project.
- I and Dr. Li Hongling designed the experiment, synthesized the materials, conducted the characterizations, analyzed the data and drafted the manuscript. Dr. Roland Tay Yingjie and Dr. Tsang Siu Hon helped revise the manuscript.

- Dr. Majid Kabiri Samani and Prof. Liu Johan helped with the thermal conductivity measurement. Dr. Liu Bo conducted the molecular dynamics simulations.
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- Prof. Edwin Teo Hang Tong and Prof. Alfred Tok ling Yoong proposed the initial research direction and guided the project.
- I and Dr. Li Hongling conceived the idea and designed the experiment, synthesized the materials, conducted the characterizations, tested the static and dynamic compressive responses, analyzed the data and drafted the manuscript.
- Dr. Roland Tay Yingjie, Mr. Lin Jinjun and Dr. Tsang Siu Hon helped with some supporting experiments and manuscript revision.

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- Prof. Edwin Teo Hang Tong proposed the initial research direction and guided the project.
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The contributions of the co-authors are as follows:

- Prof. Edwin Teo Hang Tong and Prof. Alfred Tok Iing Yoong proposed the initial research direction and guided the project.
- I and Dr. Li Hongling conceived the idea and designed the experiment, synthesized the materials, conducted the characterizations, tested the static and dynamic mechanical responses, analyzed the data and drafted the manuscript.
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Chapter 9 is published as L. Jing,[¶] H. L. Li[¶] ([¶] co-first author), R. Y. Tay, B. Sun, S. H. Tsang, O. Cometto, J. J. Lin, Teo, E. H. T. Teo,* A. I. Y. Tok*. Biocompatible Hydroxylated Boron Nitride Nanosheets/Poly (vinyl alcohol) Interpenetrating Hydrogels with Enhanced Mechanical and Thermal Responses. *ACS Nano* **2017**, 11, 3742–3751. DOI: 10.1021/acsnano.6b08408.

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- Prof. Edwin Teo Hang Tong and Prof. Alfred Tok Iing Yoong proposed the initial research direction and guided the project.
- I and Dr. Li Hongling conceived the idea and designed the experiment, synthesized the materials, conducted the characterizations, tested the mechanical and thermal properties, analyzed the data and drafted the manuscript.

- Dr. Roland Tay Yingjie, Dr. Tsang Siu Hon, Dr. Olivier Cometto and Mr. Lin Jinjun performed some supporting experiments and helped revise the manuscript.
- Dr. Sun Bo conducted the cell viability, proliferation and live/dead viability assays.

18 December 2018

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Date

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Abstract

Articular cartilage injury of the knee/ankle is one of the most common sports injuries due to the complex physiological loadings they encounter during intense activities. There are two strategies to address this: 1) to avoid, that is to protect the healthy from such injury by advancing the sports accessories (*e.g.*, footwear); 2) to cure, which means to treat the patients with appropriate therapy (*e.g.*, total cartilage replacement). However, as the most promising midsole materials, vertically aligned carbon nanotube (VACNT) arrays and three-dimensional reduced graphene oxide (3D rGO) aerogels still exhibit limited compressibility and energy dissipation, while the conventional artificial cartilages (poly (vinyl alcohol) (PVA) hydrogels) still possess insufficient mechanical strength, toughness and heat transfer. These unsatisfactory characteristics of the candidate materials have severely restricted their further applications.

To date, boron nitride nanotubes (BNNT) and nanosheets (BNNS) with superior mechanical and thermal characteristics, have demonstrated significant reinforcing effects in the physicochemical properties of carbon based architectures due to their highly coherent atomic configuration and lattice constants with graphene. In light of this, it is expected that the integration of BN nanomaterials is able to enhance the overall performances of the abovementioned candidate materials, while which has not been investigated yet. In this thesis, coaxial C@BNNT arrays with significantly improved compressive strength, shape recovery, fatigue resistance, energy dissipation and heat transfer have been firstly fabricated by encapsulating outer BNNT onto the CNT arrays. These enhancements in mechanical and thermal properties of the C@BNNT arrays endow their outstanding energy return and dissipation characteristics. Inspired by this, unique rGO/BN aerogels with ultralow density, high compressibility and excellent recoverability have been further constructed with cell walls of assembled rGO and BNNS, showing high potential as multifunctional compressible mattress.

Despite these progresses, the inadequate shape recoverability and viscoelasticity of the C@BNNT arrays under cyclic compression as well as their limited dimensions (hundreds μm in length) still cannot meet the practical application requirements. To address these issues, commercially available CNT arrays with length of ~ 4 mm were chosen and further encapsulated with outer graphene layers. Notably, the resulting CNT@Gr arrays exhibit superior compressibility ($\sim 80\%$ recovery after 1000 cycles at a 60% strain), strength, and even outstanding strain- and frequency-dependent viscoelasticity that is constant over an exceptionally broad temperature range (-100 – 500 $^{\circ}\text{C}$) in air, attributing to the more intense synergistic effect between graphene and CNT. These CNT@Gr arrays with excellent characteristics will inspire a wide range of promising mechanical support and damping applications.

On the other hand, to enable the PVA hydrogels with outstanding compressive responses to fulfill the requirements for artificial cartilages, the wafer-scale VACNTs were incorporated into the PVA hydrogels to fabricate composite VACNT/PVA hydrogels. Interestingly, such hydrogels perform outstanding mechanical responses upon both static and dynamic compressions due to the reinforcements of uniformly distributed VACNTs and large CNT-PVA interfaces. Furthermore, considering the better biocompatibility of BNNS than that of the CNT, highly hydrophilic BNNS were synthesized and subsequently introduced into the PVA to fabricate BNNS/PVA hydrogels. As expected, the resulting hydrogels exhibit not only remarkably improved mechanical properties but also excellent heat transfer, which can be attributed to the homogeneously distributed BNNS with excellent physical properties and the hydrogen bonding interactions between the BNNS and PVA chains. Therefore, these biocompatible BNNS/PVA hydrogels are promising in addressing the mechanical failure and locally overheating issues as cartilage substitutes and may also have broad utility for other biomedical applications.

Lay Summary

Articular cartilage injury of the knee/ankle is one of the most common sports injuries due to the heavy load they endure during intense activities. From the material research perspective, the strategy to address this problem is developing the sports footwear midsole materials (*e.g.*, CNT arrays, 3D rGO aerogels) with enhanced protective effect and artificial cartilage substitute materials (*e.g.*, PVA hydrogels) with improved mechanical and thermal responses. However, there still exist many obstacles, both fundamental and practical, towards practically applying these materials.

In this thesis, I developed novel fabrication approaches from both fundamental and manufacturing perspectives to address the existing problems such as limited compressibility, energy dissipation and shape recoverability under cyclic compression. By incorporation of BNNT and BNNS, the composite architectures including C@BNNT arrays, CNT@Gr arrays and rGO/BN aerogels have been successfully achieved. All these materials have shown significantly enhanced compressive strength, elasticity and energy dissipation. Particularly, the CNT@Gr arrays have demonstrated superior compressibility (~80% recovery after 1000 cycles at a 60% strain), strength, and even outstanding strain- and frequency-dependent viscoelasticity that is constant over an exceptionally broad temperature range (−100–500 °C) in air. These supercompressible CNT@Gr arrays with macroscale dimensions (~4 mm in length) will enable fabrication of midsoles with better cushioning effect, which are potentially significant to the scientific area and industry.

In addition to the midsole materials, VACNT/PVA and BNNS/PVA hydrogels have been synthesized. Compared to the bare PVA hydrogels, both of the composite hydrogels perform outstanding mechanical responses upon complex loading conditions. Especially, for the first time, highly water soluble and cytocompatible BNNS have been successfully introduced into the PVA hydrogels without affecting their biocompatibility. The resulting BNNS/PVA hydrogels possess not only remarkably improved mechanical properties but also excellent heat transfer, which are promising in addressing the mechanical failure and locally overheating issues as cartilage substitutes and may also have broad utility for other

biomedical applications, such as drug delivery, tissue engineering, biosensors, and actuators.

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Figure 4.6 Cross-sectional SEM images of the NT arrays after cyclic compressions. The CNT arrays (a, d) deformed almost plastically with heavy buckles (inset) at the bottom region, while the C@BNNT₄₀ arrays (b, e) and the C@BNNT₆₀ arrays (c, f) exhibited partial recovery with slight buckles (inset) and nearly full recovery with only curvatures formed on the tubes, respectively, showing the significantly promoted compressive resilience of the C@BNNT arrays.

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Figure 5.2 Raman spectra of CNT and corresponding C@BNNT. The crystal structure of the CNT is not altered after the introduction of outer BNNT.

Figure 5.3 SEM and EDX characterizations of the resulting C@BNNT arrays. (a) EDX spectrum, (b) SEM image and corresponding elemental maps for (c) O, (d) B, (e) C and (f) N indicate the successful introduction of BNNT and the homogeneous distribution.

Figure 5.4 (a) Schematic illustration of the PPR technique and sample structure. (b) Cross-sectional SEM image of the TiN/NT/Si shows that the aligned morphology of the NTs was well preserved after the deposition of ~ 500 nm-thick TiN layer on top. (c) Normalized surface temperature-time curves of the NT arrays measured by PPR indicate that the C@BNNT arrays dissipate heat faster than the bare CNT arrays. (d) Theoretically fitted curves of the C@BNNT arrays match reasonably well with the experimental data.

Figure 5.5 (a) Computational model (front/side view) of the coaxial C@BNNT structure. The middle region (heat source, red) and the two ending regions (heat sink, dark green) are controlled at temperatures of $T + \Delta T$ (350 K) and T (300 K), respectively. (b) Temperature distribution along the heat flow direction and (c) the cumulative energy changes vs simulation time for the coaxial C@BNNT, inner CNT and outer BNNT, respectively.

Figure 5.6 (a) Snapshots of C@BNNT, isolated CNT, and CNT cluster when the steady temperature gradient is reached under NVE ensemble, respectively. (b) Temperature distribution along the heat flow direction and (c) the cumulative energy changes vs simulation time for the inner CNT within C@BNNT, isolated CNT and individual CNT within aligned CNT cluster, respectively.

Figure 5.7 Phonon power spectra of inner CNT and outer BNNT in coaxial C@BNNT structure. The highly overlapped phonon power spectra indicates the weak interfacial phonon scattering between them, which results from their similar lattice structures.

Figure 6.1 Schematic illustration of fabricating coaxial CNT@Gr arrays by encapsulating PAN polymer and subsequently annealing to introduce conformal graphene layers onto the aligned CNTs.

Figure 6.2 Cross-sectional SEM and corresponding TEM images of CNT (a, c) and CNT@Gr (b, d) show that the outer graphene layers were uniformly encapsulated onto the CNTs without causing noticeable change in their tube areal density. EELS (e) and Raman spectra (f) further verify that the integration of pristine graphene does not alter the crystalline structure of CNTs.

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Figure 6.5 Mechanical responses of CNT@Gr arrays upon uniaxial compressions. (a) Real-time photos show that the CNT arrays collapse while the CNT@Gr arrays fully recover after compression at strain (ϵ) = 60%. Scale bar, 1 cm. (b) Loading-unloading compressive stress (σ) vs. ϵ curves of CNT@Gr and CNT arrays at various ϵ , where the hysteresis of CNT@Gr arrays increases with ϵ . Representative σ vs. ϵ curves (c), shape recovery ratios and energy dissipation ratios (d) of the CNT@Gr arrays upon cyclic compressions up to 1000 cycles at ϵ = 60% demonstrate their gradually stabilized mechanical responses with preconditioning effect. Cross-sectional SEM images (inset of (d), scale bar, 1 mm) of CNT@Gr arrays before and after 1000 compression cycles indicate their persistent shape recoverability.

Figure 6.6 Cross-sectional SEM images of CNT (a–d) and CNT@Gr (e–h) arrays before and after 1 and 1000 compression cycles at strain (ϵ) = 60%, respectively. (a, d, e, h) are the zoom-in views of (b, c, f, g), respectively.

Figure 6.7 Energy dissipated (E_d , shadow area in (a)), energy loaded (E_l , shadow area in (b)) and energy returned (E_r , shadow area in (c)) for the first compression cycle at ϵ = 60%. (d) Energy dissipation ratios of CNT@Gr arrays at various applied ϵ .

Figure 6.8 Dynamic shear tests of CNT and CNT@Gr arrays. (a) Shear sandwich clamp was used to measure the longitudinal shear viscoelastic properties of the NT arrays. (b) Storage modulus (E'), (c) loss modulus (E'') and (d) damping ratio ($\tan \delta$) of the CNT and CNT@Gr arrays as functions of applied frequency (f) (1–100 Hz, at $\varepsilon = 2\%$).

Figure 6.9 Invariant viscoelastic properties of CNT@Gr arrays over a wide temperature (T) range in ambient air. Storage modulus (E') (a, d), loss modulus (E'') (b, e) and damping ratio ($\tan \delta$) (c, f) of the CNT@Gr arrays as functions of frequency (f) (0.1–100 Hz, at $\varepsilon = 1\%$) and ε (0.1–2%, with $f = 1$ Hz), respectively, at $T = -100, 25, 300$ and 500 °C.

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Figure 8.1 Fabrication of freestanding and flexible wafer-scale VACNT/PVA composite hydrogels. Step I : VACNT arrays were firstly hydrophilized by SDBS, and then the SDBS was gradually exchanged by homogenous infiltration of aqueous PVA solution among the VACNTs. Step II : Cyclic freezing/thawing was applied to enable *in situ* hydrogelation of PVA, by which the oriented morphology and uniform distribution of the VACNTs were well preserved.

Figure 8.2 Morphology and structure characterizations of VACNTs before (a–c) and after PVA infiltration (d–f). SEM (a,d) and TEM (b,c,e,f) images of VACNTs and VACNT/PVA composites, respectively. The aligned morphology and uniform distribution of VACNTs are well retained within the VACNT/PVA composites.

Figure 8.3 (a) Raman spectra, (b) XRD patterns and (c) TGA profiles of CNT, PVA and composite VACNT/PVA. Crystalline structures of the CNT and PVA hydrogels are well preserved for the VACNT/PVA composite hydrogels with 2.23 wt% (CNT:PVA) CNT filling.

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significantly enhanced compressive strengths (C. S.) and energy dissipation ratios (E. D. R.) reinforced by VACNTs.

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Figure 9.1 (a) Schematic illustration of the preparation of the OH-BNNS *via* two-step chemical oxidation and subsequent exfoliation processes. (b–e) Representative TEM images reveal the large lateral size (2~3 μm) and few-layered structure (~3 nm, ~10 atomic layers) of the as-prepared OH-BNNS. Their SAED pattern in the inset of (e) reveals the typical 6-fold symmetry of *h*-BN, indicating the structural integrity. (f, g) EELS analysis show a gradual decrease in the oxygen content from the edge (spot 1: 9.27%) to the basal plane (spot 4: 0.24%), demonstrating that the -OH groups are predominately located along the edges of the nanosheets. (h–j) AFM images and the corresponding height profiles of isolated OH-BNNS.

Figure 9.2 SEM images of the (a, b) starting bulk BN powder and (c, d) as-prepared OH-BNNS. Compared to the starting BN powder, the as-prepared OH-BNNS become almost transparent under SEM electron beam and consist of aggregations of thin and folded nanosheets.

Figure 9.3 Physicochemical characterization of the as-prepared OH-BNNS. (a) UV-Vis spectra of bulk BN and OH-BNNS aqueous solution. Inset shows the Tyndall effect of the as-prepared OH-BNNS dispersion. (b) Raman spectra of the bulk BN and OH-BNNS. Slight red-shift of the E_{2g} vibration of the OH-BNNS indicates the few-layered structure. (c) TGA and (d–f) XPS analysis further quantify the -OH functionalization of the BNNS.

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process based on the hydrogen bonding interactions between the OH-BNNS and PVA chains. (b) The composite hydrogels can be freely shaped. Relevant (c) FTIR spectra and (d) XRD patterns indicate that the crystalline structure of the PVA hydrogel was not altered after integration of OH-BNNS.

Figure 9.6 Water contents of the as-prepared OH-BNNS/PVA hydrogels with various OH-BNNS contents.

Figure 9.7 Cross-sectional SEM images of (a) the bare PVA and (b) OH-BNNS/PVA with 0.12 wt% (OH-BNNS:PVA) OH-BNNS. Additional polymer strands can be seen for OH-BNNS/PVA, which are possibly seeded from the OH-BNNS due to the hydrogen bonding interactions between the OH-BNNS and PVA chains, contributing to strengthened matrix/filler interfaces.

Figure 9.8 (a) Compressive and (b) tensile stress-strain curves for the OH-BNNS/PVA hydrogels with OH-BNNS contents varying from 0 to 0.12 wt%.

Figure 9.9 Mechanical responses of OH-BNNS/PVA composite hydrogels. Highly (a) compressible and (d) stretchable OH-BNNS/PVA hydrogels. (b) Compressive/(e) tensile stress-strain curves of the OH-BNNS/PVA hydrogel with 0.12 wt% OH-BNNS at various applied strains. (c) Compressive/(f) tensile properties are controllably enhanced for the composite hydrogels with increasing OH-BNNS content. Improvements up to 45%, 43%, and 63% in the compressive, tensile strengths and Young's modulus can be achieved with only 0.12 wt% OH-BNNS addition.

Figure 9.10 All the as-prepared OH-BNNS/PVA hydrogels can bear high degree of various mechanical deformations such as (a) bending, (b) twisting and (c) knotting.

Figure 9.11 The thermal diffusivity and conductivity of the OH-BNNS/PVA hydrogels were controllably enhanced with increasingly incorporated OH-BNNS. Improvements of up to 15% and 5% in thermal diffusivity and conductivity, respectively, can be achieved with only 0.12 wt% OH-BNNS addition.

Figure 9.12 Thermal conductivity of OH-BNNS/PVA composites (dried) with the increasing OH-BNNS content, a significant 68% increase from 0.47 to 0.78 W m⁻¹ K⁻¹ can

be achieved with only 0.12 wt% OH-BNNS introduced, indicating the excellent reinforcing effect of the as-prepared OH-BNNS on thermal conductivity.

Figure 9.13 Cytocompatibility of the OH-BNNS/PVA hydrogels. (a) Cell viability of composite hydrogels with various OH-BNNS contents assessed by MTS assay for 24 h. Cell viability of as high as ~85–95% indicates the non-cytotoxicity of the OH-BNNS/PVA hydrogels. Cell proliferation assay (b) and representative fluorescent images of live/dead assay (c) for the OH-BNNS/PVA (0, 0.06 and 0.12 wt%) hydrogels after cell cultures of 1, 3 and 5 days, respectively. The cells proliferate and spread well for the control and OH-BNNS/PVA hydrogel samples with comparable cell density and proliferation rate, and few dead cells (red) was observed during the 5 days' culture.

Figure 10.1 Enhanced dynamic compressive responses of graphene foam (GF)/PDMS as compared to bare PDMS at 30 °C (a, c) and –130 °C (b, d), respectively.^[1]

Figure 10.2 BNNT arrays with millimeter-scale dimensions have been achieved by a template-assisted TCVD method.^[5] In this method, the BNNT arrays are prepared by a two-step route involving depositing BN over CNT arrays at a relatively low temperature (900 °C) and a subsequent annealing process.

Figure 10.3 MoS₂/PVA composites with enhanced tensile strength and modulus.^[9]

Abbreviations

0D	Zero-Dimensional
1D	One-Dimensional
2D	Two-Dimensional
3D	Three-Dimensional
AFM	Atomic Force Microscopy
BNNS	Boron Nitride Nanosheets
BNNT	Boron Nitride Nanotube
CNT	Carbon Nanotube
DMA	Dynamic Mechanical Analysis
DMEM	Dulbecco's Modified Eagle Medium
DMF	Dimethylformamide
E. D. R.	Energy Dissipation Ratio
E'	Storage Modulus
E''	Loss Modulus
EDX	Energy-Dispersive X-ray Spectroscopy
EELS	Electron Energy Loss Spectroscopy
ESR	Equilibrium Swelling Ratio
EthD-1	Ethidium Homodimer-1
FBS	Fetal Bovine Serum
FESEM	Field Emission Scanning Electron Microscopy
FT-IR	Fourier-Transform Infrared Spectroscopy
GO	Graphene Oxide
Gr	Graphene
<i>h</i> -BN	Hexagonal Boron Nitride
HeLa	HeLa Cervical Adenocarcinoma Epithelial Cells
HR-TEM	High Resolution Transmission Electron Microscopy
k	Thermal Conductivity
MD	Molecular Dynamics
MTS	3-(4,5-Dimethylthiazol-2-yl)-5-(3-carboxymethoxyphenyl)-2-(4-

	sulfophenyl)-2H-tetrazolium, inner salt
NP	Nanoparticle
OD	Optical Density
OH-BNNS	Hydroxylated Boron Nitride Nanosheets
PAN	Polyacrylonitrile
PPR	Pulsed Photothermal Reflectance
PVA	Poly (vinyl alcohol)
rGO	Reduced Graphene Oxide
SAED	Selected Area Electron Diffraction
SDBS	Sodium Dodecylbenzenesulfonates
SEM	Scanning Electron Microscopy
$\tan \delta$	Damping Ratio
TCVD	Thermal Chemical Vapor Deposition
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
UV-vis	Ultraviolet–Visible Spectroscopy
VACNT	Vertically Aligned Carbon Nanotube
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

Chapter 1

Introduction

This chapter gives the brief introduction of this thesis. The hypotheses are introduced first, based on which the objectives and scopes of this thesis are then described. Next, the dissertation overview for each chapter is presented as well. Finally, the findings and outcomes of this thesis are summarized based on top of the whole content.

1.1 Hypothesis/Problem Statement

Sports have become increasingly popular worldwide due to their benefits to human's physical and mental health.^[1] In the meantime, to protect the athletes and meanwhile boost their performance during sports, the development of sports accessories is growing exponentially (e.g., 15.58 to 47.45 billion USD from 1992 to 2016 for sporting good sales in U. S.). One of the most important parts is the sports footwear, which could vary greatly among different sports types but share common features in the shock absorption and energy return.^[2] Hence, midsole, the interlayer between the outsole and upper that provides stability, cushioning and shock absorption^[3] is required to perform outstandingly in fatigue resistance, compressive strength and resilience as well as energy damping due to the complex mechanical loadings they may encounter during sports activities.^[4] As competitive candidates, vertically aligned carbon nanotube (CNT) arrays have attracted enormous attention due to their excellent compressive responses and unique buckling phenomenon that significantly dissipate energy through structural deformation and inter-tube frictions.^[5] However, most of the as-grown CNT arrays still deform permanently at only moderate strains due to their small tube diameter, thin wall thickness and weak inter-tube interactions, which are mostly dependent on the synthesis processes.^[6] Another promising candidate is ultralight three-dimensional reduced graphene oxide (3D rGO) aerogel with promising mechanical properties.^[7] Nevertheless, additional chemical cross-linkers are usually required to help assemble the 3D graphene monoliths and most of the resulting structures still undergo significant plastic deformation or have brittle mechanical performance when going through cyclic compression, which significantly hinder their further practical applications.^[8]

On the other hand, injury is an issue that could never be ignored for sports, especially the disease in articular cartilage due to its limited self-healing ability and low metabolism.^[9] To treat this disease, total cartilage replacement with synthetic biomaterials has become a popular approach free of drawbacks such as donor site morbidity or immunological rejection.^[10] Recently, poly (vinyl alcohol) (PVA) hydrogels with tissue-like viscoelasticity, excellent biocompatibility and high hydrophilicity have been considered as promising

cartilage substitutes.^[11] However, conventional PVA hydrogels usually suffer from limited mechanical strength, toughness and heat transfer, which restrict their practical applications.

Recent studies demonstrate that the performances of aforementioned carbon based architectures can be effectively enhanced by incorporation of nanomaterials with superior mechanical and thermal characteristics such as 0D metal oxides^[12]/carbon NPs,^[13] 1D CNTs^[14, 15] and boron nitride nanotubes (BNNT),^[16] 2D GO^[17] and BN nanosheets (BNNS).^[16] Among them, BNNS and BNNT are particularly promising as reinforcing elements due to the highly coherent atomic configuration and lattice constants with graphene,^[16, 18] which enable their possible combination with special synergistic effect to achieve enhancements in overall properties.^[19] Considering all the aspects mentioned above, the following hypotheses thus are proposed in this thesis:

- 1) The compressive mechanical responses and viscoelastic properties of CNT arrays will be enhanced by encapsulating conformal BN or graphene layers onto the CNT arrays;
- 2) Incorporating BNNS into the 3D rGO monoliths will contribute to reinforced mechanical behaviour;
- 3) Integration of vertically aligned CNT arrays and PVA hydrogels will introduce intense filler-matrix interactions and contribute to effective enhancements in mechanical strength and energy dissipation;
- 4) Introduction of biocompatible BNNS will strengthen the hydrogels in both mechanical and thermal aspects while preserve the cytocompatibility, which may lead to their potential applications for cartilage replacement.

1.2 Objectives and Scope

Based on the hypotheses proposed above, the objectives and scope are listed below.

- 1) Vertically aligned CNT arrays with different densities and lengths will be prepared by TCVD method. Then, BNNTs with various wall thicknesses will be introduced onto the CNT arrays to prepare coaxial C@BNNT arrays. Their morphology, structure and composition will be systematically characterized. Their mechanical behaviours will be

investigated using uniaxial compression tests at various applied strains and compression cycles. In addition, the heat transfer of the NT arrays will be studied from both experimental and theoretical perspectives.

2) Coaxial CNT@Gr arrays will be fabricated by introducing outer graphene layers onto the vertically aligned CNTs and their physiochemical characteristics will be comprehensively analyzed. Their uniaxial compressive mechanical behaviors will be tested in both static and dynamic fashions at varying temperatures in ambient air.

3) Hydroxylated (OH-) BNNS with high hydrophilicity and large lateral size will be prepared *via* chemical oxidation and subsequent exfoliation processes. The physicochemical properties of the as-prepared OH-BNNS will be systematically characterized. Heterostructured 3D rGO/BN aerogels will be assembled by a freeze-drying and subsequent thermal annealing process. The compressive mechanical performances of the composite 3D monoliths will be investigated.

4) VACNT/PVA hydrogels will be fabricated by an *in situ* hydrogelation approach. The effect of VACNT integration on the static and dynamic compressive mechanical responses of the composite hydrogels will be studied.

5) OH-BNNS will be incorporated into PVA hydrogels to prepare composite OH-BNNS/PVA hydrogels. The mechanical, thermal responses and biocompatibility of such hydrogels will be comprehensively assessed to explore their potential in cartilage replacement applications.

1.3 Dissertation Overview

This thesis addresses why and how to synthesize novel composite architectures based on low dimensional C/BN with enhanced mechanical and thermal responses for sports applications. In general, architectures including coaxial C@BNNT arrays, CNT@Gr arrays, 3D rGO/BN aerogels, VACNT/PVA and OH-BNNS/PVA hydrogels have been developed

as potential alternative sports footwear midsole materials with enhanced protective effect and cartilage substitute materials with improved mechanical and thermal responses.

Chapter 1 provides a rationale for the research and outlines the goals and scope.

Chapter 2 reviews the literature concerning the current alternative sports footwear midsole materials and cartilage substitute materials.

Chapter 3 discusses the rationale for methods/materials selection, the synthesis and characterization techniques adopted.

Chapter 4 elaborates fabrication and characterization of C@BNNT arrays, as well as their enhanced compressive mechanical properties.

Chapter 5 studies the thermal conductivity improvement of the C@BNNT arrays from both experimental and theoretical perspectives.

Chapter 6 elaborates the fabrication and characterization of CNT@Gr arrays and demonstrates their supercompressibility and temperature-invariant viscoelastic characteristics in ambient air.

Chapter 7 shows synthesis and characterization of highly hydrophilic BNNS and further fabrication of 3D rGO/BN aerogels with enhanced cyclic compressibility.

Chapter 8 elaborates the fabrication and characterization of VACNT/PVA hydrogels and their improved static and dynamic compressive responses.

Chapter 9 elaborates the fabrication of interpenetrating OH-BNNS/PVA hydrogels with enhanced mechanical properties, thermal conductivity and well-preserved biocompatibility.

Chapter 10 concludes the dissertations and elaborates the further studies which could be

conducted in the near future.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes:

1) C@BNNT arrays with significant improvements in compressive strength, shape recoverability, fatigue resistance, energy dissipation have been fabricated by encapsulating outer BNNT onto the plastic CNT arrays *via* a TCVD method. Moreover, the resulting reinforcement can be controllably tuned by varying the wall thickness of the outer BNNT. The C@BNNT arrays with excellent mechanical behaviours would enable broad potential applications such as energy dissipative devices and compressive mechanical contacts.

2) For the first time, the enhanced thermal conductance of the C@BNNT arrays has been reported from both experimental and theoretical perspectives. As revealed by the reverse non-equilibrium MD simulation, the outer BNNT provides additional thermal conductance without affecting that of the inner CNT, which could be attributed to their coherent structures and is beneficial to their energy dissipation performance.

3) Macroscale coaxial CNT@Gr arrays with superior compressibility (~80% recovery after 1000 cycles at a 60% strain) and significantly enhanced compressive strength have been be fabricated by encapsulating uniform graphene layers onto the vertically aligned CNTs according to a two-step TCVD protocol. The resulting CNT@Gr arrays even perform outstanding strain- and frequency-dependent viscoelastic properties that are nearly constant over an exceptionally broad temperature range (−100–500 °C) in ambient air. These excellent characteristics would inspire many promising applications such as compressive mechanical/thermal contacts, electromechanical devices and energy absorption systems even in harsh environments.

4) A simple and scalable method has been developed to prepare highly water soluble hydroxylated BNNS (up to 0.6 mg mL^{−1}) with large lateral size (~2–3 μm). Furthermore,

rGO/BN aerogels have been constructed with cell walls of assembled graphene and BNNS by a facile freeze-drying and subsequent thermal annealing process. The unique 3D porous network and the synergistic effect between graphene and BNNS endow the as-prepared rGO/BN aerogel with ultralow density, high compressibility and excellent recoverability, showing high potential as multifunctional compressible mattress.

5) Wafer-scale VACNT/PVA composite hydrogels have been successfully fabricated by infiltration of PVA among VACNTs and subsequent *in situ* hydrogelation. Such hydrogels perform outstanding longitudinal compressive responses upon both static and dynamic loadings, attributing to continuous reinforcements of uniformly distributed VACNTs and the large CNT-PVA interfaces, which enable their potential in load-bearing hydrogel applications.

6) With the incorporation of as-prepared hydroxylated (OH-) BNNS, for the first time, biocompatible OH-BNNS/PVA hydrogels with significant enhancements in compressive, tensile strengths and Young's modulus, as well as improvements in thermal diffusivity and conductivity have been fabricated. These OH-BNNS/PVA hydrogels are promising in addressing the mechanical failure and locally overheating issues as cartilage substitutes.

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Chapter 2

Literature Review

This chapter presents the literature review on the recent progresses of developing candidate midsole materials and artificial cartilages. Reinforcement of CNT arrays and 3D rGO aerogels with various nanomaterials and their potential midsole applications are introduced first. Then, enhancement of PVA hydrogels by diverse nanomaterials and their cartilage replacement applications are elaborated. Finally, the questions to answer and the thesis in context based on literatures are discussed.

2.1 Overview

Lightweight CNT arrays and 3D rGO aerogels have been considered as competitive candidate midsole materials due to their high compressibility and energy dissipation that are beneficial for shock absorption and cushioning.^[1, 2] However, most of them still exhibit limited shape recovery and fatigue resistance, which severely restrict their practical applications.^[3, 4] On the other hand, PVA hydrogels with tissue-like viscoelasticity, high water contents and superior lubricity have been considered as the most promising artificial cartilage candidates, whereas limited mechanical strength and poor toughness of the bare PVA hydrogels still hinder their further applications upon complex biomechanical loadings.^[5] To address the abovementioned issues, many efforts have been made such as improving the intrinsic characteristics of these carbon based architectures by optimizing the synthesis methods and reinforcing their overall performances by incorporating nanomaterials with superior physical properties. In particular, the latter approach is more promising due to the diversity of the low dimensional nanomaterials including 0D NPs,^[6] 1D nanotubes/fibers^[7, 8] and 2D nanosheets^[5, 9, 10] with superior mechanical, thermal characteristics and large specific surface area.

To reinforce the as-grown CNT arrays, post-growth treatments involving the thickening of the tube diameter (encapsulating additional CNT walls or graphene sheets)^[11, 12] and increase in the array density of the CNT arrays (coating metal oxide NPs,^[13, 14] infiltrating polymer)^[15] have been widely studied. To strengthen 3D rGO aerogels, considerable efforts have been devoted to introducing nanomaterial linkers including polymers,^[16-19] CNTs,^[20, 21] and metal NPs^[22, 23] into the 3D networks. The detailed literatures regarding the abovementioned works will be further reviewed and summarized in section 2.1.1. As for the enhancement of PVA hydrogels, 0D hydroxyapatite NPs,^[6] 1D CNTs^[7, 8] and 2D GO^[5] have been incorporated and the resulting reinforcements have been investigated, which will be discussed in details in section 2.1.2.

2.1.1 Reinforcement of candidate midsole materials

As competitive candidate midsole materials, CNT arrays normally exhibit high mechanical strength and unique buckling phenomenon upon uniaxial compression, which contribute to their efficient energy dissipation.^[1] However, most of the as-grown CNT arrays possess limited shape recovery and fatigue resistance which are dependent on their synthesis methods, restricting their practical energy absorption applications.^[3] To reinforce the mechanical properties of the CNT arrays, conformal coatings varying from organic (polymers, *e.g.*, polyimide,^[24] epoxy,^[25] polydimethylsiloxane (PDMS)^[15]) to inorganic (*e.g.*, metal oxides including SnO₂ and MnO₂,^[14] graphene^[12]) materials with controlled thicknesses have been introduced. For example, continuous CNT/polymer composite has been fabricated by infiltrating PDMS into the interspaces of aligned CNTs (Figure 2.1),^[15] which is able to generate more than an order of magnitude increase in the longitudinal Young's modulus (up to 3300%) and energy dissipation (up to 2100%) when compared to bare CNT arrays. The “confinement effect” created by surrounding polymer chains makes the buckling of CNTs difficult, giving rise to the compressive strength and modulus. In addition, the excellent thermal conductivity of aligned CNTs facilitates the dissipation of thermal energy during compression cycles, enhancing the damping capability of the nanotube composites. Nonetheless, this polymer composite is not suitable for high temperature post-process treatment due to the relatively lower intrinsic thermal stability of polymer. Moreover, the infused PDMS decreases the porosity of CNT arrays drastically, limiting their compressibility at higher applied strains.

As an alternative reinforcing material with better thermal and mechanical properties, silicon carbide (SiC) with diamond like characteristics (crystalline structure and mechanical strengths) has been further coated onto the vertically aligned CNT arrays to simultaneously enhance their thermal and mechanical behaviours.^[26] As shown in Figure 2.2, after being coated with SiC, the porosity of the CNT arrays decreases and the connections between the tubes change from weak van der Waals interaction to amorphous SiC bonded connection. As a result, the CNT arrays modified with 21.4 nm SiC exhibit 3 orders of magnitude increases in compressive strength (~1 MPa to ~1.8 GPa) and Young's

modulus (~ 200 MPa to ~ 125 GPa) as compared to the original CNT arrays, suggesting their potential as robust high aspect-ratio structural material. Nevertheless, due to the decreased porosity, the resulting SiC coated CNT arrays are not able to endure high compressive strain (less than 20%), showing degraded flexibility and unsatisfactory shape recoverability.

Figure 2.1 “Confining effect” of the surrounding polymer chains reinforces the mechanical performance of CNT arrays.^[15] The infusion of PDMS contributes to significantly enhanced longitudinal Young’s modulus and energy dissipation with increases of 3300% and 2100%, respectively.

Figure 2.2 Compressive mechanical responses of CNT pillars coated with amorphous SiC in different thicknesses.^[26]

Figure 2.3 Mechanical responses of CNT arrays before and after modification with MnO₂ particles. Scale bar, 400 nm.^[14]

Meanwhile, to improve the energy dissipation characteristics of the CNT arrays, metal oxide NPs (SnO₂ and MnO₂) have been *in situ* synthesized among the CNT arrays *via* TCVD method without disrupting the ordered structure of the CNTs (Figure 2.3).^[14] The modified CNT arrays fracture laterally through the deposited particles upon uniaxial compression and recover elastically after load releasing, performing stable mechanical performance upon cyclic compressive loading. The frictions between the NPs during the compression cycles lead to larger amount of energy dissipation (twice that of unmodified CNT arrays), indicating their potential applications for energy cushion. However, the CNT arrays with additional heavy metal oxides exhibit increased density while do not possess sufficient shape recoverability and compressibility.

It can be noted that although various materials have been incorporated to reinforce the mechanical and thermal characteristics of the CNT arrays, there still remain several drawbacks for the resulting composite architectures. In spite of the improved shape recoverability and mechanical strength of polymer infused CNT arrays, the limited thermal stability of polymer hinders their further post treatment at high temperatures. In addition, the inorganic conformal coating has improved the mechanical strength and thermal stability of the CNT arrays, while the decreases in porosity and compressibility restrict their

potential applications where large applied strains are anticipated. Therefore, developing an alternative approach to not only improve the mechanical strength, shape recoverability and energy dissipation of the CNT arrays but also preserve their intrinsic low density and high porosity is still highly desirable.

On the other hand, as a structural analogue of CNT,^[27-29] boron nitride nanotube (BNNT) has been proved to possess superior mechanical properties^[30-32] and applied as a protective coating material for CNT.^[33, 34] Recently, it has been predicted theoretically that not only the high thermal resistance of the outer BNNT can provide protection for the inner CNT, but also the inter-wall van der Waals interactions between the CNT and BNNT will further enhance the protective effect of outer BNNT both thermally and mechanically (Figure 2.4).^[35, 36] Considering the outstanding intrinsic properties of the BNNT and its coherent structure with the CNT, it is expected that the overall performances of the CNT arrays will be enhanced by the BNNT integration. However, to the best of our knowledge, such reinforcements have not been investigated experimentally.

Figure 2.4 Simulated configurations of coaxial C@BNNT (A) and C@CNT (B) structures at various annealing temperatures.^[35]

In addition, decorating CNTs with graphitic carbon is another promising reinforcing approach because that the synergistic effect among different forms of carbon improves the overall properties.^[12] For example, petal-like multi-layer graphene has been introduced onto the vertically aligned CNTs to build up an all-carbon structure,^[12] the pristine carbon nature of which was preserved (Figure 2.5). The resulting composite CNT arrays with the additional graphene petals exhibit enhanced elastic modulus, energy absorption, shape recoverability and structural stability upon cyclic compressive loading, as compared to the as-prepared CNT arrays which plastically deform when compression is applied. Nevertheless, the majority of current carbon deposition approaches involving gaseous precursors are only applicable to laboratory-based (non-commercial) CNT arrays and encounter non-uniform carbon decoration (especially for those long and densely packed CNTs), which significantly limit their mechanical enhancements.^[11, 12, 37] As such, developing a facile process to achieve macroscale CNT arrays with uniform graphitic carbon encapsulation and further exploring their compressibility and dynamic viscoelasticity under various conditions are still in urgent demand.

Figure 2.5 CNT arrays possess higher stiffness and shape recoverability after decoration of graphene petals.^[12]

In addition to CNT arrays, 3D rGO aerogels with ultra-low density, porous structure and outstanding compressibility have also shown promising applications in mechanical support and energy absorption.^[38] However, most of the previously reported 3D structures undergo

significant plastic deformation or have brittle mechanical performance when going through cyclic compression strain,^[4] which significantly hinder their further practical applications. Thus far, considerable efforts have been devoted to improving the mechanical properties of the 3D rGO monoliths, such as introducing polymers,^[16-19] CNTs^[20, 21] and metal NPs^[22, 23] into the 3D networks. For example, a self-assembly technique has been developed to fabricate polymer reinforced GO foam (PGF), in which the GO sheets are compactly interconnected to form a network within the 3D polymer skeleton (Figure 2.6).^[18] As compared to the bare GO foam which plastically collapses upon mechanical loading, the resulting PGF performs not only outstanding mechanical performances in compression, bending and twisting but also excellent hydrophobic and electrical properties, showing broader application ranges. Moreover, as the allotrope of graphene, CNT with comparable superior mechanical properties has also been introduced into the 3D graphene networks by a synergistic assembly strategy to achieve the mechanical reinforcement (Figure 2.7).^[21] The entangled CNTs provide a linker effect by bonding the graphene sheets together to prevent the inter-sheet sliding upon compression loading, which remarkably enhances the elastic modulus of the graphene cell walls and contributes to the supercompressibility of the resulting graphene/CNT aerogels.

Figure 2.6 Polymer reinforced GO foam perform excellent shape recovery (a, b) and fatigue resistance (c). As comparison, bare GO foam collapse upon compression loading (d).^[18]

Figure 2.7 The CNT introduction contributes to the excellent shape recovery (a, b) and superior fatigue resistance (c, d) of the composite Gr/CNT aerogels, which could be attributed to the linker effect of the entangled CNTs and the synergistic effect between CNT and graphene sheets.^[21]

Figure 2.8 Molecular dynamics simulation of mechanical behaviour of bare GO sheet and GO-BNNS heterostructure upon different strains.^[39]

Despite these progresses, the performances of the resulting 3D GO aerogels are still not satisfactory. On the other hand, heterostructures assembled by two different kinds of two dimensional materials *via* van der Waals bonding could result in various extraordinary optical, electronic and mechanical characteristics.^[39-41] Such effective strategy has opened up new avenues for preparation of graphene-based 3D macrostructures, which are highly desirable for diverse practical applications. It is interesting to note that BNNS, an analogue of graphene, possesses excellent mechanical, thermal and chemical stabilities, which could be introduced into graphene frameworks to reinforce the 2D structural units and further improve the mechanical integrity of the 3D foam structure.^[39-41] Figure 2.8 shows the MD simulation on GO-BNNS heterostructures upon different applied strains.^[39] The results indicate that the atomic level interactions between GO and *h*-BN could facilitate the construction of nearly flat flexible layers. Meanwhile, the complicated stress distribution in GO-BNNS overlapped area prevents the defects/cracks propagation, contributing to the enhanced elasticity of the composite 3D GO/BNNS architectures. However, 3D interconnected heterostructures constructed from these two novel 2D materials are still at their early stage. Particularly, the reported BNNS by the exfoliation of bulk BN in organic solvents show significant restacking or aggregation,^[39-41] which significantly affect their physicochemical properties of the as-prepared GO/BNNS composite when these resultant BN products with a non-uniform thicknesses are integrated with GO. Therefore, it is highly desirable to develop an effective approach to prepare BN aqueous solution and then directly integrate the as-prepared BNNS dispersion with GO aqueous solution to build 3D GO/BNNS interconnected macrostructure with promising mechanical behaviours in a large-scale.

2.1.2 Enhancement of articular cartilage materials

To address the drawbacks of the bare PVA hydrogels as artificial cartilage substitute materials such as limited mechanical strength and poor toughness, many efforts have been done either by incorporating nanomaterials into the bare PVA hydrogels^[5-10] or developing other novel hydrogels using alternative polymers.^[42-44] To date, a lot of low dimensional nanomaterials such as hydroxyapatite (HA) nanoparticles (NPs) and carbon nanodots (C-

dot),^[6] 1D CNTs^[7, 8] and 2D GO nanosheets^[5, 9, 10] have been introduced into the PVA hydrogels to enhance the mechanical strength and rigidity. As shown in Figure 2.9, rigid HA NPs have been assembled into the PVA hydrogels by freezing-thawing method to achieve PVA-HA hydrogels. With the reinforcements of uniformly distributed HA NPs, the elastic modulus and compressive strengths of the composite hydrogels could be controllably enhanced. Meanwhile, C-dot could serve as an excellent reinforcing filler and ideal nucleating agent for PVA hydrogel crystallization (Figure 2.10).^[45] Recently, C-dot with appropriate size (~ 3 nm) and surface functional groups have been added into PVA to facilitate the formation of more dense and uniform cross-linked networks, which lead to 46.4% and 18.5% improvements in tensile strengths and strain-at-break, respectively.

Figure 2.9 (a) SEM images of the PVA-HA hydrogels. (b) Compressive stress-strain curves of PVA-HA hydrogels with various HA contents.^[6]

Figure 2.10 (a) TEM image of the C-dots. (b) Tensile strength of the PVA/C-dot hydrogel increases with the cycles of freezing-thawing process and the C-dot concentration.^[45]

As representative 1D nanomaterials, CNTs with superior mechanical properties, high

specific area, exceptionally high aspect ratio and ultralow density have been widely investigated to reinforce the overall mechanical performances of the PVA hydrogels.^[46-48] For example, CNTs have been first functionalized by poly (vinyl pyrrolidone) (PVP) to facilitate the uniform distribution of CNTs throughout the PVA matrix, resulting in a strengthened filler-matrix interface within the composite hydrogels.^[48] As a result, with less than 2% introduction of the PVP treated CNTs, significant improvements in tensile toughness, modulus strength, friction coefficient and tear strength could be achieved for the CNT/PVA composite hydrogels (Figure 2.11).

Figure 2.11 (a) SEM images of the CNT/PVA hydrogels with 2.0 wt% CNT addition, CNT-rich area was zoomed in as shown in the inset. (b) Overall tensile properties including Young's modulus, strength and strain-at-break could be controllably reinforced by the CNT introduction.^[48]

Although the mechanical properties of PVA hydrogels have been improved by integration of CNTs, it is still difficult to achieve further reinforcements by increasing the CNT content because the natural tendency of random CNTs to form agglomerates within the matrix (Figure 2.11a), which originates from the substantial inter-tube van der Waals attractions.^[49, 50] To date, many strategies have been developed to address these problems including improving the dispersion of CNTs by either significant mechanical energy input with the aid of ultrasound and ball milling, or chemical modification involving the usage of strong acids/oxidants and reactive plasma.^[51] However, the CNTs treated by such harsh processes normally suffer from shortened tube length and impaired intrinsic structures, which are detrimental to their resulting reinforcements. On the other hand, instead of random CNTs, utilizing vertically aligned CNTs (VACNTs) as continuous reinforcements could be a feasible approach to achieve uniform distribution and alignment of CNTs across the

dimensions of composite structures, without sacrificing their structural integrity or intrinsic characteristics.^[15] Considering these advantages of the continuous CNTs reinforced composites, VACNTs based composite hydrogels with large CNT-matrix interfacial area are expected to exhibit promising mechanical responses, which have not been reported thus far.

Figure 2.12 (a) Tensile strength and (b) strain-at-break of the GO/PVA hydrogels could be controllably enhanced by GO addition with various concentrations. (c) SEM images of pure PVA and GO/PVA hydrogels with 0.8 wt% of GO.^[5]

Furthermore, 2D nanomaterials with excellent mechanical properties and even larger specific surface area have also been investigated in terms of their possible reinforcing effects in the mechanical performances of the PVA hydrogels.^[15, 9, 52] For example, GO with various concentrations have been added into PVA to fabricate composite GO/PVA hydrogels by a freezing/thawing method, as shown in Figure 2.12.^[5] Interestingly, with the addition of only 0.8wt% (GO:PVA) of GO, 132% and 36% increases in the tensile and compressive strengths are performed for the composite hydrogels as compared to the bare PVA hydrogels, which could be attributed to the excellent load transfer between the GO sheets and the polymer networks.

Figure 2.13 Cytotoxicity evaluation for GO and rGO.^[53] Brightfield images ($\times 10$) of HUVEC cell morphology in control (A) and GOS1 (B), GOS2 (C), RGOS1 (D) and RGOS2 (E) after 48 h cell proliferation. MTT assay of GO/rGO with various concentrations and different treatment times are presented in (G) and (H), respectively. Both GO and RGO exhibit concentration-dependent cytotoxicity.

Despite these progresses, the abovementioned carbon/PVA nanocomposite hydrogels are still not extensively used as damaged cartilages substitutes, which can be attributed to the dose-dependent cytotoxicity of the carbon based materials (Figure 2.13).^[9, 53-55] Therefore, developing an alternative cell-friendly nanomaterial and further fabricating biocompatible PVA based composite hydrogels with adequate mechanical property and appropriate thermal conductivity are still urgent need. On the other hand, possessing comparable mechanical strength and thermal conductivity with graphene,^[56, 57] yet better biocompatibility,^[54, 58] BNNS have shown promising potential in both mechanical and thermal reinforcements.^[59, 60] However, the extremely poor solubility of the BNNS in aqueous media resulting from the high hydrophobicity makes them difficult to be uniformly incorporated into the hydrogel network.^[61] Several approaches have been developed to improve the water solubility of the BNNS by introducing hydroxyl (-OH) functional groups onto their basal plane or edges. For example, solution-phase oxygen radical functionalization has been applied for B atoms in the hexagonal BN lattice to enhance the dispersion of resulting BNNS in water (Figure 2.14).^[60] Meanwhile, ball milling of BN

powders in the presence of sodium hydroxide has also been adopted to synthesize BNNS with microscale dimension and high water solubility (Figure 2.15).^[62] In addition, other approaches such as sonication-assistant exfoliation of bulk BN powder in water,^[63] heating BN powder in air,^[64] and treating bulk BN powder with hot water steam^[65] have been demonstrated as well. Nevertheless, only OH-BNNS with limited solubility in water ($0.01\sim0.3\text{ mg mL}^{-1}$)^[61, 63, 65, 66] and small lateral size (hundreds nm)^[61, 63, 66] have been reported so far. As such, developing a facile and effective method to obtain highly water soluble OH-BNNS with relatively larger lateral size while preserve the biocompatibility of BN is crucial for the desired PVA based composite hydrogels.

Figure 2.14 UV-vis spectra of pristine BNNS and OH-BNNS in water. Inset shows the (a) photos of pure water, pristine BNNS and OH-BNNS aqueous solutions, as well as their corresponding (b) Tyndall effects.^[60]

Figure 2.15 Schematic and corresponding SEM images of the liquid phase exfoliation of *h*-BN assisted by ball milling in the presence of NaOH to achieve OH-BNNP.^[62]

2.2 Questions to Answer Based on Literature

As summarized in the aforementioned literature review, a lot of efforts have been devoted to reinforcing CNT arrays, 3D rGO aerogels and PVA hydrogels, as well as enabling their potential applications in candidate midsole materials and artificial cartilages. However, there are still several questions that remain unanswered:

First of all, theoretical studies have demonstrated that the introduction of coaxial outer BNNT onto CNT could be an effective approach to reinforce its mechanical and thermal behaviors. One may wonder that is there an effective experimental approach to prepare coaxial C@BNNT arrays and realize both enhanced mechanical and thermal properties?

Although previous works have shown that the compressive mechanical properties of CNT arrays have been improved to some extent by incorporating various nanomaterials including polymer, NPs, SiC and graphene petals, the shape recoverability, energy dissipation and viscoelastic response of the resulting composite architectures are still not satisfactory for further energy absorption applications. Moreover, most of the carbon deposition approaches involving gaseous precursors are only applicable to laboratory-based CNT arrays with limited dimension and array density. One may wonder that is there a facile process to achieve macroscale CNT arrays with uniform graphitic carbon encapsulation, which further perform stable compressibility and dynamic viscoelasticity under various conditions?

Next, 3D heterostructures constructed by 2D rGO and BNNS have been predicted to perform better mechanical stability than bare 3D rGO aerogels. However, the significant restacking or aggregation of the reported BNNS with limited solubility in water and small lateral size still significantly affect their uniform distribution in the resulting composite architectures. One may wonder that is it possible to develop an effective approach to synthesize BNNS with high water solubility and large lateral size? Moreover, will the integration of the as-prepared BNNS with GO really lead to composite architectures with outstanding mechanical properties?

In addition, although the mechanical properties of PVA hydrogels have been improved by integration of CNTs, it is still difficult to achieve sufficient reinforcements because the natural tendency of random CNTs to form agglomerates within the matrix. One may wonder that will incorporating VACNTs as continuous reinforcements be a feasible approach to achieve VACNT/PVA composite hydrogels with uniform CNT distribution and thus promising mechanical responses?

Despite the progresses in reinforcing the PVA hydrogels with carbon nanomaterials, the dose-dependent cytotoxicity of the carbon based materials still limits their further applications as cartilage substitutes. Considering the outstanding mechanical strength, thermal conductivity and excellent biocompatibility of the BNNS, will the incorporation of BNNS into the PVA networks lead to biocompatible BNNS/PVA hydrogels with enhanced mechanical and thermal responses?

2.3 PhD in Context of Literature

In this thesis, the reinforcement of mechanical and thermal properties of CNT arrays, 3D rGO aerogels and PVA hydrogels with low-dimensional C/BN nanomaterials were systematically investigated. Meanwhile, the potential sports related applications of the resulting architectures including compressible nanomattress for sports footwear midsole and hydrogel substitutes for cartilage replacement were discussed as well. The contribution of my thesis in this area is listed as follow:

First of all, it is experimentally proved for the first time that encapsulating coaxial outer BNNT onto the CNT arrays is able to controllably enhance their mechanical properties by varying the wall thickness of the outer BNNT. Significant improvements in compressive strength, shape recovery, fatigue resistance and energy dissipation were achieved for the C@BNNT arrays due to the synergistic effect between inner CNT and outer BNNT, which enable their mechanical damping related applications.

Then, it is identified that the outer BNNT provides additional thermal conductance without affecting that of the inner CNT due to their coherent structures, as supported by both the experimental measurement and reverse non-equilibrium MD simulation. This could be beneficial to the energy dissipation of C@BNNT arrays in form of heat.

Next, it is shown that conformal graphene layers could transform the plastic macroscale CNT arrays into supercompressible coaxial CNT@Gr arrays with temperature-invariant viscoelasticity in ambient air, which are attributed to the synergistic effect between the inner CNTs and outer graphene layers. These CNT@Gr arrays would enable many promising applications such as compressive mechanical/thermal contacts, electromechanical devices and energy absorption systems even in harsh environments.

Moreover, it is found that highly water soluble OH-BNNS with large lateral size could be achieved by using a two-step chemical oxidation and subsequent exfoliation method. In addition, it is experimentally proved that the incorporation of BNNS into rGO aerogels would endow high compressibility and excellent recoverability of the resulting rGO/BN aerogel, attributing to the synergistic effect between graphene and BNNS. The potential applications of the rGO/BN aerogel as multifunctional compressible mattress are expected.

In addition, it is shown that wafer-scale VACNT/PVA composite hydrogels could be successfully fabricated by an *in situ* hydrogelation approach. Meanwhile, the resulting composite hydrogels perform outstanding longitudinal compressive responses upon both static and dynamic loadings, attributing to continuous reinforcements of uniformly distributed VACNTs and the large CNT-PVA interfaces, showing potential in load-bearing applications upon complex mechanical loadings.

Last but not least, the cytocompatible OH-BNNS could serve as effective additives to fabricate OH-BNNS/PVA hydrogels with remarkably improved mechanical properties and heat transfer, attributing to the homogeneously distributed OH-BNNS and the hydrogen bonding interactions between the OH-BNNS and PVA chains. These biocompatible OH-

BNNS/PVA hydrogels show promising potential applications in artificial cartilages and tissue-engineered scaffolds.

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Chapter 3

Experimental Methodology

In this chapter, the materials and synthesis methods including freezing-thawing, freeze-drying, thermal chemical vapor deposition, hydrothermal method, chemical oxidation and sonication-assisted exfoliation are introduced that are used to synthesize the low dimensional C/BN nanomaterials such as CNT, BNNT, BNNS and graphene nanosheets, as well as to further fabricate multifunctional composite architectures including rGO/BN aerogel, coaxial C@BNNT, CNT@Gr arrays, VACNT/PVA and OH-BNNS/PVA hydrogels. Meanwhile, various techniques and equipment such as SEM, TEM, FT-IR, XRD, TGA, XPS, AFM, UV-vis and Raman spectroscopies are introduced to investigate the physicochemical characteristics of the abovementioned novel nanomaterials and corresponding hybrid nanostructures. For all these methods and techniques, the basic principles are illustrated with the help of examples.

3.1 Rationale for Selection

In this thesis, CNT arrays were first chosen as the starting materials due to their exceptional thermal and mechanical characteristics.^[1-3] Despite these advantages, their mechanical properties largely depend on geometrical structures of the CNTs and their buckling behaviour is closely associated with the interactions between individual tubes.^[4] To date, the majority of the reported CNT arrays grown by thermal chemical vapour deposition (TCVD) are known to oxidize readily at ~ 400 °C when exposed to air^[5] and usually suffer from plastic deformation upon compression,^[6] which severely limit their practical applications. An effective strategy to address these issues is integrating nanomaterials with superior mechanical and thermal properties. It is encouraging to note that BNNT not only meets all these requirements as the conformal protective material but also has been predicted that the inter-wall van der Waals interactions between the CNT and BNNT will further enhance the protective effect of outer BNNT both thermally and mechanically.^[7, 8] In the meantime, the outer BNNT is also expected to enhance the axial thermal conductivity while does not affect the intrinsic thermal conductance of the inner CNT. Therefore, it is expected that the CNT arrays encapsulated by outer BNNTs will exhibit enhanced mechanical and thermal behaviours. However, to the best of our knowledge, such reinforcements have not been investigated experimentally. On the other hand, considering that CNTs are prone to cluster upon those wet chemical modifications which may last several days to achieve the desired structure,^[9] TCVD method is more suitable for treating CNT arrays to modify their structures by introducing the BNNT as the conformal layers. Therefore, TCVD was chosen as the synthesis technology to introduce outer BNNT onto the CNT arrays under atmospheric pressure.

Another promising approach to strengthen the mechanical properties (compressive strength, shape recoverability, etc.) CNT arrays is the decoration of graphitic carbon (graphene nanosheets/coating, coaxial outer CNT, etc.) because that the resulting synergistic effect among different forms of carbon improves the overall properties.^[9] Moreover, this treatment well preserves the intrinsic characteristics of CNTs which facilitate their wide applications.^[10] However, the majority of current carbon deposition approaches involving

gaseous precursors are only applicable to laboratory-based (non-commercial) CNT arrays and encounter non-uniform carbon decoration (especially for those long and densely packed CNTs), which significantly limit their mechanical enhancements.^[9-11] Therefore, a two-step fabrication of CNT@Gr arrays was developed by encapsulating polyacrylonitrile (PAN) polymer onto the vertically aligned CNTs (~4 mm in length) and subsequently annealing to convert the PAN coating into conformal graphene layers.

To reinforce the rGO aerogels, various materials including polymers,^[12-15] CNTs,^[16, 17] and metal NPs^[18, 19] have been integrated into the 3D networks, while the obtained performance is still not satisfactory. Notably, heterostructures assembled by two different kinds of low dimensional materials *via* van der Waals bonding could result in extraordinary mechanical characteristics.^[20-22] With graphene analogous structure, BNNS show excellent mechanical properties, which inspire us to introduce them into graphene frameworks to reinforce the 2D structural units.^[20-22] However, to the best of our knowledge, the significant restacking or aggregation of the reported BNNS prepared by the exfoliation of bulk BN in organic solvents significantly affect their uniform distribution in the resulting composite architectures.^[20-22] To date, several approaches have been developed to improve the water solubility of the BNNS by introducing hydroxyl (-OH) functional groups onto their basal plane or edges, such as sonication-assistant exfoliation of bulk BN powder in water,^[23] solution-phase oxygen radical functionalization of B atoms in the hexagonal BN lattice,^[24] heating BN powder in air,^[25] ball milling of BN powders in the presence of sodium hydroxide^[26] and treating bulk BN powder with hot water steam.^[27] Nevertheless, only BNNS with limited solubility in water (0.01~0.3 mg mL⁻¹)^[23, 27-29] and small lateral size (hundreds nm)^[23, 28, 29] have been reported so far. Therefore, a two-step chemical oxidation and subsequent exfoliation process has been developed to prepare high quality BNNS with uniform size distribution and high water solubility. For the fabrication of composite aerogel, a number of approaches such as hydrothermal-mediated reduction,^[30-34] template-assisted CVD,^[35-38] chemical reduction,^[39, 40] and freeze-drying processes^[41, 42] have been developed. Among them, the freeze-drying method is a relatively facile and promising strategy to produce 3D graphene monoliths in a large-scale, which was adopted for the

fabrication of multifunctional 3D rGO/BN aerogel without the presence of any additional chemical reagents.

Many efforts have been devoted to strengthening the hydrogels by incorporating nanomaterials such as metal oxides^[43]/carbon NPs,^[44] CNTs^[45, 46] and GO nanosheets.^[47] Among them, CNTs with superior mechanical strength and modulus are particularly promising nano-fillers because of their exceptionally high aspect ratio.^[45] Nevertheless, the resulting reinforcements are still restricted by either insufficient CNT-matrix interfacial area due to the agglomeration of random CNTs^[48] or impaired intrinsic characteristics of CNTs resulting from the harsh treatments employed for dispersion.^[49] On the other hand, instead of random CNTs, utilizing vertically aligned CNTs (VACNTs) as continuous reinforcements could be a feasible approach to achieve uniform distribution and alignment of CNTs across the dimensions of composite structures, without sacrificing their structural integrity or intrinsic characteristics.^[50] Considering these advantages, VACNTs based composite hydrogels with large CNT-matrix interfacial area are expected to exhibit promising mechanical responses, while which have not been reported thus far. Therefore, we further developed a facile approach to fabricate wafer-scale VACNT/PVA hydrogels by infiltration of PVA among VACNTs and subsequent *in situ* hydrogelation.

Despite these progresses in reinforcing the PVA hydrogels with carbon nanomaterials, the resulting carbon/PVA hydrogels are still not extensively used to replace damaged cartilages due to the dose-dependent cytotoxicity of the introduced carbon based materials.^[51, 52] On the other hand, the abovementioned BNNS are found to possess comparable mechanical strength and thermal conductivity with graphene,^[53, 54] yet better biocompatibility,^[52, 55] showing great promise as a biocompatible reinforcing candidate material of PVA hydrogels.^[24, 56] Therefore, the as-prepared BNNS were further incorporated into the PVA *via* mixing and freezing/thawing to achieve biocompatible composite BNNS/PVA hydrogels with both enhanced mechanical and thermal responses.

3.2 Characterization

3.2.1 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is an electron microscope that collect signals from the interactions between atoms of sample and the electron beams to characterize the composition and surface topography of the sample. As shown in Figure 3.1,^[57] an electron beam is produced by the electron gun in the vacuum, which is accelerated under the electrical potential and pass through the condenser lens. Then, the electron beam is focused onto the sample by the objective lens. Next, the sample surface is struck by the electron beam and eject electrons, X-rays, light (cathodoluminescence) and absorbed current (specimen current) after the interactions. Among the various electrons, back-scattered electrons (BSE) and secondary electrons (SE) are the most useful electrons that can contribute to contrast in the final image. BSE is generated from the collision between the primary electron beam and the sample atom nucleus. Therefore, the BSE is sensitive to the sample atomic weight and density, which lead to contrast between the sample areas with different compositions. SE come from the inelastic collision between the electron beam and the shell electrons of the sample, which can be used to reflect the morphology and topography of the sample. The BSE and SE can be further collected and converted to form an image on the screen.

In this thesis, SE images are used for the characterization of the morphologies and microstructures of the NT arrays, aerogels, BNNS, *etc.* All the SEM characterizations were done using field emission SEM (JEOL JSM-7600F or LEO 1550). Figure 3.2 shows the representative SE images of CNT arrays before and after uniaxial compression.

Figure 3.1 Schematic of an SEM setup.^[57]

Figure 3.2 SEM images of vertically aligned CNT arrays (a) before and (b) after uniaxial compression.

3.2.2 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is a microscopy technique to form images from the interactions of the electrons transmitted through the ultra-thin specimen, after which the image is focused, magnified and further detected by a CCD camera. The small de Broglie wavelength of the electrons enables the TEM to examine the extremely fine detail that is not accessible by other microscopy techniques. As shown in Figure 3.3,^[58] an electron beam is produced by the electron gun in the vacuum, which is accelerated under the electrical potential and passes through the condenser lens. Then, the beam is focused to form a small and coherent beam by the condenser lens, the purpose of which is to exclude the high angle electrons. Next, the electron beam strikes/transmits through the specimen depending on its thickness and electron transparency. After that, the transmitted electrons are focused by the objective lens to form an image that can be further zoomed in by the projector and intermediate lenses. To enhance the contrast, the high-angle diffracted electrons can be selectively blocked by the objective apertures. Finally, the detailed morphology of the specimen can be revealed when the image hits the fluorescent screen and generates light. Typically, darker area in a TEM image indicates that fewer electrons transmit the specimen, while lighter area shows that this area is more electron transparent.

In this thesis, high resolution TEM (HR-TEM) is adopted to characterize the nanostructures of the NTs, BNNS and graphene by using either JEOL JEM-2100F or Tecnai G2 F20 X-Twin. Take the CNT samples for example, the CNTs were firstly dispersed in ethanol with the aid of ultrasonic vibration, after which the solution was directly dropped onto the 400 mesh copper grid followed by drying at ~60 °C for a few minutes. The morphology, crystallinity, inner and outer diameters, as well as number of walls of the NT can be obtained through the HR-TEM images. Figure 3.4 shows the HR-TEM images of CNTs with different diameters and morphologies.

Figure 3.3 Schematic of TEM.^[58]

Figure 3.4 Representative HR-TEM images of CNTs with different nanostructures.

3.2.3 Raman spectroscopy

Raman spectroscopy is widely used in chemistry to provide the structural fingerprint by which molecules can be identified. It relies on the Raman scattering (inelastic scattering) of the monochromatic light which usually comes from laser in the near ultraviolet, near infrared and visible ranges. When monochromatic light (laser) interacts with the phonons, molecular vibrations and other excitations in the material, the resultant inelastic scattering leads to the shift of the laser photon energy, and therefore, the vibration modes information is revealed. In a typical Raman spectroscopy characterization (Figure 3.5),^[59] a laser beam strikes the sample surface, after which a lens is applied to collect the electromagnetic radiation from the hit (illuminated) spot and further send through the monochromator. Elastic scattered radiation at the wavelength of the laser line is filtered and the rest of the light is dispersed onto a detector.

Figure 3.5 Schematic of Raman spectrometer.^[59]

In this thesis, Raman spectra were collected using WITEC CRM200 Raman system to identify the crystalline structures of the NTs, BNNS, graphene, *etc.* For CNTs with good crystallinity, the prominent peaks near ~ 1350 , ~ 1580 and $\sim 2700\text{ cm}^{-1}$ can be observed, which correspond to the D, G and 2D bands, respectively (as shown in Figure 3.6). The appearance of G band is induced by the first-order Raman scattering, the D band originates

from the second-order process and the disorder in the system, while the 2D band results from the double resonance Raman process.

Figure 3.6 Raman spectrum of as-grown CNT.

3.2.4 Fourier-transform infrared spectroscopy (FT-IR)

Fourier-transform infrared spectroscopy (FT-IR) is used to identify functional groups and bonding information in a sample by recording the characteristic frequencies of the IR that are absorbed when the light passes through. These absorptions are the resonant frequencies that match the transition energies of the groups or bonds that vibrate. The associated vibronic coupling, masses of the atoms, and also the shape of the molecular potential energy surfaces determine the energy of the bond or group, which is also affected by the strength of the bond. Therefore, characteristic bond or group can be revealed by the characteristic resonant frequencies (respective bond/group energies). Typically, as shown in Figure 3.7,^[60] the light from polychromatic infrared source firstly transmits through the interferometer with various scanning mechanisms to produce the path difference. Then, the sample is illuminated by the light and generates resulting interferogram, which is converted to a spectrum by Fourier transformation. The result of the transformation is the signal spectrum at discrete wavelengths.

Figure 3.7 Schematic of FT-IR setup.^[60]

Take CNT as example, its characteristic C=C stretching vibration appears at 1643 cm^{-1} , and usually the OH (H_2O) and C-O vibrations are observed due to wetting and partial oxidation, respectively (as shown in Figure 3.8). In this thesis, FT-IR spectra were acquired for NTs, BNNS and hydrogel samples using either Shimadzu Prestige-21 Spectrometer or PerkinElmer Frontier.

Figure 3.8 FT-IR spectrum of as-grown CNT.

3.2.5 X-ray diffraction (XRD)

X-ray diffraction (XRD) technique is used to determine the crystalline structure according to the diffraction of incident X-rays caused by the crystalline atoms. By recording the pattern (intensity and angle) of the diffracted beams, the mean positions of the atoms, ordered structure, *etc.* could be determined. Typical X-ray diffractometer consists of three main parts: X-ray source, sample holder and detector (Figure 3.9).^[61] X-ray source generates the X-rays through heating the filament to produce electrons with high energy, which are then accelerated under the applied electrical potential. When the X-rays hit the sample, some of them are diffracted and further detected by the detector. For characterization of powder and bulk samples, a θ - 2θ mode is normally applied, that is, when the sample rotates with an angle of θ to receive the incident X-rays, the detector will rotate 2θ to detect the corresponding diffracted X-ray data.

Figure 3.9 Schematic of XRD in θ - 2θ mode.^[61]

Figure 3.10 shows the typical XRD spectrum of CNTs with (002) and (004) reflections which could be assigned to the hexagonal ring structure of the graphene sheets forming CNTs.^[62] In this thesis, Shimadzu XRD-6000 is used to collect the XRD profile and thus characterize the crystalline structures of various materials including NTs, BNNS, hydrogels, etc.

Figure 3.10 Typical XRD profile of CNT.^[62]

3.2.6 Thermogravimetric analysis (TGA)

The thermogravimetric analysis (TGA) is a method to measure the sample mass as the function of increasing temperature to reflect the changes in physical and chemical properties of the samples. With the temperature increasing, the components of the sample decompose or sublime at various temperatures, and the weight of the sample is measured and recorded accordingly. Due to the mass change during physical change or chemical reaction, information regarding physical phenomena such as adsorption, desorption, absorption, sublimation and vaporization, as well as chemical phenomena such as solid-gas reactions, decomposition, desolvation and chemisorptions can be derived from the TGA. A typical thermogravimetric analyser consists of a precise balance with sample holder within a temperature controlled chamber furnace (Figure 3.11).^[63] The temperature of the furnace increases at constant rate (or controlled by a program with purpose) to stimulate the thermal reaction. The reactions could occur under various atmospheres (*e.g.*, vacuum, inert gas, ambient air, *etc.*) and various pressures (*e.g.*, high pressure, high vacuum, constant pressure, *etc.*). The collected thermogravimetric data is usually compiled to generate a plot of mass (or percentage) versus temperature (or time).

Figure 3.11 Schematic of TGA setup.^[63]

In this thesis, a Shimadzu DTG-60H thermal analyser is used for TGA analysis of the NTs, BNNS, graphene, hydrogel samples, etc. A typical TGA profile of CNT is shown as Figure 3.12, where the as-grown CNTs decompose at ~ 700 °C in ambient air.

Figure 3.12 TGA profile of as-grown CNT.

3.2.7 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a surface analysis technique that measures the chemical composition and bonding structure of a material by irradiating X-ray beam while simultaneously monitoring the number and kinetic energy of electrons that escape from the material surface (the schematic illustration is shown in Figure 3.13). Ultra high vacuum ($\sim 10^{-8}$ mbar) environment is required for the XPS measurement. XPS could be used for analyzing the surface chemistry of the material not only in its as-received state, but also after treatments including scraping, fracturing, cutting or even exposure to ion beam etching.

Figure 3.14 shows survey spectra of hydroxylated BN nanoplatelets (OH-BNNP) and as-received BN powders,^[26] as well as the high resolution B1s spectrum with fitted curves. The peak at 190.0, 284.5, 397.6 and 532.3 eV in the XPS spectra are respectively assigned to the B1s of OH-BNNP, C1s from carbon contamination, N1s from OH-BNNP and O1s from B–O bonds of OH-BNNP and the absorbed oxygen. The increase in oxygen content from 1.3 to 6.4% for as-received BN powders and OH-BNNP indicates the successful hydroxylation of the latter. In this thesis, Model PHI Quantera SXM is used for the XPS analysis of various materials.

Figure 3.13 Schematic of XPS analysis of Si wafer.^[64]

Figure 3.14 XPS survey scan of OH-BNNP on Si substrate and its high-resolution B1s spectrum.^[26]

3.2.8 Atomic force microscopy (AFM)

Atomic force microscopy (AFM) is capable of precisely characterizing the surface properties including roughness, thickness and lateral size of low-dimensional nanomaterials with a very high resolution on the order of nanometer level, which is 1000 folds higher than the optical diffraction limit. The key parts of AFM are the cantilever tip and photodiode detector (Figure 3.15).^[65] An ultra-fine needle is attached to the cantilever tip, which runs over the valleys and ridges on the sample surfaces being scanned. The cantilever deflects when the cantilever tip moves up and down. In the meantime, the laser shot on the cantilever is able to monitor its deflection by tracking the change in angle of incidence. As a result, an image reflecting the topography of the sample surface could be generated by collecting the deflection signals.

Figure 3.16a,b present typical topography image and corresponding height profile of exfoliated BNNS that are dispersed onto the Si substrate.^[66] The thickness and roughness of the BNNS could be easily extracted across the selected area and line. Meanwhile, the variations in contrast of the images which correspond to the surface height/roughness reflect the morphology of the BNNS. Therefore, the characteristics including number of

layers, smoothness and lateral sizes of the exfoliated BNNS could be comprehensively characterized using AFM by measuring the corresponding surface roughness and height profile. In this thesis, either Asylum Research MFP-3D or Cypher S was used for AFM characterization of the BNNS and GO nanosheets.

Figure 3.15 Schematic of an AFM setup.^[65]

Figure 3.16 (a) AFM topography image, scale bar = 2 μm and (b) corresponding height profile.^[66]

3.2.9 Ultraviolet-visible (UV-vis) spectroscopy

Ultraviolet-visible (UV-vis) spectroscopy refers to the absorption or reflectance spectroscopy of the material in the UV spectral region. It can be used to determine the optical band gap and concentration of the absorber in a solution. The basic parts of a UV-vis spectrometer are the light source (with monochromator), sample holder, and a detector (Figure 3.17).^[67] In a double-beam instrument, the light is separated into two beams before reaching the sample. One of the two beams serves as reference, while the other one transmits through the sample. The measurement is then presented as the ratio of the two beam intensities.

Figure 3.18 shows that BNNS dispersion is generally clear over the visible spectral region while exhibits absorption in the UV region (with peak at ~206 nm). In the meantime, the absorbance is linearly correlated with the BNNS concentration, which agrees well with the Lambert-Beer's law, indicating the homogeneous distribution of BNNS within the dispersion. In this thesis, UV-vis spectra were measured using UV-vis spectrophotometer Shimadzu 2450.

Figure 3.17 Schematic of a UV-vis spectrometer.^[67]

Figure 3.18 UV-vis absorption spectroscopy of aqueous BNNS dispersion, inset shows the correspondence between absorbance of BNNS dispersion and its concentration.^[29]

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Chapter 4

Coaxial Carbon@Boron Nitride Nanotube Arrays with Enhanced Compressive Mechanical Properties

In this chapter, coaxial C@BNNT arrays are prepared by a TCVD method to encapsulate outer BNNT with various wall thicknesses onto the CNT arrays and thus controllably tune their mechanical properties. As compared to the as-grown CNT arrays which deform plastically, the coaxial C@BNNT arrays exhibit a significant ~4-fold increase in compressive strength with nearly full recovery after first compression cycle at a 50% strain (76% recovery maintained after 10 cycles), as well as significantly high and persistent energy dissipation ratio (~60% at a 50% strain after 100 cycles), attributing to the synergistic effect between the CNT and outer BNNT. These outstanding compressive resilience and energy damping performances of the C@BNNT arrays enable their potential applications for shock absorption and energy dissipation.

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4.1 Introduction

Vertically aligned carbon nanotube (CNT) arrays have been recognized as promising multifunctional and high performance structural materials due to their exceptional electrical,^[1] thermal^[2] and in particular their mechanical properties.^[3-6] Despite their low density, CNT arrays normally exhibit high mechanical strength and stiffness.^[7, 8] In addition, CNT arrays also possess a unique buckling response upon uniaxial compression^[7, 9] that allows energy dissipates through structural deformation and friction between the individual CNTs. Owing to these interesting characteristics, CNT arrays have been applied in efficient energy dissipating systems for shockwave,^[10, 11] acoustic^[12] and vibration absorptions,^[13-16] which are highly demanded by the midsole materials of sports footwear. However, it is worth noting that their mechanical properties strictly depend on the geometrical structure of the CNTs and their buckling behaviour is closely associated with the interactions between individual tubes.^[14, 15, 17-19] Thus far, the most common method to synthesize CNT arrays is thermal chemical vapour deposition (TCVD), while this growth process usually produces CNTs with thin walls, low packing density and weak inter-tube interactions, which lead to their plastic deformation upon compression.^[14, 17, 20-22] To address the abovementioned issues, many efforts have been made either by modifying their microstructure through altering growth process^[19, 22, 23] or applying post-growth treatment to reinforce the as-grown CNT arrays.^[14, 24-27] Particularly, the latter approach which involves the thickening of the tube diameter and increase in the array density of the CNT arrays have been widely studied to strengthen arbitrary CNT arrays. Recent examples include coating metal oxide NPs onto the CNTs,^[25, 26] infiltrating polymer into the interspaces of CNTs^[27] and introducing other forms of carbon (additional CNT walls or graphene sheets) into arrays.^[14, 24]

On the other hand, as a structural analogue of CNT,^[28-30] boron nitride nanotube (BNNT) has also been proved to possess superior mechanical properties.^[31-33] However, the mechanical-related applications for as-grown BNNTs is not yet mature due to the challenges in synthesizing densely packed and high quality BNNT arrays with suitable dimensions.^[34-40] Still, due to its outstanding physicochemical stability, BNNT has been

applied as a protective coating material for CNT.^[41, 42] Recently, BN coated single-walled CNT aerogels have been prepared by solution based assembly process and exhibited enhanced elastic modulus and shape recoverability.^[43] Furthermore, it has also been predicted theoretically the inter-wall van der Waals interactions between the CNT and BNNT will enhance the protective effect of outer BNNT in mechanical perspective.^[44, 45] However, to the best of our knowledge, such reinforcement has not been investigated experimentally.

In this chapter, we demonstrate the fabrication of coaxial C@BNNT arrays with two different BN weight ratios *via* a two-step growth TCVD method by firstly, the growth of the CNT arrays and subsequently, encapsulation of the CNTs with BNNTs. Importantly, the compressive mechanical properties of the C@BNNT arrays could be tailored by varying the wall thickness of the outer BNNT. Furthermore, compressive strength, shape recoverability, cyclic compressive and energy dissipating properties, as well as structural stability have been significantly enhanced due to the synergistic effect between the CNT and the outer BNNT.

4.2 Experimental Methods

4.2.1 Preparation of vertically aligned CNT arrays

CNT arrays were grown using TCVD on Si substrate with a sandwich-structured catalyst layer consisting of 6 nm Al, 4 nm Al₂O₃ and 1 nm Fe and fabricated by electron beam deposition. CNT was grown at a pressure of 720 mbar with flowing gases including H₂ (200 sccm, using as etching gas), N₂ (160 sccm, using as carrier gas) and C₂H₂ (15 sccm, using as carbon source). Si substrate was heated up to 730 °C and held for 20 min to sustain the growth of CNT arrays with an average height of ~0.4 mm.

4.2.2 Fabrication of C@BNNT arrays

C@BNNT arrays were prepared by TCVD according to a previously reported method with slight modification.^[46] Figures 4.1 and 4.2 show the schematic of encapsulating coaxial outer BNNT onto the CNT arrays and the time-temperature plot of the TCVD process, respectively. Briefly, the CNT samples on Si wafer were firstly located in the central part of a horizontal reaction tube and boric acid powder with a specified amount was loaded at one end of the tube, followed by heating up to 150 °C in 10 min and holding for 30 min with flowing Ar (300 sccm). The temperature was then ramped up to 830 °C in 90 min and remained for another 30 min. Ammonia with a desired flow rate was introduced into the tube when boric acid started to sublimate, and the flow rate of Ar was adjusted accordingly to keep the total flow rate of gases in the tube constant. Finally, the tube was further heated up to 900 °C and held for another 1 h, followed by naturally cooling down to room temperature under protection of an Ar flow. For simplicity, C@BNNT with BN weight ratios of ~40% and 60% were designated as C@BNNT₄₀ and C@BNNT₆₀, respectively. By sintering the as-prepared samples at 400 °C for 1 h in air, annealed CNT and C@BNNT₆₀ arrays were also successfully prepared, respectively.

Figure 4.1 Schematic of the TCVD procedure for fabricating C@BNNT arrays.

Figure 4.2 Time-temperature plot of the TCVD process.

4.2.3 Mechanical test

The mechanical responses of the CNT and C@BNNT arrays before and after annealing were measured using an Instron 5567 Mechanical Tester system at room temperature. In general, the CNT or C@BNNT sample with a specified dimension was firstly loaded on the centre of the lower platen, and a compression rod with 50 mm diameter was then applied onto the sample with a controlled speed, all the compressions were conducted within the confinement of the small upper platen. Compressive strain and stress were calculated using the displacement of the compression rod divided by original height of the NT arrays and the applied compressive force over cross-sectional area of the samples, respectively. Recoverability of the NT arrays is defined as the displacement recovered over applied displacement. For the CNT, C@BNNT₄₀ and C@BNNT₆₀ arrays, the cyclic uniaxial compression experimental data were acquired at a loading-unloading rate of 0.04 mm min^{-1} at strains of 30%, 50%, 70 %, and 90%, respectively.

4.3 Principle Outcomes

4.3.1 Structure and morphology of C@BNNT arrays

Figure 4.3 Cross-sectional SEM and corresponding high resolution TEM images of (a, d) CNT, (b, e) C@BNNT₄₀ and (c, f) C@BNNT₆₀, respectively. BNNTs with increasing wall thickness were successfully encapsulated onto the CNTs without causing any observable change in the areal density of the NTs. TGA (g), FT-IR (h), and Raman (i) spectra of the various NTs, indicating the crystal structure of the CNTs was preserved after the introduction of outer BNNTs with different weight ratios.

CNT arrays were grown by a commercialized TCVD process on Si substrates with defined catalyst areas and C@BNNT arrays were prepared with the aid of another separate TCVD process as described in previous report.^[46] By varying the growth parameters, two sets of

C@BNNT arrays with specified BNNT wall thicknesses denoted by C@BNNT₄₀ and C@BNNT₆₀ were successfully fabricated. Figure 4.3a–c shows the cross-sectional SEM images of the CNT and C@BNNT arrays, respectively. It is obvious that the C@BNNT arrays retained the vertically aligned structure of the initial CNT arrays with no observable change in areal density. To investigate the wall thickness of outer BNNT, a systematic TEM study on various NTs was further carried out. Figure 4.3d–f shows representative high resolution TEM images of the individual CNT, C@BNNT₄₀ and C@BNNT₆₀, respectively. The initial CNT exhibited an inner diameter of 6.25 nm with an average wall thickness of 1.15 nm (corresponding to 3 to 4 walls). An increase in wall thickness was observed for both the C@BNNT₄₀ and C@BNNT₆₀ which were measured to be 1.60 and 2.52 nm, respectively. Based on the TEM images, outer BNNTs with wall thicknesses of 0.45 nm (~2 walls) and 1.37 nm (~5 walls) were introduced for C@BNNT₄₀ and C@BNNT₆₀, respectively. Thus, the C@BNNT arrays with outer BNNTs of varying wall thicknesses can be achieved by altering the experimental parameters.

To further determine the BN contents of the C@BNNT arrays, TGA was employed and the weight residues at temperatures lower than 700 °C were extracted. TGA tests were conducted in air from 30 to 1100 °C, as shown in Figure 4.3g. It is observed that the CNTs fully decomposed at 700 °C while 41.3% and 60.3% weight residues emerged for the C@BNNT samples, indicating that the weight ratios of BN:C were ~40:60 and 60:40 for C@BNNT₄₀ and C@BNNT₆₀, respectively, which were in good agreement with our TEM results. It should be noted that the increase in weight at ~900 °C for C@BNNT is due to the partial oxidation of BNNT forming B₂O₃.^[46] Figure 4.3h,i presents the FT-IR and Raman spectra of the CNT, C@BNNT₄₀ and C@BNNT₆₀, respectively. In Figure 4.3h, characteristic C=C stretching at 1643 cm⁻¹ is observed for CNT, while additional B–N–B and B–N vibrations located at 771 and 1358 cm⁻¹ can be clearly seen for C@BNNT, respectively.^[47] Raman spectra of all the NTs shows the characteristic D, G and 2D peaks at ~1350, 1580 and 2700 cm⁻¹, respectively (Figure 4.3i), implying that the crystal structure of the CNT was preserved after encapsulating with BNNT.^[46, 48]

4.3.2 Uniaxial compressive performance of C@BNNT arrays

Figure 4.4 Schematic illustrations of the compressive behaviours of the (a) CNT and (b) C@BNNT arrays. The as-grown CNT arrays underwent plastic deformation upon compression, while the additional outer BNNT walls facilitated the elastic recovery of the C@BNNT arrays after load releasing.

Figure 4.5a shows the compressive stress vs. strain loading-unloading curves for the CNT, C@BNNT₄₀ and C@BNNT₆₀ arrays. Similar phenomenon has also been observed in previously reported work, attributing to the small tube diameter (~ 8 nm), thin wall thickness (1.15 nm, ~ 3 walls), which were determined by the specific fabrication setup and synthesis method.^[6, 14, 17, 19-22] When the BN weight ratio of C@BNNT arrays increased to 40%, a partial recovery ($\sim 33\%$) upon unloading emerged, while $\sim 77\%$ recovery was observed for the C@BNNT₆₀ arrays after unloading of 90% compressive strain, and the two distinct paths corresponding to loading and unloading process respectively compose a hysteresis loop. In addition, the C@BNNT arrays showed a significant ~ 4 -fold increase in compressive strength (from 0.47 to 2.47 MPa) with enhanced compressive modulus, and exhibited nonlinear behaviour as observed by the increase in compressive modulus with increasing the applied strain. The recoverability of the C@BNNT arrays was further investigated at various applied strains of 30%, 50%, 70% and 90%, respectively, as shown in Figure 4.5b,c. It is observed that the C@BNNT₄₀ and C@BNNT₆₀ arrays exhibited similar strain-dependent mechanical responses under compressions where the peak compressive stress increased with increasing applied strain, while showed differences in their recovery processes. For the C@BNNT₄₀ arrays, partial recovery of $\sim 40\%$ was observed after compressions at various applied strains while with no critical strain value

for full recovery (Figure 4.5b). In contrast, the C@BNNT₆₀ arrays exhibited almost full shape recovery when a compressive strain of 50% or less was applied and partial recoveries of ~79% and 77% were observed when the applied strain was increased to 70% and 90%, respectively (Figure 4.5c).

Figure 4.5 Compressive stress vs. strain curves for the (a) CNT, C@BNNT₄₀ and C@BNNT₆₀ arrays at a 90% strain, (b, c) C@BNNT₄₀ and C@BNNT₆₀ arrays at strains of 30%, 50%, 70% and 90%, and (d) energy dissipation ratio of the C@BNNT arrays vs. applied strain. The C@BNNT arrays exhibited controllably enhanced compressive strength, modulus, and shape recoverability compared to the as-grown CNT arrays.

Considering the high porosity, resilience and compressive strength of the C@BNNT arrays, they are expected to show promising energy absorbing abilities. To quantitatively characterize the energy dissipating property of the NT arrays, their energy dissipation ratios, E_d/E_a , are extracted from their corresponding stress vs. strain curves, where E_d is the energy dissipated during the loading-unloading cycle (*i.e.* the area of the hysteresis loop), and E_a is the energy absorbed from compression loading (*i.e.* the area under loading stress-strain

curve). As shown in Figure 4.5d, both the C@BNNT₄₀ and C@BNNT₆₀ arrays showed a strain-dependent energy dissipating performance. The C@BNNT₄₀ arrays exhibited E_d/E_a of 75.27 %, 79.72%, 85.53%, and 86.25% at applied strains of 30%, 50%, 70% and 90%, respectively, while the C@BNNT₆₀ arrays with better shape recoverability exhibited relatively lower E_d/E_a of 57.33%, 71.45%, 74.86% and 78.36% at respective strains, attributing to the smaller permanent shape deformation and larger energy return. By comprehensively considering the abovementioned aspects, it is expected that the C@BNNT₆₀ arrays are more suitable for applications where both energy absorption and load recovery are critical.

4.3.3 Compression mechanism of C@BNNT arrays

To gain insights into the compression mechanisms of the NT arrays, cross-sectional SEM images were taken on the CNT, C@BNNT₄₀ and C@BNNT₆₀ arrays before and after cyclic compressions (Figure 4.6). Figure 4.6a,d and b,e show the CNT and the C@BNNT₄₀ arrays before and after 3 compression cycles at a 50% strain, respectively. It is observed that the CNT arrays collapsed with limited recovery (55% of original height was maintained) and local buckling initiated from the bottom of the CNTs which propagated upwards with a constant buckle wavelength of $\sim 4.8 \mu\text{m}$ (Figure 4.6a,d). This local buckling can be attributed to the relatively lower areal density and smaller diameter of the CNTs at the bottom region as they follow a “bottom-up growth” mechanism (*i.e.* the CNTs grow upwards from the bottom catalyst side).^[17, 19, 49] Furthermore, the frictions between the substrate and the bottom NTs could also have some contributions as well.^[18] In contrast, $\sim 54\%$ recovery was displayed (77% original height was remained) for the C@BNNT₄₀ arrays and buckles with a longer average wavelength of $\sim 9.4 \mu\text{m}$ could be observed at the bottom of the NTs (Figure 4.6b,e). The evident increase in the buckle wavelength of the compressed C@BNNT₄₀ arrays indicates that they possess higher compressive resilience compared to the starting CNT arrays.^[50] Hence, the outer BNNT played a significant role in enhancing the overall compressive resilience of the NT arrays. As additional outer BNNT was encapsulated onto the CNT, radial thickening was evident which provided additional mechanical support to the NTs.^[14, 19] More importantly, the stable van der Waals

interactions between the BNNT wall and the adjacent CNT wall upon compression protected the inner CNT from buckling, thus improved the effective compressive resistance and stiffness of the NT arrays.^[44]

Figure 4.6 Cross-sectional SEM images of the NT arrays after cyclic compressions. The CNT arrays (a, d) deformed almost plastically with heavy buckles (inset) at the bottom region, while the C@BNNT₄₀ arrays (b, e) and the C@BNNT₆₀ arrays (c, f) exhibited partial recovery with slight buckles (inset) and nearly full recovery with only curvatures formed on the tubes, respectively, showing the significantly promoted compressive resilience of the C@BNNT arrays.

Figure 4.6c,f shows the SEM images of the C@BNNT₆₀ arrays before and after 10 compression cycles at a 50% strain. It is noted that the C@BNNT₆₀ arrays exhibited a ~76% recovery (maintaining 88% of original height) even after 10 compression cycles, while only longitudinal distributed curvatures (*i.e.* buckles with ultra-long wavelength) were observed, indicating significantly enhancement in the compressive resilience when further increase the wall thickness of outer BNNT. It is noted that the curvature length was gradually decreased from upper to bottom portion (Figure 4.6f), similar gradient in buckle wavelength was also observed on compressed C@BNNT₄₀ arrays (Figure 4.6e), demonstrating the densification behaviour of the C@BNNT arrays under compression.^[7, 18] This can be attributed to the strengthened lateral interactions (*i.e.* van der Waals interactions) between the NTs due to the smaller inter-tube spacing after the introduction

of outer BNNT, resulting in the nonlinear stress-strain relationship of the C@BNNT arrays.^[8, 18] However, no additional interfacial frictions were induced between the NTs for C@BNNT arrays due to the exceptionally lower friction between the BNNTs than that between the CNTs.^[51, 52] Moreover, contact area between the adjacent NTs became larger with further increased wall thickness of outer BNNT, longitudinal sliding was hence decoupled due to the transversal deformation, resulting in lower longitudinal shear strength.^[52] Therefore, no apparent improvement in compressive strength was observed on the C@BNNT₆₀ arrays as compared to the C@BNNT₄₀ arrays (Figure 4.6a).

4.3.4 Cyclic compressive performance of C@BNNT arrays

To study the long-term cyclic mechanical performance of the C@BNNT and CNT arrays, uniaxial cyclic compression was further applied at a 50% strain. As shown in Figure 4.7a, the CNT arrays underwent serious plastic deformation during its first loading-unloading compression cycle followed by limited elastic recovery during the subsequent cycles as a result of the reversible compressions of the compressed portion,^[19] while the C@BNNT₆₀ arrays displayed almost 100% recovery after the first compression cycle with slight degradation of recoverability in the subsequent cycles (~76% remained after 10 cycles). For the as-grown CNT arrays, the unfolding or unpacking of the bent CNTs after the release of load was hindered by the strong van der Waals attraction between the compressed CNTs, while for the C@BNNT₆₀ arrays, the stronger generated restoring force upon load releasing over the van der Waals interactions among the NTs led to their significantly improved recoverability.^[14, 19] Figure 4.7b,c shows the representative stress-strain curves of the C@BNNT₄₀ and C@BNNT₆₀ arrays under 100 cycles of compression, respectively. A transient phenomenon in compressive strength (preconditioning effect) can be observed for the C@BNNT arrays. The compressive strength of the C@BNNT₄₀ arrays was measured to be up to ~0.55 MPa during the initial cycles, which gradually decreased to ~0.49 MPa and kept almost unchanged after 50 cycles. Similar strength evolution was also observed for the C@BNNT₆₀ arrays (from ~0.42 to ~0.35 MPa). This stress softening was due to the weakened van der Waals inter-tube interactions and the compression induced defects during the initial several cycles,^[16, 53, 54] after which a new equilibrium status (collectively

buckled, as shown in Figure 4.8) was gradually reached to achieve a stable stress response. In addition, the shape recoverability of the C@BNNT arrays evolved gradually with increasing cycles ($\sim 68\%$ and 78% of their original height remained for the C@BNNT₄₀ and the C@BNNT₆₀ arrays after 100 cycles, respectively), as identified by the corresponding SEM images (Figure 4.8). This persistent shape recovery performance was facilitated by the effective protection of the outer BNNT walls, as no changes in the structural dimensions of the C@BNNT were observed throughout the long-term compressive tests (Figure 4.9). Furthermore, a greater decline in the E_d/E_a of the C@BNNT₄₀ arrays (from 79.72% to 45.23%) with the increasing cycles was observed as compared to that of the C@BNNT₆₀ (from 71.35% to 61.81%), which remained somewhat consistent after 100 cycles (Figure 4.7), indicating that the enhanced shape recoverability will enable a more stable energy dissipating performance over long-term cycling.

Figure 4.7 Cyclic compressive stress vs. strain curves at a 50% strain for (a) comparison of the C@BNNT₆₀ and CNT arrays; (b, c) C@BNNT₄₀ and C@BNNT₆₀ arrays under 100 cycles of compression, respectively, and (d) energy dissipation ratio of the C@BNNT arrays as a function of cycle number. The C@BNNT arrays exhibited significantly enhanced cyclic compressive mechanical property, and the preconditioning effect was observed.

Figure 4.8 SEM images of C@BNNT₄₀ (a, b) and C@BNNT₆₀ (c, d) arrays before and after 100 cycles of compression at a 50% strain, respectively.

Figure 4.9 Representative low and high-resolution (insets) TEM images of C@BNNT₄₀ (a, b) and C@BNNT₆₀ (c, d) before and after 100 cycles of compression at a 50% strain, respectively. No observable changes in structural dimensions (average inner, outer diameters and number of walls extracted from 10 TEM images for each) were induced to the NTs by compression, proving that the outer BNNT walls encapsulated and protected the NT arrays well throughout the long-term cyclic loading.

4.4 Conclusions

CNT and coaxial BNNT encapsulated CNT (C@BNNT) arrays with two different BN weight ratios (C@BNNT₄₀ and C@BNNT₆₀) have been successfully prepared and their mechanical behaviours have been systematically investigated using uniaxial compression tests at various applied strains and compression cycles. Importantly, the compressive mechanical properties of the C@BNNT arrays can be controllably tuned by varying the wall thickness of the outer BNNT. A tremendous ~4-fold increase in the compressive strength of the C@BNNT arrays was achieved by reinforcing the CNT arrays with outer BNNT. Furthermore, as compared to the as-grown CNT arrays which deform almost plastically, the C@BNNT₆₀ (with outer BNNT of 1.37 nm wall thickness) arrays show significant enhancement in shape recoverability and cyclic compressive property (nearly full recovery after 1 compression cycle at a 50% strain, and ~76% recovery retained after 10 cycles), energy dissipating property (~60% E_d/E_a remained at a 50% strain after 100 cycles) owing to the synergistic effect between the inner CNT and outer BNNT. The remarkably enhanced compressive mechanical properties of the C@BNNT arrays would enable many potential applications such as energy dissipative devices, shock absorbers, sports footwear midsoles, *etc.*

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Chapter 5

Enhanced Heat Transfer of Coaxial Carbon@Boron Nitride Nanotube Arrays

In addition to mechanical responses, the heat transfer of C@BNNT arrays is also investigated from both experimental and theoretical perspectives. Notably, outer BNNT with 0.97 nm thickness ($\sim 3\text{--}4$ walls) could contribute to a $\sim 90\%$ increase (from ~ 15.5 to $29.5\text{ W m}^{-1}\text{ K}^{-1}$) in thermal conductivity of the C@BNNT arrays as compared to that of the bare CNT arrays, attributing to the highly coherent lattice structures of the CNT and BNNT. Further simulation results indicated that the outer BNNT can serve as additional heat conducting path without impairing the thermal conductance of inner CNT, which contributes to the outstanding energy dissipation of C@BNNT arrays.

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5.1 Introduction

Thermal interface material (TIM), a key component of thermal management for efficient heat removal, has attracted particular attention due to the rapidly increasing power density of modern electronic devices.^[1] Among the various candidates, vertically aligned carbon nanotube (CNT) arrays exhibit promising potential due to the superior thermal conductivity of the individual CNT (~ 3000 W/mK for multi-walled CNT^[2]) and the absence of inter-tube phonon scattering.^[3] However, it is still not yet successful for the CNT arrays (~ 0.1 - 220 W/mK)^[4, 5] to inherit the excellent thermal conductivity of ideal CNT due to the obstacles such as low tube volume fraction^[4, 6] and limited quality of the individual CNT,^[7] which are determined by the specific synthesis process. Nevertheless, it is still challenging to improve the heat transfer of the CNT arrays. This is because most infiltrating materials such as polymer^[3, 8-10] and metal^[11, 12] have much lower thermal conductivities, and their structural incompatibility with CNT may impair the intrinsic heat transfer of CNT as well.^[9]

On the other hand, boron nitride nanotube (BNNT) with natural advantages such as highly coherent structure with CNT, outstanding thermal conductivity (~ 350 W/mK)^[13-15] and mechanical property,^[16] superb chemical resistance^[17] and thermal stability (endure up to ~ 800 °C in air, ~ 2800 °C in inert gas)^[18] has attracted wide research interest. Our previous work (Chapter 4) has demonstrated that both the mechanical stiffness and thermal stability of CNT arrays can be enhanced by encapsulating coaxial boron nitride nanotube layers.^[19] Moreover, instead of the massive infiltration of polymer/metal into CNT arrays which dominates the thermal property of the resulting composites, the introduction of thin-walled outer BNNT is expected to not only preserve the intrinsic thermal conductivity of the inner CNT but also provide additional heat transfer channel, which has not been investigated yet.

In this chapter, outer BNNT with wall thickness of 0.97 nm (~ 3 - 4 walls) is encapsulated onto the as-prepared CNT arrays. For the first time, the thermal conductivity of the resulting C@BNNT arrays is studied both experimentally and theoretically by pulsed photothermal reflectance (PPR) technique and molecular dynamics (MD) simulation, respectively. Encouragingly, a $\sim 90\%$ increase in thermal conductivity (from ~ 15.5 to 29.5

W/mK) is observed for C@BNNT arrays compared to the bare CNT arrays. Meanwhile, the simulation results indicate that the outer BNNT serves as additional heat conducting path without influencing the thermal conductivity of the inner CNT due to their coherent structures.

5.2 Methods

5.2.1 Synthesis of vertically aligned CNT and C@BNNT arrays

Vertically aligned CNT arrays with uniform thickness of $\sim 15\ \mu\text{m}$ were grown in a 2-inch quartz tube reactor using TCVD method. Initially, 10 nm Al_2O_3 buffer layer and 1 nm Fe catalyst layer were evaporated in sequence onto Si substrate by electron beam. Then $1\ \text{cm} \times 1\ \text{cm}$ Si substrate with catalyst was put into the tube for growth at a pressure of 720 mbar with flowing gases including H_2 (100 sccm, etching gas), N_2 (1000 sccm, carrier gas) and C_2H_2 (120 sccm, carbon source). The tube was heated up to $800\ ^\circ\text{C}$ and held for 60s to sustain the CNT growth.

C@BNNT arrays were fabricated according to a previously reported TCVD process with slight modifications.^[19, 20] Firstly, the CNT samples were located in the center of the quartz tube and the boric acid powder with a specified amount was loaded at one end of the tube. Subsequently, the tube was heated up to $150\ ^\circ\text{C}$ in 10 min and held for 30 min with flowing Ar (300 sccm) to thoroughly remove the residual air and water vapour. Thirdly, the temperature was increased to $830\ ^\circ\text{C}$ in 90 min and kept for 30 min. Ammonia gas with a desired flow rate was introduced into the tube when the boric acid started to sublime, and the Ar flow was tuned accordingly to keep the tube pressure constant. Finally, the tube was ramped up to $900\ ^\circ\text{C}$ and maintained for another 60 min to realize the BNNT encapsulation.

5.2.2 Thermal conductivity measurement

Thermal properties of the CNT, C@BNNT arrays were measured by the PPR technique.^[21, 22] Prior to the test, a ~500 nm-thick TiN layer was deposited onto the top of the NT arrays by sputtering to improve the surface reflectivity and uniformity. During the measurement, the surface of the TiN was struck by a Nd:YAG (532 nm) laser pulse (pump beam) with a full width at half maximum of 7 ns, spot size of 3 mm, and pulse energy of 40 μ J. The surface temperature rose sharply just after the laser striking, which was followed by decaying to the room temperature, and the decay time is governed by the heat transfer property of the underlying NT arrays. A 1 mW HeNe laser (probe beam) with a 20 μ m spot size and 632.8 nm wavelength was focused on the TiN layer at the centre of the pump beam, and the relative changes of TiN surface temperature was linearly monitored by the reflected probe intensity.

A three-layer thermal conduction model^[23] was adopted to fit the obtained normalized surface temperature vs time curve and further extract thermal parameters. The Si substrate (~0.5 mm) is considered as infinite medium as its thickness is larger than its heat diffusion length (0.37 mm).^[24] The temperature as a function of time was Laplace transformed according to Equation 1,

$$T(s) = \frac{Q(s)}{e_1 \sqrt{s}} \left[\frac{(\cosh \eta_2 \sqrt{s} + e_{32} \sinh \eta_2 \sqrt{s}) \cosh \eta_1 \sqrt{s} + (e_{31} \sinh \eta_2 \sqrt{s} + e_{21} \sinh \eta_2 \sqrt{s}) \sinh \eta_1 \sqrt{s} + R_1 \cosh \eta_1 \sqrt{s} (e_3 \sqrt{s} \cosh \eta_2 \sqrt{s} + e_2 \sqrt{s} \sinh \eta_2 \sqrt{s}) + R_2 (e_3 \sqrt{s} \cosh \eta_1 \sqrt{s} \cosh \eta_2 \sqrt{s} + e_{31} e_2 \sqrt{s} \sinh \eta_1 \sqrt{s} \sinh \eta_2 \sqrt{s}) + R_1 R_2 e_3 \sqrt{s} e_2 \sqrt{s} \cosh \eta_1 \sqrt{s} \sinh \eta_2 \sqrt{s}}{(e_{21} \sinh \eta_2 \sqrt{s} + e_{31} \cosh \eta_2 \sqrt{s}) \cosh \eta_1 \sqrt{s} + (\cosh \eta_2 \sqrt{s} + e_{32} \sinh \eta_2 \sqrt{s}) \sinh \eta_1 \sqrt{s} + R_1 \sinh \eta_1 \sqrt{s} (e_3 \sqrt{s} \cosh \eta_2 \sqrt{s} + e_2 \sqrt{s} \sinh \eta_2 \sqrt{s}) + R_2 (e_3 \sqrt{s} \sinh \eta_1 \sqrt{s} \cosh \eta_2 \sqrt{s} + e_{31} e_2 \sqrt{s} \cosh \eta_1 \sqrt{s} \sinh \eta_2 \sqrt{s}) + R_1 R_2 e_3 \sqrt{s} e_2 \sqrt{s} \sinh \eta_1 \sqrt{s} \sinh \eta_2 \sqrt{s}} \right] \quad (1)$$

where $e_i = \sqrt{\rho_i c_i k_i}$, $e_{i,j} = e_i / e_j$, $\eta_i = d_i / \alpha_i$, $i, j = 1, 2, 3$. The subscripts 1, 2 and 3 stand for the TiN film, NT arrays and Si substrate, respectively. ρ , c , k , e , α and d are density, specific heat, thermal conductivity, thermal effusivity, thermal diffusivity and the thickness of each layer, respectively. R_1 and R_2 are the thermal boundary resistance (TBR) at TiN-NT and NT-Si interfaces, respectively. $Q(s)$ is the Laplace transformed Gaussian pulse (Nd:YAG):

$$Q(s) = \frac{1}{2} \left[1 + \operatorname{erf} \left(\frac{b}{g} - \frac{gs}{2} \right) \right] \exp \left[-bs + \frac{1}{4} g^2 s^2 \right] \quad (2)$$

where $b = 16 \times 10^{-8}$ s, $g = 4.7 \times 10^{-8}$ s are the fitted values to the Nd:YAG pulse used.

Equation 1 was inversely Laplace transformed into time domain using Stehfest numerical method.^[25] Density of 5.22×10^3 , 2.33×10^3 kg m⁻³, specific heat of 0.600×10^3 , 0.712×10^3 J kg⁻¹ K⁻¹ and thermal conductivity of 14, 148 W m⁻¹ K⁻¹ were respectively taken for TiN and Si. The fitting parameters including thermal conductivity and diffusivity of NT arrays, thermal boundary resistances at TiN-NT and NT-Si interfaces (in short, k , α , $\text{TBR}_{\text{TiN-NT}}$ and $\text{TBR}_{\text{NT-Si}}$, respectively) were varied $\pm 20\%$ and a least square optimization method was applied to minimize the fitting errors.

5.2.3 Molecular dynamics simulation

The coaxial C@BNNT structure was constructed by encapsulating three outer BNNT walls with chirality of (98, 0), (107, 0) and (116, 0) onto four inner CNT walls with chirality of (62, 0), (71, 0), (80, 0) and (89, 0). The inner and outer diameters of the coaxial C@BNNT were 4.85 nm and 9.08 nm, respectively, and the inter-wall distance was set as 3.4 Å, according to the TEM observation. For the modelling convenience, the bond lengths of CNT and BNNT were both set as 1.435 Å instead of their intrinsic values (1.42 and 1.45 Å for CNT and BNNT, respectively), and a tensile/compressive strain tolerance of $\sim 1\%$ was applied to eliminate the lattice mismatch. The corresponding x , y , z coordinates of the NT structures were generated by the Visual Molecular Dynamics package.^[26] The interactions between the C atoms, and those between the B and N atoms were described by the Tersoff potential.^[27-29] The van der Waals interactions between the various NT walls were modelled by Lennard-Jones potential.^[30-32] Periodic boundary condition was applied along the axial z direction and free boundary conditions were applied along the radial x and y directions.

The whole structure was initially well relaxed in constant volume and temperature (NVT) ensemble at 300 K for 40 ps with the time step of 0.2 fs. Next, the system was switched to

constant volume and energy (NVE) ensemble to keep the energy conserved. To extract the thermal conductivity, the coaxial C@BNNT construct was divided into many thin slabs (2.153 Å each, the width of an individual zigzag ring) along the axial z direction. The middle region (heat source, 4 slabs) and two ending regions (heat sink, 2 slabs) of the tube were controlled by Nose-Hoover thermostats at $T + \Delta T$ (350 K) and T (300 K), respectively. It took 100 ps to reach a steady temperature gradient under the NVE ensemble, and the heat flow (h) as well as temperature (T) profile were recorded in the following 100 ps. The temperature of each slab was calculated based on the kinetic energy of all the atoms within the slab. The heat flow was extracted by linearly fitting the cumulative energy changes of the heat source or heat sink regions. The thermal conductance (σ) was calculated based on $\sigma = h / \nabla T$, where ∇T is the temperature gradient (slope of the linear region of temperature distribution).

Similarly, isolated four-wall CNT (identical with the aforementioned inner CNT) and its aligned cluster (with inter-tube distance of 3.4 Å) were constructed and further simulated to study their thermal conductance behaviors. All simulations were performed using the Large-Scale Atomic/Molecular Massively Parallel Simulator.

5.3 Principle Outcomes

5.3.1 Structure and morphology of CNT and C@BNNT arrays

Figure 5.1a, b present the cross-sectional SEM images of the as-prepared CNT and C@BNNT arrays, respectively. The C@BNNT arrays retain the vertically aligned morphology of the starting CNT arrays with no observable change in tube areal density. It is also noted that the crystalline structure of the CNT is well preserved after the BNNT introduction as indicated by the corresponding Raman spectra (Figure 5.2). To clearly investigate the nanostructures of the NT before and after the BNNT encapsulation, HR-TEM study of the individual CNT and C@BNNT was further carried out. The starting CNT exhibits an inner diameter of 4.83 nm with an average wall thickness of 1.98 nm

(corresponding to ~ 4 -5 C walls, Figure 5.1c), and an increase of 0.97 nm in wall thickness can be observed for the C@BNNT (corresponding to the ~ 3 -4 outer BN layers, Figure 5.1d).

Figure 5.1 Cross-sectional SEM and HR-TEM images of (a, c) CNT and (b, d) C@BNNT, respectively. BNNT with wall thickness of 0.97 nm (~ 3 -4 walls) is encapsulated onto the CNT. (e) FT-IR and (f) EDX spectra of the NTs further confirm and quantify the introduction of BNNT for C@BNNT arrays.

Figure 5.1e shows the FT-IR spectra of CNT and C@BNNT. Besides the characteristic C=C stretching vibrations located at 1651 and 1441 cm^{-1} for CNT,^[20] additional in-plane B-N stretching and out-of-plane B-N-B bending at 1384 and 799 cm^{-1} are observed for the C@BNNT,^[19] respectively, further confirming the BNNT introduction. To better quantify

the BNNT introduced, the energy dispersive X-ray spectroscopy (EDX) was collected for the resulting C@BNNT arrays.^[33] Figure 5.1f shows the EDX spectroscopy of the C@BNNT arrays (collected from cross-sectional view), where B (0.183 keV), C (0.277 keV), N (0.392 keV) and O (0.525 keV) can be identified, and the weight fraction of each element is listed in the inset table. It is noted that the weight ratio of BN:C is ~40:50 for the C@BNNT arrays, which is consistent with the TEM results. In addition, the corresponding elemental maps show the homogeneous distribution of B, C, N within the aligned C@BNNT arrays (Figure 5.3).

Figure 5.2 Raman spectra of CNT and corresponding C@BNNT. The crystal structure of the CNT is not altered after the introduction of outer BNNT.

Figure 5.3 SEM and EDX characterizations of the resulting C@BNNT arrays. (a) EDX spectrum, (b) SEM image and corresponding elemental maps for (c) O, (d) B, (e) C and (f) N indicate the successful introduction of BNNT and the homogeneous distribution.

5.3.2 Thermal conductivity measurements of CNT and C@BNNT arrays

To study the effects of outer BNNT on the thermal conductivity of the coaxial C@BNNT arrays, PPR measurement was employed,^[34] as schematically illustrated in Figure 5.4a. To enhance the surface uniformity and reflectivity, a ~500 nm-thick titanium nitride (TiN) layer was deposited by sputtering prior to the measurement. As shown in the cross-sectional SEM image (Figure 5.4b), the uniform and dense TiN layer adheres well to the top ends of NTs without affecting their aligned morphology, which is believed to facilitate the capture of photothermal signal.^[35] During the PPR measurement, the TiN surface was struck by a Nd:YAG laser (pump beam), resulting in the sudden rise in the surface temperature and a decay to room temperature was followed. Based on the temperature dependence of the TiN's reflectivity, the surface temperature of the TiN layer was recorded by measuring the intensity of the He-Ne laser (probe beam) reflected from the centre of the pump beam. Figure 5.4c shows the obtained normalized surface temperature-time curves of the NT arrays. Obviously, the surface temperature decays faster for the C@BNNT arrays as compared to the bare CNT arrays, indicating that the heat transports more efficiently through the C@BNNT arrays. To extract the thermal properties of the NT arrays, a three-layer heat conduction model was used to fit the obtained temperature excursion files.^[34] In addition, the fitting parameters including thermal conductivity and diffusivity of NT arrays, thermal boundary resistances at TiN-NT and NT-Si interfaces (in short, k , α , $\text{TBR}_{\text{TiN-NT}}$ and $\text{TBR}_{\text{NT-Si}}$, respectively) were varied $\pm 20\%$ and a least square optimization method was applied to minimize the fitting errors.^[34] As a representative, the resulting theoretical fitted curve of the C@BNNT arrays matches well with the experimental curve (Figure 5.4d), and the latter lies in between the two fitted curves with $\pm 20\%$ variations in the best fitted values, indicating that the experimental data was reasonably fitted.

Table 5.1 Thermal properties of the CNT and C@BNNT arrays measured by the PPR technique.

NT Arrays	k ($\text{W m}^{-1} \text{K}^{-1}$)	α ($\times 10^{-5} \text{m}^2 \text{s}^{-1}$)	$\text{TBR}_{\text{TiN-NT}}$ ($\times 10^{-6} \text{m}^2 \text{K W}^{-1}$)	$\text{TBR}_{\text{NT-Si}}$ ($\times 10^{-6} \text{m}^2 \text{K W}^{-1}$)
CNT	15.50 ± 3.50	4.80 ± 2.20	0.95 ± 0.05	6.20 ± 2.50
C@BNNT	29.50 ± 4.50	4.75 ± 0.85	0.80 ± 0.10	5.75 ± 3.25

Figure 5.4 (a) Schematic illustration of the PPR technique and sample structure. (b) Cross-sectional SEM image of the TiN/NT/Si shows that the aligned morphology of the NTs was well preserved after the deposition of ~500 nm-thick TiN layer on top. (c) Normalized surface temperature-time curves of the NT arrays measured by PPR indicate that the C@BNNT arrays dissipate heat faster than the bare CNT arrays. (d) Theoretically fitted curves of the C@BNNT arrays match reasonably well with the experimental data.

Table 5.1 shows the thermal conductivity (k), thermal diffusivity (α) of the NT arrays, as well as TBR_{TiN-NT} and TBR_{NT-Si} extracted from the corresponding normalized surface temperature vs time curves. Notably, a ~90% increase in the thermal conductivity is achieved for the C@BNNT arrays (~29.5 W m⁻¹ K⁻¹) as compared to the bare CNT arrays (~15.5 W m⁻¹ K⁻¹, similar with most TCVD-grown CNT arrays³). This is expectable according to the thermal conductance model^[24] $k = \delta k_l + (1 - \delta)k_{air}$ (δ is tube volume fraction, k_l and k_{air} are thermal conductivities of individual NT and air, respectively), as the thermally conductive outer BNNT (~350 W m⁻¹ K⁻¹)^[13] squeezes the volume of thermally resistant air (~0.026 W m⁻¹ K⁻¹)^[6] between the NTs. The thermal diffusivity is generally

constant for the CNT arrays before and after the BNNT encapsulation (from $\sim 4.80 \times 10^{-5}$ to $4.75 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$), which is comparable with most TCVD-grown CNT arrays.^[5, 24, 36] Based on $C = k/\alpha$, the C@BNNT arrays have higher volumetric specific heat (C) than the bare CNT arrays, resulting from their larger tube diameter^[24] and higher tube volume fraction, which contributes to their enhanced thermal conductivity according to Debye equation^[24] $k = Cv/3$ (v and l are the velocity and mean free path of the phonons, respectively). The TBRs in the magnitudes of $\sim 10^{-6}$ – $10^{-7} \text{ m}^2 \text{ K W}^{-1}$ are consistent for the CNT and C@BNNT arrays, which are similar with those of most sandwiched metal/NT/substrate structures.^[24, 37, 38]

5.3.3 Molecular dynamics simulation

Figure 5.5 (a) Computational model (front/side view) of the coaxial C@BNNT structure. The middle region (heat source, red) and the two ending regions (heat sink, dark green) are controlled at temperatures of $T + \Delta T$ (350 K) and T (300 K), respectively. (b) Temperature distribution along the heat flow direction and (c) the cumulative energy changes vs simulation time for the coaxial C@BNNT, inner CNT and outer BNNT, respectively.

Figure 5.6 (a) Snapshots of C@BNNT, isolated CNT, and CNT cluster when the steady temperature gradient is reached under NVE ensemble, respectively. (b) Temperature distribution along the heat flow direction and (c) the cumulative energy changes vs simulation time for the inner CNT within C@BNNT, isolated CNT and individual CNT within aligned CNT cluster, respectively.

MD simulation has been found to be a very useful technique to study the thermal characteristic of CNT and BNNT.^[39] To gain deeper insights into the mechanism of heat transfer enhancement of C@BNNT arrays, corresponding MD simulation was conducted. Figure 5.5a shows the computational model of coaxial C@BNNT structure with axial length of 200 Å constructed by encapsulating three outer coaxial BNNT walls onto four inner CNT walls. Other parameters such as diameters, inter-wall distance were all set based on the TEM observations. To extract the thermal properties of the coaxial construct, reverse non-equilibrium MD simulation was further carried out, during which the middle region (heat source, red) and two ending regions (heat sink, dark green) of the NT were set at temperatures of $T + \Delta T$ (350 K) and T (300 K), respectively. A steady temperature gradient was reached in 100 ps under constant volume and energy (NVE) ensemble for the C@BNNT with slight ripples formed along the tangential and axial directions (snapshot is shown in Figure 5.6), while the coaxial NT structure was well kept without observable bending. The temperature distributions along the axial direction of the C@BNNT, inner

CNT, and outer BNNT were obtained, respectively (Figure 5.5b). It is found that dramatic temperature drops occur near the heat source and sink regions due to the intensive phonon scattering, while for the rest areas ranging from ± 25 to ± 75 Å, the temperatures decrease almost linearly from the heat source to the sink. The temperature of the BNNT is higher than that of the CNT along the tube axial direction, while the overall temperature of the C@BNNT lies in between. The cumulative energy changes in the heat source and sink regions were recorded as well (Figure 5.5c), which increase linearly with the simulation time.

Table 5.2 Thermal conductance of various NT structures extracted from MD simulation.

NT	Inner CNT	Outer BNNT	C@BNNT	Isolated CNT	CNT within Cluster
Thermal Conductance ($\times 10^5$ W m K ⁻¹)	1.89	0.65	2.26	1.88	1.97

By fitting the slopes of the linear regions of temperature distribution (Figure 5.5b) and the cumulative energy changes (Figure 5.5c), the temperature gradient (∇T) and heat flow (h) of the inner CNT, outer BNNT and C@BNNT were obtained as 0.265, 0.425, 0.345 K Å⁻¹, and 31.10, 17.35, 48.45 eV ps⁻¹, respectively. To eliminate the influence of cross-section area (A) change on the simulation of individual NT, the thermal conductance (σ , $\sigma = h / \nabla T$) instead of thermal conductivity (k , $k = h / \nabla TA$) of the individual NT was calculated for comparison. The thermal conductance of the inner CNT, outer BNNT and C@BNNT was then obtained as 1.89×10^5 , 0.65×10^5 and 2.26×10^5 W m K⁻¹, respectively (Table 5.2). To more comprehensively study the effect of the tube-tube interactions on the heat transfer of individual NT, isolated CNT and aligned CNT cluster were further constructed (Figure 5.6). The thermal conductance of the isolated CNT and individual CNT within aligned CNT cluster was extracted to be 1.88×10^5 and 1.97×10^5 W m K⁻¹, respectively (Table 5.2). Their similar thermal conductance demonstrates that the effect of tube-tube interactions on the heat transfer of NT can be neglected considering the weak van der Waals forces.^[7] In addition, the inner CNT exhibits almost same thermal conductance with that of the isolated CNT, indicating that the heat transfer of CNT is not impaired by BNNT encapsulation. On the other hand, with the additional contribution of outer BNNT, C@BNNT exhibits a 20.21% higher thermal conductance than the isolated CNT, which

shows a similar enhancement tendency with that of the experimental result. It is noted that the enhancement value obtained from simulation is lower than that of experimental result, attributing to the limited quality of the CNT arrays used in the experiment. Furthermore, the phonon power spectra of inner CNT and outer BNNT are highly overlapped (Figure 5.7) due to their similar lattice structures, which indicates the weak interfacial phonon scattering between them. Considering the negligible tube-tube interactions and the weak interfacial phonon scattering between the inner CNT and outer BNNT, it is reasonable to conclude that the improved heat transfer of as-prepared C@BNNT arrays is attributed to the outer BNNT which serves as an additional heat conducting channel while does not affect the thermal conductivity of the inner CNT.

Figure 5.7 Phonon power spectra of inner CNT and outer BNNT in coaxial C@BNNT structure. The highly overlapped phonon power spectra indicates the weak interfacial phonon scattering between them, which results from their similar lattice structures.

5.4 Conclusions

The axial thermal conductivity of the coaxial C@BNNT arrays has been measured using PPR technique and compared with that of the bare CNT arrays. Notably, a tremendous ~90% improvement (from ~15.5 to 29.5 W m⁻¹ K⁻¹) in the thermal conductivity has been achieved for the C@BNNT arrays with the introduction of 0.97 nm-thick (~3–4 walls) outer BNNT.

This enhancement is due to that the outer BNNT provides additional thermal conductance without affecting that of the inner CNT attributing to their coherent structures, as supported by the corresponding reverse non-equilibrium MD simulation. This phenomenon is beneficial to the energy dissipation performance of the C@BNNT arrays.

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Chapter 6

Supercompressible Coaxial Carbon Nanotube@Graphene Arrays with Temperature-Invariant Viscoelasticity

Despite the progresses in mechanical properties of aforementioned C@BNNT arrays, their inadequate shape recoverability, viscoelasticity under cyclic compression and limited dimensions (hundreds μm in length) still cannot meet the practical application requirements. To address these issues, in this chapter we demonstrate a facile strategy of fabricating supercompressible coaxial CNT@graphene (CNT@Gr) arrays (4 mm in length) which almost completely recover from compression at a strain of up to 80% and retain $\sim 80\%$ recovery even after 1000 compression cycles at a 60% strain. Furthermore, the CNT@Gr arrays possess outstanding strain- and frequency-dependent viscoelastic responses with storage modulus and damping ratio of up to ~ 6.5 MPa and ~ 0.19 , respectively, which are nearly constant over an exceptionally broad temperature range of -100 – 500 $^{\circ}\text{C}$ in ambient air. These supercompressibility and temperature-invariant viscoelasticity together with facile fabrication process of the CNT@Gr arrays enable their promising multifunctional applications such as energy absorbers, mechanical sensors and heat exchangers in various environments.

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6.1 Introduction

Although the aforementioned coaxial C@BNNT arrays have shown significantly enhanced compressive mechanical properties which hold promising potential in damping applications, their shape recovery could only be retained when compression with strain less than 50% and number of cycles less than 100 is applied. These unfavorable compressive behaviors of the C@BNNT arrays still limit their viscoelastic property upon dynamic compressions, which further restrict their potential mechanical damping applications.

On the other hand, decorating CNTs with graphitic carbon could be another desirable approach because that the resulting synergistic effect among different forms of carbon improves the overall properties.^[1] Moreover, this treatment well preserves the intrinsic characteristics of CNTs which facilitate their wide applications.^[2] Nevertheless, the majority of current carbon deposition approaches involving gaseous precursors are only applicable to laboratory-based (non-commercial) CNT arrays and encounter non-uniform carbon decoration (especially for those long and densely packed CNTs), which significantly limit their mechanical enhancements.^[1-3] Considering all these issues, developing a facile process to achieve macroscale CNT arrays with uniform graphitic carbon encapsulation and further exploring their compressibility and dynamic viscoelasticity under various conditions are still in urgent demand.

In this chapter, we demonstrate a simple strategy of fabricating supercompressible coaxial CNT@graphene (CNT@Gr) arrays by using a two-step route involving encapsulating polymer coating layers onto commercially available vertically aligned CNTs (~4 mm tall) and subsequent annealing processes. Different from the untreated CNT arrays that deform plastically, the resulting CNT@Gr arrays not only show a 5.6-fold increase in the compressive strength at a 60% strain, but also almost fully recover after compression at a strain of up to 80% and retain ~80% recovery even after 1000 compression cycles at a 60% strain. Notably, they also exhibit excellent strain- and frequency-dependent viscoelastic properties with storage modulus and damping ratio of up to ~6.5 MPa and ~0.19, respectively. Furthermore, these viscoelastic characteristics of the CNT@Gr arrays were

found to be nearly constant over an exceptionally broad temperature range of -100 – 500 °C in ambient air.

6.2 Experimental Methods

6.2.1 Fabrication of CNT@Gr arrays

Firstly, CNT arrays (~ 4 mm tall, Aixtron) were treated with aqueous sodium dodecyl benzene sulfonate solution (SDBS, 10 mg mL^{-1} , technical grade, Sigma-Aldrich) overnight to improve their hydrophilicity. Then, the CNT arrays were washed thoroughly with *N,N*-dimethylformamide (DMF, ACS, 99.8+%, Alfa Aesar) over 18 h (fresh DMF every 6 h) to remove any SDBS residue. Next, the treated CNT arrays were soaked in the polyacrylonitrile (PAN, MW = 150 000, Sigma-Aldrich) solution (0.5 wt%, in DMF) at 50 °C for 12 h to uniformly coat PAN. After this, ethanol washing (over 32 h, fresh ethanol every 8 h) and critical point drying were subsequently employed to obtain CNT@PAN arrays. Finally, the CNT@Gr arrays were achieved by converting the PAN coating into conformal graphene layers via an annealing process, which is composed of heating at 210 °C for 1.5 h and further annealing at 1010 °C for 1.5 h in an argon atmosphere.

6.2.2 Compression tests

Compressive mechanical performances (along tube axial direction) of CNT@Gr arrays were determined using a Universal Testing System (Instron 5567, Instron, USA) in a quasi-static fashion at room temperature. Square-shaped CNT@Gr arrays ($15 \times 15 \times 4 \text{ mm}^3$) were firstly loaded on center of lower platen, a smaller compression rod with 50 mm diameter was then applied onto the sample with a controlled speed. To comprehensively understand compressive behaviors of the CNT@Gr arrays, $\varepsilon = 20, 40, 60$ and 80% were applied at a $\dot{\varepsilon}$ rate of $100\% \text{ min}^{-1}$. In particular, compression at $\varepsilon = 60\%$ was repeated for 1000 cycles to investigate their long-term compressive performance. For comparison, compression at $\varepsilon = 60\%$ was conducted for the initial CNT arrays. ε and σ were calculated

using displacement of the compression rod divided by original height of the sample and compressive loading force over cross-sectional area of the sample, respectively.

6.2.3 Dynamic mechanical analysis

Viscoelastic properties (along tube axial direction) of CNT@Gr arrays were characterized with a dynamic mechanical analyzer (DMA Q800, TA Instruments, USA). Square-shaped CNT@Gr arrays with dimensions of $10 \times 10 \times 4 \text{ mm}^3$ were tested using a parallel-plate compression clamp to study their dynamic compressive responses. E' , E'' and $\tan \delta$ as functions of f and ε were collected under multi- f (0.1–100 Hz, at $\varepsilon = 1\%$) and multi- ε (0.1–2%, with $f = 1 \text{ Hz}$) modes with a preload force of 0.01 N, respectively. To investigate the viscoelastic behaviors of CNT@Gr arrays at varying T , all the measurements were repeatedly conducted at $T = -100, 25, 300$ and $500 \text{ }^\circ\text{C}$ in ambient air. In addition, the T -dependency of viscoelasticity of the CNT@Gr arrays was further studied by measuring E' , E'' and $\tan \delta$ over $T = -100$ – $500 \text{ }^\circ\text{C}$ in ambient air with a ramping rate of 2°C min^{-1} , where the f and ε were controlled at 1 Hz and 1%, respectively. In addition, longitudinal dynamic shear tests of the CNT and CNT@Gr arrays ($0.5 \times 4 \times 4 \text{ mm}^3$) were conducted using a shear sandwich clamp. E' , E'' and $\tan \delta$ as functions of f and ε were collected under multi- f (1–100 Hz, at $\varepsilon = 2\%$) and multi- ε (2–12%, with $f = 1 \text{ Hz}$) modes at $25 \text{ }^\circ\text{C}$ with a preload force of 0.01 N, respectively. The sample T was controlled by a bifilar wound chamber furnace with gas cooling accessory. All the samples were equilibrated at set T for 10 min prior to each test.

6.3 Principle Outcomes

6.3.1 Structure and morphology of CNT@Gr arrays

Figure 6.1 Schematic illustration of fabricating coaxial CNT@Gr arrays by encapsulating PAN polymer and subsequently annealing to introduce conformal graphene layers onto the aligned CNTs.

Figure 6.1 shows the two-step fabrication of CNT@Gr arrays by encapsulating polyacrylonitrile (PAN) polymer onto the vertically aligned CNTs and subsequently annealing to convert the PAN coating into conformal graphene layers.^[4, 5] To examine the changes in morphology and nanostructure of the CNTs before and after graphene encapsulation, SEM and TEM studies were carried out. As shown in Figure 6.2a, b, the resulting CNT@Gr arrays perfectly retain the vertical alignment without noticeable change in the tube areal density. Corresponding TEM images (Figure 6.2c, d) show that the CNT@Gr possesses similar inner diameter of ~7–9 nm while larger outer diameter of ~12–14 nm as compared to the CNT counterpart (~7–9 nm and ~9–11 nm, respectively), suggesting that outer graphene layers of ~1.5 nm (~5 layers) were encapsulated uniformly over the entire lengths of the CNTs. This can be well supported by the increased mass density of the CNT@Gr arrays (0.046 g cm^{-3}), which is 3.3-fold higher than that of the initial CNT arrays (0.014 g cm^{-3}). Meanwhile, the clear lattice fringes with a spacing of 0.35 nm (inset of Figure 6.2d) observed for CNT@Gr indicate their crystalline feature, which is also supported by the XRD characterization (Figure 6.3).

Figure 6.2 Cross-sectional SEM and corresponding TEM images of CNT (a, c) and CNT@Gr (b, d) show that the outer graphene layers were uniformly encapsulated onto the CNTs without causing noticeable change in their tube areal density. EELS (e) and Raman spectra (f) further verify that the integration of pristine graphene does not alter the crystalline structure of CNTs.

To further verify the presence of the graphene coating in the coaxial CNT@Gr structure, additional TEM/EELS characterization was carried out on an individual CNT before and after the coating process (Figure 6.2e). It is observed that EELS spectrum of CNT displays C K-edge with characteristic peaks of sp^2 materials at 286 and 292 eV corresponding to π^* and σ^* contributions,^[4, 6] respectively. After the coating process, no observable changes in the π^* and σ^* peaks as well as their ratio can be found for both the inner and outer walls of the CNT@Gr. These undisrupted sp^2 bonds in the CNT@Gr structure further confirm that the outer graphene layers are successfully introduced onto the CNTs. This is also supported

by the high-resolution C 1s XPS analysis (more details can be seen in Figure 6.4). In addition, both CNT@Gr and CNT show typical Raman characteristics and similar intensity ratio of D and G peak (~ 0.72 and 0.68 , respectively),^[1] indicating the well preserved crystallinity of CNTs after the graphene encapsulation (Figure 6.2f). Based on the above characterizations, we can reasonably conclude that pristine graphene layers were uniformly encapsulated onto the CNTs without altering their crystalline nanotube structure.^[4]

Figure 6.3 XRD profiles of CNT and CNT@Gr. The characteristic (002) and (100) diffraction peaks indicate that the crystallinity is well preserved for the CNT@Gr.

Figure 6.4 XPS survey and high resolution C 1s spectra of CNT and CNT@Gr, respectively.

6.3.2 Supercompressibility of CNT@Gr arrays

Figure 6.5 Mechanical responses of CNT@Gr arrays upon uniaxial compressions. (a) Real-time photos show that the CNT arrays collapse while the CNT@Gr arrays fully recover after compression at strain (ϵ) = 60%. Scale bar, 1 cm. (b) Loading-unloading compressive stress (σ) vs. ϵ curves of CNT@Gr and CNT arrays at various ϵ , where the hysteresis of CNT@Gr arrays increases with ϵ . Representative σ vs. ϵ curves (c), shape recovery ratios and energy dissipation ratios (d) of the CNT@Gr arrays upon cyclic compressions up to 1000 cycles at $\epsilon = 60\%$ demonstrate their gradually stabilized mechanical responses with preconditioning effect. Cross-sectional SEM images (inset of (d), scale bar, 1 mm) of CNT@Gr arrays before and after 1000 compression cycles indicate their persistent shape recoverability.

To investigate the effects of graphene encapsulation on the mechanical behaviors of the CNT@Gr arrays, uniaxial compression tests (along tube axial direction) were carried out. As shown in Figure 6.5a, both the CNT and CNT@Gr arrays can be compressed to a large strain (ϵ) due to their high porosity (Figure 6.5a, b). In contrast to some of the previously reported CNT arrays that exhibit good shape recoverability, the initial CNT arrays used in

the present work are almost plastic and collapse permanently when a compression at $\varepsilon = 60\%$ is loaded (corresponding cross-sectional SEM images are shown in Figure 6.6a–d). This is attributed to that their tube diameter ($\sim 9\text{--}11\text{ nm}$) and wall thickness ($\sim 1\text{ nm}$) are much thinner than those of the recoverable CNT arrays ($> 40\text{ nm}$ and $> 20\text{ nm}$, respectively),^[7] which are dependent on the synthesis methods. Notably, the outer graphene integration enables the CNT@Gr arrays to become resilient and fully recover to their original shape with no mechanical failure after loading-unloading of the similar compression ($\varepsilon = 60\%$). Figure 6.5b shows the plots of compressive stress (σ) vs. ε for the CNT and CNT@Gr arrays at various ε . The σ vs. ε curves obtained during the loading process display three typical deformation regimes of open-cell foams:^[8] a Hookean (linear) region for $\varepsilon \leq 7\%$, where Young's modulus of ~ 0.010 and $\sim 0.015\text{ MPa}$ are respectively performed for the CNT and CNT@Gr arrays; a plateau regime (buckling of nanotubes) at $7\% < \varepsilon < 45\%$; and a densification regime for $\varepsilon \geq 45\%$ with steeply rising σ . Upon unloading process of the compression at $\varepsilon = 60\%$, the bare CNT arrays deform almost plastically (Figure 6.5a) and recover only $\sim 8\%$ of the applied displacement. Similar observation has been reported previously, which could be due to the small tube diameter and weak inter-tube interactions originating from the specific synthesis setup and method.^[7, 9] In contrast, the CNT@Gr arrays recover more than 90% of the applied deformation even at $\varepsilon = 80\%$ and fully recover with σ returning to the origin after unloading of $\varepsilon \leq 60\%$. Meanwhile, a significant 5.6-fold increase in compressive strength from 0.095 to 0.53 MPa is exhibited for the CNT@Gr arrays as compared to CNT arrays when $\varepsilon = 60\%$ is loaded, demonstrating their significantly enhanced compressive stiffness. It can be noted that significant hysteresis loop which consists of two distinct paths corresponding to the loading and unloading processes exists among the σ vs. ε curves of the CNT@Gr arrays and increases with ε , indicating their large and ε -dependent energy dissipation.^[10] As summarized in Figure 6.7, the CNT@Gr arrays dissipate substantial 83.06, 87.53, 88.72 and 89.01% of the loaded energy when compressions at $\varepsilon = 20, 40, 60$ and 80% are applied, respectively, which are obviously higher than most previously reported CNT and graphene based arrays and aerogels ($\sim 40\text{--}60\%$) at respective ε .^[4, 8, 11-14]

Figure 6.6 Cross-sectional SEM images of CNT (a–d) and CNT@Gr (e–h) arrays before and after 1 and 1000 compression cycles at strain (ε) = 60%, respectively. (a, d, e, h) are the zoom-in views of (b, c, f, g), respectively.

Figure 6.7 Energy dissipated (E_d , shadow area in (a)), energy loaded (E_l , shadow area in (b)) and energy returned (E_r , shadow area in (c)) for the first compression cycle at $\varepsilon = 60\%$. (d) Energy dissipation ratios of CNT@Gr arrays at various applied ε .

Long-term mechanical performances of the CNT@Gr arrays are crucial to their lifetime reliability with respect to practical applications. Therefore, cyclic compressions at $\varepsilon = 60\%$ were further carried out to investigate the durability of their mechanical responses. Figure

6.5c shows the representative σ vs. ε curves of CNT@Gr arrays for the 1st, 2nd, 10th, 100th, 500th and 1000th cycles. A transient phenomenon (preconditioning effect) in compressive strength can be noted for the CNT@Gr arrays upon this continuous cyclic compression.^[9, 15] During the initial compression cycle, the compressive strength is ~ 0.53 MPa, which gradually decreases to ~ 0.28 MPa after the first 100 cycles of loading-unloading and remains almost unchanged upon further cyclic compression. This σ softening is due to the inter-tube van der Waals interactions are weakened and additional defects are induced during the initial compressions, after which a new equilibrium status is progressively reached to generate a stable σ response.^[9] Similar preconditioning effect is noted as well for the shape recovery ratio and energy dissipation ratio of the CNT@Gr arrays (Figure 3d), which respectively evolve from 100% and 88.72% for the 1st cycle to $\sim 80\%$ and $\sim 50\%$ after the initial 100 cycles and are well retained throughout the following 900 cycles of compression. The outstanding shape recovery and energy absorption over the long-term cyclic loading-unloading make the CNT@Gr arrays promising in applications that require both persistent structural support and energy damping.^[8]

To gain deep insights into the compression mechanism of CNT@Gr arrays, corresponding cross-sectional SEM images were taken before and after the long-term cyclic compression loading (inset of Figure 6.5d, more high resolution SEM images can be seen in Figure 6.6e, h). Different from the CNT arrays which permanently deform upon first cycle of compression at $\varepsilon = 60\%$ with a typical buckling initiating from the bottom and propagating upwards (Figure 6.6d), only longitudinally distributed curvatures (*i.e.* slight buckles with ultra-long wavelengths, Figure 6.6h) can be observed for the CNT@Gr arrays even after 1000 cycles of compression at $\varepsilon = 60\%$, indicating their significantly reinforced compressive resilience.^[9] The enhancement of the CNT@Gr arrays can be attributed to the rigid outer graphene layers which provide substantial mechanical supports including much higher Young's and bending modulus of the individual nanotubes.^[2, 4, 7, 9] In addition, the conformal graphene encapsulation strengthens the tube-tube bonding at bundles and decreases the segment length, which further improves the critical buckling load of the CNT@Gr arrays.^[2] Moreover, the effectively enlarged tube diameter promotes more tube-tube contacts that significantly increase the vertical shear strength of the CNT@Gr arrays

upon axial compression,^[1] which can be supported by their enhanced longitudinal shear viscoelastic properties (more details can be seen in Figure 6.8).

Figure 6.8 Dynamic shear tests of CNT and CNT@Gr arrays. (a) Shear sandwich clamp was used to measure the longitudinal shear viscoelastic properties of the NT arrays. (b) Storage modulus (E'), (c) loss modulus (E'') and (d) damping ratio ($\tan \delta$) of the CNT and CNT@Gr arrays as functions of applied frequency (f) (1–100 Hz, at $\varepsilon = 2\%$).

6.3.3 Temperature-invariant viscoelasticity of CNT@Gr arrays

In addition to excellent static compressive performances, outstanding dynamic mechanical responses are also desirable for damping materials. Therefore, systematic compression loadings with varying frequency (f) and ε over a wide temperature (T) range were applied to further study the viscoelastic responses of the CNT@Gr arrays. Figure 6.9a–c show the storage modulus (E'), loss modulus (E'') and damping ratio ($\tan \delta$) of the CNT@Gr arrays as functions of f (0.1–100 Hz) at $T = -100, 25, 300$ and 500 °C in ambient air, respectively. When $\varepsilon = 1\%$ is loaded over such a substantially broad f range, a notable and stable E' of ~ 1.5 MPa is performed for the CNT@Gr arrays, which is ~ 6 -fold and ~ 2 orders of magnitude higher than those of the entangled CNT aerogels (~ 0.25 MPa)^[16] and the graphene based aerogels (~ 0.01 MPa)^[17, 18] at the same ε , respectively. This excellent E' is

attributed to their highly oriented morphology which makes full use of the superior axial elastic modulus of the individual nanotubes.^[19] On the other hand, the E'' of ~ 0.12 MPa remains generally unchanged over $f = 0.1$ – 10 Hz, while shows an abrupt 2.3-fold increase to ~ 0.28 MPa when higher $f = 10$ – 100 Hz is applied. As a result, the $\tan \delta = E'' / E'$ displays a similar tendency with E'' , where a stable value of ~ 0.08 over $f = 0.1$ – 10 Hz followed by a sudden 2.4-fold increase to ~ 0.19 over $f = 10$ – 100 Hz can be observed. These increases in E'' and $\tan \delta$ could be due to that the higher loading f induces stress accumulation along the compression direction, which results in the breaking and deformation of nanotubes and thus leads to a larger energy consumption.^[20] It should be noted that this $\tan \delta$ of the CNT@Gr arrays is ~ 1 order of magnitude higher than that of the graphene coated entangled CNT aerogels (~ 0.02)^[4, 16] (Table 6.1) and is better than or comparable with those of the previously reported dense and short CNT brushes (~ 0.04 – 0.17),^[19, 21] indicating the promising potential of CNT@Gr arrays in energy absorption applications. This energy dissipation is attributed to the significant van der Waals adhesion energy consumed by zipping-unzipping between the aligned nanotubes with increased tube diameter and contact area during the compression loading-unloading process.^[22] It is worthy to note that these f -dependent viscoelastic behaviors of the CNT@Gr arrays remain nearly constant when exposed to drastically varied $T = -100, 25, 300$ and 500 °C in ambient air.

Figure 6.9 Invariant viscoelastic properties of CNT@Gr arrays over a wide temperature (T) range in ambient air. Storage modulus (E') (a, d), loss modulus (E'') (b, e) and damping ratio ($\tan \delta$) (c, f).

f) of the CNT@Gr arrays as functions of frequency (f) (0.1–100 Hz, at $\varepsilon = 1\%$) and ε (0.1–2%, with $f = 1$ Hz), respectively, at $T = -100, 25, 300$ and 500 °C.

Table 6.1 Comparison of physical and mechanical properties of the CNT@Gr arrays with those of the existing materials.

Material	ρ (g cm ⁻³)	Max. T (° C)	Mechanical Properties		
			σ (MPa)	E' (MPa)	$\tan \delta$
CNT@Gr Arrays (This work)	0.046	500	1.5	~1.5–6.5	~0.08–0.19
CNT Aerogels ^{4, 16}	~0.014	500	~0.3	~0.2–1.0	~0.02
CNT Brushes ^{19, 21, 23}	~0.95	N/A	~0.4–800	~70–240	~0.04–0.17
Polymeric Foam ²⁷	~0.7–1.5	~30–250	~5–50	~0.01–3	~0.05–0.5
Elastomeric Rubber ²⁷	~0.8–2.5	~0–230	~1–20	~1–10 ³	~0.02–0.25
Metals and Alloy ²⁷	~1.5–20	~0–1000+	~5–10 ³	~10 ⁴ –10 ⁶	~10 ⁻⁵ –10 ⁻²
Ceramics ²⁷	~1.2–13	~160–2000+	~10 ³ –10 ⁴	~10 ⁴ –10 ⁶	~10 ⁻⁵ –10 ⁻⁴

The effect of applied ε on the dynamic mechanical responses of the CNT@Gr arrays was further investigated ($\varepsilon = 0.1$ –2%, $f = 1$ Hz). As shown in Figure 6.9d, the E' remains nearly unchanged at ~1.5 MPa over $\varepsilon = 0.1$ –1%, but suddenly increases to ~6.5 MPa (a 4.3-fold increase) at higher $\varepsilon = 2\%$. This is because considerable elastic energy is stored within the spring-like CNT@Gr arrays when larger ε (within the Hookean regime) is loaded.^[23] Similar ε -dependency is also observed for both E'' and $\tan \delta$ (Figure 6.9e, f), which show dramatic 12.2-fold (from ~0.09 to ~1.1 MPa) and 2.8-fold (from ~0.06 to ~0.17) increases, respectively. These phenomena can be attributed to the nanotubes that are more prone to contact with each other at higher ε , resulting in significantly intensified inter-tube interactions which dissipate energy efficiently.^[19] Meanwhile, these ε -dependent viscoelastic characteristics of CNT@Gr arrays are also nearly T -invariant in ambient air, as indicated by the systematic measurements at $T = -100, 25, 300$ and 500 °C.

To further characterize the thermal stability of the viscoelasticity of CNT@Gr arrays in ambient air, their E' , E'' and $\tan \delta$ were further measured as functions of $T = -100$ – 500 °C (Figure 6.10). The ε and f were controlled as 1% and 1 Hz throughout the measurement, respectively. It can be observed that the E' remains nearly unchanged (from ~ 1.29 to 1.25 MPa, $\sim 3\%$ decrease) over this broad T range. On the other hand, E'' and $\tan \delta$ drop at $T = \sim 200$ °C with $\sim 18\%$ (from ~ 0.133 to 0.109 MPa) and $\sim 17\%$ (from ~ 0.103 to 0.085) decreases, respectively, while which are almost stable upon further heating to $T = 500$ °C. These moderate degradations in E'' and $\tan \delta$ are due to that less energy is consumed by the mediated intercalation between graphitic walls, resulting from the defects induced by the oxidation of nanotubes.^[24] Similar constant compressive mechanical behaviors over such a wide T range have only been reported for entangled CNT aerogels under the protection of inert gas.^[16] This thermo-mechanical stability of the CNT@Gr arrays in air is due to their outstanding thermal stability that is well preserved with the encapsulation of oxidation resistant graphene layers (corresponding TGA profiles are shown in Figure 6.11).^[2, 25] Meanwhile, the large specific area of porous CNT@Gr arrays allows for rapid and efficient heat dissipation, preventing the severe heat accumulation that usually causes property degradation.^[22] In addition, the inter-tube van der Waals interactions that mainly contribute to the viscoelasticity of CNT@Gr arrays are insensitive to temperature changes.^[22, 26] Further comparison with the conventional materials^[27] (Table 6.1) shows that the CNT@Gr arrays possess σ , E' and $\tan \delta$ which are comparable with the polymeric foam and elastomeric rubber while have much lower density (ρ , ~ 15 – to ~ 55 –fold lower) and higher maximum service temperature (Max. T , more than 250 °C higher). On the other hand, the metal and ceramic related materials with high Max. T are generally rigid and tough with nearly no energy dissipation capability. Therefore, the outstanding T -invariant viscoelastic properties over the exceptionally broad T range in ambient air make the CNT@Gr arrays highly promising for lightweight energy absorption applications in wide conditions ranging from cold interstellar spaces to high temperature furnaces.^[22]

Figure 6.10 Viscoelastic properties (E' , E'' and $\tan \delta$) of CNT@Gr arrays over $T = -100$ – 500 °C with ramping rate of 2 °C min^{-1} in ambient air. The ε and f were controlled at 1% and 1 Hz, respectively.

Figure 6.11 TGA analysis of CNT and CNT@Gr under a constant air flow of 50 mL min^{-1} . With the encapsulation of oxidation resistant graphene layers, the CNT@Gr generally retains the thermal stability of CNT in ambient air.

6.4 Conclusions

Coaxial CNT@Gr arrays have been successfully fabricated by encapsulating uniform graphene layers of ~1.5 nm (~5 layers) onto the vertically aligned CNTs (~4 mm tall) and their mechanical behaviors upon static and dynamic compressions have been systematically investigated. Different from the initial CNT arrays that deform plastically, the resulting CNT@Gr arrays exhibit superior compressibility (almost full recovery after compression at a 80% strain and ~80% recovery even after 1000 cycles at a 60% strain) and significantly enhanced compressive strength (5.6-fold increase at a 60% strain). More importantly, the CNT@Gr arrays perform outstanding strain- and frequency-dependent viscoelastic properties with storage modulus and damping ratio of up to ~6.5 MPa and ~0.19, respectively, which are nearly constant over an exceptionally broad temperature range of -100 to 500 °C in ambient air. These distinguished compressibility and temperature-invariant viscoelasticity of the CNT@Gr arrays are attributed to the synergistic effect between the inner CNTs and outer graphene layers, and would enable many promising applications such as compressive mechanical/thermal contacts, electromechanical devices and energy absorption systems even in environments with large temperature variations.

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Chapter 7

Ultralight and Highly Compressible Reduced Graphene Oxide/Boron Nitride Composite Aerogel

In addition to nanotube arrays, ultralight graphene based aerogel is another alternative candidate midsole material. This chapter presents a simple approach to fabricate 3D reduced graphene oxide/boron nitride (rGO/BN) aerogels in a large-scale by directly freeze-drying aqueous solutions of GO and BNNS without the presence of any additional chemical reagents. The macroscopic-assembled aerogel exhibits ultralow density, high compressibility and excellent compressive recoverability, which can be attributed to the unique 3D interconnected porous network as well as the synergistic effect between graphene and BNNS, showing promising applications as multifunctional compressible mattress.

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7.1 Introduction

Recently, macroscopic 3D graphene monoliths constructed by 2D graphene oxide (GO) nanosheets have attracted considerable attention due to their fascinating mechanical, electrical and thermal properties.^[1-5] In particular, the ultra-low density, porous structure and outstanding compressibility together with the ease of scalable synthesis of 2D GO nanosheets from natural graphite make the 3D graphene monoliths show promising applications in mechanical support and energy-absorbing materials.^[6] To date, a number of approaches have been devoted to the synthesis of 3D graphene monoliths such as hydrothermal-mediated reduction,^[7-11] template-assisted CVD,^[1, 12-14] chemical reduction,^[15, 16] and freeze-drying processes.^[17, 18] Among them, the freeze-drying method is a relative facile and promising strategy to produce 3D graphene monoliths in a large-scale. However, additional chemical cross-linkers are usually required and most of the previously reported 3D structures undergo significant plastic deformation or have brittle mechanical performance when going through cyclic compression strain, which significantly hinders its further practical applications.

Currently, considerable efforts have been devoted to improve the mechanical properties (shape recoverability, compressive strength, fatigue resistance, etc.) of the 3D graphene monoliths, such as introducing polymers,^[19-22] CNTs^[23, 24] and metal NPs^[25, 26] into 3D networks, whereas the obtained performance is still not satisfactory in certain cases (e.g., harsh environments) due to the introduction of additional cross-linkers and the impaired intrinsic characteristics of graphene. Notably, heterostructures assembled by two different kinds of low dimensional materials *via* van der Waals bonding can result in various extraordinary optical, electronic and mechanical characteristics.^[27-29] Such effective strategy has opened up new avenues for preparation of graphene-based 3D macrostructures, which are highly desirable for diverse practical applications. On the other hand, BNNS with graphene analogous structure and excellent mechanical, thermal and chemical stabilities, show promising potential in reinforcing the 2D structural units, and further improve the mechanical integrity of the 3D foam structure.^[27-29] However, 3D interconnected heterostructures constructed from these two novel 2D materials is still at

their early stage. Particularly, the reported BNNS by the exfoliation of bulk BN in organic solvents show significant restacking or aggregation,^[27-29] which will significantly affect their physicochemical properties of the as-prepared GO/BN composite when these resultant BN products with a non-uniform thicknesses are integrated with GO. Therefore, several approaches have been developed to improve the water solubility of the BNNS by introducing hydroxyl (-OH) functional groups onto their basal plane or edges, such as sonication-assistant exfoliation of bulk BN powder in water,^[30] solution-phase oxygen radical functionalization of B atoms in the hexagonal BN lattice,^[31] heating BN powder in air,^[32] ball milling of BN powders in the presence of sodium hydroxide^[33] and treating bulk BN powder with hot water steam.^[34] Nevertheless, only hydroxylated BNNS with limited solubility in water ($0.01\sim0.3\text{ mg mL}^{-1}$)^[30, 34-36] and small lateral size (hundreds nm)^[30, 35, 36] have been reported so far. As such, it is highly desirable to develop an effective approach to prepare BNNS with high water solubility and large lateral size and then directly integrate the as-prepared BNNS dispersion with GO aqueous solution to build 3D GO/BN interconnected macrostructure in a large-scale, which are expected to perform promising and stable mechanical behaviour in various environments.

Based on the above considerations, in this chapter, hydroxylated BNNS with high water solubility (up to 0.6 mg mL^{-1}) and large lateral size ($\sim 2\text{-}3\text{ }\mu\text{m}$) are synthesized *via* two-step chemical oxidation and subsequent exfoliation processes. Then, a very simple approach is demonstrated to fabricate multifunctional 3D reduced GO (rGO)/BN aerogel in a large-scale by directly freeze-drying aqueous solutions of GO and BNNS without the presence of any additional chemical reagents. The macroscopic-assembled aerogel exhibits ultralow density, high compressibility and excellent compressive recoverability in both air and organic solvents, which can be attributed to the unique 3D interconnected porous network as well as the synergistic effect between graphene and BNNS.

7.2 Experimental Methods

7.2.1 Preparation of GO

GO was synthesized from natural graphite flake (Alfa Aesar, 325 mesh) by a modified Hummers method.^[37] As-prepared GO was dispersed in water by ultrasonication for 60 min, followed by a low-speed centrifugation (3000 rpm/min) to get rid of any aggregated particles. Finally, a stable GO suspension with a concentration of 14.6 mg mL^{-1} was obtained.

7.2.2 Synthesis of hydroxylated BNNS

Firstly, BN powder (3 g, Grade AC6004, Momentive Performance Materials, Inc.) was put into an 80°C mixture of concentrated H_2SO_4 (12 mL, 99.99 %, Sigma-Aldrich), $\text{K}_2\text{S}_2\text{O}_8$ (2.5 g, 99 %, Sigma-Aldrich), and P_2O_5 (2.5 g, 99 %, Sigma-Aldrich) and stirred for 4.5 h. The mixture was then cooled to room temperature, which was further diluted with 0.5 L of water and left overnight. Subsequently, the mixture was filtered and washed with water to remove any residual acid. Next, the pre-oxidized BN was dried in air at room temperature and introduced into an ice bathed concentrated H_2SO_4 (120 mL). KMnO_4 (15 g, 97 %, Sigma-Aldrich) was slowly added under vigorous agitation to proceed further oxidation. After that, the mixture was heated in a water bath at 35°C for 2 h, and 250 mL of water was gradually introduced followed with another 2 h stirring. The reaction was terminated by adding 0.7 L of water and 20 mL of 30 wt% H_2O_2 (Sigma-Aldrich). The resultant white colour mixture was filtered and washed with 10 wt% HCl solution (Sigma-Aldrich) to remove possible metal ions. The precipitate was then washed with water, and dried in a vacuum oven at 60°C overnight. The as-prepared hydroxylated BN was further exfoliated in the water by ultrasonication for 1 h, which was followed by a $3000 \text{ rpm min}^{-1}$ centrifugation to get rid of aggregated particles. Finally, a stable hydroxylated BNNS suspension with a concentration of $\sim 0.6 \text{ mg mL}^{-1}$ was obtained.

7.2.3 Fabrication of rGO/BN aerogel

Typically, to a 10 mL beaker containing GO aqueous dispersion (14.6 mg mL^{-1} , 3 mL), BNNS aqueous solution (0.6 mg mL^{-1} , 3 mL) was added. The mixture was homogenized in a bath sonicator for 1 h, and then placed in a refrigerator to freeze overnight. Next, the resultant GO/BN monolith was subjected to freeze-drying in a freeze dryer (Labconco FreeZone 4.5 L Benchtop Freeze-Dry System) overnight to form GO/BN aerogel. Finally, the reduced GO/BN (rGO/BN) aerogel with a density of 3.6 mg cm^{-3} was obtained by annealing the GO/BN aerogel in a tubular furnace at 300°C for 2 h at a heating rate of $10^\circ\text{C min}^{-1}$ in H_2 atmosphere.

7.2.4 Mechanical test

The compressive properties of the rGO/BN aerogels were measured using an Instron 5567 Mechanical Tester system at room temperature. Typically, a rGO/BN aerogel with a density of 3.6 mg cm^{-3} (21.7 mm in diameter and 12.8 mm in height) was firstly loaded on the centre of the lower platen, and a compression rod with diameter of 50 mm was then applied onto the sample with a controlled speed, all the compressions were conducted within the confinement of the small upper platen. Compressive strain and stress were calculated from the displacement of the compression rod divided by original height of the rGO/BN aerogels and the applied compressive force over cross-sectional area of the samples, respectively. Recoverability of the rGO/BN aerogel is defined as the displacement recovered over applied displacement. The cyclic uniaxial compression data were acquired at a loading-unloading rate of 0.04 mm min^{-1} at strains of 10%, 20%, 30%, 40% and 50%, respectively.

7.3 Principle Outcomes

7.3.1 Physicochemical characteristics of rGO/BN aerogel

Figure 7.1 Schematic illustration of preparation procedure of rGO/BN aerogel. It includes (1) preparation of GO from natural graphite flake using a modified Hummers method, (2) synthesis of BNNS from bulk BN by using oxidation and subsequent exfoliation process, (3) homogenization of aqueous solutions of GO and BNNS by ultrasonication, (4) preparation of GO/BN nanocomposite by freeze-drying process, and (5) formation of rGO/BN aerogel by thermal annealing in H₂ atmosphere.

The typical synthesis process of rGO/BN aerogel is illustrated in Figure 7.1. Firstly, exfoliated GO and BNNS were prepared and homogeneously mixed together with the aid of the bath sonication. Second, the mixture was subjected to freeze-drying process overnight to form the GO/BN aerogel. Finally, the desired rGO/BN aerogel was obtained by annealing the GO/BN aerogel in a tubular furnace at 300 °C for 2 h at a heating rate of 10 °C min⁻¹ in H₂ atmosphere. It is noted that the resulting aerogel exhibits negligible volume shrinkage after assembly and is not distorted significantly from their original shape

by processing. Also, the resulting rGO/BN aerogel with a density of 3.6 mg cm^{-3} is freestanding and can well rest on the tip of a fire tree flower, indicating its ultra-lightness. Considering the simplicity of template-free self-assembly process and the large-scale availability of the exfoliated GO and BNNS, the integrated rGO/BN aerogels with desired size and shape are easily accessible.

Figure 7.2a-e displays a cylinder rGO/BN aerogel and its corresponding microstructures which are identified by SEM. Clearly, the rGO/BN aerogel possesses honeycomb-like 3D porous architectures and exhibits open-cell geometry with interconnected pores ranging from tens to hundreds of micrometres. The pore structures within the entire aerogel distribute uniformly at a large-scale as identified by the top-view and side-view SEM images (Figure 7.2b and c). Compared with the reported graphene based 3D materials,^[18, 38, 39] these relatively larger pores are attributed to the strong physical interactions between larger sized GO sheets (up to several tens of micrometers in size and with average thickness less than 3 nm) and smaller sized BNNS (up to several micrometres in size and with average thickness less than 3.5 nm) which can result in uniform distribution of BNNS throughout the porous network and the existence of BNNS also effectively prevents the GO sheets from crumbing together and thus binds them to form large porous networks.^[27] The enlarged views of SEM images (Figure 7.2d and e) clearly demonstrate that the cell walls made up of assembled graphene and BNNS are formed during the freezing process where individual sheets are pushed together with the formation of ice crystals and the in-plane size of these assembled sheets can be up to several hundreds of micrometres, leading to an enhanced elastic stiffness.^[9, 40, 41] In addition, twists and wrinkles can be obviously seen along the surfaces of the graphene sheets, which may account for the outstanding macroscopic mechanical robustness and self-supported structural stability of the as-prepared rGO/BN aerogel.^[40, 42]

Figure 7.2 Morphology, microstructure and chemical composition characterizations of GO, BNNS and rGO/BN aerogel. (a) Digital photograph shows the macroscopic structure of the rGO/BN sponge ($\rho = 3.6 \text{ mg cm}^{-3}$). Top-view (b) and (c-e) side-view SEM images of the rGO/BN sponge show the porous network structure. (f) FT-IR, (g) Raman and (h) XPS survey spectra. The inset of (h) shows the enlarged spectrum of rGO/BN in the range of 170 to 420 eV. High-resolution C 1s spectra of (i) GO and (j) rGO/BN, respectively. (k) TGA spectra.

The chemical composition, microstructure and thermal stability of the as-prepared rGO/BN aerogel are further investigated by employing FT-IR, Raman, XPS and TGA. After being homogeneously mixed with BNNS and subsequent thermal treatment, the intensity of characteristic peaks for GO including O-H (3420 cm^{-1}), C=O (1730 cm^{-1}), epoxy C-O (1224 cm^{-1}), and alkoxy C-O (1053 cm^{-1}) are obviously reduced, while new vibration bands observed at 1380 and 1193 cm^{-1} correspond to the B-N stretching and B-O deformation modes, respectively (Figure 7.2f).^[33, 43, 44] The Raman spectrum of the rGO/BN aerogel is presented in Figure 7.2g. It can be observed that the centre of the D band of rGO in the as-prepared rGO/BN aerogel is shifted to 1356 cm^{-1} due to the overlapping of the D

band of rGO and the E_{2g} phonon mode of BNNS.^[27, 37] Compared to the intensity ratio of D and G bands of GO ($I_D/I_G = 0.87$), I_D/I_G of the rGO/BN aerogel (0.94) is slightly higher, indicating an increase in disordered structures/defects in the rGO/BN aerogel after introduction of BNNS and thermal treatment.^[37] The chemical composition of the rGO/BN aerogel is further identified by XPS. As shown in the survey spectrum (Figure 7.2h), except for the existence of C, B and N elements in the rGO/BN aerogel, the observable O 1s peak at binding energy of 532 eV clearly demonstrates the presence of oxygen-containing groups. The extracted weight ratio of BN in rGO/BN aerogel from the survey spectrum is ~4 %, which is similar with that of the as-prepared GO/BN nanocomposite. Notably, the atomic ratio of C/O is obviously increased from 2.17 to 5.90, indicating most of the oxygen-containing groups have been successfully eliminated by the thermal reduction process. As shown in Figure 7.2i and j, both the GO and rGO/BN aerogel display four deconvoluted peaks in the high-resolution C 1s spectrum located at around 284.5, 284.6, 288.2 and 289.6 eV corresponding to C-C, C-O, C=O, and O-C=O bonds, respectively,^[10] whereas the ratio of C-O and C-C bonds in the rGO/BN aerogel is obviously lower than that of GO, which is consistent with the above mentioned XPS analysis. The thermal behaviours of the GO, BNNS and rGO/BN aerogel are further explored by TGA analysis (Figure 7.2k). GO are not thermally stable and exhibit rapid weight loss of 60% below 350 °C corresponding to the decomposition of oxygen-containing groups. In the case of BNNS, 30% weight loss at around 100-200 °C is observed, arising from the oxygen-containing groups of BNNS after oxidation and exfoliation processes and is in agreement with the above mentioned XPS analysis. As expected, for the rGO/BN aerogel, it exhibits better thermal stability with the main weight loss occurring at a much higher decomposition temperature (around 627 °C), which is attributed to the well-assembled heterostructure of the rGO with BNNS *via* van der Waals bonding as well as less amounts of oxygen-containing groups after the thermal treatment. By combining all the aforementioned characterization and analysis, we can conclude that 3D rGO/BN aerogel with desired morphology, microstructure and chemical composition, has been successfully prepared.

7.3.2 Compressibility of rGO/BN aerogel

Figure 7.3 The compression tests of rGO/BN aerogel. (a) Digital images show the recovering process of a compressed rGO/BN aerogel at 50% strain in air for the first compression cycle. (b) The stress-strain curves of the rGO/BN aerogel with different set strains. The inset shows the calculated energy loss coefficients of the rGO/BN aerogel compressed to different strains. (c) The stress-strain curves of the rGO/BN aerogel in air at 50% strain for 100 cycles. (d) The stress-strain curves of the rGO/BN aerogel in hexane at 50% strain for 50 cycles. (e) The corresponding maximum compressive strength and energy loss coefficients of the rGO/BN aerogel derived from (c) and (d), respectively.

It is well-known that excellent mechanical behaviour is one of core interests for a graphene-based aerogel material in practical applications. Therefore, uniaxial compressive tests are systematically conducted to evaluate mechanical compressive properties of the as-prepared rGO/BN aerogel (Figure 7.3). The rGO/BN aerogel with a density of 3.6 mg cm^{-3} exhibits

a full shape recovery upon compression up to 50% strain, indicating its good mechanical strength and flexibility (Figure 7.3a). Figure 7.3b shows the stress (σ) vs. strain (ε) curves of the rGO/BN aerogel at maximum applied strain varying from 10% to 50% during the first compression cycle, respectively. The loading process for the as-prepared rGO/BN aerogel displays characteristic mechanical response of the porous material,^[3] *i.e.* initial linear elastic region ($\varepsilon < 30\%–35\%$) with a Young's modulus of 1.99 kPa due to the elastic bending deformation of the graphene/BN composite cell walls, and then followed by the steep slope region ($\varepsilon > 30\%–35\%$) with rapidly increasing stress due to the densification of the graphene/BN cells where the cell walls started to contact with each other.^[11] It is well-known that hysteresis behaviour is very important in materials used for absorption.^[40, 45] Notably, the energy loss coefficient (η), defined as the area of the hysteresis loop over the area under the loading curve, is found to ramp up with the increase of the applied strain and reaches as high as 75.13% at a 50% strain. The observed energy dissipation is due to the van der Waals adhesion and friction between the graphene and BNNS or movement of air through the large porous aerogel.^[27, 46] The cyclic strain-stress curves of the as-prepared rGO/BN aerogel for 100 cycles (in air) and 50 cycles (in hexane) at a 50% strain are shown in Figure 7.3c and d, respectively. It is noted that the first compression cycle is different from the subsequent ones showing a higher Young's modulus, maximum stress and large energy loss coefficient. Transient degradation behaviour in the mechanical response is observed both in air and hexane in the initial 10 cycles, while the σ vs. ε curves remains almost unchanged after the tenth cycles. It is noted that ~10% residue deformation is left after 10 cycles of compression in air, which only slightly increases to ~15% even after further 90 cycles. Interestingly, the as-prepared rGO/BN aerogel shows enhanced σ vs. ε response in hexane corresponding to its ultralow density, high porosity as well as well-kept structure integrity created with the assembled 2D graphene and BNNS. Meanwhile, this aerogel exhibits smoother σ – ε relationship due to the buffer effect of hexane and is able to totally recover even after 50 cycles of compression, which makes it a promising candidate for mechanical related applications where an organic liquid environment is involved. In addition, as shown in Figure 7.3e, the compressive strength of the aerogel is found to decrease rapidly both in air (~1.57 to 1.30 kPa) and hexane (~1.67 to 1.33 kPa) in the first 10 cycles, and gradually becomes constant in the subsequent cycles (~1.04 kPa after 100

cycles in air, ~ 1.17 kPa after 50 cycles in hexane). This stress softening behaviour can be referred to as preconditioning effect, resulting from the reconfiguration/bending of the cell walls (graphene/BNNS) and the possibly induced defects during the cyclic loading.^[3] Similar evolution is also observed for the energy loss coefficient, which decreases from 75.13% to 56.83% after the first 10 compression cycles in air and then remains fairly constant ($\sim 50\%$) even after 100 cycles, implying good mechanical robustness of the as-prepared aerogel.

Figure 7.4 Side-view (a-c) and top-view (d-f) SEM images of the rGO/BN aerogels. (a and d) As-prepared, (b and e) After 10 uniaxial compressive cycles at 50% strain, (c and f) After 100 uniaxial compressive cycles at 50% strain.

In order to gain further insights on how the microstructure change affects their compressive behaviour, side-view and top-view SEM images of the rGO/BN aerogel before and after two different compressive cycles in air (10 and 100 cycles) at a 50% strain are carefully collected and compared (Figure 7.4). The as-prepared rGO/BN aerogel possesses a well ordered isotropic structure with an average pore size of ~ 200 to $300 \mu\text{m}$ (Figure 7.4a). Once the strain is applied, bending or buckling of the cell walls decreases the interlayer distances in the graphene/BNNS network and increases the contact area, eventually leading to an

enhanced interconnection between graphene/BN cell walls which results in the restacking of each other. Therefore, the average pore sizes of the aerogel decreases to ~ 150 to $200\ \mu\text{m}$ and the appearance of flat cells are observed after 10 cycles of uniaxial compression at 50% strain, resulting from the reorganized graphene layers around the BNNS, and permanent deformation is therefore introduced (Figure 7.4b). This phenomenon is consistent with the aforementioned mechanical properties of the as-prepared rGO/BN aerogel during the first 10 compressive cycles. After 10 compressive cycles, the resultant aerogel with smaller pore size exhibits an enhanced interlayer interaction between the cell walls, and gradually a stable network with certain pore sizes is formed, which can well support the persistent mechanical response. Therefore, no observable structure changes can be seen during subsequent 90 cycles of compression (Figure 7.4c). In addition, the top-view SEM images of the aerogel show that there is no obvious microstructure changes even after 100 uniaxial compression cycles. This is a good indication of the structural robustness of the as-prepared rGO/BN aerogel (Figure 7.4d–f). Firstly, the evenly distributed smaller sized BNNS can effectively inhibit the restacking of larger sized GO sheets thus resulting in unique 3D large porous network with cell size in the same range, which maximizes the elastic strength and modulus. Secondly, the $\pi - \pi$ interaction between BNNS and graphene sheets existed in the cross-linking sites of cell walls as well as the $\pi - \pi$ interaction in the curved ridges or crumples, which tightly bind them together and the existence of BNNS hinders the free rotation or reconstruction of the graphene sheets upon compression loading, and thus can greatly enhance the strength and elastic stiffness of cell walls. According to the above results and analysis, the stable compressive mechanical performance of the as-prepared rGO/BN aerogel can be attributed to the unique 3D network macroscopic structure, as well as the interaction between graphene and BNNS.^[24, 27]

7.4 Conclusions

In this chapter, we have successfully prepared ultralight and highly compressive aerogels constructed with cell walls of assembled graphene and BNNS by a facile freeze-drying and subsequent thermal annealing process. The unique 3D porous network and the synergistic effect between graphene and BNNS endow the as-prepared rGO/BN aerogel with ultralow

density, high compressibility and excellent recoverability. It is noted that the simplicity of the present synthesis and the large-scale availability of exfoliated GO and BNNS allow us to easily achieve the integrated rGO/BN aerogel with desired size and shapes, enabling their potential applications as compliant mechanical contacts and energy dissipation systems.

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Chapter 8

Wafer-Scale Vertically Aligned Carbon Nanotubes/Poly (vinyl alcohol) Hydrogels with Strengthened Static and Dynamic Compressive Responses

To enable the poly (vinyl alcohol) (PVA) hydrogels with outstanding compressive responses to fulfill the requirements for artificial cartilages, wafer-scale vertically aligned carbon nanotube/PVA (VACNT/PVA) hydrogels are fabricated by infiltration of PVA among VACNTs and subsequent in situ hydrogelation. Compared to bare PVA hydrogels, such composite hydrogels with large CNT-PVA interfaces perform significantly enhanced longitudinal compressive responses upon both static and dynamic loadings, achieving improvements of up to 25.2– and 9.0–fold in strength and loss modulus, respectively. The scalable fabrication of VACNT/PVA hydrogels and their attractive performances hold great potential for load-bearing applications.

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8.1 Introduction

Hydrogels, three-dimensional polymer networks with high water contents, flexibility and lubricity have been considered as good candidates for various applications such as substitutes for bio-tissues,^[1] cushion materials for sports shoes^[2] and artificial muscles in soft robotics.^[3] However, bare hydrogels usually suffer from limited mechanical strength and damping due to lack of an efficient energy dissipation mechanism,^[4] which severely hinder their further practical applications. As such, many efforts have been devoted to strengthening the hydrogels by incorporating nanomaterials such as metal oxides^[5]/carbon nanoparticles,^[6] CNTs^[7, 8] and GO nanosheets.^[2] Among them, CNTs with superior mechanical strength and modulus are particularly promising nano-fillers because of their exceptionally high aspect ratio. Nevertheless, the resulting reinforcements are still unsatisfactory attributing to the limited CNT-matrix interfacial area, resulting from agglomeration of random CNTs within matrix due to substantial inter-tube van der Waals attractions.^[9, 10]

To date, many strategies have been developed to address the abovementioned problems, including improving the dispersion of CNTs by either significant mechanical energy input with the aid of ultrasound and ball milling, or chemical modification involving the usage of strong acids/oxidants and reactive plasma.^[11] However, the CNTs treated by such harsh processes normally suffer from shortened tube length and impaired intrinsic structures, which are detrimental to their resulting reinforcements. On the other hand, instead of random CNTs, utilizing vertically aligned CNTs (VACNTs) as continuous reinforcements could be a feasible approach to achieve uniform distribution and alignment of CNTs across the dimensions of composite structures, without sacrificing their structural integrity or intrinsic characteristics.^[12] Considering these advantages of the continuous CNTs reinforced composites, VACNTs based composite hydrogels with large CNT-matrix interfacial area are expected to exhibit promising mechanical responses, while which have not been reported thus far. This is because structural collapse would occur for the VACNTs once they are treated with aqueous solutions due to their hydrophobic nature.^[9]

In this chapter, wafer-scale continuous VACNTs reinforced poly (vinyl alcohol) (VACNT/PVA) composite hydrogels are fabricated by infiltration of PVA among hydrophilized VACNTs and subsequent *in situ* hydrogelation. The as-prepared composite hydrogels perform significantly enhanced longitudinal compressive responses upon both static and dynamic loadings.

8.2 Experimental Methods

8.2.1 Fabrication of VACNT/PVA hydrogels

Firstly, VACNT arrays (5-mm tall, Aixtron) were treated with aqueous sodium dodecyl benzene sulfonate (SDBS, technical grade, Sigma-Aldrich) solution with concentration of 10 mg mL^{-1} overnight to improve their hydrophilicity. Next, the SDBS was gradually exchanged with aqueous PVA (MW = 89 000–98 000, 99%, Sigma-Aldrich) solution with concentration of 13.6 wt% assisted by mechanical shaking, achieving a homogeneous infiltration of PVA among the VACNTs. Finally, the VACNT/PVA composite hydrogels were achieved by *in situ* hydrogelation of PVA after 5 cycles of freeze/thaw process, which is composed of a freezing step (21 h at -20°C) and a subsequent thawing step (3 h at 25°C). For comparison, bare PVA hydrogels were also prepared with similar process.

8.2.2 Measurements of Water Content and Swelling Ratio

First, the hydrogel samples ($15 \times 15 \times 5 \text{ mm}^3$) were dried at 40°C in vacuum for 10 h to ensure that all the water component have been removed. Then, the dried samples were immersed in DI water to swell until their masses became unchanged. Next, the samples were taken out from the water and blotted with filter paper before weighing. The water content and the equilibrium swelling ratio (ESR) of the hydrogel sample were respectively calculated according to $\text{water content} = (m_0 - m_1) / m_0 \times 100\%$ and $\text{ESR} = (m_2 - m_1) / m_1 \times 100\%$, where m_0 , m_1 and m_2 are the masses of the hydrogel sample, dried sample and swollen sample, respectively.

8.2.3 Static compression tests

Static compressive properties (longitudinal, along CNT alignment direction) of VACNT/PVA hydrogels were determined using a Universal Testing System (Instron 5567, Instron, USA) in a quasi-static fashion at room temperature. Square-shaped VACNT/PVA hydrogel sample ($15 \times 15 \times 5 \text{ mm}^3$) was firstly loaded on center of lower platen, a compression rod with 50 mm diameter was then applied onto the sample with a controlled speed. The compressions were all conducted within confinement of the smaller upper platen. To comprehensively investigate compressive behaviors of the VACNT/PVA hydrogels, strains of 25, 50 and 75% were applied at a strain rate of $100\% \text{ min}^{-1}$. Corresponding tests were also done for bare PVA hydrogels as comparison. Strain and stress were calculated using displacement of the compression rod divided by original height of the sample and compressive loading force over cross-sectional area of the sample, respectively. All the measurements were repeated at least three times to extract average values.

8.2.4 Dynamic mechanical analysis

Dynamic compressive viscoelastic properties (longitudinal, along CNT alignment direction) of VACNT/PVA hydrogels were characterized with a dynamic mechanical analyzer (DMA Q800, TA Instruments, USA) at room temperature. Square-shaped VACNT/PVA hydrogel samples with dimensions of $10 \times 10 \times 5 \text{ mm}^3$ were tested using a parallel-plate compression clamp. Storage and loss moduli as functions of applied strain and frequency were respectively collected under multi-strain (0.3–10%, at 1 Hz) and multi-frequency (0.1–100 Hz, at 0.5% strain) modes with a preload force of 0.01 N. Corresponding tests were also carried out for bare PVA hydrogels as comparison. All the measurements were repeated at least three times to obtain average values.

8.3 Principle Outcomes

8.3.1 Physicochemical characteristics of VACNT/PVA hydrogels

Figure 8.1 Fabrication of freestanding and flexible wafer-scale VACNT/PVA composite hydrogels. Step I: VACNT arrays were firstly hydrophilized by SDBS, and then the SDBS was gradually exchanged by homogenous infiltration of aqueous PVA solution among the VACNTs. Step II: Cyclic freezing/thawing was applied to enable *in situ* hydrogelation of PVA, by which the oriented morphology and uniform distribution of the VACNTs were well preserved.

Figure 8.2 Morphology and structure characterizations of VACNTs before (a–c) and after PVA infiltration (d–f). SEM (a,d) and TEM (b,c,e,f) images of VACNTs and VACNT/PVA composites,

respectively. The aligned morphology and uniform distribution of VACNTs are well retained within the VACNT/PVA composites.

Figure 8.1 illustrates the fabrication process of VACNT/PVA composite hydrogels. The 5-mm long VACNTs grown on a 4-inch Si wafer were firstly treated with sodium dodecyl benzene sulfonate (SDBS) to improve their hydrophilicity. Then the SDBS was gradually exchanged with aqueous PVA solution until a homogeneous infiltration of PVA among the VACNTs was obtained. Next, cyclic freezing/thawing was applied to enable *in situ* hydrogelation of PVA, by which freestanding and flexible wafer-scale VACNT/PVA composite hydrogels were successfully fabricated. The morphology and structure changes of the VACNTs before (Figure 8.2a–c) and after PVA infiltration (Figure 8.2d–f) were further studied by scanning SEM and TEM characterizations. It is observed that the highly oriented structure of VACNTs within the VACNT/PVA composites was not affected by PVA infiltration. Meanwhile, the CNT-PVA interfaces display intimate contact without physical gaps, indicating strong adhesion between CNTs and PVA polymer chains.^[13]

Figure 8.3 (a) Raman spectra, (b) XRD patterns and (c) TGA profiles of CNT, PVA and composite VACNT/PVA. Crystalline structures of the CNT and PVA hydrogels are well preserved for the VACNT/PVA composite hydrogels with 2.23 wt% (CNT:PVA) CNT filling.

Next, Raman, XRD and TGA were further employed to verify crystalline structure and thermal behavior of the VACNTs before and after PVA infiltration. As shown in the Raman spectra (Figure 8.3a), characteristic D (1334.3 cm^{-1}) and G (1571.8 cm^{-1}) peaks with high G/D intensity ratio (I_G/I_D)^[14] of initial CNTs could be clearly identified with no noticeable changes for the VACNT/PVA composites, indicating that the good crystalline structure of CNTs is not altered by PVA infiltration. It is noted that the XRD pattern (Figure 8.3b) of VACNT/PVA hydrogels exhibits similar diffraction peaks with that of bare PVA hydrogels,^[15] suggesting that the crystalline structure of composite hydrogels is not

affected by CNTs. As shown in Figure 8.3c, the VACNT/PVA hydrogels exhibit dramatic 86.27% weight loss before 160 °C attributing to the water evaporation, showing similar water content with bare PVA hydrogels (86.60%).^[15] Upon continuous heating, further weight losses of 13.43% at 650 °C and 0.30% at 800 °C can be observed due to the decompositions of PVA and CNT, respectively. The weight fraction of CNT (CNT:PVA) was then calculated to be 2.23 wt% (corresponding to volume fraction of 1.28%). In addition, the VACNT/PVA hydrogels possess improved swelling capability than the bare PVA hydrogels (with equilibrium swelling ratios of 338.43% and 287.28%, respectively), which is beneficial for their practical applications.

8.3.2 Static compressive performance of VACNT/PVA hydrogels

To investigate reinforcing effects of VACNTs on mechanical responses of composite hydrogels, systematic longitudinal compressions were carried out. Similar with bare PVA hydrogels, VACNT/PVA hydrogels are able to fully recover after compression up to a 75% strain (Figure 8.4a), showing their excellent shape-recovery characteristics resulting from highly cross-linked polymer chains formed after cyclic freezing/thawing (Figure 8.2d). Meanwhile, corresponding stress-strain curves at strains of 25, 50 and 75% (Figure 8.4b) exhibit a nonlinear stress-strain relationship (strain stiffening^[16]) of the hydrogels, indicating their natural viscoelastic characteristic.^[15] Upon continuous compression, PVA chains within hydrogels tend to become uniformly oriented, while the interactions between PVA chains and H₂O molecules lead to a hardening effect. In the meantime, VACNT/PVA hydrogels perform significantly higher compressive stresses and larger hysteresis loops than bare PVA hydrogels at respective strains, suggesting their better performances in mechanical strength and energy dissipation.

Figure 8.4 (a) VACNT/PVA hydrogels are able to fully recover after longitudinal compression at a strain of as high as 75%. (b) Compressive stress-strain curves of the viscoelastic composite hydrogels at various applied strains demonstrate their (c) significantly enhanced compressive strengths (C. S.) and energy dissipation ratios (E. D. R.) reinforced by VACNTs.

As summarized in Figure 8.4c, compressive strengths (C. S.) of 0.081, 0.16 and 0.47 MPa can be achieved when strains of 25, 50 and 75% are applied for composite hydrogels, which are respectively 25.2–, 7.8– and 2.4–fold higher than those of bare PVA hydrogels. These significant reinforcements contributed by 2.23 wt% VACNTs are obviously better than those of randomly dispersed CNTs or GO within hydrogels (3.5 wt% and 0.8 wt% additions lead to 113% and 36% increases in C. S.,^[17, 18] respectively). As reported, the crystallinity and water content have significant impacts on mechanical properties of hydrogels.^[15] Considering that the crystalline structure (Figure 8.3b) and water content (from 86.60% to 86.27%) of the composite hydrogels are not affected by CNTs, the enhanced mechanical performances of VACNT/PVA hydrogels can be attributed to the reinforcing effects of VACNTs. As identified by the abovementioned SEM and TEM analysis (Figure 8.2), the VACNT/PVA composites exhibit well-bonded interfaces between CNT and PVA. Therefore, a commonly used theoretical model $Y_c = (\eta_o \eta_l Y_f - Y_m) V_f + Y_m$ could be applied for the as-prepared VACNT/PVA hydrogel, where Y is modulus, V is volume fraction, c , f and m stand for composite, filler and matrix, respectively.^[19] η_o is the orientation efficiency factor, which has values of 0.2, 0.375 and 1 for random distributed, in plane aligned and

aligned fibers, respectively. The uniform distribution and continuous alignment of VACNTs enable the composite hydrogels take full advantages of their superior axial mechanical strength and modulus.^[12, 19] Meanwhile, the VACNTs with ultra-high aspect ratio of $\sim 3 \times 10^5$ maximize the length efficiency factor η_l (approaches 1 when fiber aspect ratio is larger than 10),^[19] which facilitate the homogeneous stress distribution and minimize the presence of stress concentration centers, leading to the efficient load transfer upon loading. In addition, the VACNT/PVA hydrogels perform excellent energy dissipation ratios (E. D. R.) of 39.76, 51.46 and 61.15% at 25, 50 and 75% strains, respectively, which are 5.7–, 4.3– and 1.5–fold higher than the counterparts of bare PVA hydrogels. This is attributed to the large interfacial areas resulting from nanoscale dimension and high aspect ratio of CNTs,^[20] which contribute to significant frictional energy loss caused by additional CNT-PVA and CNT-CNT interactions upon compression.^[12, 21–23] Moreover, the nanotube structure and excellent thermal conductivity of VACNTs enable immediate dissipation of strain energy through on-tube oscillations and in form of heat, respectively.^[24, 25]

8.3.3 Dynamic compressive response of VACNT/PVA hydrogels

Figure 8.5 VACNT/PVA and bare PVA hydrogels show (a) frequency and (b) strain dependent storage (E'), loss (E'') modulus and damping ratio ($\tan \delta$) upon dynamic longitudinal compressions. Moreover, the composite hydrogels perform effective improvements in E' and E'' over entire ranges of applied frequency and strain, which are particularly significant at larger strains.

In addition to static loading, complex dynamic compressions with various frequencies or strains are also anticipated for structural hydrogels.^[26-28] Therefore, the viscoelastic responses (longitudinal) of the VACNT/PVA hydrogels were further characterized. Figure 8.5a shows storage (E'), loss modulus (E'') and damping ratio ($\tan \delta$) of the VACNT/PVA and bare PVA hydrogels as functions of frequency at a 0.5% strain. Besides the positive frequency dependence of E' and E'' ,^[29] both hydrogels show the E' that is more than 1 order of magnitude higher than respective E'' over entire applied frequency range (0.1–100 Hz), suggesting their elasticity and rigidity.^[30] Meanwhile, the VACNT/PVA hydrogels exhibit stably higher E' and E'' (1.9– and 1.4–fold, respectively) than bare PVA hydrogels at respective frequencies, which agrees well with what observed during static compressions. To study the effect of strain on E' and E'' of hydrogels, dynamic compressions at strains varying from 0.3 to 10% were further carried out (Figure 8.5b). Upon loading frequency of 1 Hz, both PVA and VACNT/PVA hydrogels show strain-dependent E' and E'' , which are generally stable at strains less than 1% and increase when strain is larger. Particularly, the reinforcements in E' and E'' (especially for E'') of VACNT/PVA hydrogels become more obvious at higher strains. When applied strain reaches 10%, significant enhancements of 4.5–fold in E' (from 0.08 to 0.36 MPa) and 9.0–fold in E'' (from 0.008 to 0.072 MPa) can be achieved for the composite hydrogels as compared to bare PVA hydrogels, respectively. The strengthened van der Waals interactions and mechanical interlocking at strong CNT-PVA interfaces under larger strains contribute to better load transfer and thus higher E' .^[31] On the other hand, more interaction sites are activated at CNT-PVA and CNT-CNT interfaces upon larger applied strains, which greatly facilitate stick-slip frictional energy dissipation^[22, 23, 31-33] of the VACNT/PVA hydrogels and lead to comparable damping (E'' and $\tan \delta$) improvements with those of the aligned CNT/polymer composites.^[22, 34]

8.4 Conclusions

Wafer-scale VACNT/PVA composite hydrogels have been successfully fabricated by infiltration of PVA among VACNTs and subsequent *in situ* hydrogelation. By using this

method, the uniform distribution, aligned morphology and crystallinity of CNTs are well preserved within the composite structure. As a result, the as-prepared composite hydrogels perform outstanding longitudinal compressive responses upon both static and dynamic loadings, attributing to continuous reinforcements of uniformly distributed VACNTs and the resulting large CNT-PVA interfaces. Particularly, significant enhancements of up to 25.2-, 5.7-, 4.5- and 9.0-fold in compressive strength, energy dissipation ratio, storage and loss moduli, respectively, can be achieved for the VACNT/PVA hydrogels. This work not only provides a novel scalable fabrication approach for various VACNT/polymer hydrogels, but also highlights their great potential in load-bearing applications.

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Chapter 9

Biocompatible Hydroxylated Boron Nitride Nanosheets/Poly (vinyl alcohol) Interpenetrating Hydrogels with Enhanced Mechanical and Thermal Responses

To further address the biocompatibility issue of composite PVA hydrogels and enable their practical cartilage replacement applications, biocompatible and highly hydrophilic hydroxylated boron nitride nanosheets (OH-BNNS) are synthesized and subsequently introduced into the PVA to fabricate OH-BNNS/PVA interpenetrating hydrogels via freezing/thawing approach. The resulting composite hydrogels exhibit controllable reinforcements in both mechanical and thermal responses by simply varying the OH-BNNS contents, attributing to the synergistic effect of intrinsic superior properties of the as-prepared OH-BNNS and strong hydrogen bonding interactions between the OH-BNNS and PVA chains. These biocompatible OH-BNNS/PVA hydrogels are promising in addressing the mechanical failure and locally overheating issues of artificial cartilage substitutes.

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9.1 Introduction

Despite those progresses in reinforcing the mechanical properties of PVA hydrogels with carbon nanomaterials, the resulting carbon/PVA nanocomposite hydrogels are still not extensively used to replace damaged cartilages due to the dose-dependent cytotoxicity of carbon based materials.^[1, 2] In addition, local temperature increase^[3-5] upon cyclic physiological mechanical loading, resulting from the low heat transfer coefficient of the current cartilage substitutes,^[6-8] has always led to the mechanical failure and affected the normal metabolism of surrounding bio-tissues.^[8-10] Therefore, developing an alternative cell-friendly nanomaterial and further fabricating biocompatible PVA based composite hydrogels with adequate mechanical property and appropriate thermal conductivity are in urgent demand.

On the other hand, the abovementioned BNNS is found to possess comparable mechanical strength and thermal conductivity with graphene,^[11, 12] yet better biocompatibility,^[2, 13] showing great promise as a biocompatible reinforcement candidate material of PVA hydrogel.^[14, 15] However, the extremely poor solubility of the BNNS in aqueous media resulting from the high hydrophobicity makes them difficult to be uniformly incorporated into the hydrogel network.^[16] In chapter 7, we have demonstrated the synthesis of hydroxylated (OH-) BNNS with high water solubility (up to 0.6 mg mL^{-1}) and large lateral size ($\sim 2\text{-}3 \text{ }\mu\text{m}$) *via* two-step chemical oxidation and subsequent exfoliation processes.^[17] Nevertheless, the potential reinforcing effects of these OH-BNNS on the mechanical and thermal characteristics of the PVA hydrogels, as well as the biocompatibility of the resulting composite hydrogels have not been investigated yet.

In this chapter, for the first time, these highly water soluble OH-BNNS with large lateral sizes have been integrated into the PVA to obtain OH-BNNS/PVA composite hydrogels, which perform significant reinforcements in both mechanical and thermal responses attributing to the homogeneous incorporation. More importantly, the high “cleanness” of the OH-BNNS enables the resulting OH-BNNS/PVA hydrogels with outstanding biocompatibility, which further supports their cartilage replacement applications.

9.2 Experimental Methods

9.2.1 Preparation of OH-BNNS

OH-BNNS were prepared with the same method as described in chapter 7 (7.2.2).

9.2.2 Fabrication of OH-BNNS/PVA hydrogels

Firstly, aqueous 13.6 wt% PVA solution was prepared by dissolving PVA powder (5.0 g, MW=89,000~98,000, 99%, Sigma-Aldrich) in water (31.7 mL) and then refluxing at ~95 °C for 3 h. Then, 10.0 mL of OH-BNNS aqueous solution (~0.6 mg mL⁻¹) was introduced into the as-prepared PVA solution, followed by further ultrasonic treatment at 60 °C for 1 h. The resulting homogenous composite solution was ultrasonic bathed at 50 °C for another 0.5 h to get rid of air bubbles. Next, 4 mL and 10 mL of the clear mixture were poured into beaker or petri dish at room temperature, respectively. Finally, the OH-BNNS/PVA hydrogels with a OH-BNNS concentration of 0.12 wt% (OH-BNNS:PVA) and different dimensions (cylinder with 25 mm in diameter and 10 mm in height, thin film with 80 mm in diameter and 2 mm in thickness) were prepared by a cyclic freeze/thaw process, which is composed of a freezing step (21 h at -20 °C) and a subsequent thawing step (3 h at 25 °C). For each hydrogel, 5 freeze/thaw cycles were applied. Similar process was conducted to prepare OH-BNNS/PVA hydrogels with OH-BNNS concentrations of 0, 0.03, 0.06 and 0.09 wt%.

9.2.3 Mechanical property evaluation

The mechanical properties of the OH-BNNS/PVA hydrogels with various OH-BNNS contents were determined using a Universal Testing System (Instron 5567, Instron, Canton, MA) at room temperature. To evaluate the uniaxial compressive mechanical performance, the cylinder-shaped OH-BNNS/PVA hydrogel sample (25 mm in diameter and 10 mm in height) was firstly loaded on the center of the lower platen, a compression rod with 50 mm

diameter was then applied onto the sample with a controlled speed. The compressions were all conducted within the confinement of the small upper platen. All the OH-BNNS/PVA hydrogel samples were compressed to a 75% strain at a strain rate of $100\% \text{ min}^{-1}$. For the OH-BNNS/PVA hydrogels with 0.12 wt% OH-BNNS, additional compressive strains of 10%, 25% and 50% were applied to thoroughly investigate their compressive mechanical performance. For the uniaxial tensile tests, dumbbell-shaped tensile bars of various OH-BNNS/PVA hydrogels with 2 mm thickness were prepared strictly adhering to the ASTM D638-V standard. The tensile strengths of the hydrogel samples were acquired at a strain rate of $1000\% \text{ min}^{-1}$ until breaking, and additional cyclic tests at tensile strains of 200%, 400%, 600% and 800% were conducted for the OH-BNNS/PVA hydrogels with 0.12 wt% OH-BNNS to thoroughly evaluate their tensile mechanical performance. For all the mechanical tests, strain and stress were calculated using the displacement of the compression rod/tensile grip divided by original height/length of the sample and the compressive/tensile loading force over cross-sectional area of the sample, respectively. All the measurements were repeated at least three times to extract the average values.

9.2.4 Thermal diffusivity/conductivity measurement

Thermal conductivity and diffusivity of the composite hydrogel samples with different OH-BNNS contents were measured using the transient plane source method (TPS 500 S, Hot Disk, Gothenburg, Sweden) in accordance with the ISO 22007-2.2. During the measurement, a 3.19 mm diameter C5465 TPS sensor was placed between the flat surfaces of two identical hydrogel samples (25 mm in diameter, 4 mm in thickness) at room temperature. The power output from the sensor heated up the samples, after which the electrical resistance of the sensor was monitored to determine the transient temperature. The sensor was assumed to be in an infinite sample medium for the subsequent analysis as the experimental measurement time is shorter as compared to the characteristic thermal diffusion time. Finally, the thermal conductivity and diffusivity parameters of the samples were calculated by successively iterating the detected transient temperatures. Multiple (at least 5) measurements were done for each sample to confirm the reproducibility.

The OH-BNNS/PVA composite hydrogels were further freeze dried to obtain the corresponding OH-BNNS/PVA composites, which were then cut into disks with diameter of 12.7 mm and thickness of 2 mm and measured using Laser Flash technique (DLF 1200, TA Instruments, USA). Prior to the measurement under Ar atmosphere at room temperature, spray coating of a thin graphite layer was applied on two sides of the samples to maximize absorption and emissivity. The data was fitted using Cowan model with pulse correction to extract the thermal diffusivity. The thermal conductivity was finally obtained according to $\lambda = \alpha \cdot \rho \cdot C_P$, where λ is the thermal conductivity, α is thermal diffusivity (as extracted), ρ is density (as measured) and C_P is heat capacity (measured by Modulated Differential Scanning Calorimeter, MDSC, TA 2920, TA Instruments, USA). The measurements were repeated three times for each sample to verify the reproducibility.

9.2.5 Cell culture

The HeLa cells were cultured in Dulbecco's Modified Eagle Medium (DMEM, Gibco, Life Technologies, USA) supplemented with 10% fetal bovine serum (FBS, Gibco, Life Technologies, USA) in a humidified environment containing 5% CO₂ and 95% air at 37 °C.

9.2.6 Cell viability assay

HeLa cells were seeded on 96-well plates with a density of around 10,000 cells per well and allowed to adhere for 24 h prior to the assays. The cells were co-incubated with a series of OH-BNNS/PVA hydrogel (0, 0.03, 0.06, 0.09 and 0.12 wt%) sample disks with diameter of 2.5 mm and thickness of 1 mm at 37 °C for 24 h. Next, 120 μ L MTS indicator dye (MTS, 0.1 mg/mL, Promega, USA) was added to each well, and the cells were incubated for another 4 h at 37 °C in the dark. The absorbance of MTS at 490 nm was measured using a microplate reader (Bio-Rad, Hercules, CA, USA) to determine the cell viability. The values obtained were expressed as a percentage of the control cells to which no hydrogel sample was introduced.

9.2.7 Cell proliferation assay

HeLa cells were seeded on 96-well plates with a density of around 3,000 cells per well and allowed to adhere for 24 h prior to the assays. MTS assay of 1, 3 and 5 days was further applied on OH-BNNS/PVA hydrogels (0, 0.06 and 0.12 wt%) to evaluate the cell proliferation. Similarly, after certain time of cell culture, MTS was introduced and the corresponding optical density (OD, proportional to the number of viable cells) was read. The OD values of different samples and varying culture time were obtained and normalized to that of the control experiment at day 1.

9.2.8 Live/dead viability assay

HeLa cells were seeded on μ -Slide 8 well glass bottom plates (ibidi, Munich, Germany) with a density of 5,000 cells per well and allowed to adhere for 24 h prior to the assays. After 1, 3 and 5 days of cell culture on the OH-BNNS/PVA hydrogels (0, 0.06 and 0.12 wt%), the spent media was aspirated. The respective cells were rinsed twice with PBS and incubated for 45 min in 400 μ L LIVE/DEAD Viability/Cytotoxicity Kit (Gibco, Life Technologies, USA) prepared by dissolving calcein AM (2 μ M) and ethidium homodimer-1 (EthD-1; 4 μ M) according to the protocol. Finally, the cells were washed with the PBS and observed with laser confocal microscope (Olympus Fluoview F300, Japan) to obtain the fluorescent images, in which live and dead cells were labeled with green (calcein AM) and red (EthD-1), respectively.

9.3 Principle Outcomes

9.3.1 Physicochemical characteristics of OH-BNNS

Figure 9.1a shows the preparation scheme of OH-BNNS by two-step chemical oxidation and subsequent exfoliation processes (see Experimental Methods for more details).^[18] To

evaluate the exfoliation of OH-BNNS from bulk BN, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used. Compared to the starting BN powder, the as-prepared OH-BNNS become almost transparent under SEM electron beam and consist of aggregations of thin and folded nanosheets (Figure 9.2), which were further verified by representative TEM images of several stacked OH-BNNS thin layers (Figure 9.1b) and an individual OH-BNNS layer (Figure 9.1c) with a lateral size of $\sim 2\text{--}3\ \mu\text{m}$. It is noted that the lateral size of the as-prepared OH-BNNS is much larger than most of those reported in the references ($\sim 200\text{--}500\ \text{nm}$),^[16, 19, 20] which can be beneficial for effective thermal and mechanical reinforcements.^[21]

Figure 9.1 (a) Schematic illustration of the preparation of the OH-BNNS *via* two-step chemical oxidation and subsequent exfoliation processes. (b–e) Representative TEM images reveal the large

lateral size ($2\sim3\ \mu\text{m}$) and few-layered structure ($\sim3\ \text{nm}$, ~10 atomic layers) of the as-prepared OH-BNNS. Their SAED pattern in the inset of (e) reveals the typical 6-fold symmetry of *h*-BN, indicating the structural integrity. (f, g) EELS analysis show a gradual decrease in the oxygen content from the edge (spot 1: 9.27%) to the basal plane (spot 4: 0.24%), demonstrating that the -OH groups are predominately located along the edges of the nanosheets. (h–j) AFM images and the corresponding height profiles of isolated OH-BNNS.

Figure 9.2 SEM images of the (a, b) starting bulk BN powder and (c, d) as-prepared OH-BNNS. Compared to the starting BN powder, the as-prepared OH-BNNS become almost transparent under SEM electron beam and consist of aggregations of thin and folded nanosheets.

Figure 9.3 Physicochemical characterization of the as-prepared OH-BNNS. (a) UV-Vis spectra of bulk BN and OH-BNNS aqueous solution. Inset shows the Tyndall effect of the as-prepared OH-

BNNS dispersion. (b) Raman spectra of the bulk BN and OH-BNNS. Slight red-shift of the E_{2g} vibration of the OH-BNNS indicates the few-layered structure. (c) TGA and (d–f) XPS analysis further quantify the -OH functionalization of the BNNS.

Figure 9.1d, e shows the high-resolution TEM images of the edge and interior of an individual OH-BNNS, respectively. The edge region of the nanosheets exhibits a few defects and 9–10 parallel fringes corresponding to 9–10 BN layers (Figure 9.1d), while the hexagonal lattice remains intact without defective holes or dislocations on the basal plane (Figure 9.1e), which is further verified by the corresponding selected area electron diffraction (SAED) pattern (inset of Figure 9.1e). To gain deeper insights into the exfoliation mechanism of the OH-BNNS, electron energy-loss spectroscopy (EELS) were further used to identify the -OH groups' distribution in the as-prepared OH-BNNS. As shown in Figure 9.1f, g, the oxygen content gradually decreases from 9.27% (spot 1 at edge) to 0.24% (spot 4 on the basal plane) when the probe moves from the edge to the interior of the sheet, suggesting that the BNNS are mainly -OH functionalized on the edges rather than on the basal plane. The atomic force microscopy (AFM) images and the height profiles (Figure 9.1h–j) further show that the OH-BNNS possess smooth surface with average lateral size of $\sim 2\text{--}3\ \mu\text{m}$ and uniform thickness of $\sim 3\ \text{nm}$, which are consistent with abovementioned TEM results, demonstrating the successful exfoliation of OH-BNNS from bulk BN.

UV-Vis spectroscopy was used to determine the change in solubility of the BN before and after the functionalization procedure. As shown in Figure 9.3a, both the OH-BNNS and bulk BN water dispersion exhibit an absorption peak at around 204.5 nm, while the peak intensity of the former is much higher than the later, indicating the successful modification of the BN surface chemistry by introduction of hydrophilic -OH functional groups. The concentration of the OH-BNNS was found to be $\sim 0.6\ \text{mg mL}^{-1}$, which is two times the highest reported so far.^[16, 20, 21] This excitingly high solubility is attributed to the effective functionalization during the peroxidation with persulfate followed by oxidation with permanganate.^[18] In addition, the cloudy dispersion of OH-BNNS displays an obvious Tyndall effect (inset of Figure 9.3a) and is highly stable over six months (Figure 9.4), suggesting the successful exfoliation of the OH-BNNS. As shown in Raman spectra

(Figure 9.3b), the bulk BN and exfoliated OH-BNNS exhibit typical E_{2g} mode vibration of *h*-BN at 1365.9 and 1367.5 cm^{-1} , respectively. The slight red-shift of $\sim 2 \text{ cm}^{-1}$ for the OH-BNNS is due to the reduced interlayer interactions after exfoliation of the bulk BN.^[21] To quantify the -OH fraction grafted to the BNNS, thermogravimetric analysis (TGA) was performed. As shown in Figure 9.3c, the bulk BN was observed to be thermally stable upon heating up to 800 °C, while approximately 25% weight loss can be observed for the OH-BNNS between 100 and 200 °C, attributing to the decomposition of -OH functional groups.^[16] X-ray photoelectron spectroscopy (XPS) was further employed to characterize the chemical composition and bonding state of the as-prepared OH-BNNS. As can be seen from the survey spectrum (Figure 9.3d), the OH-BNNS consist of B (43.9%), N (45.5%), O (5.5%) and C (5.1%). Except for the existence of C which can be explained by the carbon contamination, no evidence of any other contaminant elements was found in the as-prepared OH-BNNS. Multi-peak Gaussian method was used to fit the high-resolution spectra of B 1s and N 1s. As shown in Figure 9.3e, the B 1s spectrum could be deconvoluted into two peaks located at 191.3 and 190.2 eV, which are attributed to the B-O and B-N bondings, respectively. While only one peak centered at 397.5 eV assigning to the N-B bonding is observed for the N 1s spectrum (Figure 9.3f). According to the XPS and above TEM/EELS analysis, it is reasonable to conclude that the -OH groups are bonded to B atoms at the edges of BNNS.

Figure 9.4 The as-prepared OH-BNNS water dispersion is stable over 6 months.

9.3.2 Structure and morphology of OH-BNNS/PVA hydrogels

Figure 9.5 Preparation of OH-BNNS/PVA hydrogels and their structure characterization. (a) OH-BNNS/PVA interpenetrating hydrogels were fabricated by a cyclic freeze/thaw process based on the hydrogen bonding interactions between the OH-BNNS and PVA chains. (b) The composite hydrogels can be freely shaped. Relevant (c) FTIR spectra and (d) XRD patterns indicate that the crystalline structure of the PVA hydrogel was not altered after integration of OH-BNNS.

Figure 9.6 Water contents of the as-prepared OH-BNNS/PVA hydrogels with various OH-BNNS contents.

Figure 9.7 Cross-sectional SEM images of (a) the bare PVA and (b) OH-BNNS/PVA with 0.12 wt% (OH-BNNS:PVA) OH-BNNS. Additional polymer strands can be seen for OH-BNNS/PVA, which are possibly seeded from the OH-BNNS due to the hydrogen bonding interactions between the OH-BNNS and PVA chains, contributing to strengthened matrix/filler interfaces.

Considering the outstanding solubility of the as-prepared OH-BNNS in water and expected hydrogen bonding interactions between the OH-BNNS and PVA chains, OH-BNNS/PVA interpenetrating hydrogels were successfully fabricated using the aqueous mixture of OH-BNNS and PVA through a simple cyclic freeze/thaw method (see Experimental Methods) as presented in Figure 9.5a. To fully understand the reinforcing effects of the OH-BNNS, OH-BNNS/PVA composite hydrogels with different amounts of OH-BNNS (0, 0.03, 0.06, 0.09 and 0.12 wt%, OH-BNNS:PVA), high water contents of ~90% (Figure 9.6) and various dimensions/shapes were prepared (Figure 9.5b). The morphology difference between the bare PVA and the OH-BNNS/PVA composite (0.12 wt%) hydrogels were analyzed using their cross-sectional SEM images. It is observed that OH-BNNS/PVA shows the additional polymer strands seeded from the OH-BNNS as compared to the bare PVA (Figure 9.7), which might be due to the strong bonding interactions between the introduced OH-BNNS and PVA chains. To identify the presence of OH-BNNS within the composite hydrogels and the crystalline structures of the OH-BNNS/PVA hydrogels, Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD) spectra of the bulk BN, OH-BNNS, OH-BNNS/PVA and bare PVA hydrogels were acquired. As shown in the FT-IR spectra (Figure 9.5c), besides two characteristic peaks of *h*-BN at 1373 and 802 cm^{-1} , additional B-OH stretching at 3217 cm^{-1} and B-O deformation at 1192 cm^{-1} can be clearly seen for the OH-BNNS as compared to the bulk BN, confirming the -OH functionalization of the BNNS.^[22, 23] In addition, not only the typical peaks of bare PVA located at 3410, 2931, 1651 and 1083 cm^{-1} , but also slight additional B-N stretching at 1373 cm^{-1} can be observed for the OH-BNNS/PVA hydrogels with 0.12 wt% OH-

BNNS,^[24] demonstrating the successful incorporation of OH-BNNS. It is noted that the XRD pattern (Figure 9.5d) of as-prepared OH-BNNS exhibits characteristic diffraction peak at 26.9° assigned to (002) crystallographic plane of the *h*-BN, demonstrating its high crystallinity.^[25] However, except for characteristic diffraction peaks of bare PVA, no obvious deviation or difference in the diffraction peaks was found for all the OH-BNNS/PVA composite hydrogels as compared to the bare PVA hydrogel, suggesting that the addition of OH-BNNS with relatively low amount do not have noticeable effect on the crystallinities of the composite hydrogels formed after 5 freeze/thaw cycles.

9.3.3 Mechanical properties of OH-BNNS/PVA hydrogels

It is well known that outstanding mechanical properties of the cartilage replacement materials are of great significance considering the diverse physiological loads they may encounter. Therefore, systematic compression and tensile tests were conducted on both the bare PVA (Figure 9.8) and as-prepared OH-BNNS/PVA hydrogels with different OH-BNNS contents (Figure 9.9). As shown in Figure 9.9a, OH-BNNS/PVA hydrogels are able to endure uniaxial compression up to a 75% strain and recover fully after the release of load, indicating their outstanding shape-recovery characteristic resulting from the highly crosslinked polymer chains. In addition, a nonlinear stress-strain relationship can be derived from the compressive stress-strain curves of the OH-BNNS/PVA hydrogels with 0.12 wt% OH-BNNS at different applied strains (Figure 9.9b), indicating their natural cartilage-like viscoelastic mechanical characteristic.^[4, 26, 27] When the compression continues, the orientation of PVA chains within the hydrogel tends to become uniform, while the frictions among the polymer chains, H₂O molecules and OH-BNNS lead to a hardening effect.^[28] Additionally, it is noted that the mechanical strength is gradually enhanced with the increase of the OH-BNNS content and a significant 45% improvement (from 0.29 to 0.42 MPa) could be achieved even with only 0.12 wt% OH-BNNS addition (Figure 9.9c, see Figure 9.8 for more details). This reinforcement is competitively better when compared with that of the GO within GO/PVA hydrogels (0.8 wt% GO addition led to a 36% increase in compressive strength).^[29] It is reported that both water content and the crystallinity of the hydrogels have very important influences on their mechanical

performance.^[29] Since the as-prepared OH-BNNS/PVA composite hydrogels possess similar water contents and crystalline structures with the bare PVA, the enhancement in compressive strength can be mainly attributed to the exceptional mechanical properties of the introduced OH-BNNS and the strong hydrogen bonding interactions between the PVA chains and the OH-BNNS.^[16, 29] The strengthened matrix/filler interfaces^[15] lead to promoted load transfer among them and hinder the possible sliding between the PVA chains upon compression. Furthermore, the intrinsically ultra-strong OH-BNNS help effectively bear the applied load,^[16] contributing to the improved compressive stiffness of the composite hydrogels.

Figure 9.8 (a) Compressive and (b) tensile stress-strain curves for the OH-BNNS/PVA hydrogels with OH-BNNS contents varying from 0 to 0.12 wt%.

Figure 9.9 Mechanical responses of OH-BNNS/PVA composite hydrogels. Highly (a) compressible and (d) stretchable OH-BNNS/PVA hydrogels. (b) Compressive/(e) tensile stress-

strain curves of the OH-BNNS/PVA hydrogel with 0.12 wt% OH-BNNS at various applied strains. (c) Compressive/(f) tensile properties are controllably enhanced for the composite hydrogels with increasing OH-BNNS content. Improvements up to 45%, 43%, and 63% in the compressive, tensile strengths and Young's modulus can be achieved with only 0.12 wt% OH-BNNS addition.

In addition to the compressive performance, tensile mechanical property of the cartilage substitutes plays a significant role in their practical load bearing as well. Figure 9.9d shows the real-time photos of the OH-BNNS/PVA hydrogels under tensile test at a strain of as high as 600%. Notably, the composite hydrogels recover almost fully (~90%) after the load release, showing their outstanding shape recoverability. The excellent tensile elasticity and stretchability are also revealed by the tensile stress-strain curves of OH-BNNS/PVA hydrogels with a 0.12 wt% OH-BNNS addition at strains of 200%, 400%, 600%, 800% and strain-at-break (~930%), respectively (Figure 9.9e). As shown in Figure 9.9f, same tendency of mechanical strength varying with the OH-BNNS content is found in the tensile and compressive processes (see Figure 9.8 for more details). It is noted that 43% and 61% increases in the tensile strength (from 0.19 to 0.27 MPa) and Young's modulus (from 28 to 46 KPa), respectively, can be achieved for the composite hydrogels with only 0.12 wt% OH-BNNS introduction, which are comparable to or better than those of the GO/PVA hydrogels.^[29-33] These exciting enhancements are attributed to the distinguished intrinsic tensile properties of the OH-BNNS (with 2D elastic modulus and breaking strength of as high as ~220-510 N/m and ~8.8-15.7 N/m, respectively^[34]), as well as the frictions between the OH-BNNS and the PVA matrix upon loading. Moreover, the exactly matched chemical compatibility of the PVA and OH-BNNS ensures the homogeneous dispersion of OH-BNNS within the polymer network, contributing to the proper stress transfer upon tensile loading.^[15] Furthermore, the close hydrogen bonding interactions between PVA and the OH-BNNS can effectively resist the stretching and thus promote the tensile resistance.^[29] In addition, complex loadings such as bending, twisting and knotting were also applied. As expected, the as-prepared OH-BNNS/PVA hydrogels can withstand these various shape deformations, demonstrating their superior flexibility, stiffness and toughness that are beneficial for mechanical supports under various loading conditions (Figure 9.10).

Figure 9.10 All the as-prepared OH-BNNS/PVA hydrogels can bear high degree of various mechanical deformations such as (a) bending, (b) twisting and (c) knotting.

9.3.4 Thermal responses of OH-BNNS/PVA hydrogels

To study the effect of introduced OH-BNNS on the thermal performance of the composite hydrogels, their thermal diffusivity and conductivity were further studied using a transient plane source method.^[35] As shown in Figure 9.11, an effective 15% improvement in thermal diffusivity (from 0.1532 to 0.1738 mm² s⁻¹) can be observed for the composite hydrogel with only 0.12 wt% OH-BNNS added, implying that the OH-BNNS/PVA hydrogels are able to “smoothed out” the temperature concavity faster than bare PVA hydrogel, enabling a faster response upon temperature change.^[36] This enhanced thermal diffusivity is due to the excellent reinforcing effect of the OH-BNNS on elastic modulus.^[37] In addition, an expectable 5% increase in the thermal conductivity (from 0.6198 to 0.6432 W m⁻¹ K⁻¹, apparently higher than ~0.21-0.48 W m⁻¹ K⁻¹ of the natural cartilages^[38] or other substitutes^[8, 39]) was achieved for the OH-BNNS/PVA hydrogel with the introduction of only 0.12 wt% OH-BNNS, which agrees well with the parallel thermal conduction model^[39] (0.6464 W m⁻¹ K⁻¹ as estimated). Meanwhile, a significant 68% improvement in thermal conductivity was also observed for the OH-BNNS/PVA composite (dried) with 0.12 wt% OH-BNNS (Figure 9.12), which is comparable with or better than those of the previously reported BNNS/polymer composites.^[40-42] The more efficient heat transfer along the uniform thermal conductive network composed of OH-BNNS and PVA^[40] is attributed to the high thermal conductivity of OH-BNNS (as high as 360 W m⁻¹ K⁻¹ for 11-layered *h*-BN^[12]) and strong hydrogen bonding interactions between the OH-BNNS and

PVA chains.^[21] Moreover, the large contact area between the PVA and OH-BNNS minimizes the phonon dispersion/thermal contact resistance at the interfaces.^[21] The improved thermal conductivity of the OH-BNNS/PVA hydrogels makes the extra heat transfer out more immediately to keep the temperature balanced instead of locally overheated during the cyclic physiological mechanical loading, which is expected to cause less influence on the normal metabolism of the surrounding bio-tissues.

Figure 9.11 The thermal diffusivity and conductivity of the OH-BNNS/PVA hydrogels were controllably enhanced with increasingly incorporated OH-BNNS. Improvements of up to 15% and 5% in thermal diffusivity and conductivity, respectively, can be achieved with only 0.12 wt% OH-BNNS addition.

Figure 9.12 Thermal conductivity of OH-BNNS/PVA composites (dried) with the increasing OH-BNNS content, a significant 68% increase from 0.47 to 0.78 W m⁻¹ K⁻¹ can be achieved with only

0.12 wt% OH-BNNS introduced, indicating the excellent reinforcing effect of the as-prepared OH-BNNS on thermal conductivity.

9.3.5 Cytocompatibility of OH-BNNS/PVA hydrogels

To further investigate the potential of the as-prepared composite OH-BNNS/PVA hydrogels as cartilage substitutes, the cytocompatibility of composite OH-BNNS/PVA hydrogels with various OH-BNNS contents was assessed by *in vitro* culture of HeLa cervical adenocarcinoma epithelial (HeLa) cells. Cells seeded without hydrogel extracts served as controls. As shown in Figure 9.13a, the MTS assay for OH-BNNS/PVA hydrogels with various OH-BNNS contents (0, 0.03, 0.06, 0.09 and 0.12 wt%) shows the excellent cell viability as high as ~85-95%, indicating their non-cytotoxicity. It should be noted that some cells under the hydrogel disks may perish due to the external pressure instead of the toxicity of the hydrogel. To further study the cell compatibility and visualize the cell viability of the composite hydrogels, cell proliferation and live/dead viability assays for 1, 3 and 5 days were respectively employed on OH-BNNS/PVA hydrogels with 0, 0.06 and 0.12 wt% OH-BNNS additions. As shown in Figure 9.13b, all the control and hydrogel samples show similar cell density after first day's culture, which increases dramatically during the following culture. After culture for 5 days, no significant variation in cell density can be observed among the various samples. Representative live/dead fluorescence images are shown in Figure 9.13c. After culture for 1 day, similar live cell (green) density was observed for all the control and hydrogel samples without noticeable dead cells (red) could be found, indicating that all the hydrogels are not cytotoxic, which is consistent with the abovementioned MTS results. Later, cells continuously proliferated and spread homogeneously for the various hydrogels till almost full coverage after 5 days of culture, and few dead cells was observed during this extended culture. This indicates that outstanding cell viability of the composite OH-BNNS/PVA hydrogels are perfectly maintained after the introduction of OH-BNNS. Combining with the excellent mechanical and thermal performances, the outstanding cytocompatibility of the OH-BNNS/PVA hydrogels further supports their potential in cartilage replacement and other biomedical

applications.

Figure 9.13 Cytocompatibility of the OH-BNNS/PVA hydrogels. (a) Cell viability of composite hydrogels with various OH-BNNS contents assessed by MTS assay for 24 h. Cell viability of as high as ~85–95% indicates the non-cytotoxicity of the OH-BNNS/PVA hydrogels. Cell proliferation assay (b) and representative fluorescent images of live/dead assay (c) for the OH-BNNS/PVA (0, 0.06 and 0.12 wt%) hydrogels after cell cultures of 1, 3 and 5 days, respectively. The cells proliferate and spread well for the control and OH-BNNS/PVA hydrogel samples with comparable cell density and proliferation rate, and few dead cells (red) was observed during the 5 days' culture.

9.4 Conclusions

A simple and scalable method has been successfully developed to prepare highly water soluble ($\sim 0.6 \text{ mg mL}^{-1}$) OH-BNNS with large lateral size ($\sim 2\text{--}3 \text{ }\mu\text{m}$). The outstanding hydrophilicity and well-preserved structural integrity of the as-prepared OH-BNNS make them effective additives in PVA hydrogels. Notably, significant 45%, 43% and 63% increases in compressive, tensile strengths and Young's modulus, as well as 15 % and 5% improvements in the thermal diffusivity and conductivity, respectively, can be achieved for the composite hydrogels when only 0.12 wt% (OH-BNNS:PVA) OH-BNNS were incorporated. The homogeneously distributed OH-BNNS with excellent physical properties, as well as the hydrogen bonding interactions between the OH-BNNS and PVA chains collectively contribute to the efficient load transfer and heat conduction. Moreover, the excellent cytocompatibility of the composite hydrogels is not affected by the incorporation of OH-BNNS, due to the non-toxicity of the as-prepared OH-BNNS to cells. These biocompatible OH-BNNS/PVA hydrogels with excellent mechanical and thermal responses show promising potential in biomedical applications including artificial cartilages, drug delivery vehicles and tissue-engineered scaffolds.

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Chapter 10

Conclusions and Future Work

This chapter gives a general discussion to conclude the whole thesis and discusses the originality of the research work in this thesis. Based on the current research progress, future work that can be conducted is also looked into.

10.1 Conclusions

In this thesis, reinforcing the mechanical and thermal properties of CNT arrays, 3D rGO aerogels and PVA hydrogels with low-dimensional C/BN nanomaterials have been systematically investigated. Meanwhile, the potential sports related applications of these composite architectures such as midsole materials for sports footwear and artificial substitutes for cartilage treatment have been explored as well.

First of all, coaxial C@BNNT arrays have been fabricated for the first time by encapsulating outer BNNT onto the CNT arrays *via* a TCVD method. In the meantime, the outer BNNTs with varying thicknesses contribute to controllable and significant improvements in compressive strength, shape recovery, fatigue resistance and energy dissipation of the C@BNNT arrays due to the synergistic effect between inner CNT and outer BNNT. In addition, the outer BNNT provides an additional thermal conductance without affecting that of the inner CNT attributing to their coherent structures, as revealed by both the experimental measurement and the reverse non-equilibrium MD simulation. These overall enhancements in compressive mechanical properties and heat transfer of the C@BNNT arrays would endow their potential energy dissipation and mechanical damping related applications.

Then, a simple strategy has been developed to fabricate supercompressible coaxial CNT@graphene (CNT@Gr) arrays by using a two-step route involving encapsulating polymer coating layers onto commercially available vertically aligned CNTs (~4 mm tall) and subsequent annealing processes. Different from the untreated CNT arrays that plastically deform, the resulting CNT@Gr arrays exhibit superior compressibility (~80% recovery after 1000 cycles at a 60% strain), significantly enhanced compressive strength, and even outstanding strain- and frequency-dependent viscoelastic properties that are nearly constant over an exceptionally broad temperature range (−100–500 °C) in ambient air. These excellent characteristics would inspire many promising applications such as compressive mechanical/thermal contacts, electromechanical devices and energy absorption systems in various environments (even in area with extreme temperatures).

Meanwhile, hydroxylated BNNS with large lateral size ($\sim 2\text{--}3\ \mu\text{m}$) and high water solubility (up to $0.6\ \text{mg mL}^{-1}$) have been achieved by using a two-step chemical oxidation and subsequent exfoliation method. Furthermore, ultralight and highly compressive rGO/BN aerogels have been constructed with cell walls of assembled graphene and BN nanosheets by a facile freeze-drying and subsequent thermal annealing process. The unique 3D porous network and the synergistic effect between graphene and BN sheets endow the as-prepared rGO/BN aerogel with ultralow density, high compressibility and excellent recoverability, showing high potential as compressible mattress.

In addition, wafer-scale VACNT/PVA composite hydrogels have been successfully fabricated by infiltration of PVA among VACNTs and subsequent *in situ* hydrogelation. Meanwhile, the as-prepared composite hydrogels perform outstanding longitudinal compressive responses upon both static and dynamic loadings, attributing to continuous reinforcements of uniformly distributed VACNTs and the large CNT-PVA interfaces. The scalable fabrication approach and excellent mechanical responses of the VACNT/PVA hydrogels endow their potential in load-bearing applications.

Last but not least, the as-prepared hydroxylated (OH-) BNNS could serve as effective additives to fabricate OH-BNNS/PVA hydrogels with remarkably improved mechanical properties and heat transfer, attributing to the homogeneously distributed OH-BNNS with excellent physical properties and the hydrogen bonding interactions between the OH-BNNS and PVA chains. These biocompatible OH-BNNS/PVA hydrogels show promising potential as artificial substitutes for cartilage treatment and tissue-engineered scaffolds.

10.2 Future Work

Although some interesting works have been done in this thesis, there are still some opportunities remaining in this promising field. Based on the current status discussed in this thesis, a general discussion is given below on some topics that could be further looked into in the near future.

Figure 10.1 Enhanced dynamic compressive responses of graphene foam (GF)/PDMS as compared to bare PDMS at 30 °C (a, c) and -130 °C (b, d), respectively.^[1]

Chapter 4-7 of this thesis have demonstrated some ultralight compressible structures with good damping characteristics that are promising candidates for midsole materials of sports footwear. On the other hand, previous studies have shown that these multi-dimensional composite architectures are also effective reinforcing fillers for polymer based composites. Ci *et al.*^[2] has infiltrated VACNTs into polydimethylsiloxane (PDMS) to achieve VACNT/PDMS composites with effectively improved longitudinal compressive strength and modulus. Ghosh *et al.*^[1] has fabricated graphene foam (GF)/PDMS composites and further explored their temperature dependent viscoelastic properties (Figure 10.1). Inspired by this, the other option to produce eligible materials for midsole fabrication could be to refine the current materials (ethylene vinyl acetate (EVA),^[3] polyurethane (PU),^[4] etc.) by incorporating the C@BNNT arrays, CNT@Gr arrays, graphene aerogels and improve their mechanical performances. Considering the obtained large filler-matrix interfacial area and the superior mechanical properties of the fillers, the resulting composites are expected to perform effectively reinforced mechanical responses upon either static or dynamic compressions. In addition, the outstanding physiochemical stability of the C/BN

nanomaterials are anticipated to improve the thermo-mechanical stability of the resulting composite materials, which may endow their more stable mechanical properties in environments with extreme temperatures.

Figure 10.2 BNNT arrays with millimeter-scale dimensions have been achieved by a template-assisted TCVD method.^[5] In this method, the BNNT arrays are prepared by a two-step route involving depositing BN over CNT arrays at a relatively low temperature (900 °C) and a subsequent annealing process.

Chapter 9 has identified the biocompatibility of the OH-BNNS and their effective effects in reinforcing the mechanical and thermal characteristics of the PVA hydrogels, which enable their potential cartilage replacement applications. Considering that significant improvements have been achieved with the relatively small lateral size (micron scale) of the as-prepared OH-BNNS and the limited incorporated concentration (up to 0.12 wt%, BN:PVA), more significant enhancements in mechanical/thermal properties are expected if BN nanomaterials with larger dimensions and amounts could be introduced. It has been reported by our group that vertically aligned BNNT arrays up to millimeter-scale (~5 mm in length) could be obtained *via* a facile template-assisted TCVD method (Figure 10.2).^[5] Meanwhile, excellent thermal conductivity of up to $170 \text{ W m}^{-1} \text{ K}^{-1}$ ^[6] has been reported for the as-grown BNNT arrays. Based on the aforementioned information and the superior mechanical characteristics^[7] and cytocompatibility^[8] of the BNNT, BNNT arrays are expected to be effective reinforcing fillers for the PVA hydrogels to fabricate VABNNT/PVA hydrogels with both enhanced mechanical and thermal responses, which are highly demanded for cartilage replacement applications, tissue-engineered scaffolds and other related biomedical applications.

Figure 10.3 MoS₂/PVA composites with enhanced tensile strength and modulus.^[9]

In addition to graphene and BNNS, other 2D nanomaterials such as ultrathin 2D transition metal chalcogenides (TMD; *e.g.*, MoS₂, WS₂, TiS₂, MoSe₂, WSe₂, *etc.*) nanosheets have attracted considerable research attention due to their unique properties and wide potential applications.^[10] Particularly, some of them have been reported to possess exceptional mechanical, thermal properties and thus could serve as effective additives in preparing polymer based composites. As shown in Figure 10.3, MoS₂ nanosheets have been incorporated into polymer matrix to obtain MoS₂/PVA,^[9, 11] MoS₂/epoxy,^[12] MoS₂/poly(ethylene oxide)^[13] *etc.* with significantly improved tensile strength and modulus. Moreover, MoS₂ nanosheets have been reported to be biocompatible^[14] and introduced into hydrogels to fabricate biocompatible flexible anisotropic actuators.^[15] Together with their scalable synthesis approaches^[10] such as liquid exfoliation, ion-intercalation and exfoliation, more efforts could be devoted to developing TMD nanosheets reinforced polymer or hydrogel composites with strengthened mechanical and thermal properties as well as good biocompatibility, which could further enable wide sports related applications.

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Publication List

Awards

1. **2nd Place in Poster Competition of 2nd International Conference in Sports Science and Technology** (ICSST, Dec. 2016, Singapore) for “Coaxial Carbon@Boron Nitride Nanotube Arrays with Enhanced Compressive Mechanical Property”.
2. **2nd Place in Poster Competition of ACS On Campus-Nanyang Technological University** (Aug. 2018, Singapore) for “Biocompatible Hydroxylated Boron Nitride Nanosheets/Poly (vinyl alcohol) Interpenetrating Hydrogels with Enhanced Mechanical and Thermal Responses”.

Journals

1. **L. Jing**,[¶] H. L. Li[¶] ([¶] co-first author), R. Y. Tay, B. Sun, S. H. Tsang, O. Cometto, J. J. Lin, E. H. T. Teo, A. I. Y. Tok, Biocompatible Hydroxylated Boron Nitride Nanosheets/Poly (vinyl alcohol) Interpenetrating Hydrogels with Enhanced Mechanical and Thermal Responses, *ACS Nano* 2017, 11, 3742–3751.
2. **L. Jing**,[¶] H. L. Li[¶] ([¶] co-first author), J. J. Lin, R. Y. Tay, S. H. Tsang, E. H. T. Teo, A. I. Y. Tok, Supercompressible Carbon Nanotube@Graphene Arrays with Invariant Viscoelasticity over –100 to 500 °C in Ambient Air, *ACS Appl. Mater. Interfaces* 2018, 10, 9688–9695.
3. **L. Jing**,[¶] M. K. Samani,[¶] B. Liu[¶] ([¶] co-first author), H. L. Li, R. Y. Tay, S. H. Tsang, O. Cometto, A. Nylander, J. Liu, E. H. T. Teo, A. I. Y. Tok, Thermal Conductivity Enhancement of Coaxial Carbon@Boron Nitride Nanotube Arrays, *ACS Appl. Mater. Interfaces* 2017, 9, 14555–14560.
4. **L. Jing**, R. Y. Tay, H. L. Li, S. H. Tsang, J. F. Huang, D. L. Tan, B. W. Zhang, E. H. T. Teo, A. I. Y. Tok, Coaxial Carbon@Boron Nitride Nanotube Arrays with Enhanced Thermal Stability and Compressive Mechanical Properties, *Nanoscale* 2016, 8, 11114–11122.
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