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**SENSITIVITY OPTIMIZATION
STRATEGIES OF CARBON-BASED
FLEXIBLE STRAIN SENSORS FOR LOW
STRAIN SENSING: FROM 1D CARBON
NANOTUBE TO 2D GRAPHENE**

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Sensitivity optimization strategies of carbon-based flexible strain sensors for low strain sensing: from 1D carbon nanotube to 2D graphene

WENG ZENGSHENG

**A Thesis Submitted in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy**

April 2024

A CERTIFICATE OF ORIGINALITY

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ABSTRACT

Flexible strain sensors have gained prominence for their ability to detect and monitor mechanical deformations in various applications. These sensors, typically made from flexible and stretchable materials, offer advantages in wearable technology, structural health monitoring, and robotics by providing real-time feedback on strain, making them crucial for dynamic and adaptable systems.

Carbon-based nanomaterials like carbon nanotubes (CNTs) and graphene are valued for their strength, conductivity, and surface area, ideal for sensor technologies. Their mechanical and electrical properties enable precise strain detection. The tunnelling effect in these materials enhances sensor sensitivity, making them ideal for optimizing strain sensors in various applications.

This thesis proposes strategies for optimizing the sensitivity of (CNTs or graphene)-based strain sensors to meet the increasing demand for high sensitivity in various applications. The strategies involve modifying and combining nanofillers, such as applying viscous polymer nanolayers, surface modifications, hybrid nanofiller combinations, and sandwiched-like structures. These strategies aim to enhance sensitivity and enable more accurate and precise strain detection in the sensors.

For CNT-based sensors, this research focuses on optimizing thin-film strain sensors based on multi-walled carbon nanotubes (MWNTs) nanocomposites. The goal is to detect low deformations and micro-vibrations generated by ultrasonic waves, where the tunnelling effect plays a crucial role. To improve the dispersion of MWNTs, a thin viscous polydopamine (PDA) nanolayer is coated on the surface of MWNTs, resulting in a 40% increase in sensitivity compared to uncoated MWNTs. Also, nanocomposite sensors constructed from hybrid carbon nanofillers (PDA@MWNTs and graphene) exhibited significantly enhanced low deformation signal acquisition. Both types of nanofillers contribute significantly to the improved sensitivity of the proposed sensor,

leading to increased geometrical contact between the nanofillers and thereby intensifying the tunneling effect.

To overcome the non-conductive nature of PDA nanolayers, which limits electron tunneling, silver nanoparticles (AgNPs) are immobilized on the surfaces of MWNTs through a PDA-assisted process. Material characterizations confirm the effective incorporation of AgNPs into the PDA nanolayers on the surfaces of MWNTs, enhancing the electron transport ability of the PDA nanolayers and facilitating electron tunneling between adjacent nanofillers. Static tensile tests demonstrate that sensor specimens made from nanofillers with immobilized AgNPs exhibit a sensitivity up to 37% higher than those made with PDA nanolayers alone. Moreover, high-frequency vibration tests reveal that the AgNP content in a sensor specimen positively impacts its sensitivity across a wide frequency spectrum.

For graphene-based sensors, this study is the first time to attempt the feasibility of graphene oxide (GO), equipped with great dispersion ability, in preparing Pen-on-paper (PoP) inks with high sensitivity in multitype strain sensing. First, graphene was oxidized by the Hummer's method to different degree of oxidation and then put into the home-made print pen as the writable instruments to fabricate drawing-made sensors. The materials characterizations confirm that the GO have been separated into different degree. The GO-based paper strain sensors show the ability to capture the strain signals of tensile , compression and pressure. It is also found that the paper sensors show a similar GF value even when the sensor were placed on boards in sensing the same strains, which illustrating the reliability of the GO-based paper sensors.

To further enhance sensitivity of graphene-based strain sensors, a 2-step PDA nanolayer coating method, that is to reduce DA first on graphene and then conduct the PDA coating, is proposed for controlling the tunnelling distance between graphene flakes. The surface of PDA-coated reduced graphene oxide (rGO) prepared using the 2-step method is shown to be smoother compared to direct PDA coating. Thin-film full-

filler strain sensors are fabricated using the coated nanofillers, and an improvement of 21% in sensitivity is observed compared to sensors with direct PDA coating. By adjusting the number of coating cycles, different thicknesses of PDA nanolayers on graphene can be obtained, affecting the surface roughness and agglomeration of graphene nanofillers. The sensitivity of PDA-coated rGO sensors exhibits an initial increase and then a decline as the PDA content increases, indicating an optimal distance between neighbouring graphene flakes for achieving the tunnelling effect.

Moreover, a hybrid approach is explored by combining PDA-coated rGO with black phosphorene (BP) nanosheets to create hybrid full-filler strain sensors due to the excellent piezoresistive effect of BP. The PDA nanolayers on rGO control the distance between graphene nanofillers, enhancing the tunnelling effect. The thickness of BP nanofillers, achieved through centrifugation, negatively impacts sensitivity, with thicker BP resulting in higher piezoresistivity. The hybrid strain sensors demonstrate varying sensitivity due to the synergy between the piezoresistivity of BP and the tunnelling effect of graphene. A hybrid BP-PDA@rGO full-filler sensor with a sensitivity of up to 1300 is achieved, highlighting the potential for obtaining strain sensors with even higher sensitivity through the use of different nanofillers and their mechanisms.

In conclusion, this thesis proposes strategies to optimize the sensitivity of (CNT and graphene)-based strain sensors through nanofiller modifications and/or combinations. The research findings lead to significant improvements in sensitivity, enabling more precise strain detection in various valuable applications. Those advancements contribute to the overall progress of strain sensing research.

LIST OF PUBLICATIONS

Related Journal Publications

[1] Weng Z, Guan R, Zou F, et al. A highly sensitive PDA@ hybrid carbon nanofillers based nanocomposite sensor for acquiring high-frequency ultrasonic waves[J]. Carbon, 2020, 170: 403-413.

[2] Weng Z, Zou F, Li D, et al. A high-sensitivity thin-film MWNT@ PDA-AgNP nanocomposite sensor for acquiring microscopic deformations[J]. Composites Science and Technology, 2022, 229: 109689.

[3] Guan R, Zou F, Weng Z, et al. On a highly reproducible, broadband nanocomposite ultrasonic film sensor fabricated by ultrasonic atomization - assisted spray coating[J]. Advanced Engineering Materials, 2020, 22(11): 2000462.

Conference Presentations

1.WENG Zengsheng, Zou Fangxin, “A highly sensitive strain sensor based on polydopamine@hybrid carbon nanofillers/polyvinylidene fluoride composites for acquiring high-frequency ultrasonic waves”, 2020 MRS Fall Meeting and Exhibit, November 28 - December 04, 2020, Online.

2.WENG Zengsheng, Zou Fangxin, “Writable sensitive strain sensors fabricated by graphene oxide inks for multitype slight deformation sensing”, 2023 MRS Spring Meeting and Exhibit, April 10 - 14 ,2023,San Francisco, USA

3. WENG Zengsheng, Zou Fangxin, “Optimization strategies of MWNTs-based nanocomposite modified by PDA nanolayers to microscopy strain sensing”, 2023 Material Today Conference, August 02 - 05,2023, Singapore.

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As I pen down those words, it is already the late night of early Spring. In the past five years, my journey has been filled with ups and downs, like a roller coaster ride. I have faced numerous challenges, stumbling blocks and unexpected detours. And now the light boat has sailed across countless mountains. I believe I can express those experiences in a more lighthearted manner with graceful words.

First and foremost, I want to express my heartfelt appreciation to my family for their unwavering support and care, both in the past and the future. Their unwavering presence and unconditional love have been the foundation of my strength and resilience. Specifically, I am deeply grateful for the childlike kindness and innocence of my nieces and nephews, as their pure hearts have healed my moments of sadness, and I hope they grow up happily.

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Just as in my favorite movie, "The Secret Life of Walter Mitty," which states, "To see the world, things dangerous to come to, to see behind walls, to draw closer, to find each other and to feel. That is the purpose of life." I will strive to embrace these ideals and embark on meaningful journeys, both physically and emotionally, as I continue to grow and explore the world around me.

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LIST OF ABBREVIATIONS

1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
-NH ₂	Amino
-COOH	Carboxyl
-OH	Hydroxyl
A ₀	Fundamental anti-symmetric Lamb wave mode
ABS	Acrylonitrile–butadiene–styrene
AFM	Atomic force microscopy
Ag	Silver
AgNPs	Silver nanoparticles
BE	Binding energy
BP	black phosphorene
CB	Carbon black
CNTs	Carbon nanotubes
CVD	Chemical vapor deposition
DA	Dopamine
DMF	N, N-dimethylformamide
DT	Direct tunneling
EDS	Energy dispersive X-ray spectroscopy
FNT	Fowler-Nordheim tunneling

FTIR	Fourier transform infrared spectroscopy
GF	Gauge factor
GFRP	Glass fiber reinforced polymer
GO	Graphene oxide
H ₂ O ₂	Hydrogen peroxide
H ₂ SO ₄	Sulphuric acid
HCl	Hydrochloric acid
KMnO ₄	Potassium permanganate
LIG	Laser-induced graphene
MCG	Molybdenum carbide-graphene
MWNTs	Multiwall carbon nanotube
NMP	N-Methyl-2-pyrrolidone
rGO	reduced GO
PC	Polycarbonate
PDA	Polydopamine
PDDA	Poly-diallyl-dimethyl-ammonium
PDMS	Polydimethylsiloxane
PECVD	Plasma-enhanced chemical vapor deposition
PET	Polyethylene terephthalate
PI	Polyimide
PoP	Pen-on-Paper
PMMA	Polymethyl methacrylate
PU	Polyurethane

PVDF	Polyvinylidene difluoride
PSS	Polystyrene sulfonate sodium
PZT	Lead Zirconium Titanate
TEM	Transmission electron microscopy
Tris-HCl	Tris hydroxymethyl aminomethane hydrochloride
S ₀	Fundamental symmetric Lamb wave mode
SBS	Styrene-butadiene-styrene
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscopy
SiC	Silicon carbide
SWNTs	Single-walled carbon nanotubes
TiO ₂	Titanium oxide
UV-Vis	Ultraviolet-visible spectroscopy
WCNT	Whisker carbon nanotube
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction analysis
ZnONW	Zinc oxide nanowire

Chapter 1 Introduction

1.1 Background

Throughout history, humans have demonstrated an innate ability to perceive and harness the signals produced when an object experiences external stress or pressure, leading to either static or dynamic deformation depending on the nature of the forces applied. Those deformed signals have been recognized and utilized in various sensory forms. For instance, by striking the surface of a metal object, different frequencies of vibrations can be generated, giving rise to pleasant musical compositions. Similarly, the observation that rubber-like materials possess a wide range of tolerance for external forces has enabled the creation of slingshots for hunting. Those examples highlight the pervasive role of recognizing and leveraging deformation signals in numerous aspects of human life and technological advancements.

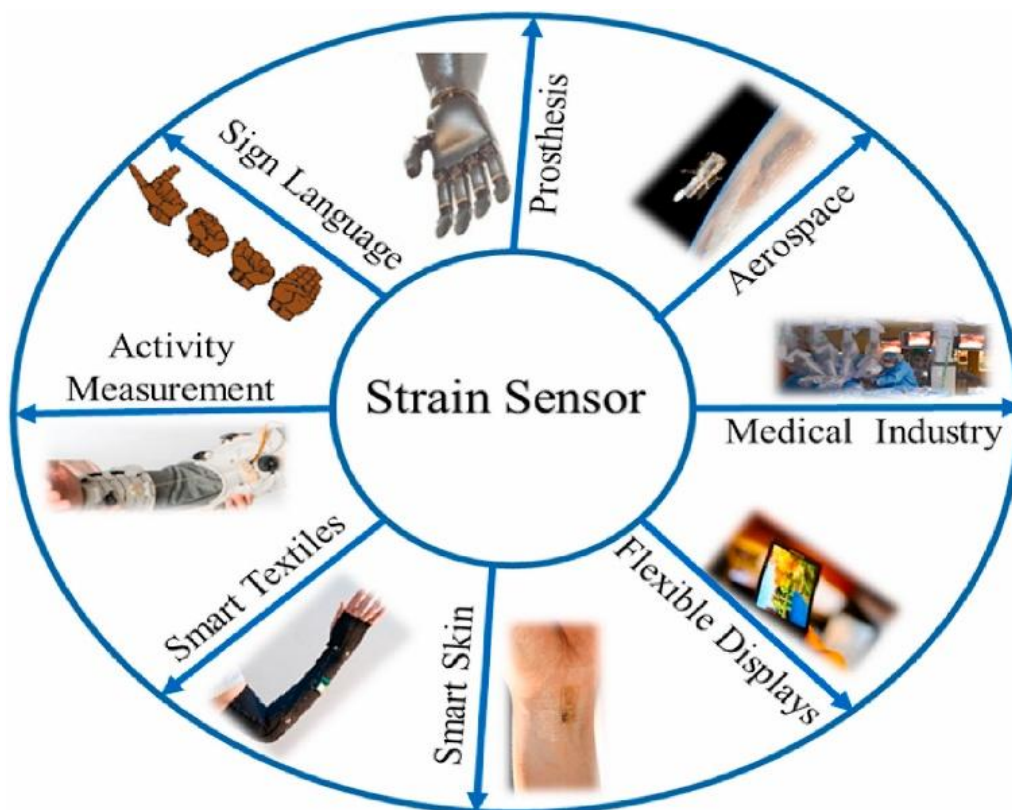


Figure 1.1. Strain sensor applications[1].

Strain sensors have significantly advanced, becoming essential tools for monitoring mechanical deformations in various fields. These sensors are categorized based on their sensing mechanisms, with distinct types offering unique advantages in measuring and analysing strain levels accurately. The classifications of strain sensors include resistive, capacitive, inductive, optical, piezoelectric, and acoustic sensors[2]. Resistive sensors measure strain through resistance changes, capacitive sensors detect capacitance variations, and inductive sensors gauge strain via inductance alterations. Optical sensors use light properties, piezoelectric sensors convert mechanical strain to electrical signals, and acoustic sensors detect strain through acoustic waves. These diverse sensor types cater to a wide range of applications, providing specialized solutions for precise and efficient strain measurement in various industries. Each type operates on specific principles, catering to diverse industry requirements and applications.

Resistive strain sensors are favored for their ease of integration into different systems, providing real-time feedback on structural integrity and performance. They are widely used in applications requiring high sensitivity, such as structural health monitoring[3], robotics [4], and wearable technology [5]. Their compatibility with diverse materials and structures, along with their ability to offer continuous and reliable strain measurements, makes them indispensable in dynamic environments where accurate strain detection is critical. The simplicity of their design and their cost-effectiveness further contribute to their widespread adoption across industries, showcasing their importance in modern engineering and monitoring processes.

In 1850, Lord Kelvin introduced a relationship between strain and electrical resistance. However, it was not until 1930 that Charles Kearns developed the first strain gauge using carbon resistors mounted on an insulating strip. Unfortunately, those early gauges exhibited poor accuracy and were unable to measure static strains effectively [6]. In 1938, Arthur Ruge and Edward Simmons independently reported the development of strain gauges using small diameter wires [7], which showed improved responsiveness to static strains.

As technology advanced, in 1950, Saunders-Roe introduced a strain gauge that utilized etched patterns on a thin foil [7]. This innovation resulted in reduced size and production costs, making those types of gauges the most commonly used in current applications, as depicted in **Fig. 1.1** [1]. Previously, conventional strain sensors were designed using metal or semiconducting piezoresistors. However, those sensors were fragile and rigid, making them unsuitable for sensing curved surface.

As technology continues to advance, there is a growing trend of replacing human labor with multifunctional artificial sensors. Those sensors, known as strain sensors, possess exceptional deformation capturing capabilities that surpass human abilities. Consequently, they have found widespread application in various domains, including daily life, manufacturing, and production. Generally, a typical strain sensor is utilizing a resistance strain gauge to convert strain into changes in resistance. It consists of an elastic element with a pasted resistance strain-sensitive component, which converts the applied physical quantity into resistance changes. When the measured physical quantity acts on the elastic element, it deforms, causing the resistance of the sensitive component to vary. This electrical output is then converted through a circuit, with the level of electrical change reflecting the magnitude of the measured physical quantity. Strain sensors are capable of measuring physical quantities such as strain stress, bending moment, torque, acceleration, and displacement.

The field of nanotechnology-based devices has experienced significant growth at the end of the 20th century. Various types of nanomaterials have been employed to create sensors for both domestic and industrial applications [8-10]. Traditional large-scale integrated circuits used for sensing applications were highly influenced by their immediate environment, affecting their sensitivity and durability [11]. To overcome those limitations, researchers have turned to the development of small-scale sensors with enhanced characteristics that can be utilized in a broader range of applications [12, 13]. Initially, those sensors were prototyped using semiconducting materials, with substrates made of silicon [14] and electrodes composed of metallic nanoparticles like

gold, chromium, and platinum [15]. The fabrication of those silicon sensors involved microelectromechanical system techniques, including conventional photolithography for electrode formation [16]. While those sensors found use in environmental and engineering sensing applications, they had drawbacks in terms of high fabrication costs [17]. The development of those sensors necessitated expensive cleanrooms and foundry facilities, increasing the overall assembly cost even for a limited number of sensors. Consequently, researchers began exploring sensors that incorporated flexible materials. Extensive printing techniques such as screen printing [18], inkjet printing [19, 20], 3D printing [21, 22] and offset lithography [23] have been employed to fabricate those sensors.

Moreover, the field of nanotechnology has allowed for the development of advanced flexible strain sensors using various nanofiller-based composite materials [24, 25]. Those nanocomposite strain sensors operate at atomic and molecular scales, capitalizing on the exceptional properties of nanomaterials such as high efficiency [24, 26], toughness [27], and super plasticity [28]. Consequently, they exhibit high sensitivity even under significant deformations, while consuming low power and offering intelligence and multifunctional integration [29]. Nanocomposite strain sensors address the demands of ultra-miniaturization, intelligence, component integration, high-density storage, and ultrafast transmission inherent in current scientific and technological developments [30]. As a result, they have found extensive application in fields such as biology [31], chemistry [32, 33], machinery [34], aviation [35, 36], and military [37].

In recent times, there has been a growing need to capture extremely small deformations, reaching scales of micrometers [38, 39]. This requirement stems from the necessity to understand the mechanical properties of engineering structures operating in demanding environments and evaluate their service life [40, 41]. While strain sensors have been widely used in engineering and structural monitoring for detecting large strains, their application to low strain ranges presents unique advantages and challenges.

One significant application of strain sensors in the low strain range is in the field of wearable technology and human health monitoring [42-44]. By integrating strain sensors into wearable devices, such as smart garments or wristbands, it becomes possible to monitor subtle movements and biomechanical changes in real-time. Those sensors can detect low strains in joints, muscles, and tendons, providing valuable insights into body movements, posture, and physical performance. This information can be utilized for sports performance analysis, injury prevention, rehabilitation monitoring, and optimizing human-machine interactions. Another area where strain sensors in the low strain range find relevance is in structural health monitoring and material characterization [45, 46]. Those sensors can be used to detect micro-level strains in infrastructure components, such as bridges, buildings, and pipelines. By continuously monitoring low strains, it becomes possible to identify early signs of structural degradation, fatigue, or damage, allowing for timely maintenance and preventing catastrophic failures. Additionally, strain sensors in the low strain range can be employed in material testing and characterization to study the behaviours of materials under minimal deformation [47, 48], enabling the development of more efficient and durable materials.

Furthermore, the application of strain sensors to low strain ranges holds promise in the field of robotics and automation [49, 50]. By integrating those sensors into robotic systems, it becomes possible to detect and adapt to low changes in the environment or object manipulation. This allows for more precise control, improved object recognition, and enhanced safety in human-robot interaction. Strain sensors can also be utilized in the field of soft robotics, where they can provide feedback on deformations and enable the development of more flexible and adaptable robotic systems.

Despite the potential benefits, working with strain sensors in the low strain range presents challenges related to sensitivity, accuracy, and signal processing. Among those challenges, low sensitivity to low strain is the most important factor for casting the real-world application and intelligent application of flexible strain sensors. The unsatisfied

sensitivity may be resulted from the limited interaction between the nanofillers, the presence of mechanical hysteresis, inadequate dispersion or alignment of nanofillers and the choice of materials with inherently low gauge factors [51-54]. Addressing those problems is to have the challenges like optimizing the interface between the sensing elements and the substrate, improving the dispersion and alignment of nanofillers, and selecting materials with higher gauge factors potential. Overcoming those challenges is crucial to enhance the sensitivity of flexible strain sensors, and it serves as the primary focus of this study.

Above all, we believe that continued research and development in sensitivity of flexible strain sensors will further unlock the potential of strain sensors in the low strain range, driving innovation and benefiting society as a whole.

1.2 Research objectives and Outline of thesis

The detail research objective are as follows:

1. To fabricate MWNT-PDA core-shell nanostructure nanofillers through the in-situ self-polymerization of dopamine (DA) and prepare PDA@MWNT-graphene hybrid nanofillers.
2. To synthesize the functional MWNT-based composite nanofillers by a PDA-assisted procedure for AgNPs immobilization.
3. To explore the utilization of GO as dispersed nanofillers in the preparation of inks for strain sensing.
4. To create PDA-coated rGO (PDA@rGO) through 2-step coating process (involving DA reduction process and in-situ self-polymerization of DA).
5. To prepare BP nanofillers with different thickness by peeling black phosphorus and obtain the BP-PDA@rGO sandwiched-like nanofillers through self-assembly process.
6. To respectively prepare above nanofillers-based thin-film strain sensors by specific solution-processed means and investigate the low deformation capturing performance.

This report is structured as follows:

Chapter 1 provides an overview of the research background, including the development history, current status and applications of flexible strain sensors.

In chapter 2, a comprehensive review of the literature is presented. It focuses on the properties and synthesis of one-dimensional (1D) carbon nanotubes and two-dimensional (2D) graphene. This chapter discusses flexible strain sensors based on those materials and explores current optimization strategies for improving the sensitivity of flexible strain sensors to low strains. It also states the research objectives of the study.

Chapter 3 provides a detailed overview of the materials and methodology utilized in this thesis. It includes an in-depth examination of the characterization methods employed to assess the properties and structures of the nanofillers. Additionally, the experimental setup used to evaluate the performance of strain sensors under minimal strains is presented.

Chapter 4 focuses on the preparation of polydopamine (PDA)-coated multiwall carbon nanotube (MWNTs) and hybrid carbon nanofillers for acquiring micro-deformation. It describes the process of coating MWNTs with a 10 nm thick viscous PDA layer to improve their compatibility with polyvinylidene fluoride substrates. Moreover, the mixing of one-dimensional PDA@MWNTs with two-dimensional single-layer graphene can be used to enhance the geometric contact between the nanofillers.

Chapter 5 discusses the immobilization of silver nanoparticles (AgNPs) onto the surfaces of MWNTs using a PDA-assisted process. The material characterizations performed show that AgNPs are compounded, in their elemental state, with the PDA nanolayers on the surfaces of MWNTs, and help to lower the potential barriers between nanofillers. As such, the tunneling of electrons across adjacent nanofillers, which underpins the sensing of low deformations, is promoted.

Chapter 6 presents the feasibility study of graphene oxide (GO) in preparing Pen-on-Paper (PoP) inks for multitype strain sensing. To implement the idea, graphene was oxidized by the Hummer's method to different degree of oxidation and then put into the home-made print pen as the writable instruments to fabricate drawing-made sensors.

Chapter 7 focuses on the 2-step coating method used to achieve evenly distributed PDA nanolayers on reduced graphene oxide (rGO). The PDA coating helps control the distance between neighbouring graphene nanofillers, enhancing the tunnelling effect from graphene.

Chapter 8 study the preparation of hybrid fillers strain sensors using PDA-coated rGO and black phosphorene (BP) nanosheets. It is proven that dual mechanisms (that is piezoresistivity of BP and tunnelling effect of graphene) synergistically contribute to varying sensitivity of hybrid strain sensors.

Chapter 9 provides a summary of the conclusions drawn from this study and presents future perspectives for further research.

Chapter 2 Literature review

In this chapter, a comprehensive literature review is presented, which focuses on the properties and the synthesis of 1D carbon nanotubes (CNTs) and 2D graphene, fabrication techniques of (CNTs or graphene)-based flexible strain sensors to low strain, the current nanomaterials modification strategies to improving the sensitivity of flexible strain sensors.

2.1 Introduction

The transition from conventional sensors to specialized strain sensors represents a significant leap in sensor technology, enabling the precise measurement of mechanical deformations crucial for structural health monitoring and performance evaluation. Strain sensors are finely tuned instruments designed to detect and quantify minute changes in material strain, playing a vital role in industries ranging from civil engineering to healthcare. This evolution has paved the way for advanced sensing capabilities, offering unparalleled insights into the behavior of materials under stress and strain.

Beyond resistive strain sensors, a diverse array of sensor technologies exists, each tailored to unique application needs and operational principles. Capacitive, piezoelectric, and optical strain sensors are among the various types available, each offering distinct advantages in terms of sensitivity, accuracy, and response time. The versatility of these sensor variants allows for a broad spectrum of applications, from structural health monitoring in infrastructure to intricate motion detection in robotics, highlighting the multifaceted nature of modern strain sensor technologies in addressing a wide range of industrial and scientific challenges.

Sensitivity stands at the core of strain sensor performance, defining the sensor's ability to convert applied stimuli into measurable output signals with accuracy and responsiveness. This critical parameter, indicative of the sensor's precision and

reliability, is essential for detecting subtle changes in strain levels and ensuring timely responses to varying environmental conditions. By assessing sensitivity, engineers and researchers can fine-tune strain sensors to meet specific application requirements, optimizing their performance for diverse scenarios.

In general, sensitivity refers to the relationship between the change in quantitative output signals and the applied stimuli. To determine sensitivity, a curve is typically plotted to analyse the performance of sensors by comparing the input values of pressure or strain with the corresponding electric signal output. For flexible pressure/strain sensors, the sensitivity is measured in kPa^{-1} when the stimuli are pressure, while it is dimensionless and referred to as the gauge factor (GF) when the stimuli are strain. The GF represents the ratio of the relative change in output to the applied strain. Therefore, the method of defining sensitivity varies depending on the sensing mechanisms employed and the specific quantity being measured [55]. This study focuses on the sensitivity optimization strategies of resistive-type carbon-based flexible strain sensors to extremely low strain sensing, thus the following literature suggest the sensitivity of the ratio of the relative resistance change in output to the applied strain.

The challenges encountered in strain sensors is their low sensitivity to low deformations [56-58]. This issue arises may be due to several factors. Firstly, the limited interaction between the nanofillers or sensing elements and the substrate material can lead to reduced strain transfer efficiency. Insufficient contact or weak bonding between the sensing elements and the substrate restricts the transmission of strain-induced changes, thereby diminishing the sensitivity of sensors [51]. Additionally, inadequate dispersion or alignment of nanofillers within the sensor matrix can limit strain transfer and compromise sensitivity. Non-uniform distribution of nanofillers or their agglomeration in certain areas hinders the efficient transmission of strain, leading to reduced sensitivity to low deformations [59, 60].

Furthermore, the choice of materials with inherently low gauge factors (a measure of sensitivity to strain) can also contribute to the low sensitivity of strain sensors [58]. Certain materials may exhibit limited changes in electrical or mechanical properties in response to strain, resulting in diminished sensitivity. Carbon-based nanofillers with specific properties is suitable for preparing flexible strain sensors to low strain sensing and that is also the reason why the literature review will start with the introduction of 1D carbon nanotube and 2D graphene and their progress in sensing low strain.

Different types of nanofillers exhibit distinct electronic behaviours in response to low deformations, which can be attributed to the underlying mechanisms. The specific carbon-based nanofillers have been identified to demonstrate mechanisms such as piezoresistivity, disconnection mechanism, and tunnel effect under low deformations [58, 61, 62]. Those mechanisms govern the nanofillers response to low strain and will be discussed in the following sections.

To further enhance the sensitivity of strain sensors, optimization strategies can be employed. Structural design, surface modification, and the utilization of hybrid fillers are potential approaches to increase the interface between the sensing elements and the substrate or to improve the dispersion and alignment of nanofillers. Those strategies aim to maximize the interaction and strain transfer efficiency, thereby enhancing the sensitivity of the sensors to low deformations.

By implementing those optimization strategies, the overall performance and sensitivity of flexible strain sensors is expected to be significantly improved.

2.2 Carbon nanotubes

CNTs are fascinating nanoscale structures that exhibit extraordinary properties due to their unique geometry and atomic arrangement. Those cylindrical structures are formed by rolling layers of graphite sheets at a specific angle, resulting in seamless and hollow tubes [63]. The walls of CNTs are primarily composed of hexagonal carbon atom grids, which give them their remarkable properties [64].

There are two main types of CNTs (**Fig. 2.1**⁴): single-walled carbon nanotubes (SWNTs) and MWNTs. SWNTs consist of a single layer of graphene rolled into a tube, resembling a straw. They typically have diameters ranging from 1 to 2 nanometers and lengths between 0.2 to 5 micrometers. SWNTs possess exceptional mechanical strength, electrical conductivity, and thermal conductivity, making them highly desirable for various applications in nanotechnology and materials science [65].

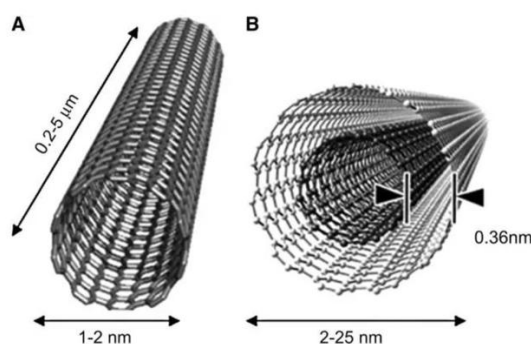


Figure 2.1. Length and radius of typical SWNTs and MWNTs [4].

On the other hand, MWNTs are analogous to coaxial cables, consisting of multiple layers of graphene concentrically arranged. The layers are separated by a distance of approximately 0.36 nanometers, similar to the spacing between graphite layers. MWNTs can have 2 to 50 layers, with diameters varying from 2 to 25 nanometers. The lengths of MWNTs range from 0.1 to 50 micrometers [66]. Due to their unique layered structure, MWNTs exhibit enhanced mechanical properties and can withstand higher tensile forces compared to SWNTs [67].

In addition to the number of layers, CNTs can also be classified based on the presence of defects in their walls. Perfect CNTs are defect-free, with all carbon atoms arranged in a pristine hexagonal lattice. However, during the synthesis process, structural imperfections such as vacancies, Stone-Wales defects, or sidewall deformations can occur, resulting in defective CNTs [65]. Those defects can significantly alter the properties of CNTs and may be intentionally introduced for specific applications.

Furthermore, CNTs can exhibit diverse shapes and structures beyond the typical cylindrical form. Straight tubes are the most common and well-known configuration. However, CNTs can also form bundles, where multiple tubes are held together by van der Waals forces. Y-shaped tubes are another intriguing structure, where two tubes merge at a junction and form a Y-like shape. Additionally, snake-like tubes with highly curved or helical geometries have also been observed [68]. Those different shapes and structures of CNTs provide a rich playground for exploring their unique properties and developing tailored applications.

SWNTs and MWNTs are selected for strain sensor applications based on their distinct characteristics. SWNTs are preferred when high sensitivity and rapid response times are crucial due to their exceptional electrical properties and high surface-to-volume ratio, making them ideal for detecting subtle changes in strain. On the other hand, MWNTs are chosen when a balance between sensitivity and mechanical robustness is required, as their multi-layered structure provides improved mechanical strength while maintaining good electrical conductivity. Therefore, for applications where high sensitivity is paramount, SWNTs may be favored, whereas MWNTs could be more suitable when durability and mechanical strength are key considerations in strain sensor design.

In summary, CNTs represent a remarkable class of tubular structures, categorized into SWNTs and MWNTs, offer an array of possibilities for various applications. Understanding the different types, defects, and shapes of CNTs is essential for harnessing their full potential and advancing nanotechnology and materials science.

2.2.1 Properties of CNTs

CNTs possess remarkable physical properties, making them ideal candidates for flexible strain sensors. CNTs exhibit exceptional values for Young's modulus and tensile strength, measuring approximately 1 TPa and 100 GPa, respectively. Moreover, they exhibit impressive elongation at break, reaching up to 30%. Beyond their

mechanical properties, CNTs also showcase outstanding electrical conductivity, thermal conductivity, and semiconductor characteristics. The electrical conductivity of CNTs is exceptionally high, registering at approximately 10 S/m. Similarly, their current carrying capacity is remarkable, reaching levels as high as 10 °A/cm². In terms of thermal conductivity, CNTs exhibit an impressive value of approximately 3500 W/(K·m). [69, 70]

One of the key advantages of CNTs is their stability, enabling them to maintain their original electrical properties even when subjected to stretching or bending. This durability ensures that CNTs are resistant to damage and can withstand various deformations without compromising their electrical properties. Consequently, CNTs are exceptionally well-suited for the fabrication of flexible strain sensors. Expanding on the topic, the unique combination of mechanical strength, electrical conductivity, and stability exhibited by CNTs makes them highly desirable for a wide range of applications [71]. Those properties enable CNT-based strain sensors to accurately detect and measure mechanical deformations while retaining their functionality even under extreme conditions.

The high Young's modulus and tensile strength of CNTs ensure that the sensors can withstand substantial strains without structural failure. Additionally, their excellent elongation at break allows the strain sensors to endure significant stretching before reaching their maximum limit, enhancing their flexibility and resilience. The exceptional electrical conductivity of CNTs enables efficient transmission of electrical signals within the strain sensor, facilitating accurate measurement and detection of strain [72, 73]. This property is particularly advantageous in applications where real-time monitoring and precise strain analysis are required. Furthermore, impressive thermal conductivity of CNTs enables efficient dissipation of heat generated during sensor operation [74]. This feature is particularly beneficial in high-performance applications, preventing thermal buildup and ensuring reliable and accurate strain measurements over extended periods.

CNTs possess unique 1D structures with extraordinary mechanical strength and flexibility. Their electrical conductivity can be influenced by mechanical deformations, making them ideal candidates for strain sensing. When subjected to strain, CNTs undergo changes in their interatomic distances and bond angles, resulting in alterations in their electronic band structure and electrical resistance.

Researchers around the world have demonstrated the effectiveness of CNTs-based strain sensors in detecting low strains [75-78]. Generally, carbon nanotube-based films can be classified into two types: CNTs film and CNTs/polymer composite film. Initially, research focused on the fabrication of conductive CNTs networks. Early studies on strain sensors primarily involved SWNTs. For example, Kang et al.[79] synthesized SWNTs buckypapers through vacuum filtration and observed a linear strain response within a range of 500 microstrain. Beyond 500 microstrain, the strain behaviour saturated due to slippage among the CNTs bundles. Dharap et al.[80] fabricated thin films of pristine SWNTs via vacuum filtration through a Teflon membrane, attaching the film to a brass specimen. Characterization results indicated a linear change in voltage across the film with applied strain.

MWNTs have garnered significant attention due to their lower cost, relatively higher purity, and superior electrical properties. And consequently, there has been a shift towards utilizing MWNTs as a promising material for CNTs-based strain sensors. For instance, Vemuru et al.[81] synthesized MWNTs films using the vacuum filtration method and attached them to a brass specimen to study the strain response under tensile loading. They found a linear relationship between the change in voltage and applied microstrain. However, the gauge factor of the MWNT film was only 0.3482, which is low compared to conventional metallic strain gauges (GF:2). Bu et al. [82] synthesized CNT films from MWNTs and SWNTs, and non-covalently functionalizing them with sodium dodecyl sulfate (SDS) surfactant. The MWNT films exhibited higher sensing performance than SWNT films, with a GF of 2.5 for strains below 0.1% and a

sensitivity of 5 for strains ranging from 0.1% to 1%, while maintaining good reproducibility.

At the same time, the advancement of flexible strain sensors has predominantly focused on utilizing CNTs/polymer composite films [83-85]. In those composites, CNTs serve as conductive fillers within various polymer matrices, including thermoplastic polymers like PMMA, PVA, PSF, thermosets like epoxy resin, and elastomers such as PDMS and natural rubber. For polymers like epoxy resin, in-situ polymerization with the addition of a curing agent is commonly employed [86]. The curing agent enables covalent bonding between functionalized CNTs and the polymer matrix. The incorporation of CNTs into the polymer matrix significantly enhances the mechanical and electromechanical properties of the composite films.

Overall, the exceptional physical properties of CNTs, including their mechanical strength, electrical conductivity, and stability, make them a highly attractive material for the development of flexible strain sensors capable of withstanding various deformations while maintaining excellent performance.

2.2.2 Synthesis of CNTs

The synthesis of CNTs is a complex and sophisticated process that requires precise control over various parameters. Several methods have been developed to produce CNTs, including chemical vapor deposition (CVD) [87], arc discharge [88], laser ablation [89], and catalytic chemical vapor deposition [90] (Schematic representation of those methods were shown in **Fig. 2.2** [91]).

Arc discharge: In this method, a high electrical current is passed through two graphite electrodes in an inert gas atmosphere. The intense heat generated causes the vaporization of graphite, leading to the formation of carbon nanotubes.

CVD: CVD is one of the most widely used techniques for synthesizing CNTs. It involves the decomposition of hydrocarbon gases in the presence of a catalyst at high temperatures. The catalyst, typically transition metal nanoparticles such as iron, cobalt,

or nickel, acts as a nucleation site for the growth of carbon nanotubes. The hydrocarbon gas, such as methane or ethylene, is introduced into a reactor chamber along with the catalyst, and upon heating, carbon atoms are deposited on the catalyst surface, leading to the formation of CNTs.

Laser ablation: Laser ablation entails the use of a high-power laser to vaporize a graphite target in a reaction chamber filled with an inert gas. The vaporized carbon atoms condense and form carbon nanotubes on a cooler surface within the chamber.

Hydrocarbon flames: In this method, hydrocarbon gases such as methane or acetylene are combusted in the presence of a metal catalyst. The high-temperature flame promotes the formation of carbon nanotubes through the catalytic decomposition of the hydrocarbon molecules.

Regardless of the synthesis method, achieving control over the diameter, length, and quality of CNTs remains a challenge. The specific synthesis conditions, including temperature, gas composition, catalyst type, and growth time, greatly influence the characteristics of the produced CNTs. Thus, extensive research and optimization are conducted to tailor the synthesis parameters and obtain CNTs with desired properties for various applications.

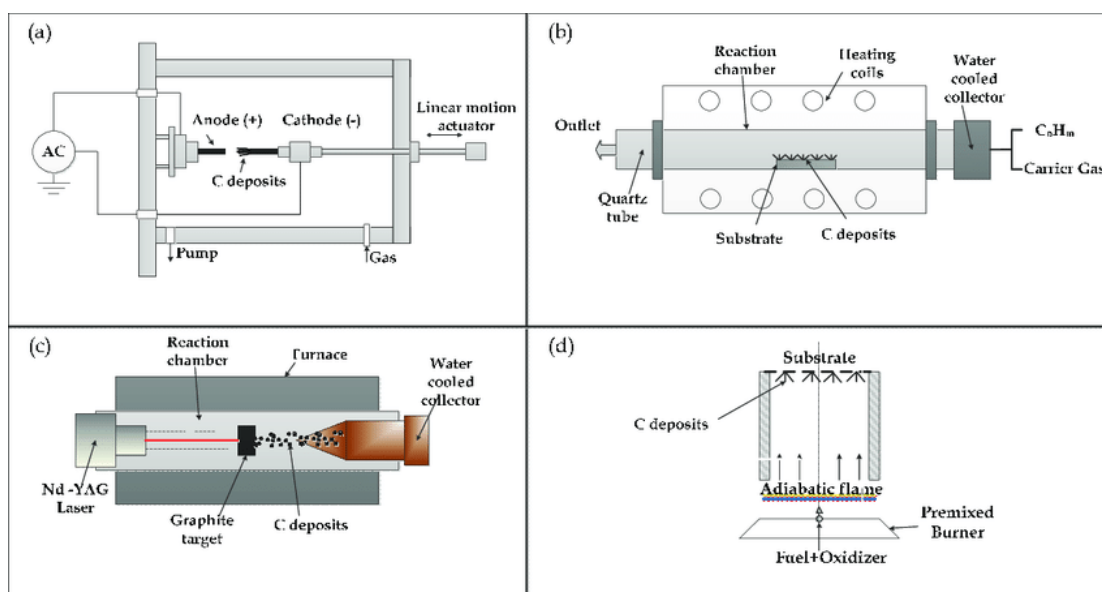


Figure 2.2. Schematic representation of methods used for carbon nanotube synthesis (a) Arc discharge (b) Chemical vapor deposition (c) Laser ablation (d) hydrocarbon flames [91].

In conclusion, the synthesis of CNTs is a dynamic and continually evolving field, driven by the need to understand and control the growth mechanisms for producing high-quality nanotubes. Continued research and development in this area will further enhance our ability to synthesize CNTs with precise control over their properties, opening up new possibilities for their application in various industries.

2.3 Graphene-based nanofillers

Graphene, firstly isolated by Geim and Novoselov in 2004 [92-95], has attracted great attention due to its prominent 2D electro-mechanical properties and become a suitable candidate for developing strain sensors of various types [96-99]. In this study, graphene not only refer to pristine graphene flakes but include their related materials such as GO and rGO (the structure of those graphene nanomaterials can be found in **Fig. 2.3** [100]). Those materials have shown promise in electro-mechanical sensors due to their high strain sensitivities resulting from their excellent mechanical properties and the significant changes in interlayer distances in response to external strains. Integrating graphene into composite matrices not only enhances the properties of the composites but also generates novel functionalities for diverse applications.

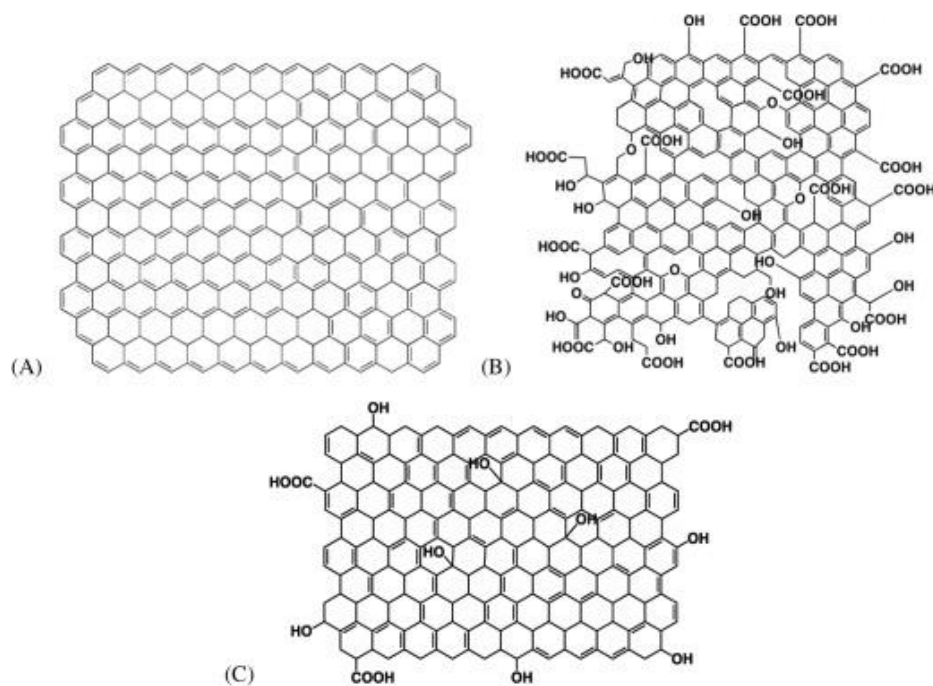


Figure 2.3. Representative structures of (A) graphene, (B) GO, and (C) reduced GO [100].

2.3.1 Properties of graphene-based nanofillers

The unique properties of graphene-based sensors arise from multiple factors. Firstly, the intrinsic characteristics of graphene itself, such as its exceptional electrical conductivity, thermal conductivity, and mechanical strength, contribute to the performance of prepared sensors. 2D nature of graphene and graphene-based nanofillers allows for efficient charge transport, enabling high sensitivity and rapid response in sensing applications [101]. Secondly, the combined functionalities of graphene and other elements incorporated into the substrate further enhance its capabilities. For instance, the integration of graphene with other nanomaterials, such as metal nanoparticles or semiconducting materials, can enhance sensing performance through synergistic effects and tailored material interactions. Those hybrid structures can exhibit improved selectivity, stability, and sensitivity, making them suitable for specific sensing applications [102, 103]. Lastly, graphene derivatives, such as GO and rGO, offer additional possibilities for sensor design and fabrication [104]. Those derivatives possess unique chemical and physical properties, making them suitable for

applications ranging from gas sensing to biosensing. The key chemical and physical properties of graphene, GO, and rGO can be shown as follows respectively [105, 106]:

Graphene:

Single-layer Structure: Graphene is a two-dimensional material consisting of a single layer of carbon atoms arranged in a hexagonal lattice.

Exceptional Mechanical Strength: Graphene exhibits extraordinary mechanical strength, with a tensile strength of about 130 GPa and Young's modulus of approximately 1 TPa.

High Electrical Conductivity: Graphene is an excellent conductor of electricity due to its unique electronic structure, allowing for efficient charge transport.

High Thermal Conductivity: Graphene also exhibits exceptional thermal conductivity, making it an excellent material for thermal management applications.

Flexibility: Graphene is a highly flexible material, enabling its integration into flexible electronics and wearable devices.

Chemical Stability: Graphene is chemically stable and resistant to various environmental factors, making it durable for a wide range of applications.

GO:

Oxygen-Functionalized Graphene: GO is derived from graphene through the introduction of oxygen-containing functional groups, such as hydroxyl, epoxy, and carboxyl groups.

Exfoliation and Dispersion: GO can be easily dispersed in water and other polar solvents, allowing for its integration into various composite materials.

Tunable Properties: The oxygen functional groups in GO can be modified to tailor its properties, such as electrical conductivity and hydrophilicity.

Insulating Behavior: Due to the presence of oxygen functional groups, GO exhibits reduced electrical conductivity compared to pristine graphene.

Reduced GO:

Restoration of Graphene-Like Properties: rGO is obtained by reducing GO, which removes a significant portion of the oxygen functional groups, thereby restoring some of the properties of graphene.

Enhanced Electrical Conductivity: rGO exhibits improved electrical conductivity compared to GO, although it is still lower than pristine graphene.

Improved Hydrophobicity: The reduction process reduces the hydrophilicity of GO, resulting in increased hydrophobicity of rGO.

Retained Mechanical Strength: While the reduction process may reduce the mechanical strength of rGO compared to graphene, it still retains considerable strength.

From above comparison, it can be shown that while graphene possesses the most desirable properties, GO and rGO offer additional advantages. Dispersibility of GO and tunability make it suitable for composite materials, while rGO retains some of properties of graphene while being easier to process and having improved hydrophobicity. However, it is important to consider the specific requirements of each application and select the appropriate material accordingly.

Overall, those remarkable properties of graphene family have led to its exploration and utilization in a wide range of fields, including electronics, energy storage, strain sensors, biomedical devices, aerospace, and many more. As researchers continue to uncover new ways to harness and optimize its properties, graphene-based nanomaterials hold tremendous potential for revolutionizing numerous industries and driving technological advancements

2.3.2 Preparation methods of graphene and graphene-based nanomaterials

The synthesis of graphene-based nanomaterials has been a subject of intense research and development since its discovery. Several methods have been established to produce graphene, each with its own advantages and limitations. The methods can be shown as follows (**Fig. 2.3**¹⁶):

Mechanical Exfoliation [107-109]: The mechanical exfoliation method was the pioneering technique for isolating graphene. It involves repeatedly peeling off layers of graphene from graphite using adhesive tape. This method yields high-quality graphene flakes but is limited in terms of scalability and production volume.

CVD [110, 111]: CVD is a widely used method for large-scale production of graphene. It involves depositing carbon precursors onto a substrate, such as copper or nickel, at high temperatures. The precursors decompose, and graphene layers form on the substrate surface. CVD offers excellent control over the growth parameters, allowing for the synthesis of high-quality graphene films with large areas.

Epitaxial Growth on Silicon Carbide [112, 113]: Graphene can be synthesized by heating silicon carbide (SiC) crystals to high temperatures in a controlled environment. The heat causes the silicon atoms to evaporate, leaving behind a layer of graphene on the SiC surface. This method produces high-quality graphene with good electronic properties, but it is limited to SiC substrates.

Chemical Exfoliation: Chemical exfoliation involves the use of chemical agents to separate graphene layers from bulk graphite. One popular method is the Hummers' method, where graphite is oxidized and subsequently sonicated to obtain GO. Chemical exfoliation allows for the production of graphene in solution form, which is advantageous for various applications.

Plasma-Enhanced Chemical Vapor Deposition (PECVD) [114-116]: PECVD is a variation of CVD that utilizes plasma to enhance the growth of graphene. Plasma provides additional energy to the carbon precursors, facilitating the formation of

graphene. PECVD offers better control over the growth process and can be used on various substrates, making it a versatile method for graphene synthesis.

Laser-Based Techniques [117, 118]: Laser-based methods, such as laser ablation and laser-induced graphene (LIG), utilize high-energy lasers to convert carbon-containing materials into graphene. Laser ablation involves vaporizing a carbon target, while LIG involves directly patterning graphene on a substrate using a laser. Those methods offer simplicity and scalability but may have limitations in terms of quality and uniformity.

Bottom-Up Synthesis [119]: Bottom-up approaches aim to synthesize graphene from small carbon-containing molecules, such as hydrocarbons or carbon nanotubes. Those methods typically involve chemical reactions or self-assembly processes to build graphene structures atom by atom. While bottom-up synthesis holds great potential for precise control over graphene properties, it is still an active area of research and development.

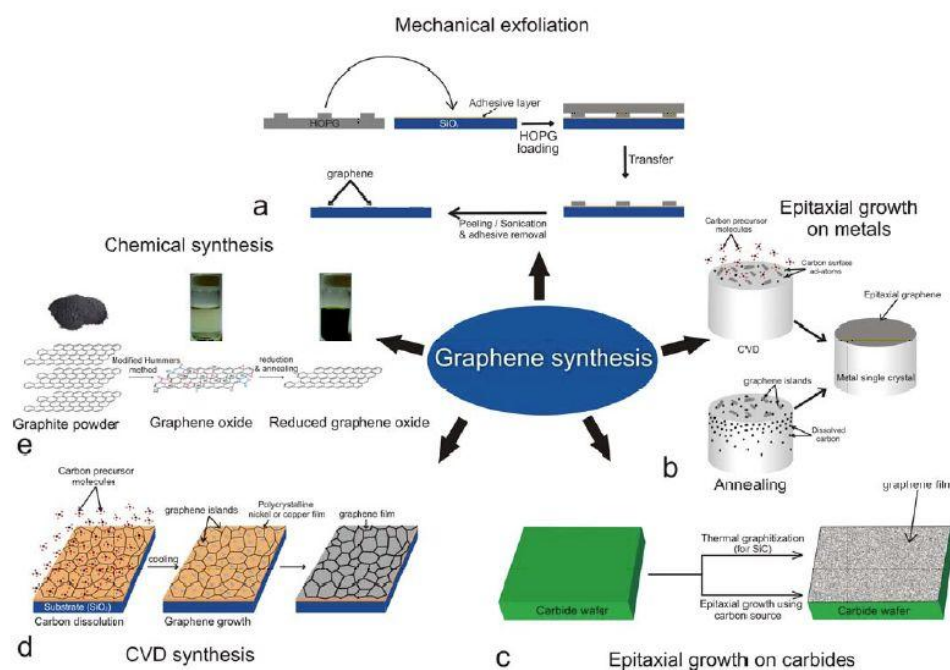


Figure 2.4. Fabrication schemes for the preparation methods of graphene and graphene-based nanomaterials ¹⁶.

It is worth noting that each synthesis method has its own strengths and limitations in terms of scalability, quality, cost, and compatibility with specific applications.

Researchers continue to explore and refine those methods to improve the synthesis efficiency, yield high-quality graphene, and enable its integration into various technologies. The choice of synthesis method depends on the desired application, production scale, and specific requirements of the graphene material.

Overall, the distinct dimensional structure, adjustable electromechanical properties, and versatile synthetic techniques of CNTs or graphene nanomaterials have been extensively utilized to create flexible sensors of different configurations. Those nanomaterials, with their exceptional sensor fabrication technology, have showcased their capability to accurately detect low strains.

2.4 Fabrication techniques of (CNTs or graphene)-based flexible strain sensors for sensing low strains

In recent years, there has been a remarkable increase in research on (CNTs or graphene)-based flexible strain sensors, as reflected in the exponential growth of publications in this field[51, 61, 120-122]. The choice of fabrication techniques plays a crucial role in shaping the design and substrate of strain sensors, ultimately influencing their sensitivity to low strain.

In dry fabrication, CVD is commonly used for thin film deposition in flexible sensors [123-125]. CVD involves the reaction of gaseous materials in the vapor phase or on the substrate surface, resulting in the formation of a controlled thin film. The thickness of the film can be adjusted by manipulating parameters such as temperature, gas flow rate, and chamber pressure. As this process does not involve residual solvents, additional curing and drying steps are not necessary. CVD has shown excellent results for depositing (CNTs or graphene)-based materials like graphene and carbon nanotubes, but it requires high temperature and pressure, limiting substrate selection [126]. The transfer process in CVD can also pose challenges such as increased costs and potential cracks during substrate replacement.

Solution-based methods, such as coating, printing, casting et al., involve formulating nanofillers dispersions by combining functional materials with specific solvents and surfactants in low-temperature environments. Those methods have been employed in the development of flexible electronics using advanced functional (CNTs or graphene)-based nanomaterials and their composite solutions, particularly on non-planar surfaces. Additives such as solvents, surfactants, or adhesives are used to enhance the stability of the solution, although their presence can affect the electrical properties of the deposited film.

Coating is a well-known and straightforward solution process that allows for the deposition of a uniform thin film on a flat substrate. Researchers have successfully utilized spinning coating and twisting techniques to fabricate graphene-based yarn strain sensors using pure carbon nanomaterials [127, 128]. Those techniques involve the controlled assembly and alignment of graphene into yarn-like structures. The resulting graphene-based yarn strain sensors demonstrate excellent mechanical and electrical properties, making them suitable for accurate and sensitive strain detection. The spinning and twisting techniques enable the production of yarn sensors with enhanced flexibility, stretchability, and durability, enabling them to withstand repeated deformations while maintaining their sensing capabilities [121, 129]. Another advantage of coating fabrication is the ease of controlling the film thickness through coating parameters [130]. The preparation method conditions (e.g., sonication time), membrane filter types, and volume of solvent used can influence the tensile properties and quality of the film.

Spray coating is efficient and rapid method for depositing thin layers [131]. In this technique, a spray gun is used to spread the sample onto a hot substrate, and the uniformity of the deposition is controlled by spray pressure. Spray coating is compatible with various nanomaterials (such as graphene, carbon nanotubes and carbon black) and polymer substrates (such as silicone elastomer, Polydimethylsiloxane (PDMS), polyurethane, cotton fabric). However, a challenge in this method is achieving a smooth

flow of liquid through the nozzle, which depends on the physical and chemical properties of the solution or ink.

Drop casting and dip coating are additional solution-based techniques . In drop casting, a droplet is simply placed on the substrate and left for the solvent to evaporate, while dip coating involves immersing the substrate in the desired solution to achieve thin film fabrication. Dip coating offers better control compared to other coating techniques and is suitable for large-scale preparations. Spin coating, on the other hand, produces more uniform and repeatable layers than drop casting and dip coating.

Vacuum filtration is another technique used in the fabrication of strain sensors for flexible devices [1, 51, 60, 132, 133]. In this method, a homogeneously dispersed carbon solution is vacuum-filtered through a suitable membrane. The filtration process results in a thin film formation through the van der Waals force of attraction at the carbon-carbon interface. The film is subsequently washed in distilled water or methanol and dried in an oven before being peeled off.

Printing techniques, such as screen printing and inkjet printing, are commonly employed for graphene-based sensor fabrication [134]. Inkjet printing is a low-cost and flexible method, offering fast printing, digital patterning, and high repeatability. It is particularly suitable for sensing large deformations. However, nozzle clogging can be an issue in inkjet printing due to particle aggregation. Solution-processed techniques, including printing methods, have shown great potential for the fabrication of flexible graphene-based strain sensors due to their low cost and high production capabilities [135-137].

Flexible strain sensors, crafted through diverse fabrication techniques, represent a groundbreaking advancement in sensor technology. These sensors, designed to bend and stretch without compromising performance, are manufactured using methods such as screen printing, inkjet printing, and microfabrication processes. The versatility of these fabrication techniques enables the production of sensors that can conform to

irregular surfaces, making them ideal for applications in wearable devices, healthcare monitoring systems, and structural health monitoring.

Various fabrication techniques are employed in the manufacturing of (CNTs or graphene)-based sensors, depending on the desired structures and the availability of functional materials and substrates. Those methods can be classified into solution-based and dry processes based on the physical state of the precursor and the thin-film deposition mechanism. The advance of fabrication techniques will be discussed as follows and the typical strain sensors by different fabrication techniques are shown in **Table.2.1.**

Table 2.1 Flexible strain sensors made by different fabrication techniques.

Material	Fabrication Technique	Max GF	Max Strain (%)	Remarks	References
Graphene / PDMS	CVD	151	5	The resistance initially decreased by 2.47% due to wrinkle relaxation. Between 2.4% and 4.5% strain, the resistance increased. Above 5% strain, an irreversible resistance change occurred, indicating complete structure destruction.	[138]
Graphene	Ink-jet printing	125	1.25	The inkjet process of fabrication offers fast and direct fabrication on the surface with a larger sensing area. Drop casting with 99 printing layers has been found to be the optimum condition for synthesizing highly sensitive sensors, with a thickness of approximately 20 μm .	[139]
rGO/ Titanium oxide (TiO ₂)	Spray coating	23	5	The strain-resistance behavior exhibited a linear response across a wide strain range of up to 5%. However, it was observed that the sensitivity improvement was limited to a narrow range of TiO ₂ content, specifically up to 37.5% by weight.	[140]
MWNTs/ PDMS	Spin coating	25	2.3	The percolation threshold for the MWNTs in the PDMS composite films was found to be at 0.5 wt. %. Within the strain range of 0% to 2.5%, the MWNTs/PDMS	[141]

				composite films demonstrated a quasi-linear piezoresistive response.	
Graphene /MWNTs	Spray/ Vacuum Filtration Method	181.3	7.5	The sensor, fabricated using 30 wt.% loading of graphene nanoplates, exhibits an electrical conductivity of 104 S/m. Additionally, the sensor demonstrates a tensile strength of 5.4 MPa and a remarkable strain sensing linearity of 99.545% with excellent reproducibility over 5000 cycles.	[142]
MWNTs/ polymethyl methacrylate (PMMA)	Solution casting	15	1	As the tensile strain increased, the sheet resistivity of the films exhibited an increase. This can be attributed to the reduction in the density of the conductive network and the widening of inter-tube distances within the film structure.	[143]
Graphene	Vacuum Filtration	473	1.4	The sensor showed a 40% relative resistive change at a 0.1% tension. During test cycles of approximately 1000 within a 0.16% strain range, the relative resistance changes varied by up to 75% across measurements.	[144]
Graphene	Spray coating	100	1	The flexible strain sensor demonstrates impressive characteristics, including a fast response with a response time ranging from 400 to 700 μ s. It also exhibits good stability, enduring 1000 cycles without degradation. Additionally, the sensor	[145]

showcases low overshoot, with a value below 5%.

It can be seen from above table that fabrication techniques of strain sensors play an important role in determining the performance. The selection and optimization of fabrication techniques significantly affect the sensitivity of strain sensors. Factors such as sub material choice, deposition methods, film thickness, and structural design have a substantial impact on sensor sensitivity. By carefully considering those fabrication parameters, it becomes possible to develop strain sensors with heightened sensitivity. This enables the strain sensors to accurately detect even the smallest changes in strain, providing enhanced precision in various applications such as structural health monitoring, wearable devices, and robotics.

Solution-processed techniques, characterized by their affordability and scalability, exhibit immense promise for fabricating flexible strain sensors based on (CNTs or graphene)-based materials. Consequently, this kind of fabrication techniques has been chosen to be employed in this thesis to develop and explore the potential of such sensors.

2.5 Mechanisms of (CNTs or graphene)-based resistive strain sensors to low strains

Different mechanisms come into play in resistive strain sensors, responding to applied strain based on material type, micro/nano structure, and manufacturing process. Those mechanisms include geometric effects, piezoresistive effect, disconnection between sensing elements, crack effect, and tunneling effect [26, 56, 58]. The response of strain sensors is often a combination of those mechanisms, which varies with different strain ranges and composite or nanofiller structures. For instance, Yang et al. [146] developed a strain sensor using graphene/PDMS composite materials. The sensing mechanism can be divided into three regions: At 5% strain, the increase in resistance is primarily due to the overlapping of graphene nanosheets in the composite material. During the 5% to

15% strain range, the resistance change is mainly influenced by disconnection between graphene sheets and the development of cracks in the rigid graphene. As the strain increases further, resistance changes are solely determined by the occurrence and propagation of cracks.

Moreover, the presence of multiple conductive mechanisms leads to nonlinear resistance changes in stretchable strain sensors. However, in (CNTs or graphene)-based strain sensors with minimal deformations, the piezoresistive effect, disconnection mechanism and tunneling effect are considered to play dominant roles. Those mechanisms have distinct impacts on the resistance of strain sensors and will be discussed separately.

2.5.1 Piezoresistive effect

Piezoresistivity refers to the change in resistance of materials caused by structural deformations. In the equation $\Delta R/R = (1+2\nu) \varepsilon + \Delta\rho/\rho = (1+2\nu) \varepsilon - 2\Delta V_F/V_F$, where ρ resistivity, ε is the applied strain, ν is Poisson's ratio and V_F is the Fermi velocity, the relative change in resistance is expressed as a combination of the influence of geometrical changes and the intrinsic piezoresistivity of the (CNTs or graphene)-based nanomaterials [147-149]. Moreover, it can be seen from the formula that the sensitivity is influenced by both the geometric effect $(1+2\nu)$ and the intrinsic factor $((\Delta\rho/\rho)/\varepsilon)$. The Poisson's ratio of polymer typically falls between 0.35 and 0.5, indicating that the geometric contribution to GF should range from 1.7 to 2. Therefore, a GF value below 2 can be attributed to the geometric contribution, while a value above 2 may be due to the inherent resistivity change and the deformed strain of the composite[150].

Building upon this understanding, Costa et al. [150] developed a resistive strain sensor based on CNTs/styrene-butadiene-styrene (SBS) composite. The inclusion of carbon nanotubes enhances the mechanical properties of the composite while also conferring electrical properties. The sensor exhibits the ability to accurately measure large deformations of up to 20% with minimal hysteresis. The CNTs/SBS composites,

prepared through extrusion and spray printing, demonstrated notable GF values of up to 4 and 2, respectively. The percolation thresholds for the extruded and spray-printed CNTs/SBS composites were found to be approximately 6% and 1% by weight, respectively. Those materials exhibit excellent reproducibility, processing capabilities, and ease of integration. Consequently, this kind of piezoresistive sensors have been effectively applied to gloves, allowing for accurate measurement of finger motions (**Fig. 2.5** [150]).

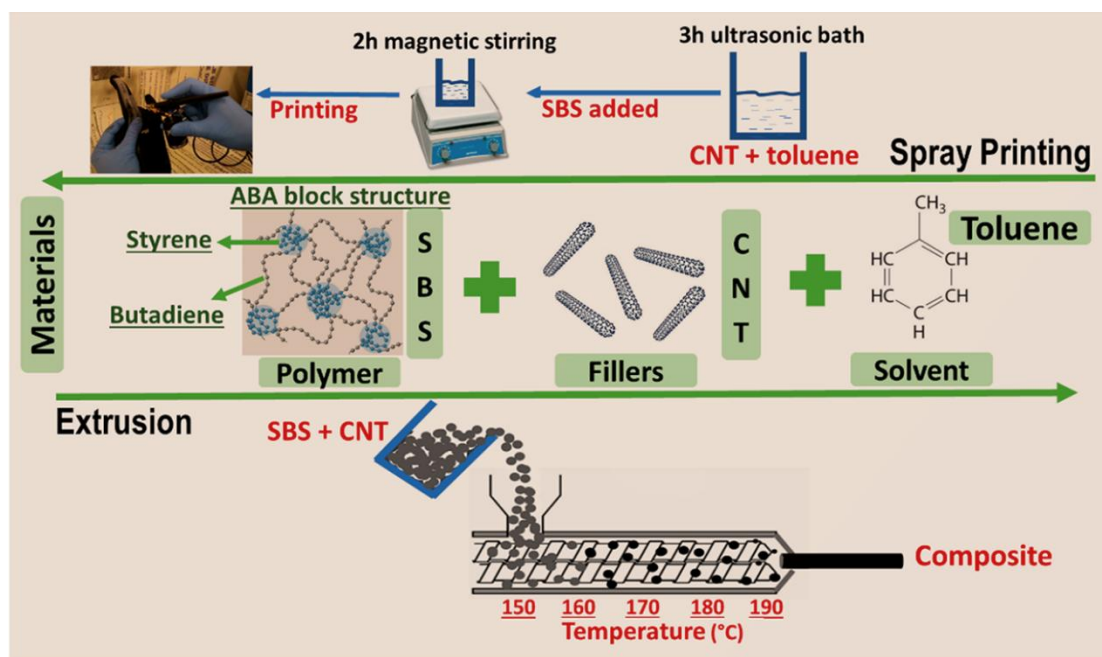


Figure 2.5. Materials and methods used for the preparation of the piezoresistive composites. (above) Spray-printing procedure; (middle) materials; (below) extrusion procedure [150].

In 2010, Hu et al. [151] proposed that the piezoresistive effects of (CNTs or graphene)-based nanofillers are influenced by the compactness of the conductive networks formed by CNTs. Specifically, sparse conductive networks, which result from lower weight percentages of CNTs or the presence of agglomerated nanotubes, are more susceptible to tensile strain due to looser connections or fewer contacts between neighbouring nanotubes. In contrast, denser networks exhibit greater resistance to strain. Therefore, the network structure of CNTs, including the compactness of the filler

networks and connections between nanotubes, plays a crucial role in the piezoresistive behavior of nanofiller-polymer nanocomposites under mechanical stress. The piezoresistive properties of conductive nanofillers-polymer nanocomposites can be tailored by manipulating the network structure of conductive nanofillers. One approach involves incorporating secondary conductive fillers to modify the network structure of CNT-filled nanocomposites with CNTs contents around the percolation threshold [121, 152]. By adjusting the compactness of the filler networks and the interconnections among nanotubes, researchers can control the piezoresistive effects and optimize the sensing performance of strain sensors.

Additionally, challenges such as technical difficulties, inhomogeneous electromechanical properties, and poor stretchability have hindered the widespread use of single nanotubes or nanowires as strain sensors [56]. To overcome those limitations, approaches have been proposed to develop highly stretchable and sensitive strain sensors by forming composites of functional nanomaterials and stretchable polymers. However, in such cases, the contribution from the piezoresistivity of nanomaterials to the overall resistance-strain behavior of stretchable strain sensors may be limited due to the significant elastic mismatch and weak interfacial adhesion strength between nanomaterials and polymers [153, 154]. As a result, the deformations experienced by the nanomaterials upon stretching are negligible, impacting their effectiveness in strain sensing applications.

2.5.2 Disconnection mechanism

In conductive thin films composed of a nanomaterial conductive network, the passage of electrons occurs through overlapped nanomaterials within the percolation network. When those thin films are stretched, some connected nanomaterials lose their overlapped area and electrical connection, resulting in an increase in electrical resistance. From a microstructural perspective, the disconnection of overlapped nanomaterials during stretching is caused by the slippage of nanomaterials due to weak

interfacial binding and a significant stiffness mismatch between the nanomaterials and stretchable polymers [56]. For example, when compression or tension strain applied to a graphene film, it causes changes in resistance due to the corresponding alteration in the overlap area between neighbouring flakes (As shown in **Fig. 2.6** [155]). Compression reduces the overlap area, leading to increased resistance, while tension increases the overlap area, resulting in decreased resistance [155]. Thus, resistance serves as an indicator of the applied strain, reflecting the changes in the graphene film.

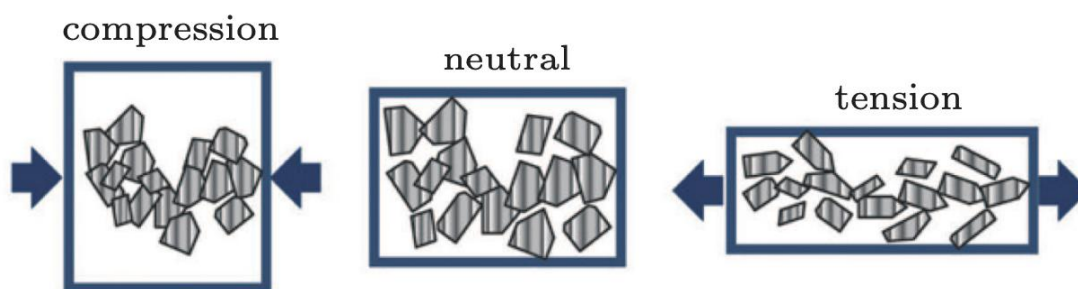


Figure 2.6. Schematic illustration of disconnection mechanism of graphene sheets [155].

Several research groups have utilized this mechanism to develop a variety of (CNTs or graphene)-based strain sensors with different GFs [155-157]. For example, Amjadi et al. [56, 158] investigated the strain sensing mechanism of AgNWs- PDMS nanocomposites, where AgNWs with Young's modulus of 81-176 GPa were embedded in a much softer PDMS layer with a Young's modulus of 0.4-3.5 MPa. During the stretching cycle, the AgNWs fillers slid within the PDMS matrix due to the significantly larger elongation of the PDMS. This sliding of the NWs resulted in disconnection at certain NW-NW junctions, leading to an increase in electrical resistance as the stretching was continued. A similar mechanism was identified for the piezoresistivity of zinc oxide nanowire (ZnONW) thin films coated on PDMS substrates.

Hempel et al. [155] introduced a model to analyse the voltage drop at a fixed current in a graphene film subjected to various levels of strain. In their experimental setup, a spray-deposited graphene was utilized to fabricate the gauge sensor. The researchers

employed Kirchhoff equations to calculate the resistance of the entire flake network. To account for the influence of strain, they displaced the flakes based on the elongation of the entire device and recalculated the network resistance. Upon applying strain, the connections between graphene sheets decreased, leading to a reduction in conductive paths. As a result, the resistance change was higher, indicating the sensitivity of the strain sensor to strain-induced alterations in the conductive network.

Another way of improving sensitivity of strain sensors based on disconnection mechanism is by involved (CNTs or graphene)-based nanoflakes coated on flexible support materials. When those composite films were stretched, the graphene flakes slid in the direction of elongation, reducing the overlapped area between connected flakes and increasing the contact resistance at the flake-flake junctions [53, 56, 158-160]. Recently, microstructure-based strain sensors utilizing interlocked microstructures have also been reported. In those cases, instead of disconnection between overlapped nanomaterials upon stretching, the deformation of the microstructure itself was used to alter the output electrical signal. For example, when two opposing conductive interlocked microdome arrays were laminated and stretched laterally, the contact area between the microdomes decreased significantly, resulting in a considerable increase in electrical resistance.

Disconnections of nanofillers in strain sensors can also arise from a significant stiffness mismatch between two different kinds of nanomaterials. This mismatch can result in the slippage and debonding of nanomaterials when subjected to substantial stretching. This disconnection mechanism is particularly advantageous in strain sensors based on nanowires and flakes. The resistance shift observed in stretchable strain sensors composed of MXene/CNTs films coated on a latex substrate [153, 154], for example, is attributed to changes in overlapping areas and interconnecting pathways during cyclic stretching and releasing. A similar behavior has been observed in strain sensors containing a conductive network of gold nanosheets drop cast on a paper substrate. Under tensile, the nanosheets slide in the direction of the external load, reducing the

contact area between them and consequently increasing the overall resistance of the strain sensor.

2.5.3 Tunneling effect

The phenomenon of electrons crossing a nonconductive barrier is known as tunneling. In the context of nanomaterials, electrons have the ability to tunnel through closely spaced adjacent nanomaterials. Recent experiments have observed very thin insulating polymer layers in CNTs-polymer nanocomposites, where several CNT-CNT junctions were physically separated but still allowed for potential tunneling conduction [161, 162]. This suggests that within a specific distance between neighbouring nanomaterials, electrons can traverse through thin polymer layers and create quantum tunneling junctions. The tunneling resistance between two adjacent nanomaterials can be approximately estimated using Simmons's theory for tunneling resistance as shown in following[56]:

$$R_t = \frac{h^2 d}{\sqrt{2m\lambda} A e^2} \exp\left(\frac{4\pi d}{h} \sqrt{2m\lambda}\right) \quad 1.1$$

Where V represents the electrical potential difference, A is the cross-sectional area of the tunneling junction, J is the tunneling current density, h is Planck's constant, d is the distance between adjacent nanomaterials, e is the charge of a single electron, m is the mass of an electron, and λ is the height of the energy barrier for polymers.

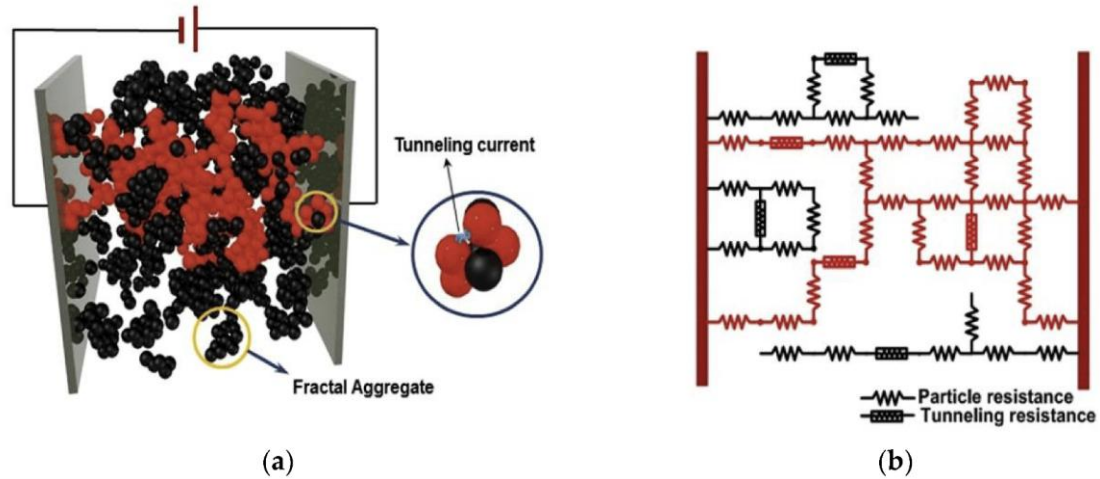


Figure 2.7. (a) Schematic of nanofillers conductive model response to low strain; (b) Equivalent resistor network (formed by directly-contacted nanoparticles and indirectly-contacted nanoparticles via the quantum tunneling effect) [163].

The tunneling effect has been identified as the primary strain-responsive mechanism in strain sensors based on (CNTs or graphene)-polymer nanocomposites in sensing low deformation [164]. When an external strain is applied, the unfolding of those entangled elastic nanomaterials is more likely to occur than sliding in their axial directions, leading to changes in tunneling resistance. This mechanism differs from the disconnection mechanism mentioned earlier, where several connected junctions are separated due to the sliding of rigid nanomaterials (as shown in **Fig. 2.7** [163]).

Regarding tunneling resistance, studies by Hu et al. [165] indicated that the resistance change with CNTs is primarily influenced by the increase in tunneling resistance between neighbouring nanotubes, particularly at small strains or micro-strains. Additionally, Rahman et al. [166] and Wang et al. [167] found that the alignment, aspect ratio, and weight percentage of CNTs in the polymer matrix before stretching also impact the tunneling resistance change. Conducted by Hu et al. [151], both numerical and experimental results of polymer/CNTs composite sensors were examined. It was found that a higher tunneling resistance or a higher ratio of the tunneling resistance to the total resistance of the sensor leads to increased sensor

sensitivity. Processing conditions and material properties such as weight fraction, diameter, and conductivity of CNTs, curing temperature, mixing rate, and barrier height of the polymer matrix were identified as factors that determine the sensor sensitivity. Those results emphasize the significance of controlling and optimizing those factors to enhance the performance and sensitivity of (CNTs or graphene)-based strain sensors. Above studies indicate that there are many factors in determining the tunneling resistance contributing to sensitivity, in this study, the tunneling distance and height of the barrier height are taken into account for improving the GF of strain sensors as discussed in Chapter 4, Chapter 5 and Chapter 7.

The tunneling distance is influenced by various factors, including the type of conductive materials, type of insulating media, and processing parameters. For instance, the tunneling distances for channels like CNT-polymer-CNT have been reported to be approximately 1.8 nm. In the case of parallel graphene sheets insulated with polymers, the tunneling cutoff distance is around 2-3 nm, which is larger than that of CNTs due to the highly crumpled nature of graphene sheets [56]. Xia et al. [168] investigated the tensile and compressive gauge factors of MWNTs/epoxy nanocomposite sensors using an electromechanically coupled homogenization scheme. They revealed the discrepancy in sensing performance between tensile and compressive loading through the loading-dependent tunneling effect, which is influenced by a unified strain-dependent tunneling distance between adjacent MWNTs. The predicted GF and resistance change ratio of the sensors were calibrated using experimental data from compressive to tensile loadings. The results showed that the tensile GF was higher than the compressive gauge factor. The absolute values of the resistance change ratio for both tensile and compressive loading increased with MWNT waviness, strain loading, and the height of the potential barrier between adjacent MWNTs.

Different types of tunneling effect can be used to improve the GF of the resulted strain sensors. For example, Gao et al.[169] used prepared tunable-sensitivity graphene nanoparticle films achieved by modulating the tunneling mechanism. The output

characterization reveals that direct tunneling (DT) and Fowler-Nordheim tunneling (FNT) are the dominant charge carrier transport mechanisms in different voltage regions. At low voltages (0 V - 4 V), DT is the primary mechanism, resulting in a gauge factor of approximately 79. In contrast, at high voltages (20 V - 40 V), FNT becomes dominant, leading to a higher gauge factor of approximately 110, which demonstrate a profound dependence of the strain sensors' sensitivity on the types of tunneling, highlighting the need to consider and manipulate those mechanisms for performance optimization. This study suggests that there is a theoretical basis for optimizing the performance of tunneling strain sensors through the manipulation of the tunneling type. Overall, despite the limited piezoresistivity of (CNTs or graphene)-based nanomaterials, the disconnection mechanism and tunneling effect play significant roles in enhancing the sensitivity of strain sensors. When optimizing specific nanomaterials, it is crucial to consider the underlying mechanism contributing to sensitivity improvement. For instance, incorporating sticky polymers onto the (CNTs or graphene)-based nanofiller hinders the separation or movement between fillers. By reducing the separation between fillers through the addition of sticky polymers, the contribution of disconnection mechanics is minimized compared to fillers without a polymer layer. Consequently, the resistance change is predominantly governed by the tunneling effect. As the tunneling resistance exponentially changes with the distance between fillers, reducing the polymer layer thickness to a nanometers scale that aligns with the filler characteristics can further enhance sensor sensitivity based on the tunneling effect. This concept serves as the foundation for the idea explored in Chapter 4 and Chapter 6 of this thesis.

2.6 Nanofiller modification/combination strategies of (CNTs or graphene)-based nanomaterials for improving sensitivity

Above sections discussed the factors that affect the sensitivity of (CNTs or graphene)-based strain from sensor fabrication techniques to sensing mechanisms of nanofillers.

CNTs and graphene, two prominent carbon-based nanomaterials, exhibit distinct performance characteristics in sensing applications. CNTs, with their unique tubular structure, offer high aspect ratios and excellent mechanical strength, making them sensitive to mechanical deformations. On the other hand, graphene, with its two-dimensional honeycomb lattice structure, provides exceptional electrical conductivity and surface area, enhancing its sensitivity to subtle changes in strain. While CNTs excel in detecting macroscopic deformations due to their structure, graphene's high electrical conductivity enables it to detect even minute strains, making it exceptionally suitable for ultra-sensitive sensing applications. The choice between CNTs and graphene for sensing applications often depends on the specific requirements of the sensing task, with each material offering distinct advantages based on the nature and scale of the strain being measured. However, research around the world have also put a lot of effort into making the (CNTs or graphene)-based nanomaterials more sensitive by different nano-scale techniques, that is nanofillers modification/combination strategies of (CNTs or graphene)-based nanomaterials in this subsection. Those strategies focus on enhancing the sensing abilities of (CNTs or graphene)-based nanomaterials or composites by manipulating their structural and compositional aspects. By employing those sensitivity optimization strategies, researchers aim to unlock the full potential of (CNTs or graphene)-based composites for advanced sensing technologies.

One common approach is optimizing the microstructure and morphology of nanofillers inside composite or not can significantly impact its sensing performance [62, 170]. By controlling factors such as filler morphology, filler component, and orientation, researchers can tailor the mechanical and electrical properties of nanofillers, resulting in enhanced sensitivity. Techniques like controlled blending, annealing, and templating have been utilized to achieve desired microstructures and morphologies. By tuning the network structure of the composite by controlling the dispersion and alignment of the (CNTs or graphene)-based fillers to achieve a well-dispersed and interconnected network within the composite matrix is crucial for optimal sensing performance.

Techniques such as solution processing, melt blending, and electrospinning have been employed to achieve uniform dispersion and alignment of the fillers, thereby enhancing the sensing response.

Surface functionalization of (CNTs or graphene)-based fillers has shown promise in improving sensitivity [102, 171-173]. By modifying the surface chemistry of the fillers, researchers can enhance their compatibility with the polymer matrix and promote stronger filler-polymer interactions. This approach improves the charge transfer efficiency and reduces the contact resistance, leading to improved sensitivity and signal-to-noise ratio.

Furthermore, the incorporation of hybrid conductive fillers, such as CNTs, graphene, or carbon black, into the composites is also positive for improving the sensitivity. The combination of different fillers can lead to improved electrical conductivity and piezoresistive sensitivity [174, 175]. This approach allows for the exploitation of the unique properties of each filler, such as high aspect ratios, excellent electrical conductivity, and enhanced interfacial interactions, resulting in enhanced sensing performance.

2.6.1 Structural design

The performance of strain sensors is significantly influenced by the conductive network formed by nanomaterials. By designing and manipulating the structure of the conductive network, various aspects of the sensing performance, including sensitivity, conductivity, and flexibility, can be modified[53, 176].

One prevalent approach is to establish a percolation conductive network topology[177, 178]. Increasing the content of nanomaterials in the polymer substrate up to the percolation threshold allows for the transition from an insulator to a conductor. Additionally, designing specific conductive networks, such as double-permeable networks or isolated structures, can lower the percolation threshold of the nanomaterials and enhance conductivity. For example, the combination of dual percolation and

isolation structures exhibits a synergistic effect, resulting in a reduction in the percolation threshold, excellent electrical conductivity, and improved toughness and flexibility of the composites. **Fig. 2.8(a)** illustrates the approach used by Wu et al. [179], where they employed a solution mixing method to incorporate MWNTs into acrylonitrile–butadiene–styrene (ABS). The ABS/MWNTs mixture serves as a conductive and permeable polymer phase, which naturally coats the surface of polycarbonate/acrylonitrile–butadiene–styrene (PC/ABS) pellets through mechanical mixing, thereby creating a double percolation and isolated structure. This arrangement effectively separates the PC/ABS particles and enhances the percolation of the conductive phase. Notably, the presence of ABS in both the polymer matrix and the conductive filler mitigates the issue of poor compatibility between the matrix and filler materials. In **Fig. 2.8(b)–(d)**, the black area represents ABS/MWNTs, while the white space corresponds to PC/ABS particles in the polymer matrix. The synergistic effect of the isolation and double percolation structures contributes to the achievement of a low percolation threshold and high electrical conductivity in the resulting composite material, referred to as PCC.

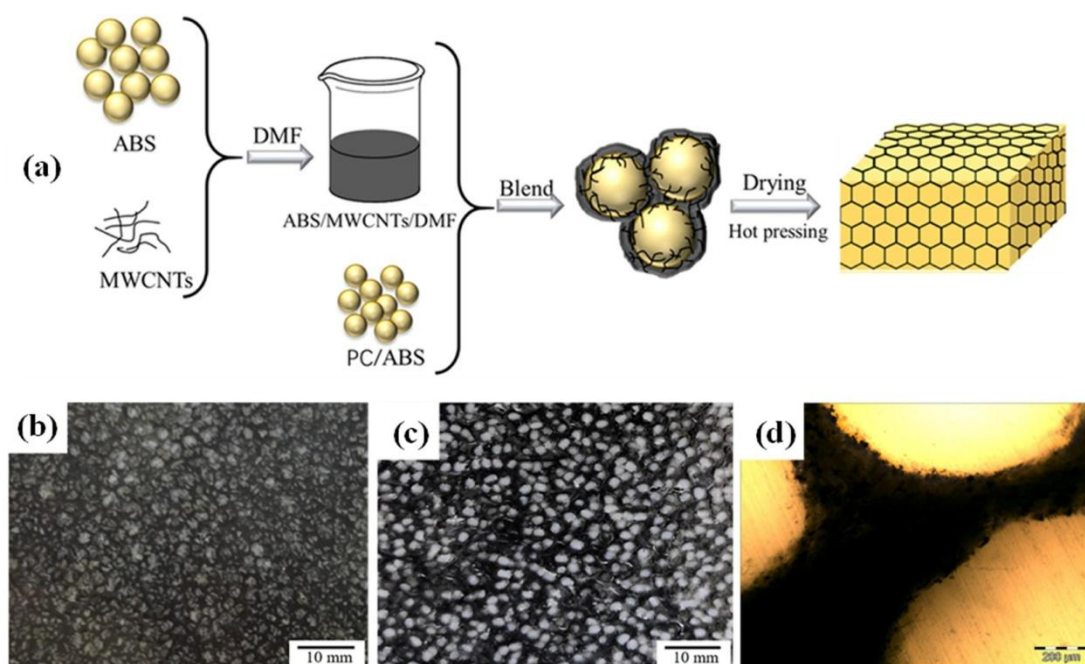


Figure 2.8. (a) Schematic for the fabrication procedure of the composites. (b) Optical photographs of PC/ABS/MWNTs specimens prepared by solution-mechanical mixing. (c) PC/ABS pellets coated with ABS/MWNTs generated plastic deformation in the hot-pressing process. (d) high-resolution images of PC/ABS/MWNTs [179].

Another example is Zhang et al. [180] utilized a simplified Langmuir-Blodgett process for the fabrication of conductive whisker carbon nanotube (WCNT) films, as depicted in **Fig. 2.9(a)-(b)**. By sandwiching WCNTs between two layers of elastic PDMS, a flexible and stretchable strain sensor was created. WCNTs exhibit improved dispersion and conductivity compared to typical CNTs due to their reduced entanglement and flaws (**Fig. 2.9(c)-(d)**). This property allows WCNT films to withstand greater mechanical deformation. The conductivity of WCNT films is influenced by their thickness. Thicker films offer fewer conductive pathways for external mechanical stimulation, resulting in increased conductivity. As a result, those MWNTs-based sensors demonstrate high sensitivity.

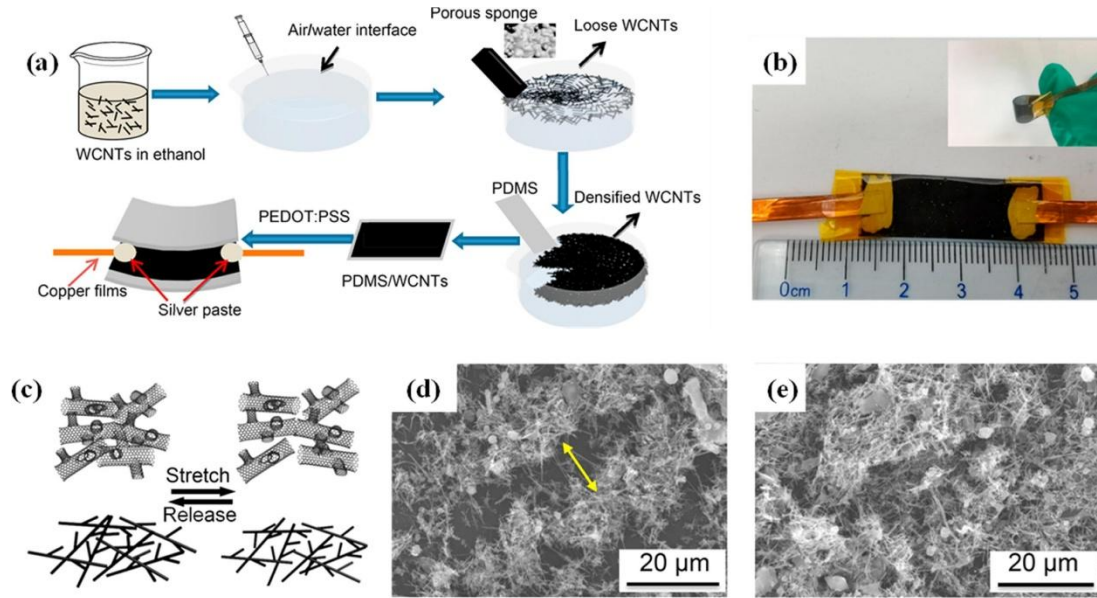


Figure 2.9. (a) Schematic of the fabrication of WCNT nanocomposite films and the structure of strain sensor. (b) The pictures of flexible WCNT-based strain sensor. (c) The schematic diagram of the deformation of the 3D networks of WCNT films during stretching and releasing. (d) SEM image of WCNT films during stretching and releasing. (e) SEM image of WCNT films during stretching and releasing [180].

Further microstructure design techniques, including surface microcrack treatment [181, 182] and wrinkling [183], can simultaneously enhance sensitivity and sensing performance. For instance, conductive nanomaterials can fill micro-grooves on flexible substrates, enabling the achievement of ultra-high sensitivity even under minor stresses and enhancing the ability of strain sensors to detect vibrations.

Creating specific patterns or structures on nanofillers is also an effective approach to enhance the strain sensitivity of sensors [25, 51, 184]. Patterning techniques [185-187], such as lithography or laser ablation, can be utilized to generate micro- or nano-scale features that optimize stress distribution and strain transfer within the sensor material. Those patterns or structures play a crucial role in improving the ability of sensor to detect and measure low strains. The generated patterns or structures on the nanofiller surface can have different configurations, such as lines, grids, or arrays. Those patterns

can influence the strain transfer mechanisms within the sensor material. For instance, a grid pattern can effectively distribute and concentrate the strain, enhancing the sensor's sensitivity to low strains. Similarly, an array of pillars or cavities can modify the stress distribution and strain transfer paths, optimizing the response of sensors.

For example, lithography techniques [188] involve selectively modifying the surface of the nanofillers using photolithography or electron beam lithography. Photolithography utilizes light-sensitive materials and masks to selectively expose and develop desired patterns on the nanofiller surface. On the other hand, electron beam lithography employs a focused electron beam to directly write patterns with high precision. By patterning the nanofiller surface, stress distribution within the sensor material can be optimized. The specific patterns can be designed to guide and redistribute the strain, leading to enhanced strain transfer to the sensor [189]. This optimization of stress distribution ensures that the strain is effectively channelled to the sensing elements, maximizing the sensitivity of the sensor. For instance, Gorissen et al. [190] conducted a study on a strain sensor utilizing vertically CNT filler elements embedded in a rubber matrix. The use of vertically aligned CNTs allows for patterning through lithography, enabling the scaling down of sensor size to the micrometers range.

Laser ablation [191] is another technique that can be used to create patterns or structures on the nanofiller surface. In laser ablation, a high-energy laser beam is focused on the nanofiller surface to selectively remove or modify the material. This technique allows for precise control over the size, shape, and distribution of the patterns or structures. An example of the application of patterned nanofillers is in flexible electronics, where strain sensors are integrated into wearable devices. By patterning the nanofiller surface, the strain sensors can be made more sensitive and responsive to the movements and deformations experienced by the wearable device[25, 192, 193]. The patterns can be designed to align with the expected strain distribution, maximizing the detection of specific movements or strains.

Patterning techniques such as lithography or laser ablation can be employed to generate micro- or nano-scale features that optimize stress distribution and strain transfer within the sensor material in low deformation. By tailoring the patterns to the desired strain distribution, the sensitivity of the sensor can be significantly improved, enabling the detection and measurement of even low strains with higher accuracy.

2.6.2 Surface modification

Surface modification techniques play a crucial role in optimizing the sensitivity of strain sensors to detect even low strains. Those techniques aim to enhance the interaction between the nanofillers and/or polymer substrates to the external strain, thereby improving the sensitivity. Some common surface modification approaches include:

Functionalization: Functionalization involves attaching specific functional groups or molecules to the surface of the nanofiller materials or nanocomposite to enhance its sensitivity to strain [194]. This modification enables better adhesion and interaction between the sensor and its surrounding environment. By introducing functional groups, such as amino (-NH₂), carboxyl (-COOH), or hydroxyl (-OH) groups, the surface chemistry of the sensor is altered, leading to improved strain sensing capabilities [83].

In the case of (CNTs or graphene)-based nanofillers, functionalization can be achieved by attaching organic molecules to the nanofiller surface. Those molecules can have specific functional groups that interact with the surrounding environment or the strained object. The functional groups can provide additional binding sites for the strained object, promoting stronger adhesion and better strain transfer [195, 196]. For example, Zhang et al.[197] developed flexible composites by employing a swelling/permeating method to combine PDMS with CNTs. The process involved the diffusion of CNTs into the surface layer of PDMS. The interior core of PDMS contained only a minimal amount of CNTs, giving rise to a sandwich-like structure within the composite (as shown in **Fig. 2.10** [197]). To enhance the interaction between CNTs and PDMS, the researchers

performed surface modification of the CNTs using surface chemical agent. This modification led to improved permeation and greater dispersion of CNTs within the PDMS matrix, resulting a higher GFs.

In this functionalization process, the functional molecules are typically chemically bonded to the surface of the carbon nanotubes through covalent or non-covalent interactions. Covalent functionalization involves forming strong chemical bonds between the functional groups and the carbon nanotube surface, ensuring long-term stability and improved sensitivity. Non-covalent functionalization, on the other hand, relies on weak intermolecular forces, such as *Van Der Waals* interactions, hydrogen bonding, or π - π stacking, to attach the functional molecules to the nanotube surface [198].

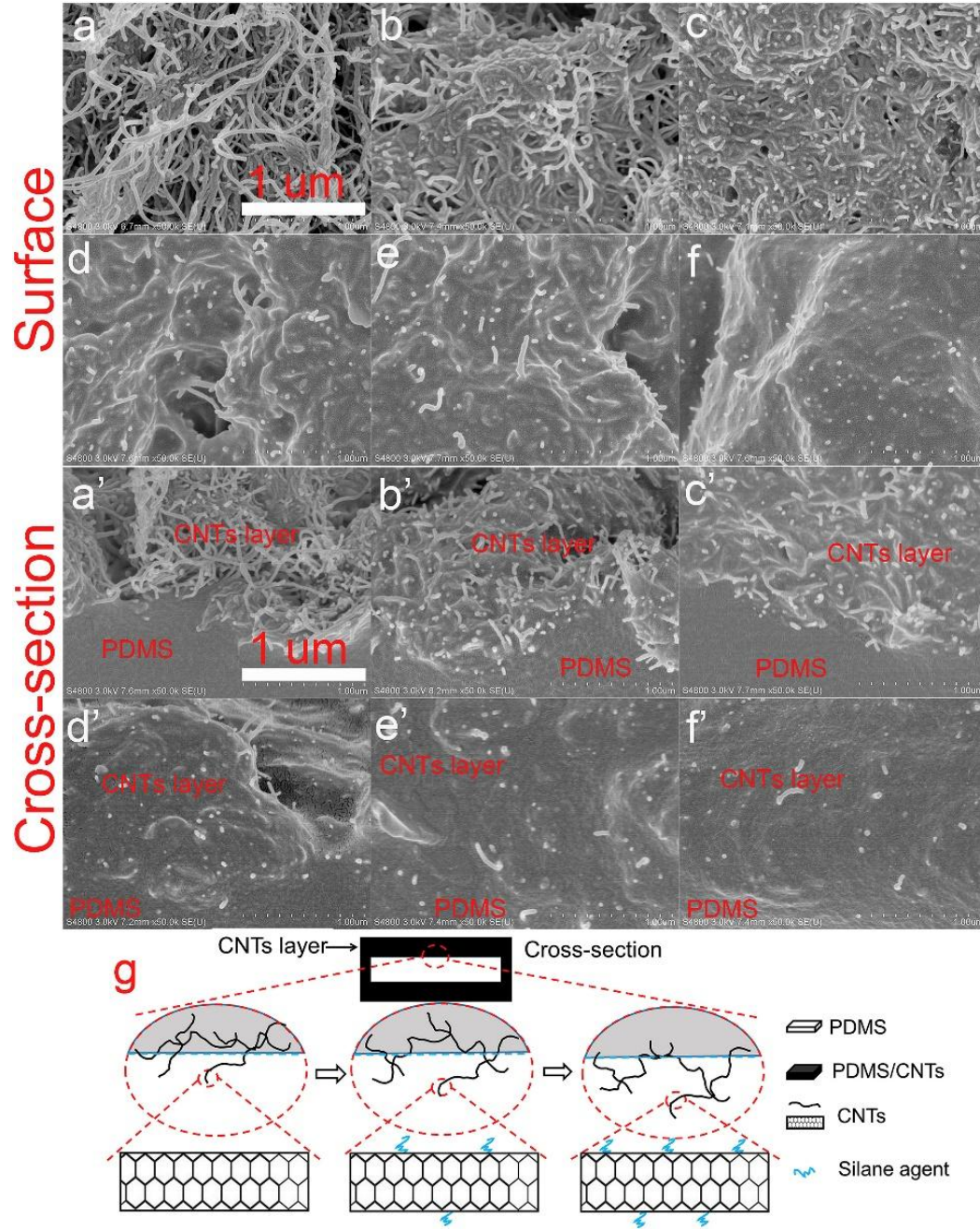


Figure 2.10. SEM images for the surface (a) to (f) and cross-section (a) to (f) of composites of CNTs modified with 0, 0.5, 0.8, 1.0, 1.5, 2.0 wt. %; a proposed model showing the permeation of CNTs into PDMS with surface modification (g) [197].

The introduction of functional groups through surface functionalization increases the available surface area for strain transfer, allowing the sensor to effectively detect and respond to low strains. The functional groups can also alter the electronic properties of the sensor material, leading to changes in its electrical conductivity or piezoresistive

behaviour, further enhancing its sensitivity to strain. Functionalization through attaching specific functional groups or molecules to the sensor surface is a powerful approach to optimize the sensitivity of strain sensors. It improves adhesion, increases surface area for strain transfer, and promotes stronger bonds with the strained object, resulting in enhanced strain sensing capabilities [199].

Surface roughening: Creating micro-scale or nano-scale roughness on the surface of nanofillers is an effective method to enhance its sensitivity to low strains [200]. The introduction of surface roughness increases the effective contact area between the sensor and the strained object, allowing for better strain transfer and improved detection capabilities.

One example of surface roughening is the use of techniques like sandblasting or etching to generate controlled surface features on the sensor material [201, 202]. Those techniques can create micro-scale or nano-scale roughness, such as pits, grooves, or protrusions, on the sensor surface. The roughened surface alters the stress distribution and strain transfer mechanisms, leading to improved sensitivity. The increased contact area resulting from surface roughness enhances the mechanical interaction between the sensor and the strained object. When a low strain is applied to the object, the roughened surface allows for more points of contact and a greater distribution of strain across the sensor surface. This amplifies the effect of the low strain, making it easier for the sensor to detect and measure.

Additionally, the roughened surface introduces stress concentration points, which are regions where stress tends to accumulate. Those stress concentration points act as localized amplifiers, further magnifying the effect of low strains [203]. As a result, the sensor becomes more responsive and sensitive to even the smallest changes in strain. The choice of roughening technique and the scale of roughness depend on the specific requirements of the strain sensor and its intended application. For example, in the field of flexible electronics, micro-scale roughness introduced through techniques like

nanoimprinting or laser ablation can enhance the sensitivity of strain sensors integrated into wearable devices or biomedical sensors.

By incorporating surface roughness, strain sensors can achieve improved sensitivity to low strains. The increased contact area and the introduction of stress concentration points optimize the strain transfer and enhance the sensor's ability to detect and quantify even subtle changes in strain.

Nanomaterial integration: Introducing nanomaterials, such as nanoparticles or nanolayers formed by polymer, metal or organic matter, onto the surface of (CNTs or graphene)-based nanofillers is a promising approach to significantly enhance their sensitivity to low strains [83, 96]. Those nanomaterials can act as stress concentrators, effectively transferring strain to the sensor and greatly improving its detection capabilities and enhance the dispersion ability of the nanofillers within a matrix.

When nanomaterials are incorporated onto the surface of strain sensors, such as within a polymer matrix, they play a crucial role in amplifying the strain signals. Nanoparticles, with their small size and high surface-to-volume ratio, are particularly effective stress concentrators. As strain is applied to the surrounding material, the stress becomes concentrated at the nanoparticle sites, causing localized deformation. This localized deformation leads to a more efficient transfer of strain to the sensor, thereby enhancing its sensitivity. Similarly, nanolayers, which are thin layers of nanomaterials deposited onto the sensor surface, can also act as stress concentrators. Those nanolayers can effectively capture and redistribute the strain, enabling its efficient transmission to the sensor. By acting as stress concentrators, nanolayers enhance the strain detection capabilities of the sensor, allowing it to accurately measure even subtle changes in strain.

Integrate (CNTs or graphene)-based nanofillers with a polymer nanolayer is also an effective approach to enhance the dispersion ability of the nanofillers within a matrix [204]. Carbon nanofillers have a high tendency to agglomerate or form clusters due to

their high surface energy and strong van der Waals forces. The polymer coating nanolayers provides a physical barrier between the nanofillers, preventing them from coming into direct contact and forming agglomerates. The polymer layer surrounds each individual nanofiller, reducing interparticle interactions and promoting a more even distribution throughout the matrix [205]. Additionally, the polymer coating can introduce functional groups or surface modifications that enhance the compatibility between the nanofillers and the polymer matrix. This improved compatibility reduces the interfacial energy between the nanofillers and the matrix, further discouraging agglomeration and facilitating their dispersion. In some cases, the polymer coating also increases the effective size and surface area of the nanofillers, making them more easily dispersible in the matrix. Such as, PDA polymer layer acts as a spacer, preventing direct contact between the nanofillers and allowing for a more efficient dispersion process [1]. Moreover, the polymer coating can provide a lubricating effect, reducing the friction between the nanofillers and enabling them to move more freely within the matrix. This dynamic movement helps to break up agglomerates and promotes a more uniform dispersion thus improve the sensitivity of resulted strain sensors. For example, Sankar et al. [59] proposes a method of polymer integration to balance the stable dispersion of nanofillers while maintaining their inherent characteristics. By using oppositely charged polymers, polystyrene sulfonate sodium salt (PSS) and poly-diallyl-dimethyl-ammonium chloride (PDDA), to functionalize CNTs, they achieve better dispersion of PSS-CNT compared to PDDA-functionalized CNTs in a poly (vinylidene difluoride) (PVDF) matrix as shown in **Fig. 2.11** The PVDF/PSS-CNT composite exhibits significantly higher electrical conductivity and gauge factor (9.8) compared to PVDF/PDDA-CNT. The improved dispersion of PSS-CNTs is attributed to the repulsive forces between individual CNTs facilitated by the charged polymer functional groups, resembling the intrinsic functional groups of pristine CNTs.

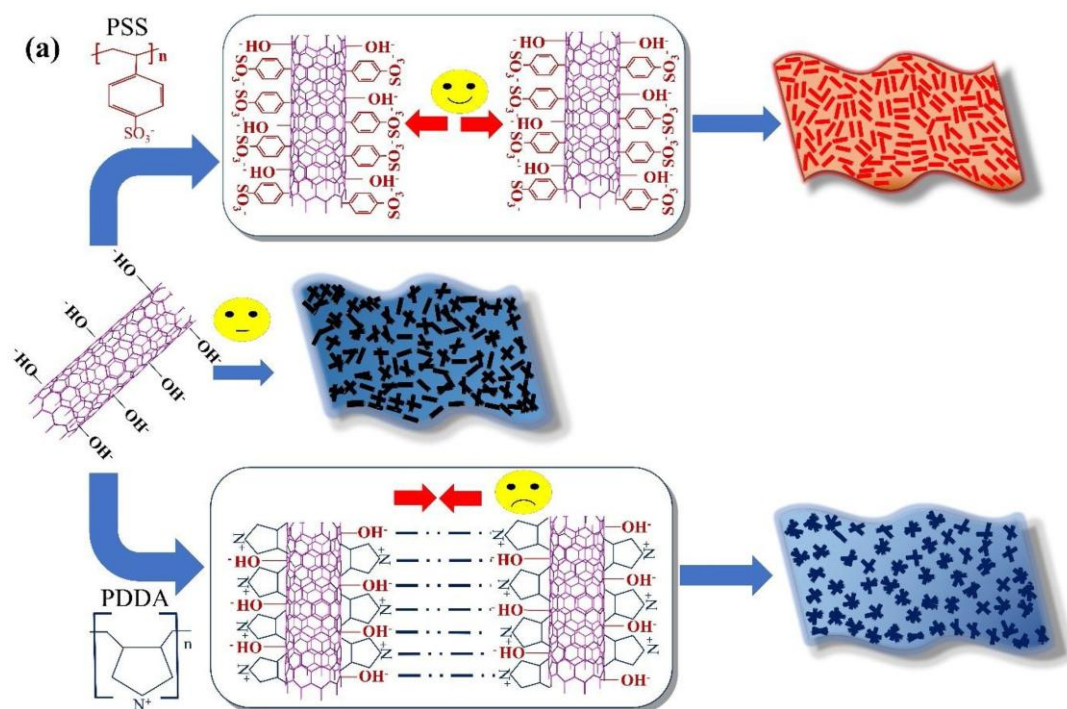


Figure 2.11. Schematic of functionalized nanofillers and its dispersion in the polymer matrix [59].

By comparing various surface modification methods for (CNTs or graphene)-based nanofillers, it becomes evident that integrating them with polymer nanolayers is a mature and efficient approach to reduce aggregation of the nanofillers [61]. Additionally, the polymer nanolayers act as spacers, effectively separating the nanofillers from each other at the nanoscale. Considering the mechanisms discussed in **Chapter 2 Section 2.5**, it is the tunneling resistance that appears to be the primary factor contributing to resistance changes, which in turn reflects changes in sensitivity.

Polymer coating nanolayers demonstrate dual benefits: improving the dispersion ability of (CNTs or graphene)-based nanofillers and influencing the tunneling resistance change. This makes them highly promising for optimizing the sensitivity of strain sensors to sensing low strains. Consequently, this strategy becomes the starting point for ideas discussed in **Chapter 4** and **Chapter 7**, where polymer-coating strategies are applied to 1D MWNTs and 2D graphene, respectively.

2.6.3 Hybrid-nanofillers strategy

In recent years, researchers have explored the incorporation of hybrid conductive fillers in polymers as a means to achieve higher electrical conductivity in conductive filler-polymer nanocomposites at a given loading or below the percolation threshold of individual fillers. For example, Ma et al. [206] demonstrated that the percolation threshold in epoxy nanocomposites containing 0.2 wt.% CNTs combined with various amounts of carbon black (CB) was lower than those filled with CNTs or CB alone. Similarly, Chen et al. [207] found that a lower percolation threshold was achieved in nanocomposites of a polyamide 6 (60%)/ABS blend (40%) filled with hybrid fillers of CNTs and CB (mass ratio CNTs/CB = 1/1) compared to those filled with CNTs or CB individually. However, obtaining such synergy effects in terms of decreased percolation thresholds relies heavily on the dispersion of fillers and the interconnections between the hybrid fillers in Conductive polymer nanocomposites, making it challenging to achieve consistently.

In general, it is more common to observe similar or even higher electrical conductivity in conductive nanofiller-polymer nanocomposites containing hybrid conductive fillers compared to those with single fillers at the same total filler content. Socher et al. [208] reported that samples containing hybrid MWNTs and CB exhibited higher volume conductivities at filler loadings well above the percolation threshold compared to samples with single fillers. Additionally, the improvement in electrical conductivity in conductive polymer nanocomposites is influenced by the composition of hybrid fillers, such as the mass ratio of CNTs to CB ($m_{\text{CNTs}}/m_{\text{CB}}$), with higher ratios generally resulting in higher electrical conductivity. Similar trends can be observed with other hybrid fillers in Conductive polymer nanocomposites, offering the potential for achieving higher electrical conductivity through their incorporation.

The electrical conductivity of conductive polymer nanocomposites filled with (CNTs or graphene)-based conductive nanofillers is well-known to arise from the creation of conductive pathways formed by the contacts between neighbouring nanofillers [61, 209]. This conductivity is facilitated through tunneling or electron hopping effects

within insulating polymers. However, the sensing performance of conductive nanofiller-polymer nanocomposites is affected by the increase in tunneling resistance between nanotubes and the loss of contacts between them. As a result, the piezoresistive effect observed in conductive nanofiller-polymer nanocomposites is closely linked to their initial electrical conductivity, both of which can be influenced by the network structure formed by the conductive fillers within the conductive polymer nanocomposites.

For example, Ke et al. [210] prepared PVDF nanocomposites filled with hybrid CNTs and CB using a micro-compounder through melt mixing. It is found that for nanocomposites with a CNTs content below the percolation threshold of 0.53 wt.%, there is a noticeable decrease in electrical resistivity with an increase in the content of carbon black. This can be attributed to the formation of hybrid conductive networks, where the CB particles bridge the gaps between CNTs when the CNTs content alone is insufficient to form continuous conductive pathways. Those nanocomposites with such hybrid conductive networks exhibited high susceptibility to strain, resulting in a significantly higher change in resistance compared to nanocomposites containing only CNTs. For nanocomposites with CNTs contents above 0.53 wt.%, the addition of CB did not have a notable impact on the increase in electrical conductivity. In this scenario, CB served to compact the existing conductive networks. The more compact networks displayed enhanced resistance against mechanical deformation during stretching due to higher network compactness and stronger entanglement of CNTs. As a result, the piezoresistive sensitivity decreased. The above study not only prove that the feasibility of collaborative mechanism of hybrid (CNTs or graphene)-based nanofillers, but also emphasize it is both mechanise affecting hybrid structure to low strain.

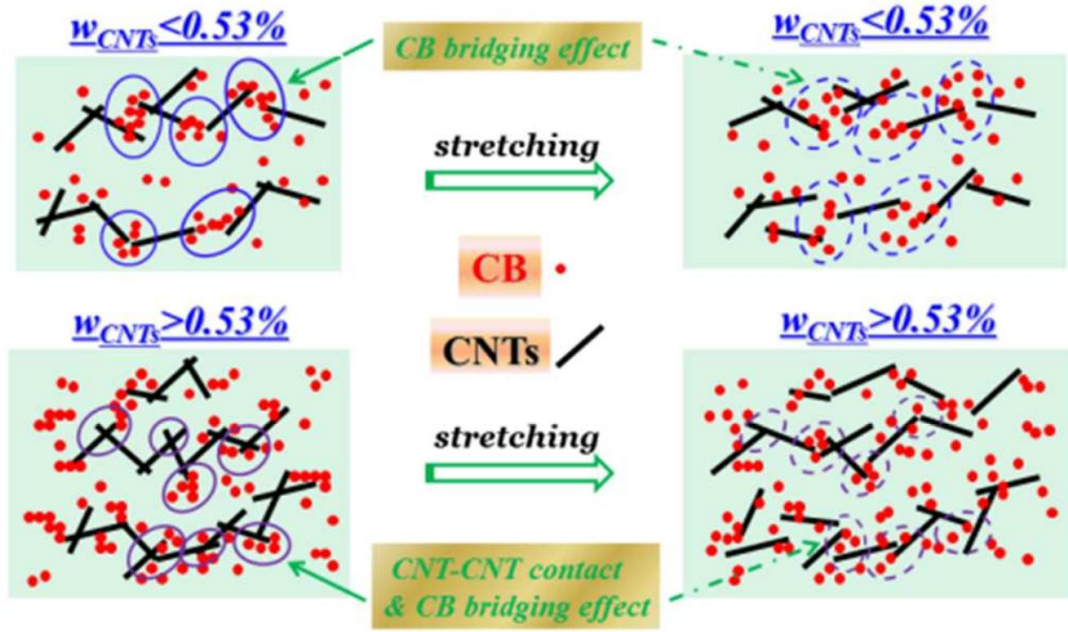


Figure 2.12. Schematic illustration of the network structure consisting of CNTs and CB before and after stretching for PVDF nanocomposites containing CNT contents [210].

However, previous studies have not given much attention to the impact of individual resistance-change mechanisms inside hybrid conductive filler systems to the sensitivity [210]. As discussed before, individual nanofillers is given different mechanisms for resistance change. By combining different individual nanofillers into hybrid nanofillers, the mechanisms behaviours may change as well. For example, Lin et al. [211] discovered that thermoplastic polyurethane nanocomposites, filled with a hybrid filler comprising 7 wt.% CB and 3 wt.% MWNTs, exhibited higher piezoresistive sensitivity compared to nanocomposites filled with 10 wt.% MWNTs alone. The researchers attributed this improvement to the reduction of entanglements between CNTs in the network structure when CB particles were added. It is worth noting that although the nanocomposites filled with hybrid fillers had higher initial resistivity than those filled with 10% CNTs, this difference could also contribute to the enhancement of piezoresistive sensitivity with strain. Additionally, Zhao et al. [212] conducted a study where they prepared PDMS nanocomposites using a three-roll mill. Those

nanocomposites were filled with hybrid fillers consisting of graphite nanoplates and CNTs, forming a hub-like structure. The resulting nanocomposites exhibited excellent sensitivity by connecting conductive network where both piezoresistive effect of graphite nanoplates and CNTs become affect collaboratively. Those findings highlight the potential of hybrid conductive nanofiller systems in enhancing sensitivity by applying mechanisms from both individual nanofillers.

In general, the use of hybrid conductive fillers presents a promising approach to enhance the sensitivity by improving electrical conductivity, optimizing the percolation threshold, creating more conductive pathways or changing/adding resistance-change mechanisms of hybrid system.

Overall, above sections discussed various nanomaterial-functional strategies for optimizing the sensitivity of (CNTs or graphene)-based strain sensors. The ways in which those strategies become effective mainly include: (1) achieving a well-dispersed and interconnected network, (2) tailoring the mechanical and electrical properties, (3) creating conductive pathways, (4) improving compatibility with the polymer matrix, and (5) promoting stronger interactions between fillers and the polymer matrix or between fillers themselves. Those approaches have demonstrated positive effects on improving the sensitivity of flexible strain sensors.

2.7 Conclusion

This thesis is focused on the sensitivity improvement of functionalised nanofillers (from 1D carbon nanotubes to 2D graphene) strain sensors for low strains sensing.

In this chapter, we first reveal the properties and the synthesis methods of the 1D CNTs and 2D graphene, respectively. Their unique electronic and mechanical properties endue the abilities to sensing the low deformations, which have been selected as the research objects of this thesis.

Then varied factors that contribute to the sensitivity change of the (CNTs or graphene)-based strain sensors have been discussed. Those discussions form the basis for the ideas explored in this thesis.

The first one is sensor fabrication techniques. The selection of fabrication techniques significantly affects the sensitivity of prepared strain sensors and already explained through examples. The utilization of solution-processed techniques, known for their affordability and scalability, holds great potential in the production of (CNTs or graphene)-based strain sensors. Those fabrication techniques have been selected for implementation in this thesis to advance the development of those sensors.

The second one is mechanisms of (CNTs or graphene)-based nanofillers to low strains. The piezoresistivity effect, disconnection mechanism and tunneling effect of CNTs or graphene nanomaterials play significant roles in changing the sensitivity of strain sensors and research around the world has demonstrated promising outcomes in enhancing the sensitivity of strain sensors through the implementation of those mechanisms.

The third one is nanofillers modification/combination strategies. Structural design, surface modification and hybrid-nanofillers strategy have been shown to be positive approaches in improving the sensitivity of (CNTs or graphene)-based strain sensors for low strain sensing. The ways that those strategies affect the sensitivity mainly include establishing a well-dispersed network, tailoring properties, creating conductive pathways, improving compatibility or promoting stronger interactions between nanofillers. Those factors mentioned serve as the foundational ideas utilized to enhance the sensitivity of (CNTs or graphene)-based strain sensors in this thesis.

Inspired by above research outcomes, this thesis proposed sensitivity optimization strategies based on following discussion:

(i) From mechanisms-applying perspective, sensitivity improvement was achieved by applying tunneling effect in sensing low strains. By creating nanoscale separation

between the nanofillers, it is possible to reduce the impact of disconnection mechanics and emphasize the tunneling effect, ultimately enhancing the sensitivity of the sensor. This concept is explored in **Chapter 4** and **Chapter 7** for 1D CNTs and 2D graphene respectively.

(ii) From the perspective of nanofiller modification/combination, different strategies were introduced. 1. Viscous polymer nanolayers was coating to the surface of MWNTs or graphene to improve nanofillers dispersion state and/or improve bonding with polymers substrate. 2. Surface modifications were introduced for tailoring electronic properties of the surface of nanofillers. 3. Hybrid nanofillers were also applied for creating more conductive pathways. 4. Sandwiched-like structure design were applied to promote stronger interactions between nanofillers.

Chapter 3 Materials and methodology

In this chapter, an overview of the materials that will be utilized throughout this thesis is provided. Subsequently, an in-depth examination of the characterization methods employed to assess the properties and structures of nanofillers is conducted. Lastly, the experimental setup utilized to evaluate the performance of strain sensors when subjected to minimal strains is presented.

3.1 Chemical materials

MWNTs (inner diameter: 5 - 10 nm, outer diameter: 10 - 20 nm), graphite, and graphene (thickness: 4 - 7 nm, diameter: 6 mm, purity: 99.7%) were acquired from Shanghai Aladdin Bio-Chem Technology Co., Ltd., China. Likewise, DA hydrochloride, silver nitrate (AgNO_3), PVDF, and PI films were sourced from the same supplier. N-Methyl-2-pyrrolidone (NMP) and N, N-dimethylformamide (DMF) originated from Fu Chen, Inc. in Tianjin, China. Moreover, bulk black phosphorus (99.99%) was provided by Smart-Elements in England. For additional materials like ethanol absolute agent, Tris-HCl, and 1H,1H,2H,2H-per-fluorodecyltrichlorosilane (volume fraction: 0.025%), acquisitions were made from Aladdin reagent Co. Ltd. These elements played a pivotal role in the experimental procedures, greatly influencing the research outcomes.

The selection of these specific materials from various reputable suppliers ensured the reliability and consistency of the experimental results. Each component, from MWNTs to graphene and the supporting chemicals, was meticulously chosen to meet the stringent requirements of the study. This comprehensive procurement strategy not only guaranteed the quality and authenticity of the materials but also underscored the meticulous approach taken in the experimental design and execution.

3.2 Material Characterization

The characterization techniques used for the nanocomposite sensors included:

Scanning Electron Microscopy (SEM): The microscopic morphologies of the nanocomposite and the corresponding energy dispersive X-ray spectroscopy (EDS) mapping were taken on JSM-6700F scanning electron microscope from Japan. SEM allows for high-resolution imaging of the surface topography and structure of the sensors.

Transmission Electron Microscopy (TEM): TEM or TEM-EDS analysis was performed using a JOEL JEM-1230 Transmission Electron Microscope from the USA. TEM provides detailed information about the internal structure, crystal lattice, and composition of materials at the nanoscale.

X-ray Photoelectron Spectroscopy (XPS): XPS measurements were conducted using a Thermo Scientific K-Alpha Spectrometer System from the USA. The spectrometer utilizes a monochromatic Al K α X-ray source operating at 100 W. XPS analysis provides information about the elemental composition and chemical bonding states of the samples. The spectra were acquired under vacuum conditions, and the peaks were calibrated using the C1s peak for adventitious carbon.

X-ray Diffraction Analysis (XRD): XRD experiments were performed using a Rigaku D/MAX-3C X-ray Diffractometer from Japan with Cu K α radiation. The samples were scanned at a rate of 10°/min, and the diffraction angle 2 θ was measured in the range of 5–90°. XRD is utilized to determine the crystallographic structure and phase composition of the materials.

Raman Spectroscopy: Raman spectroscopy measurements were carried out using a Renishaw inVia Confocal Raman Microscope from the UK. The samples were excited with a 632.8 nm NeHe laser, and the Raman spectra were acquired in the range of 100–4000 cm⁻¹. Raman spectroscopy provides information about the vibrational modes and molecular structure of the samples.

Fourier Transform Infrared Spectroscopy (FTIR): FTIR spectroscopy is a technique used to analyse the chemical composition and molecular structure of materials based

on their distinct infrared absorption patterns. In this case, FTIR spectra of the samples were recorded on a Bruker Vector33 spectrometer. The samples were prepared as KBr pellets, where the sample material is mixed with a KBr powder and pressed into a thin disc. The FTIR spectra were collected using a Nicolet iS50 FT-IR spectrometer with a DTGS detector on a Smart Orbit ATR accessory. The ATR crystal allows for direct contact between the sample and the diamond crystal, enabling efficient infrared measurements.

Atomic Force Microscopy (AFM): AFM is a high-resolution imaging technique used to visualize the surface topography and properties of materials at the nanoscale. In this case, AFM characterization was performed using an MFP-3D-SA AFM system. AFM involves scanning a sharp tip across the sample surface and detecting the forces between the tip and the sample. The resulting data provides detailed information about surface roughness, height variations, and even mechanical properties such as elasticity and adhesion.

Zeta Potential: Zeta potential is a measure of the electric potential at the interface between a solid surface and a surrounding liquid medium. It is a crucial parameter for understanding the stability and behavior of colloidal particles. In this case, the Zeta potential was measured using a nanoparticle analyzer (HORIBA Nanopartica SZ-100). The nanofiller samples were mixed with distilled water, and the Zeta potential was calculated by the microprocessor unit of the instrument. Multiple measurements were taken, and the average of four measurements at 22.5 °C was considered for each data point.

Ultraviolet-Visible Spectroscopy (UV-Vis): UV-Vis spectroscopy involves measuring the absorption of ultraviolet and visible light by a sample. It provides information about the electronic transitions and optical properties of materials. In this case, UV-Vis spectra were analyzed using a Shimadzu UV-1800 spectrophotometer. The analysis was performed over a range of wavelengths from 450 to 200 nm, using both tungsten

and deuterium lamps as light sources. The UV-Vis spectrum provides information about the absorbance and transmittance characteristics of the samples in this specific wavelength range.

Those characterization techniques enable the researchers to gain insights into the morphology, structure, elemental composition, crystallography, and chemical properties of the provided nanofillers or composite.

3.3 Performance tests setup

3.3.1 Measurement of responses of flexible strain sensors to ultrasonic waves

The experimental setup employed to investigate the sensitivities of nanocomposite sensors to micro-vibrations generated by ultrasonic waves is depicted in **Fig. 3.1**. Each experiment involved affixing a nanocomposite sensor and a piezoelectric wafer onto a 1 mm thick glass fibre reinforced polymer (GFRP) panel, with a separation distance of 150 mm between them. The nanocomposite sensor featured a pair of electrodes created using silver paste, and wires were connected to those electrodes. To generate the ultrasonic waves, a waveform generator (PXI-5412, National Instruments, USA) produced a 5-cycle Hanning-windowed sinusoidal toneburst. Prior to exciting the piezoelectric wafer, the signal was amplified using a linear amplifier (US-TXP-3, Ciprian, France). The resulting ultrasonic waves propagated along the GFRP panel and interacted with the nanocomposite sensor, inducing imperceptible micro-vibrations [213].

Those micro-vibrations caused variations in the sizes of the nanofillers within the sensor and the distances between adjacent nanofillers, resulting in minute changes in the electrical resistance of the sensor. An in-house bridge circuit/amplifier unit was used to convert the change in electrical resistance into an electrical voltage signal, which could be visualized on an oscilloscope (DSO 9064A, Agilent Technologies, Inc., USA). The home-made internal bridge circuit/amplifier unit connected to the nanocomposite sensor consisted of a voltage divider, a capacitor, and an amplifier.

During the ultrasound experiment, the resistance of the voltage divider needed to be adjusted to balance it with the baseline resistance of the nanocomposite sensor. To mitigate the effects of instrument noise and ambient noise from the surroundings, a Fourier transform-based bandpass filter was employed to eliminate noise from the received signals.

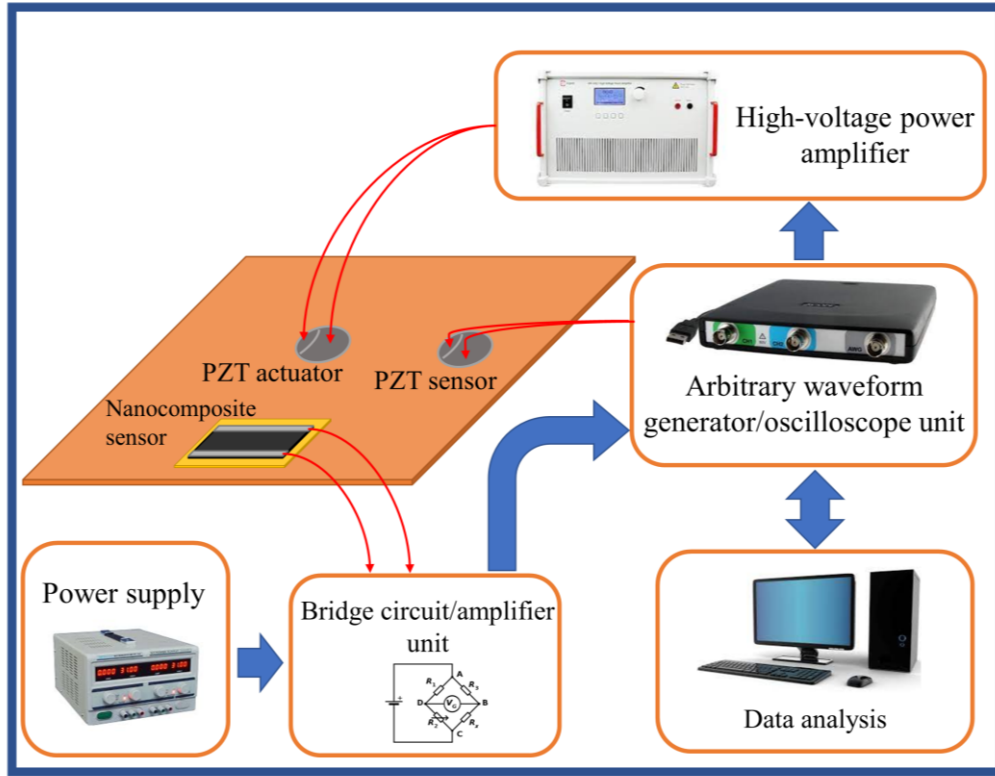


Figure 3.1. Schematic diagram of ultrasonic experimental setup.

The strain experienced by the strain sensors during the ultrasonic experiment in high frequency (more than 100 kHz) is characterized by an exceptionally low magnitude. This value can be determined using the following formula:

For each of the ultrasound-based vibration tests performed, the peak in-plane displacement (d) of the Lead Zirconium Titanate (PZT) actuator used is given by [214]

$$d(x) = \frac{V d_{31} a \sin(\gamma x)}{t(\gamma a \cos(\gamma a) + r \sin(\gamma a))}, \quad x = a$$

where V is the peak excitation voltage (100 V), d_{31} is a piezoelectric charge coefficient of the PZT actuator ($1.8 \times 10^{-10} \text{ C} \cdot \text{N}^{-1}$), a is the radius of the PZT actuator (0.0065 m),

t is the thickness of the PZT actuator (0.0005 m), r is the ratio between the stiffness of the GFRP panel used and that of the PZT actuator (158.52), and γ is the wavenumber of the S_0 Lamb wave mode in the PZT actuator (200 kHz: 431.32 m⁻¹, 250 kHz: 539.15 m⁻¹, 300 kHz: 646.98 m⁻¹). Therefore, the peak in-plane strain (ε) of the ultrasonic wave that was excited by the PZT actuator can be calculated by

$$\varepsilon = \frac{Vd_{31} \sin(\gamma a)}{t(\gamma a \cos(\gamma a) + r \sin(\gamma a))}$$

The applied strain is corresponding to the excitation frequency. For example, the peak in-plane strains of the ultrasonic waves induced in the vibration tests are found to be 0.0000239% (200 kHz), 0.0000215% (250 kHz) and 0.0000224% (300 kHz).

3.3.2 Measurement of responses of flexible strain sensors to static tensile strain

The experimental setup that utilized for conducting static tensile tests is illustrated in **Fig. 3.2**. To prepare the experimental sample, a strain sensor specimen with attached electrodes is affixed at the center of one side of a dog-bone-shaped aluminum alloy substrate. Simultaneously, at the corresponding position on the other side of the substrate, a strain gauge (BFLA-5-3-1LJB, Tokyo Sokki Kenkyujo Co., Ltd., Japan) is adhered.

During the tensile test, the resistance of the nanocomposite sensor specimen (R) and the strain measured by the strain gauge (ε) are monitored in real-time. The resistance is measured using a digital multimeter (DMM6500, Keithley Instruments, USA), while the strain is recorded by the universal testing machine (5982, Instron, USA) used for the experiment. Subsequently, the relative change in resistance of the nanocomposite sensor specimen, expressed as $(R-R_0)/R_0$ (where R_0 represents the initial resistance of the sensor specimen), is plotted against the strain measured by the strain gauge. The gradient of this plot corresponds to the GF of the nanocomposite sensor specimen. The gauge factor represents the sensitivity of the sensor specimen to strain. During the static

tensile experiment, the strain experienced by the strain sensors is found to be less than 1%.

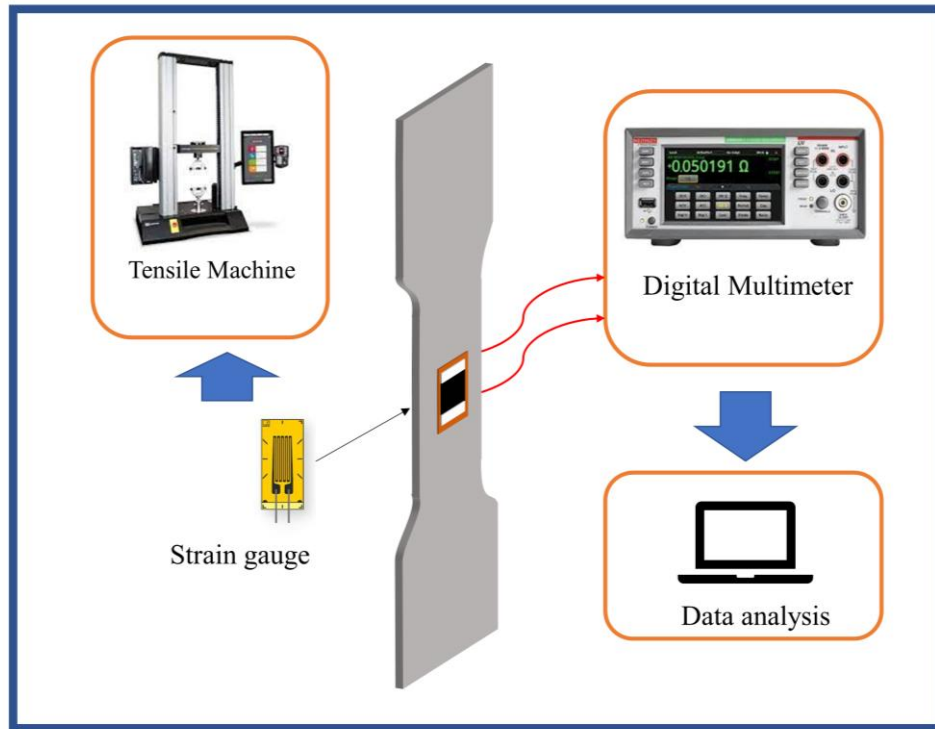


Figure 3.2. Schematic diagram of static tensile experimental setup.

3.3.3 Measurement of responses of flexible sensors to low-frequency vibration strain

The configuration of the platform is illustrated in **Fig. 3.3**. To begin, the prepared sensor devices are affixed at a distance of 10 cm from the end of a polymer reinforced epoxy panel. At the corresponding position on the other side of the panel, a commercial strain gauge (BFLA-5-3-1LJB, Tokyo Sokki Kenkyujo Co., Ltd., Japan) is adhered. During the experiment, a digital multimeter (DMM6500, Keithley Instruments, USA) is used to measure the resistance of both the prepared strain sensors and the commercial strain gauge. This allows for the relative changes in resistance of both the prepared strain sensors and the commercial strain gauge to be recorded under different frequencies. The other end of the panel is securely fixed to the vibration shaft of the shaker. An arbitrary waveform generator unit (Handyscope HS5, TiePie Engineering, Netherlands)

is connected to the shaker (Shiao, SA-JZ005) to generate cyclic vibrations within a low frequency range spanning from 0.25 Hz to 10 Hz.

During the vibration experiment, the strain experienced by the strain sensors can be evaluated by referencing the measurements obtained from the commercial strain gauge. Consider the example of the 1 Hz result: The GF for the commercial strain gauge is determined to be 2. The recorded relative resistance change for the commercial strain gauge is approximately 0.0033. By using the formula $GF = (\Delta R/R_0)/\epsilon$, where ΔR represents the resistance change, R_0 is the initial resistance, and ϵ denotes the strain. In this case, the calculated strain based on the commercial strain gauge measurements would be approximately 0.165%.

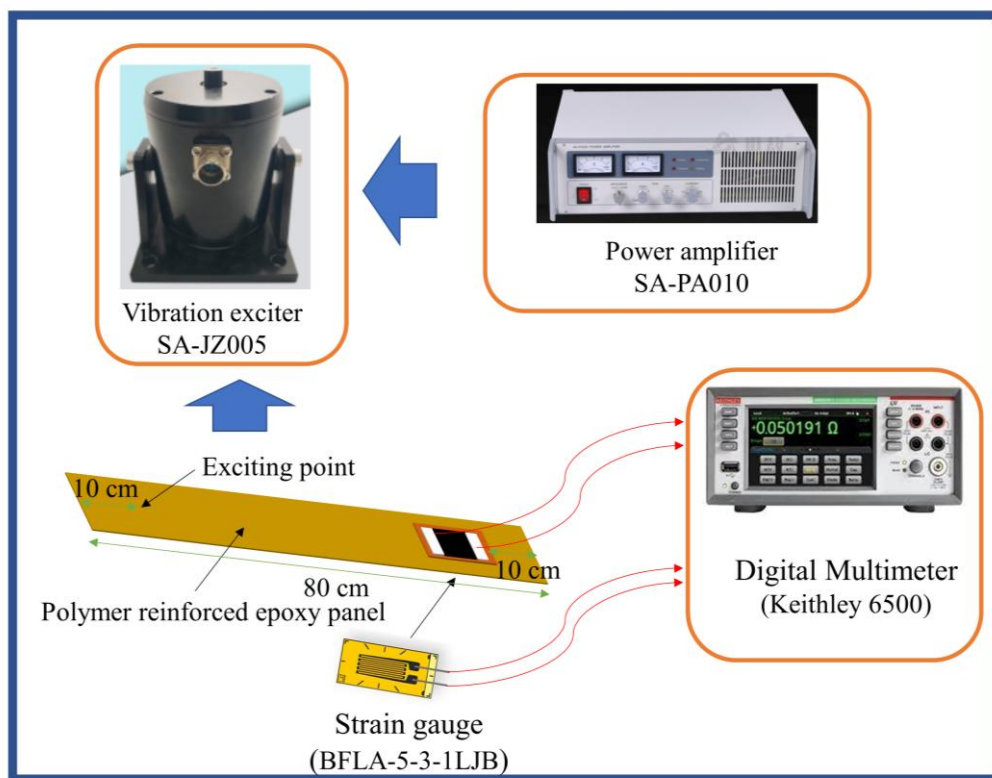


Figure 3.3. Schematic diagram of vibration experimental setup.

Chapter 4 A highly sensitive PDA@MWNT based nanocomposite sensor for acquiring extremely low deformation

4.1 Introduction

In this pivotal chapter, our research endeavours focus on the strategic utilization of surface modification techniques to amplify the sensitivity and efficacy of one-dimensional MWNTs in detecting subtle tensile signals and micro-scale ultrasonic vibrations. The foundation of this exploration lies in the recognition of the inherent capabilities of MWNTs to serve as exceptional sensors, particularly when appropriately tailored through surface modifications. By delving into the realm of nanomaterial engineering, we aim to harness the unique properties of MWNTs to enhance their responsiveness to minute mechanical stimuli, thereby revolutionizing their applicability in the realm of sensor technology.

The decision to employ surface modification strategies stems from the understanding that the surface characteristics of nanomaterials play a pivotal role in dictating their sensing capabilities [215]. Through deliberate alterations at the nanoscale level, we aspire to fine-tune the interactions between MWNTs and the surrounding environment, optimizing their ability to capture and interpret even the most nuanced tensile forces and ultrasonic signals. This research initiative not only seeks to push the boundaries of sensor sensitivity but also underscores the significance of tailored modifications in unlocking the full potential of MWNTs in micro-scale sensing applications. By elucidating the intricate interplay between surface modifications and sensor performance, our exploration aims to pave the way for cutting-edge advancements in sensor technology, offering unprecedented precision and reliability in detecting subtle mechanical cues.

Since Phillip B. Messersmith carried out the first synthesis of multifunctional PDA adhesive coating that was inspired by the mussel foot silk protein [216], PDA has attracted widespread research interest [217-221]. Related research has found that PDA can be deposited on inorganic substrates, including various types of nanomaterials, as uniform coating layers, and can be further functionalized. The polymerization and cross-linking reactions of PDA can be carried out slowly and spontaneously under weakly alkaline conditions (pH: 8.5). This phenomenon can be well explained by the equilibrium movement mechanism proposed by the predecessors, which embodies a series of reactions, including a step for forming an indole structure through a 3,4-dihydroxyphenylalanine cyclization reaction [222, 223].

PDA is a preferred choice as a coating material for CNTs to sensing low strain due to its unique properties and advantages. One of the key reasons for selecting PDA as a CNT coating nanolayer is its excellent adhesive properties [224, 225]. PDA exhibits strong adhesion to various surfaces, including CNTs, which improves the dispersion and stability of CNTs in composite materials. This prevents the agglomeration of CNTs and ensures their uniform distribution throughout the matrix, leading to enhanced mechanical and electrical properties of the nanocomposite [226, 227]. Another advantage of PDA is its chemical reactivity. PDA contains functional groups, such as amine, catechol, and quinone, which can undergo reactions with other compounds. This reactivity enables further functionalization of the PDA-coated CNTs, allowing for the attachment of additional molecules or polymers. Furthermore, PDA exhibits moderate electrical conductivity, which is beneficial when coating CNTs. The PDA coating acts as a conductive layer surrounding the CNTs, preserving their inherent electrical conductivity. This allows for efficient transfer of electrical signals within the nanocomposite, making PDA-coated CNTs suitable for applications such as conductive films, electrodes, or electronic devices [228, 229].

In term of detecting ultrasonic signals, the tunneling effect and piezoresistive effect are the key physical principles [230]. When exposed to dynamic strains from ultrasonic

waves, the conductive nanofillers within the sensor vibrate at a microscopic level. Those vibrations induce two microscopic phenomena: (i) dimensional changes in the nanofillers, altering their intrinsic electrical resistances through the piezoresistive effect, and (ii) fluctuations in the distances between adjacent nanofillers, leading to oscillations in tunneling resistances across the nanofillers via the tunneling effect. Those phenomena cause a microscopic change in the overall electrical resistance of the sensor, making the effective conversion of high-frequency micro-vibrations into resistance changes crucial for designing nanocomposite strain sensors to capture ultrasonic waves.

Carbon-based nanofillers have shown promise in capturing ultrasonic waves. Nanocomposite strain sensors exhibit higher sensitivities compared to conventional sensors, particularly when the nanofiller content is close to the percolation threshold [231, 232]. At this threshold, the nonlinear change in electrical resistance of the sensor is primarily influenced by the tunneling effect between adjacent nanofillers rather than the conductive network splitting [233, 234]. However, existing nanocomposite strain sensors still have limited sensitivities to ultrasonic waves, hindering their practical applications in this regime. This limitation can be attributed to factors such as poor dispersion of nanofillers due to agglomeration or unfavourable capacitive compatibility with polymer matrices, as well as the lack of effective tunneling nodes within the nanocomposite structures to reflect micro-vibrations as resistance changes.

The dimensionalities of carbon nanofillers used in nanocomposite strain sensors directly impact their electrical and mechanical properties [235]. Mixing nanofillers of different dimensionalities enhances the geometric contact between nanofillers at the microscale, leading to more significant changes in tunneling resistances under micro-vibrations. Hybrid nanocomposite materials combining CNTs and graphene flakes exhibit excellent properties, such as high stretchability, wide strain-dependent sensitivity, and linear current-voltage behavior [236]. The complex network formed by tangled and folded CNTs and graphene flakes inside the polymer matrix enhances the likelihood of changes in electrical resistance when external tensile strains are applied.

The stacking of hybrid nanofillers increases the number of tunneling nodes at the nanoscale, further improving the sensitivity to micro-vibrations generated by ultrasonic waves [236-238].

In this study, our focus centers on introducing a pioneering approach to heighten the sensitivity of nanocomposite strain sensors towards detecting low to micro-scale strains. Our novel methodology entails the creation of a unique nanostructure by applying a PDA coating onto the surfaces of MWNTs through an innovative in-situ DA self-polymerization process. The introduction of this PDA coating serves a dual purpose: mitigating MWNT entanglement and serving as a protective buffer layer between MWNTs and the PVDF matrix. This strategic intervention significantly enhances the receptiveness of strain sensors to low strains by tunneling effect, marking a significant advancement in sensor technology.

By amalgamating the PDA-coated MWNTs with single-layer graphene to generate a precursor, and subsequently blending this with PVDF, we establish a novel composite material. Through the fabrication process employing blade coating, we craft hybrid PDA@MWNT/graphene nanocomposite strain sensors. This innovative approach not only refines sensor performance but also underscores the importance of synergistic material interactions in sensor design. Moreover, the incorporation of both 1D MWNTs and 2D graphene nanofillers within the nanostructure amplifies the number of tunneling nodes, thereby elevating the sensor's responsiveness to ultrasonic vibrations. This pioneering work not only showcases the potential for enhanced sensor sensitivity but also underscores the transformative impact of nanoparticle engineering on sensor design and functionality.

4.2 Experimental

4.2.1. Synthesis of PDA@MWNTs

0.06 g - 0.15 g of DA was dispersed in 30 mL of Tris Hydroxymethyl Aminomethane Hydrochloride (Tris-HCl) buffer (pH: 8.5), and 0.1 g of MWNTs were then added. The

re- action was performed at 25 °C for 12 h. The product of the reaction was washed with distilled water 3 to 5 times, dried, immersed in 20 mL of n-hexane solution containing 1H,1H,2H,2H-per-fluorodecyltrichlorosilane (volume fraction: 0.025%), washed with absolute ethanol 3 times, and dried at 60 °C for 2 h. The solid PDA@MWNTs that were obtained were placed in a dry box overnight to remove excess water.

4.2.2. Fabrication of nanocomposite sensors

In this study, the fabrication process of the nanocomposite sensors involved the following steps: Carbon nanofillers and PVDF were combined in a 10 mL solution of dimethylformamide (DMF). The mixture was mechanically stirred at 30 °C for 4 hours to ensure thorough mixing. A polyimide (PI) film was placed on a table and flattened using a vacuum pump. A mold measuring 20 mm x 10 mm was positioned on the PI film. The nanocomposite solution was then dropped onto the PI film within the mold and scraped back and forth using a blade at a fixed height of 50 mm. Throughout this process, the temperature of the table was maintained at 25°C. After the volatile solvent in the nanocomposite solution evaporated, a nanocomposite sensor film with a thickness of 50 µm was obtained. The film was subsequently cut into individual sensors of the desired dimensions, resulting in uniform thicknesses.

Three sets of nanocomposite sensors were fabricated, all with a nanofiller content of 15 wt.%. The first set comprised a sensor made solely from uncoated MWNTs, as well as a couple of sensors created by coating MWNTs with PDA at mass fractions of 10% and 15% (referred to as PDA10%@MWNT and PDA15%@MWNT). The second set of sensors was formed by mixing graphene with uncoated MWNTs, PDA10%@MWNT, or PDA15%@MWNT at a mass ratio of 1:1 (labelled as Gra/MWNT, Gra/PDA10%@MWNT, and Gra/PDA15%@MWNT). The third set included a pure graphene sensor, as well as three other sensors created by mixing graphene with

PDA15%@MWNT at mass ratios of 1:2, 1:1, and 2:1. (labelled as $m_{\text{Gra}}/m_{\text{PDA15\%@MWNT}}=1:2$, $m_{\text{Gra}}/m_{\text{PDA15\%@MWNT}}=1:1$ and $m_{\text{Gra}}/m_{\text{PDA15\%@MWNT}}=2:1$).

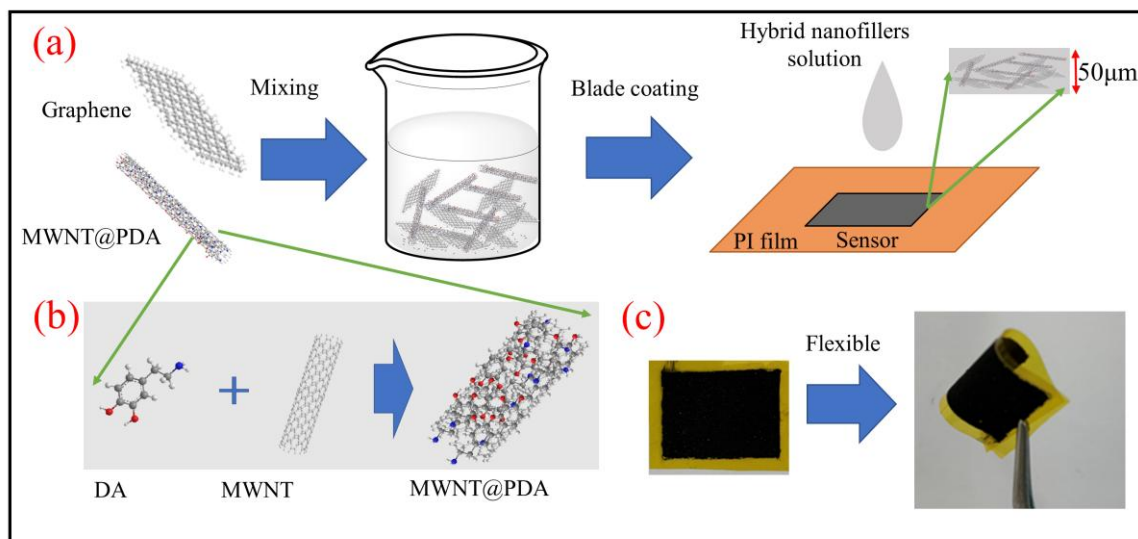


Figure 4.1. (a) The fabrication procedure of the proposed nanocomposite sensor with hybrid nanofillers. (b) In situ polymerization of DA on the surfaces of MWNTs. (c) A typical flexible nanocomposite sensor.

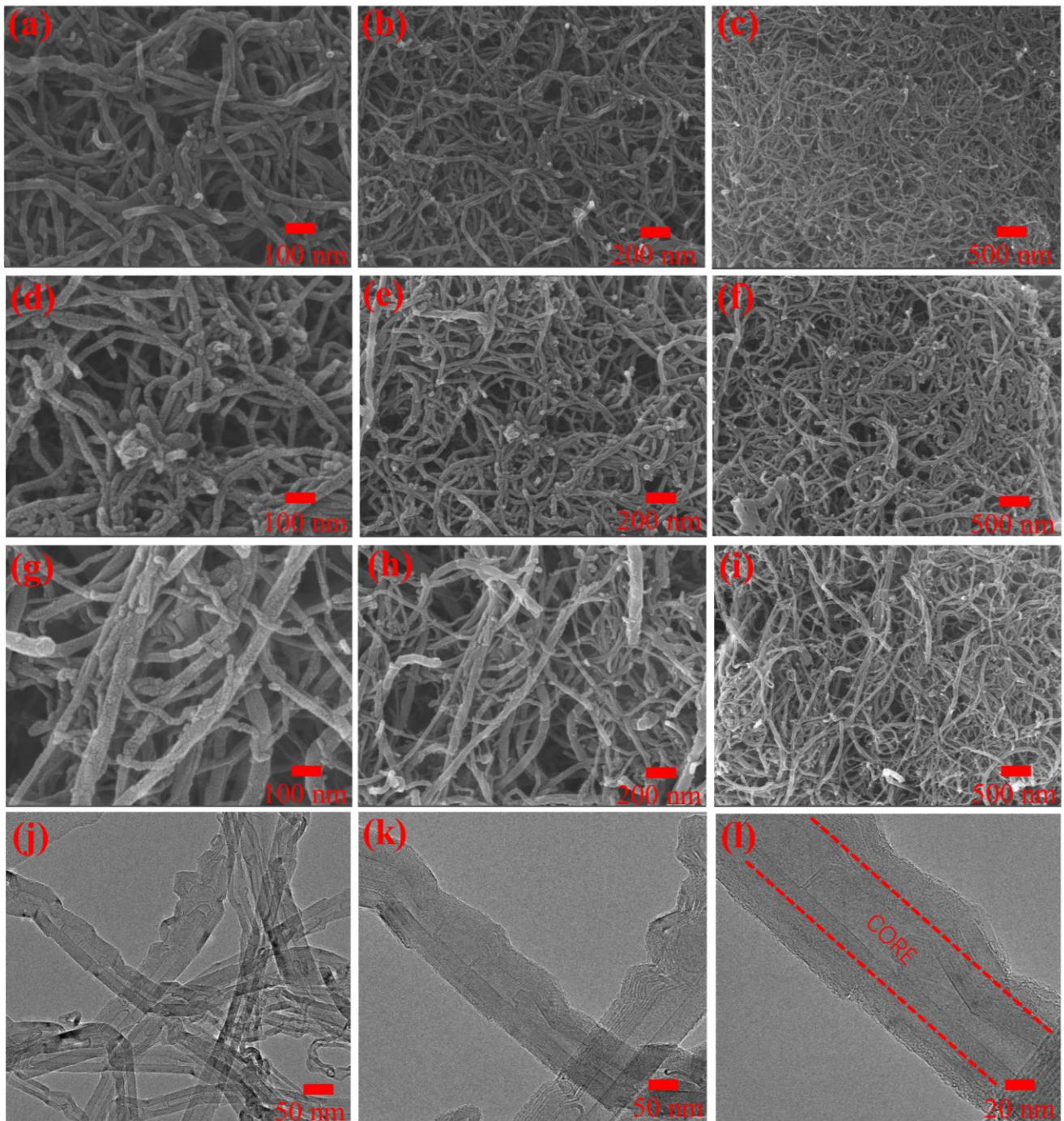
4.3 Results and discussion

4.3.1 Characterization of PDA@MWNT nanofillers

In this Chapter, we use different tests to characterize the PDA@MWNT nanofillers, such as SEM, XRD tests. The specific test methods have been demonstrated in Chapter 3, Section 2.

Figs. 4.2(a)-(c) show the SEM images of uncoated MWNTs. It can be seen that pure MWNTs exhibit a long rod-like shape with a smooth surface and a rigid crystal structure. The length of a MWNT is generally about 10s μm while its radius is between 300 nm and 500 nm. Normally MWNTs are prone to aggregation because there are few functional groups on their surfaces which can prevent aggregation from happening. Due to their rigid rod-like structures, MWNTs can only give rise to weak piezoresistive effect when subjected to external strains. In this study, our goal is to increase the rates

of change of the tunneling resistances of nanocomposite materials in response to micro-vibrations, as opposed to simply improving the conductive properties of the materials.



However, entangled MWNTs are not conducive to the occurrence of the tunneling effect. Therefore, nanocomposite sensors that are made of MWNTs generally possess weak sensitivities to ultrasonic signals.

Figure 4.2. The SEM images of (a)-(c) uncoated MWNTs, (d)-(f) PDA10%@MWNTs and (g)-(i) PDA15%@MWNTs at different magnifications; (j)-(l) The TEM images of PDA15%@MWNTs at different magnifications.

Due to the insolubility of MWNTs, the compatibility between MWNTs and polymer matrices is poor. Also, the content of functional groups on the surfaces of MWNTs is low. Those, together, would result in weak interfacial bonds between MWNTs and substrates in nanocomposite strain sensors, hindering the effective transmission of external strains to nanofillers. In this work, PDA was coated on MWNTs in order to improve the compatibility and the interfacial adhesion between MWNTs and substrates. Since the polymer chains of PDA are highly similar to polymer substrates, they would allow MWNTs to covalently graft to substrates, in turn improving the compatibility of MWNTs in substrates and enhancing the adhesion of MWNTs to substrates. Since synthesized PDA is insoluble in solvents, it would precipitate on the surfaces of MWNTs through physical binding. As seen from the **Fig. 4.2 (d)-(f)** and **Fig. 4.2 (g)-(i)**, after PDA coating had been done, the MWNTs became rough with their surfaces exhibiting a layered structure, and the diameters of the MWNTs increased by 10-20 nm. The amount of increase depended on the temperature of the reaction, the stirring speed, and the concentration of PDA. At a more microscopic scale, it can be seen from **Fig. 2 (j)-(l)** that PDA forms a layered crystalline structure covering the surface of MWNTs, and its thickness is stable between 10 nm and 20 nm. Because of the strong viscosity of PDA, MWNT and PDA crystal are closely combined. The PDA coating would function as buffer layers between the conductive nanofillers and the PVDF substrates, allowing high-frequency micro-vibrations that are induced by ultrasonic waves to appear as elastic vibrations as opposed to rigid vibrations.

In order to determine the crystal structures of PDA@MWNTs, XRD pattern were obtained. As observed from **Fig. 4.3(a)**, the addition of PDA did not give rise to new crystalline peaks, and this confirms that no residual PDA in PDA@MWNTs existed as a single phase. It further illustrates that strong physical bonds were formed between

PDA and MWNTs, due to the strong viscosity of PDA. In the XRD patterns, the strongest crystalline diffraction peaks appear at 26.6° , which corresponds to the plane (0 0 2), echoing with the rod-shaped graphitized MWNT crystals [239]. The spurious peaks, which arose from the entanglement between MWNTs, did not change with PDA content, indicating that the dispersion of MWNTs remained the same with the addition of PDA. It is inferable from the small number of impurity peaks and the stronger graphite peak that the purities and the degrees of perfection of the nanocomposite materials are high.

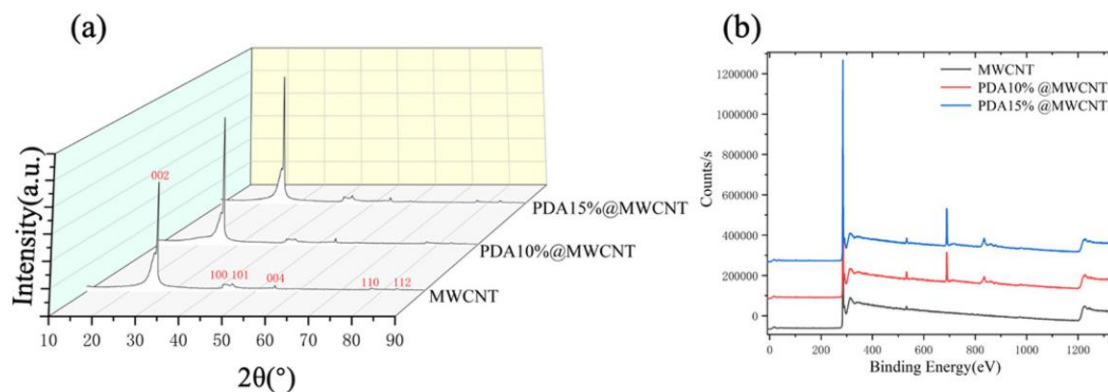


Figure 4.3. (a) The XRD patterns and (b) the XPS patterns of uncoated MWNTs and PDA@MWNTs.

Moreover, by using the JADE software, the crystallization information of the nanocomposite materials at 26.6° was obtained as shown in **Table 4.1**. As the amount of PDA used in the reaction was increased, the average grain size of PDA@MWNTs also increased from 32.6 nm to 44.4 nm, in line with the increase in the amplitude of the graphite peak in the XRD patterns. This means that PDA formed a perfect crystalline phase which existed on the surfaces of crystallized MWNTs. The increase in the grain size of PDA was attributed to the thickening of PDA coating. Together with the SEM images, we can conclude that relatively pure PDA@MWNTs were obtained and PDA coating was very well done. The effect of PDA coating was evident through

the difference between the ultrasonic signals that were acquired by nanocomposite sensors with uncoated MWNTs and with PDA@MWNTs.

Table 4.1. The crystallization information of uncoated MWNTs and PDA@MWNTs.

	2θ(°)	Crystal plane distance(nm)	Average grain size(nm)
Uncoated MWNT	26.668	3.3399	32.6
PDA10%@MWNT	26.607	3.3474	43.2
PDA15%@MWNT	26.645	3.3551	44.4

In order to obtain further information of the pad surface, surface analysis of the nanocomposite sensors was carried out using XPS. As shown in **Fig. 4.3(b)**, those additional peaks (697.5 eV for the coexistence of O(1s) and 846.3 eV the coexistence of N(1s)) for PDA@MWNTs samples indicate the existence of PDA[240]. The fact that those peaks did not change with PDA content demonstrates that the chemical environments of PDA10%@MWNT and PDA15%@MWNT were the same. The coexistence of C(1s) in is evidenced by a shoulder observed on the main peak at 285.0 eV[240]. With the addition of PDA, this peak becomes higher without shift, which means that there is a strong physical binding between PDA layer and MWNTs and the surface of MWNTs still retains the same chemical atmosphere.

4.3.2 Performances of PDA@MWNT nanocomposite sensors in low strain sensing

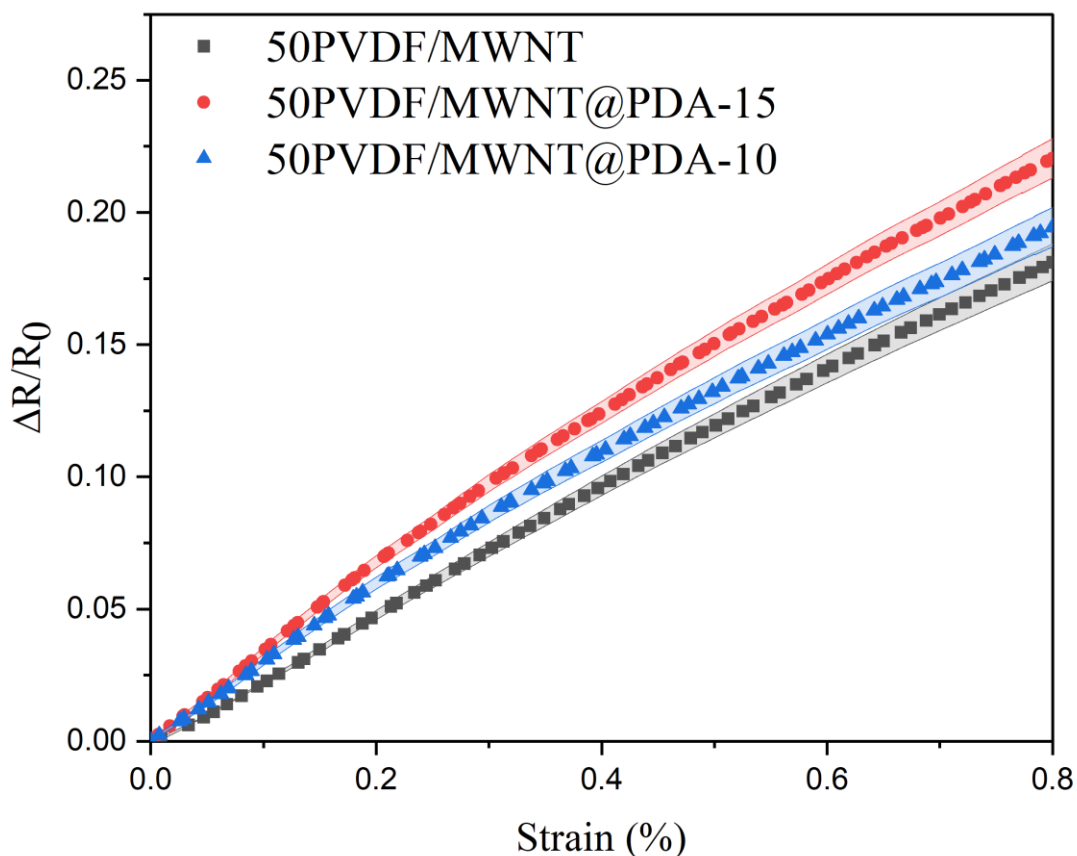


Figure 4.4. Relative resistance changes vs. strain curves of 50PVDF/MWNT@PDA with different PDA content and 50PVDF/MWNT sensor specimens (shaded areas: ± 1 standard deviation).

The specific experimental process and experimental setup for sensing static tensile tests can be found in **Chapter 3 Section 3.3.2**.

The PDA@MWCTs nanocomposite sensors that has been proposed exhibits the capability to detect resistance changes even under minor deformations ($\epsilon: <1\%$). As depicted in **Fig. 4.4**, all the sensor specimens tested display a reasonably linear relationship between resistance change and strain. It is noteworthy that the 50PVDF/MWNT@PDA sensor specimens (GF: 26.85) show higher sensitivity compared to the PVDF/MWNT sensor specimens (GF: 23.13). This enhanced sensitivity can be attributed to two main factors.

On one hand, the MWNT@PDA nanofillers are better dispersed within the composite, which is a result of the viscosity of the PDA. This improved dispersion ensures a more

uniform and effective response to strain, leading to more accurate resistance changes [223,228]. On the other hand, under minor deformations, the PDA nanolayers facilitate the formation of tunneling junctions. These junctions play a crucial role in dictating the resistance changes across adjacent nanofillers. The tunneling junctions allow for electron movement between nanofillers, even in the presence of an energy barrier [215]. This phenomenon, known as quantum tunneling, is particularly effective under low deformations [230] and contributes to the increased sensitivity of the 50PVDF/MWNT@PDA sensor specimens.

4.3.3 Performances of PDA@MWNT nanocomposite sensors in acquiring ultrasonic waves

The experimental process and experimental setup for sensing ultrasonic signals can be found in **Chapter 3 Section 3.3.1**.

The first diagram in **Fig. 4.5(a)** shows the excitation signal that was used, which is a 5-cycle Hanning-windowed sinusoidal toneburst with a central frequency of 100 kHz. It can be seen from the subsequent diagrams that the nanocomposite sensors are able to capture the two modes of ultrasonic waves that propagate in plate-like structures, i.e. the fundamental symmetric Lamb wave mode (denoted by S_0) and the fundamental anti-symmetric Lamb wave mode (denoted by A_0). It was discussed earlier that the thickness of the cladding layer on the surfaces of MWNTs increased with the amount of PDA that was added during the reaction. Here, it is observed that the amplitudes of ultrasonic signals also increased with PDA content. Compared to the sensor with uncoated MWNTs, an increase of 40% was obtained by the sensor with PDA15%@MWNT. This implies that PDA coating has a positive effect on the changes in electrical resistance of the nanocomposite sensors under high-frequency micro-vibrations. With the addition of nanofillers, the conductive network inside the material would be more filled by the contact points between nanofillers. Although the PDA coating on the surfaces of MWNTs would negatively affect electron transport, this elastic coating layer would

enable MWNTs to move closer to each other at the nanoscale but without making contact, leading to a stronger tunneling effect that is conducive to electron transport under micro-vibrations. At the same time, the highly viscous PDA would help the nanofillers to keep up with the movement of the PVDF substrates under high-frequency micro-vibrations, hence increasing of the amplitudes of the ultrasonic signals that were the outputs.

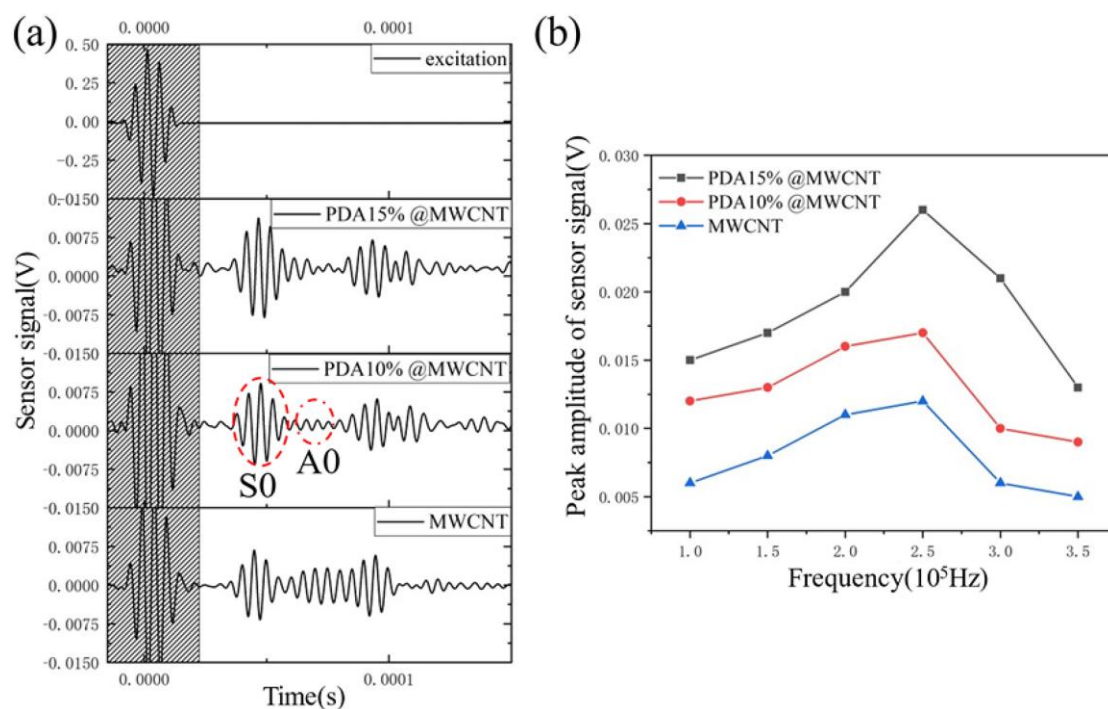


Figure 4.5. (a) The ultrasonic signals that were captured by nanocomposite sensors with uncoated MWNTs and PDA@MWNTs under an excitation frequency of 100 kHz (the shaded parts refer to either the excitation signal or cross-talks). (b) The peak amplitudes of the ultrasonic signals that were captured by nanocomposite sensors with uncoated MWNTs and PDA@MWNTs under various excitation frequencies.

Further, we observed the peak amplitudes of the ultrasonic signals that were acquired, at different excitation frequencies, by PDA@MWNT nanocomposite sensors with different PDA loadings, as shown in **Fig. 4.5(b)**. Since the resonance frequency of the piezoelectric wafer that was used to excite ultrasonic waves is at 250 kHz, the peak amplitudes of the ultrasonic signals that were acquired by each of the nanocomposite

sensors reach the maximum at 250 kHz. It is seen from the result that the nanocomposite sensor with a higher PDA coating level always demonstrates a higher sensitivity regardless of excitation frequency. This shows that the viscous PDA buffer layer is able to effectively transmit micro-vibrations from PVDF substrates to nanofillers over a very wide frequency range.

4.3.4 Characterization of Gra/PDA@MWNTs hybrid nanofillers

Generally speaking, due to their long aspect ratio and high electrical conductivity, CNTs exhibit satisfactory rates of change in electrical resistance under relatively large strains. However, when receiving the microscopic strains (between 10s to 100s of nanometers) that are generated by ultrasonic waves, although the sensitivity of MWNTs had been improved by PDA coating in this work, it still would not meet the requirement of real-world applications. This could be due to the high electron transport capacity of MWNTs, and the lack of effective tunneling nodes which could be led to by the entanglement and the poor dispersion of the nanofillers^{58,59}. Under micro-vibrations, the change in electrical resistance of a sensor would be small, leading to a weak electrical voltage signal. Based on previous research work and theoretical analysis⁶⁰, it was found that single-layer graphene has a better capability in receiving ultrasonic wave signals. In this work, a nanocomposite material with hybrid nanofillers is proposed. By stacking one-dimensional MWNTs and two-dimensional planar graphene, it would be possible to give rise to a larger number of effective tunneling nodes within a unit volume.

Fig. 4.6(a) shows the Raman spectra of nanocomposite strain sensors with hybrid nanofillers mixed at different mass ratios. Three peaks were observed, namely a D peak at $\sim 1355\text{ cm}^{-1}$, a G peak at $\sim 1586\text{ cm}^{-1}$ and a 2D peak at $\sim 2670\text{ cm}^{-1}$ [241]. The first peak indicates a structural defect due to structural edge effects, while the second peak indicates the tangential vibrational mode of carbon atoms in the graphite structure. For a nanocomposite sensor, a high intensity ratio between the D and the G peaks (I_D / I_G)

calculated from the Raman spectrum would correspond to a large number of inherent microstructural defects in the sensor, indicating a low local conductivity that is not conducive to electron movement. On one hand, an extremely low I_D / I_G would represent a high-density and saturated conductive network, in which case the tunneling effect between nanofillers would not be triggered when the sensor is subjected to external strains. It can be seen from the figure that with an increase in the mass fraction of graphene, the G peak rapidly increased, while the D peak remained at the original order of magnitude, meaning that the number of defects inside the material decreased and the remaining defects were largely attributed to the intrinsic defects of MWNTs. Due to the geometric structure and the steric hindrance effect, the hybrid nanofillers can be effectively stacked on each other in a limited space to form a dense conductive network. However, it would be difficult for pure rod-shaped MWNTs or flake graphene to form a perfect stacking.

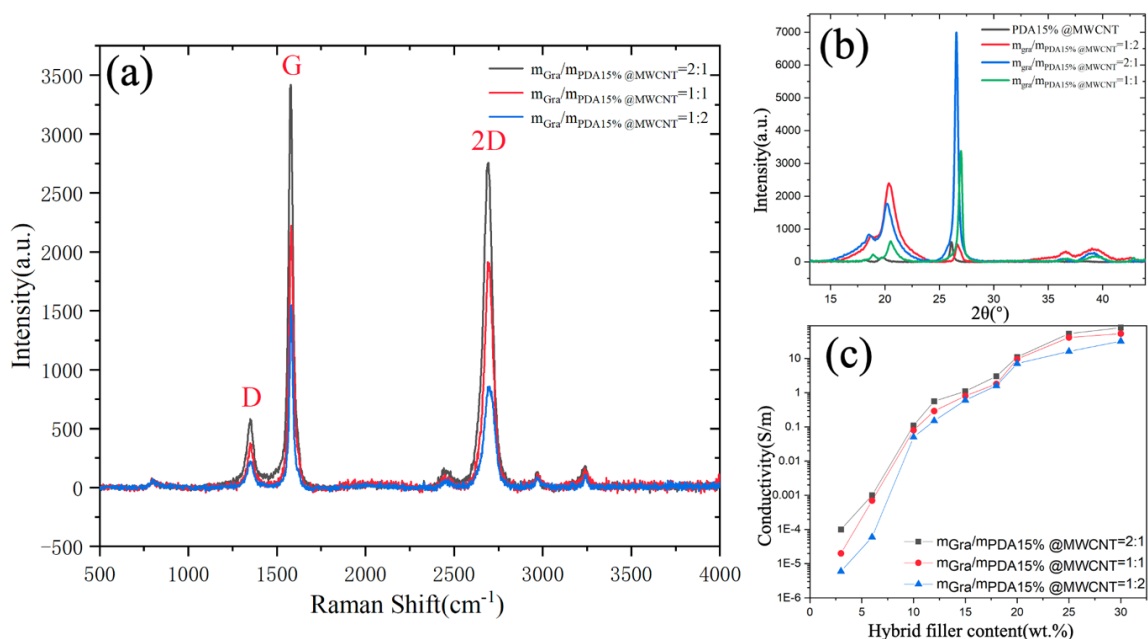


Figure 4.6. (a) The Raman spectra, (b) the XRD patterns and (c) the electrical conductivities of nanocomposite sensors with hybrid nanofillers mixed at different mass ratios.

The crystal morphologies of the sensors were further observed by XRD analysis. The XRD patterns, given in **Fig. 4.6(b)**, show that the diffraction peaks of the PVDF substrate at 2θ are 17.6° , 18.5° , 20.0° , and 26.6° , which correspond to the faces (1 0 0), (0 2 0), (1 0 0) and (0 2 1) of the α -phase crystal, respectively [245]. This is related to the absence of heating during the synthesis of the nanocomposite materials since the evaporation of the solvent at room temperature is conducive to the formation of α phase crystals of PVDF. From **Fig. 4.6(c)**, it can be seen that sensors with higher graphene contents possess higher electrical conductivities, but the difference is within the same order of magnitude. Also, the conductivities of the sensors, which contain hybrid nanofiller mixed at different ratios, followed the same trend, meaning that the nanocomposite structures of the sensors had similar conductive paths and the differences in conductivity mainly originated from the variations in the geometrical contact between the hybrid nanofillers. Moreover, it is worth mentioning that the sensors with a hybrid nanofiller content of 15 wt.%, which were used for the subsequent assessment of the performance of the proposed nanocomposite sensor in acquiring ultrasonic waves, have a conductivity close to 1 S/m. Based on previous experimental research⁶¹ and the characteristics of the inhouse bridge circuit / amplifier unit, it was found that sensor with a conductivity of 1 S/m would lead to the best performance in signal acquisition.

4.3.5 Performance of Gra/PDA@MWNT hybrid nanocomposite strain sensors in low strain sensing and acquiring ultrasonic waves

The specific experimental process and experimental setup for sensing static tensile tests can be found in **Chapter 3 Section 3.3.2**.

The Gra/PDA@MWNTs nanocomposite sensors that has been proposed exhibits the capability to detect resistance changes even under minor deformations (ϵ : $<1\%$). As depicted in **Fig. 4.7**, all the sensor specimens tested display a reasonably linear relationship between resistance change and strain. First, it is clear that the sensitivity of

Gra/MWNT hybrid nanocomposite strain sensors (GF: 82) is at least 10% lower than the Gra/PDA@MWNT hybrid nanocomposite strain sensors, which confirmed with the conclusion that the PDA coating is conducive to the dispersion of nanofillers inside the composite, resulting a higher GF. It is also noteworthy that the Gra/PDA15%MWNT sensor specimens (GF: 104) show higher sensitivity compared to the Gra/PDA10%MWNT sensor specimens (GF: 91).

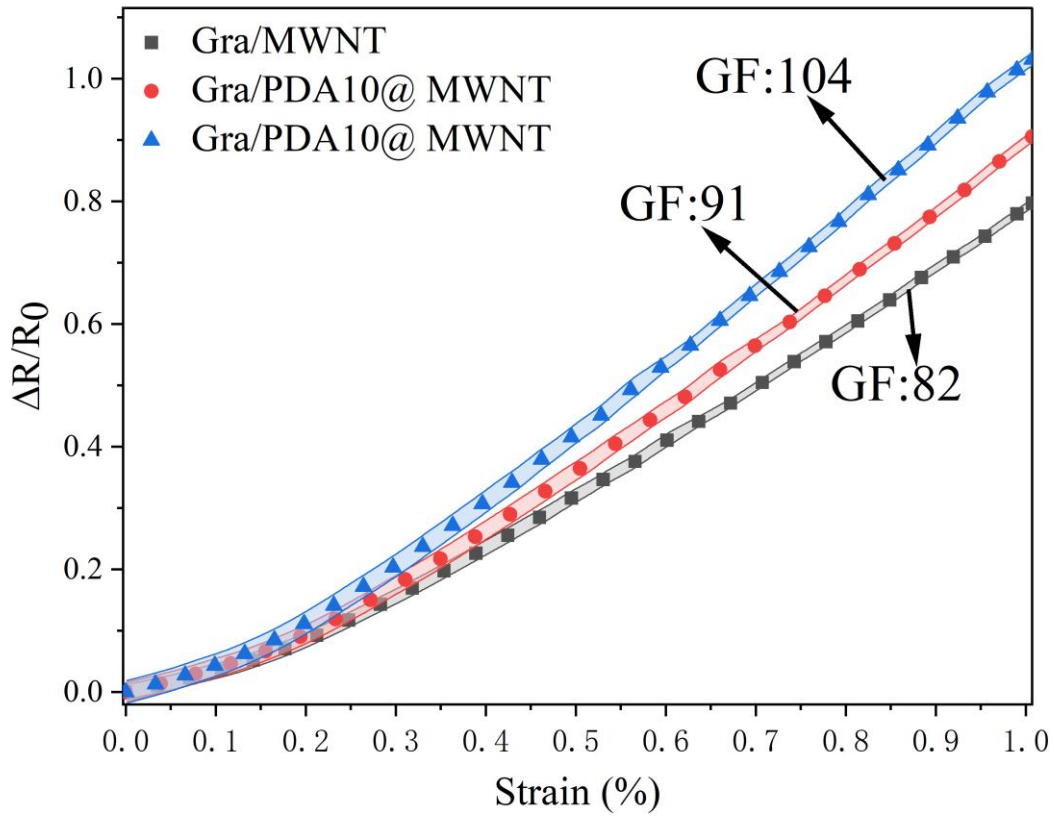


Figure 4.7. Relative resistance changes vs. strain curves of Gra/MWNT, Gra/PDA10%MWNT and Gra/PDA15%MWNT sensor specimens (shaded areas: ± 1 standard deviation).

The experimental process and experimental setup for sensing ultrasonic signals can be found in **Chapter 3 Section 3.3.1**.

Fig. 4.8(a) compares the ultrasonic signals that were acquired by nanocomposite sensors with hybrid nanofillers at different PDA coating levels. The excitation signal that was used is a 5-cycle Hanning-windowed sinusoidal toneburst with a central

frequency of 200 kHz. It can be seen from the signals that the S_0 and the A_0 Lamb wave modes that propagated along the GFRP panel were faithfully captured. The positive effect of increasing the amount of PDA on the sensitivity of sensors, which was demonstrated and discussed in the previous section, remained qualitatively the same. However, quantitatively the effect of increasing the amount of PDA was much more significant for sensors with hybrid nanofillers since the improvement that was brought about by using PDA15%@MWNTs in the hybrid nanofillers over using uncoated MWNTs is as high as 180%. Owing to the fact that the graphene contents of the three sensors are the same, it can be concluded that among the three types of contact modes of hybrid nanofillers, the stacking of graphene and MWNTs has the most significant impact on the number of effective tunneling nodes.

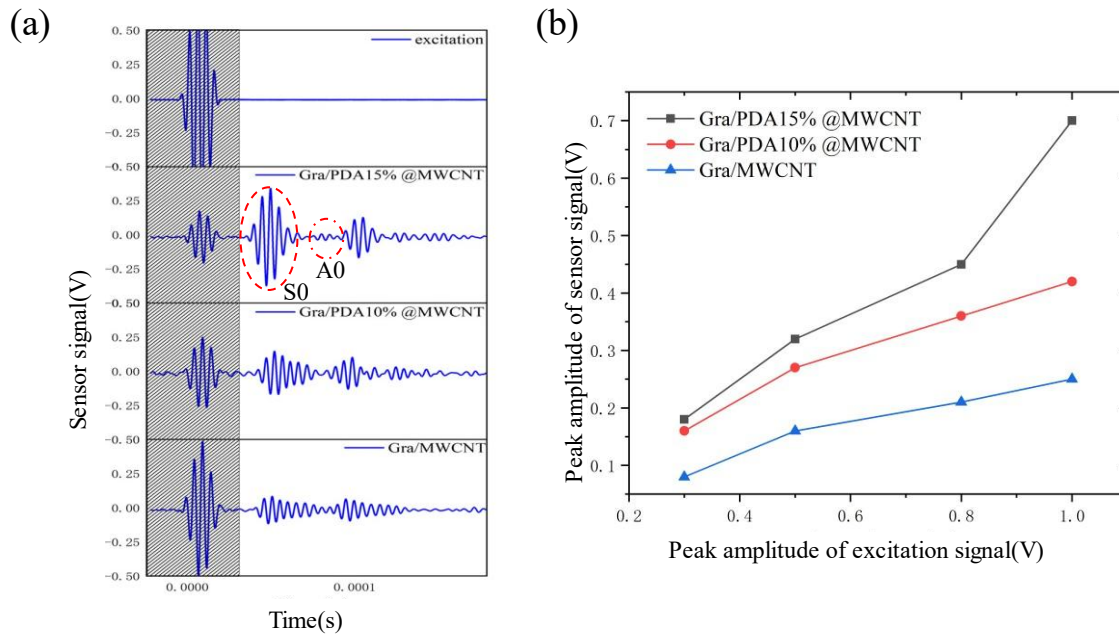


Figure 4.8. (a) The ultrasonic signals that were captured under an excitation frequency of 200 kHz by nanocomposite sensors with hybrid nanofillers with different PDA coating levels (the shaded parts refer to either the excitation signal or cross-talks). (b) The peak amplitudes of the ultrasonic signals that were acquired under various

excitation voltages by nanocomposite sensors with hybrid nanofillers with different PDA coating levels.

In order to further evaluate the sensitivity of the nanocomposite sensors with hybrid nanofillers to ultrasonic waves, 5-cycle Hanning-windowed sinusoidal tonebursts with a central frequency of 200 kHz but different peak voltages were used to excite ultrasonic waves. As the peak excitation voltage was increased from 0.2 V to 1 V, the ultrasonic signals that were acquired became stronger, as shown in **Fig. 4.9**. **Fig. 4.8(b)** depicts the linear trends between the peak excitation voltages and the peak amplitudes of the ultrasonic signals that were acquired, proving that the proposed nanocomposite sensor is highly sensitive to ultrasonic waves, capable of responding quantitatively to ultra-weak micro-vibrations. In addition, the slopes for sensors with higher levels of PDA coating are larger, meaning that the addition of PDA increases the sensitivities of sensors to ultrasonic waves. It further illustrates that the high sensitivity of the nanocomposite sensors with hybrid nanofillers was not just derived from graphene, which is known to be more sensitive than MWNTs, but also the morphology and the structure of PDA@MWNTs.

In order to illustrate the effect of graphene on the sensitivity of nanocomposite sensors with hybrid nanofillers, the ultrasonic waves that were acquired by nanocomposite sensors with hybrid nanofillers mixed at different ratios were examined, as shown in **Fig. 4.10(a)**. It can be seen that even the pure graphene nanocomposite sensor exhibits a far more superior sensitivity than the sensor that was made from uncoated MWNTs. On the other hand, the sensitivity of the nanocomposite sensors with is on par with that of the pure graphene sensor. As the mass fraction of graphene in hybrid nanofillers was increased from 33% to 66%, the peak amplitude of the ultrasonic signals that were acquired by the sensors rose from 0.7 V to 1.5 V, exceeding the peak amplitude of the ultrasonic signal that was acquired by the pure graphene sensor. This shows that graphene plays an important role in determining the sensitivity the nanocomposite sensors with hybrid nanofillers.

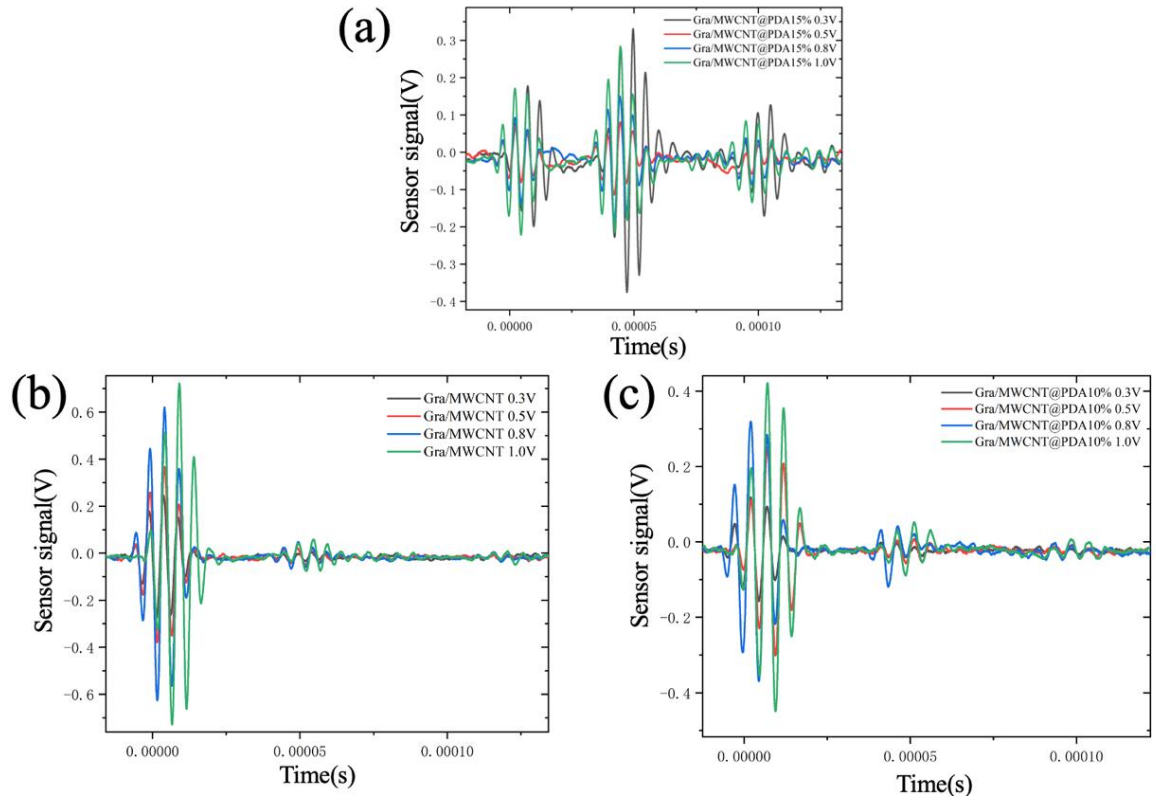


Figure 4.9. The raw ultrasonic signals that were captured under various excitation voltages by nanocomposite sensors with hybrid nanofillers. The first wave packet in each of the signals is cross-talk.

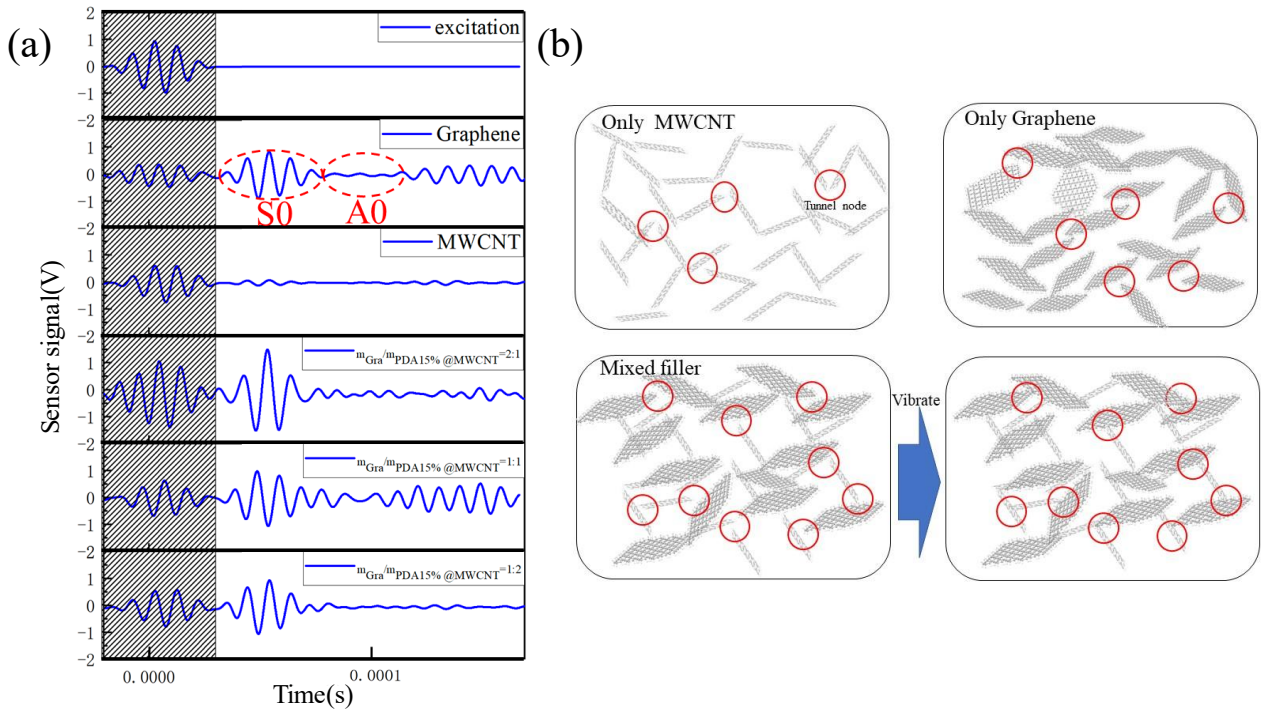


Figure 4.10. (a) The ultrasonic signals that were captured under an excitation frequency of 200kHz by a nanocomposite sensor that was made from uncoated MWNTs, a pure graphene nanocomposite sensor, and nanocomposite sensors with hybrid filler mixed at different mass ratios (the shaded parts refer to either the excitation signal or cross-talks). (b) The schematic model of the stacking of the nanofillers in different types of nanocomposite sensors. The red circles highlight the possible contact modes of the nanofillers. In the nanocomposite sensors with hybrid nanofillers, the three type of contact modes are CNTs-CNTs, CNTs-Gra and Gra-Gra.

Based on the experimental results and the analysis that have been presented, it is shown that a nanocomposite strain sensor with hybrid nanofillers, which achieves a higher sensitivity than pure graphene sensors to the micro-scale vibrations that are generated by ultrasonic waves, has been successfully developed. The proposed sensor, which utilizes a lower graphene content, benefits from the synergy between the two different types of nanofillers which are of different dimensionalities, as shown in **Fig. 4.10(b)**. It would be difficult for pure MWNT sensors or pure graphene sensors to gain sufficient

tight and effective tunneling nodes due to poor stacking and the steric hindrance effect which would be crucial to the acquisition of ultrasonic waves. Mixing nanofillers of two different dimensionalities can provide more ways for nanofillers to make contact with each other and increase the probability of forming tunneling nodes. Therefore, a higher sensitivity to ultrasonic waves was observed.

4.4 Conclusion

PDA coating was adopted and hybrid carbon nanofillers were used in this research to improve the sensitivity of nanocomposite strain sensors to sensing low tensile strain and ultrasonic signals. PDA@MWNTs were analysed by XRD and XPS, and it was shown that PDA was precipitated on the surfaces of the MWNTs as single-crystal layers with a thickness of 10s nm. Through ultrasonic measurements over a wide range of frequencies, it was found that the thickness of PDA layers has a positive effect on the sensitivities of sensors. An improvement of approximately 40% was achieved over uncoated MWNTs when the amount of PDA added was 15 wt.%. This indicates that PDA buffer layers positively influence tunneling processes because the tunneling effect is more likely to work only when the distances between conductive nanofillers are at the nanometre level. The static tensile results also confirm the same conclusion. Nanocomposite sensors that were made from hybrid carbon nanofillers acquired ultrasonic signals at even more pronounced levels, demonstrating a sensitivity that is at least one order of magnitude higher than that of MWNT based sensors. It was deduced that both types of nanofillers play an important role in improving the sensitivity of the proposed sensor, giving rise to enhanced geometrical contact between the nanofillers which intensified the tunneling effect. Also, as the mass fraction of graphene was increased from 33% to 66%, the sensitivity of the proposed sensor increased by approximately 120%. It surpasses that of pure graphene sensors, while a lower graphene content is used.

In summary, we put forward a new approach for optimizing the sensitivity of nanocomposite strain sensors to low strain sensing and the micro-vibrations that are generated by ultrasonic waves. The feasibility of the idea has been validated by a series of experiments that encompass both material characterizations and measurements of ultrasonic signals.

Chapter 5 A high-sensitivity thin-film MWNT@PDA-AgNP nanocomposite sensor for acquiring microscopic deformations

5.1 Introduction

The tunneling effect has been shown to be an important physical phenomenon which enables carbon nanomaterial-based strain sensors to capture low deformations [230, 242]. Under a micro-strain, the distances between the adjacent nanofillers in a sensor would change, resulting in changes in the tunneling resistances across the adjacent nanofillers and, hence, a microscopic change in the overall electrical resistance of the sensor. There are a number of possible reasons behind the unsatisfactory performance of nanocomposite sensors in capturing low deformations. Among those, poor dispersion, or agglomeration, of nanofillers inside a sensor would lead to a deficiency in the number of effective tunneling junctions [243-245]. Also, the relatively high potential energy between the nanofillers and the polymer matrix of the sensor would hinder the tunneling of electrons across the nanofillers, further reducing the effectiveness of the tunneling junctions [246, 247].

In previous works [248-250], MWNTs-based nanocomposite strain sensors have demonstrated the capability to capture low deformations, due to the high aspect ratio and the superior electron transport ability of MWNTs. Moreover, nanoscale PDA layers were coated on the surfaces of MWNTs to improve the dispersion of nanofillers and to function as buffer layers between nanofillers and polymer matrices, with a view to increase the number of effective tunneling junctions in a sensor [251]. However, the presence of PDA nanolayers in a sensor could have further lifted the electron transport barriers between the nanofillers and the polymer matrix [252, 253]. Therefore, in this work, our focus will be on increasing the conductivity of PDA nanolayers in order to promote the tunneling of electrons across adjacent nanofillers.

Surface modification is considered to be an effective approach for offsetting for the high potential barriers between nanofillers and polymer matrices [254]. In particular, binding conductive nanoparticles onto the surfaces of nanofillers can improve the electron transport ability of the interfaces of nanofillers at the nanometers scale. Htwe et al. [255] fabricated a strain sensor by inkjet-printing a hybrid conductive ink, produced from graphene and AgNPs, on a polyvinyl alcohol substrate. The sensitivity of the hybrid sensor was shown to be higher than that of a sensor that is made from either graphene or AgNPs alone, up to 20% strain. Min et al. [256] printed a microscale porous conductive pattern, which consists of MWNTs and AgNPs, on a polydimethylsiloxane substrate. They fabricate a strain sensor that can achieve a high sensitivity (gauge factor: 58.7) under a large deformation (strain: 74%).

In view of the outstanding electron transport ability of silver nanoparticles [257-259] and the reduction ability of PDA [252-254, 260, 261], there exists the possibility of immobilizing silver nanoparticles onto the PDA nanolayers of the previously reported MWNT@PDA core-shell nanostructures [251], which have been shown to exhibit a superior dispersion than pure MWNTs. The silver nanoparticles would take the role of lowering the electron transport barriers of the PDA nanolayers, rendering the tunneling effect more probable under micro-strains. It is expected that the proposed MWNT@(PDA/Ag) core-shell nanostructure would demonstrate an enhanced sensitivity to low deformations.

In this work, PDA nanolayers that are coated on the surfaces of MWNTs were used as versatile platforms for secondary reactions, during which silver ions were reduced to AgNPs and AgNPs were compounded with the PDA nanolayers in the first time for preparing strain sensors. The quantity of AgNPs in a PDA nanolayer could be varied by adjusting the concentration of the silver nitrate solution used in the reduction process. The nanofillers synthesized, which possess a MWNT@(PDA/Ag) core-shell nanostructure, were mixed with PVDF matrix. Flexible strain sensor specimens were then fabricated by blade coating the nanocomposite mixture on PI films. The specimens

were attached on different types of substrates, and their responses to different kinds of real-world low deformations were acquired. Through a series of material characterizations and performance testing experiments, the influences of AgNPs on the sensitivities of the new nanocomposite sensor to microscopic static deformations and microscopic high-frequency vibrations were scrutinized. Moreover, the effect of AgNP content on the response of the new sensor to static deformations was explored by employing specimens with different thicknesses.

5.2 Experimental

Fig. 5.1(a)-(d) outlines the whole fabrication process of the proposed nanocomposite sensor.

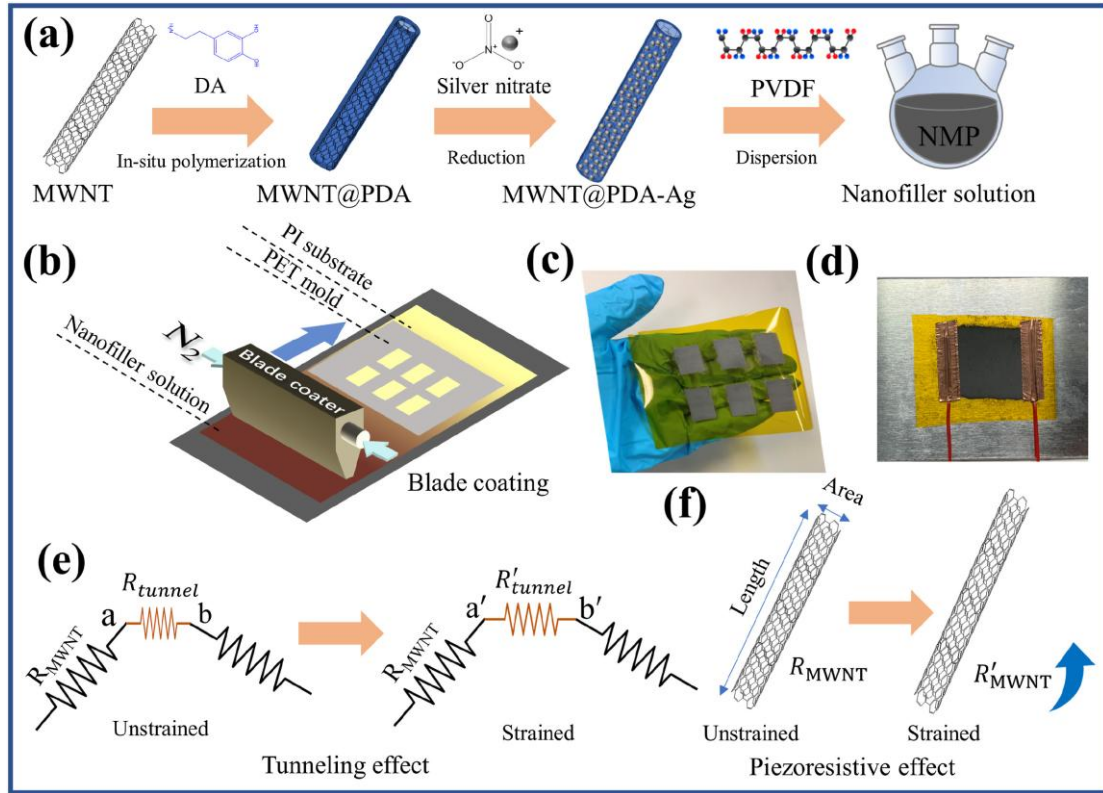


Figure 5.1. (a) Preparation of nanocomposite solutions with AgNP-modified PDA-coated MWNTs and PVDF. (b) Blade coating of the proposed nanocomposite sensor. (c) An actual batch of blade-coated sensor specimens. (d) A functional sensor specimen with electrodes connected. Schematics diagrams of (e) the tunneling effect and (f) the piezoresistive effect.

5.2.1. Synthesis of PDA-coated MWNTs

0.15 g of DA and 0.85 g of MWNTs were dispersed into 50 mL of Tri-HCl buffer solution (pH: 8.0–8.5). The self-polymerization reaction of DA was performed at 35 °C for 12 h. The product of the reaction was washed with deionized water 5 times, dried, and immersed in 20 mL of n-hexane solution that contains 1H,1H,2H,2H-perfluorodecyltrichlorosilane (volume fraction: 0.025%). The solution was filtered, and the solid product was washed with absolute ethanol 3 times and dried under vacuum at 60 °C for 2 h. The PDA-coated MWNT nanofillers obtained, hereinafter referred to as MWNT@PDA, were placed in a dry box overnight to remove excess solvent.

5.2.2. Immobilization of AgNPs on PDA-coated MWNTs

A silver/ammonia solution was prepared by dropping ammonia into a silver nitrate solution (concentration: 0.05–0.15 mol/L) until the solution had become transparent. Polyvinylpyrrolidone (mass fraction: 1%) was added to the silver/ammonia solution as a dispersant and stabilizer, and MWNTs@PDA nanofillers were put into the solution. The mixture was stirred for 12 h at 60 °C and centrifuged. The supernatant mixture was rinsed thoroughly with deionized water and dried under vacuum at 40 °C for 24 h. During this process, the catechol groups and the nitrogen-containing groups on the surfaces of PDA nanolayers would have attracted $\text{Ag}(\text{NH}_3)_2^+$ ions. The silver ions would then have been reduced to AgNPs due to the reduction ability of PDA. The resultant PDA-coated MWNT nanofillers with immobilized AgNPs are hereinafter referred to as MWNT@PDA-Ag.

Three groups of MWNT@PDA-Ag nanofillers, each with a distinct AgNP content, were prepared. The concentrations of the silver nitrate solutions used are 0.05 mol/L, 0.1 mol/L and 0.15 mol/L, respectively. The resultant nanofillers labelled as MWNT@PDA-Ag-0.5, MWNT@PDA-Ag-1.0 and MWNT@PDA-Ag-1.5.

5.2.3. Forming of nanocomposite sensors

Nanofillers (i.e., pure MWNTs, MWNT@PDA or MWNT@PDA-Ag) and PVDF were mixed at a mass ratio of 1:9 and put into 10 mL of DMF solution. To ensure thorough mixing, the nanocomposite solution was mechanically stirred for 1 h and ultrasonically dispersed for 0.5 h. A PI film was fixed on a platform and flattened by a vacuum pump. A polyethylene terephthalate (PET) mold with multiple 20 mm × 10 mm openings was placed on the PI film. The nanocomposite solution was dropped into the openings of the mold and scraped back and forth by a blade that was precisely positioned at a constant height. After the volatile solvent in the nanocomposite solution had evaporated, a batch of thin-film nanocomposite sensor specimens were obtained (**Fig. 5.1(c)**). The sensor specimens were cut out from the PI film. In order to measure the resistances of

the sensor specimens, silver paste was used to paint electrodes at the two ends of each sensor specimen, and a copper wire was attached on each electrode (**Fig. 5.1(d)**).

The nanocomposite sensor specimens fabricated were labelled as α PVDF/MWNT, α PVDF/MWNT@PDA or α PVDF/MWNT@PDA-Ag- β , where α represents the thickness of a sensor specimen and β represents the concentration of the silver nitrate solution used (if any). For instance, if a sensor specimen is 25 μ m thick and fabricated with a 0.05 mol/L silver nitrate solution, it would be labelled as 25PVDF/MWNT@PDA-Ag-0.5. The variation in thickness was achieved by using different PET molds.

It is worth mentioning that the strain-induced resistance change of the proposed sensor could be attributed to the tunneling effect and/or the piezoresistive effect. When a sensor specimen is deformed, the distances and, hence, the tunneling resistances between adjacent MWNTs would change (**Fig. 5.1(e)**). Meanwhile, the MWNTs themselves could also undergo deformations, causing their intrinsic resistances to change (**Fig. 5.1(f)**). As a result, the overall resistance of the sensor specimen would change.

5.3 Results and discussion

5.3.1 Characterization of AgNP-modified PDA-coated MWNTs

In this Chapter, we use different tests to characterize the AgNP-modified PDA-coated MWNTs nanofillers, such as TEM, XPS tests. The specific test methods have been demonstrated in Chapter 3, Section 2. **Fig. 5.2** and **Fig. 5.3** show the morphologies of the MWNT@PDA-Ag nanofillers at various stages of the fabrication process, captured using a TEM characterization. Pure MWNTs exhibit a rod-like strip shape and their radii vary from 10 nm to 20 nm (**Fig. 5.2(a)-(b)**). Under an alkaline condition, DA would have undergone self- polymerization to form PDA, and PDA then was deposited on the surfaces of MWNTs as colorless nanolayers (**Fig. 5.2(c)-(d)**). During the oxidative spontaneous polymerization of DA, the color of the solution slowly became

dark, indicating that DA was chemically cross- linking and the formation of PDA was proceeding along a similar pathway to that of melanin.

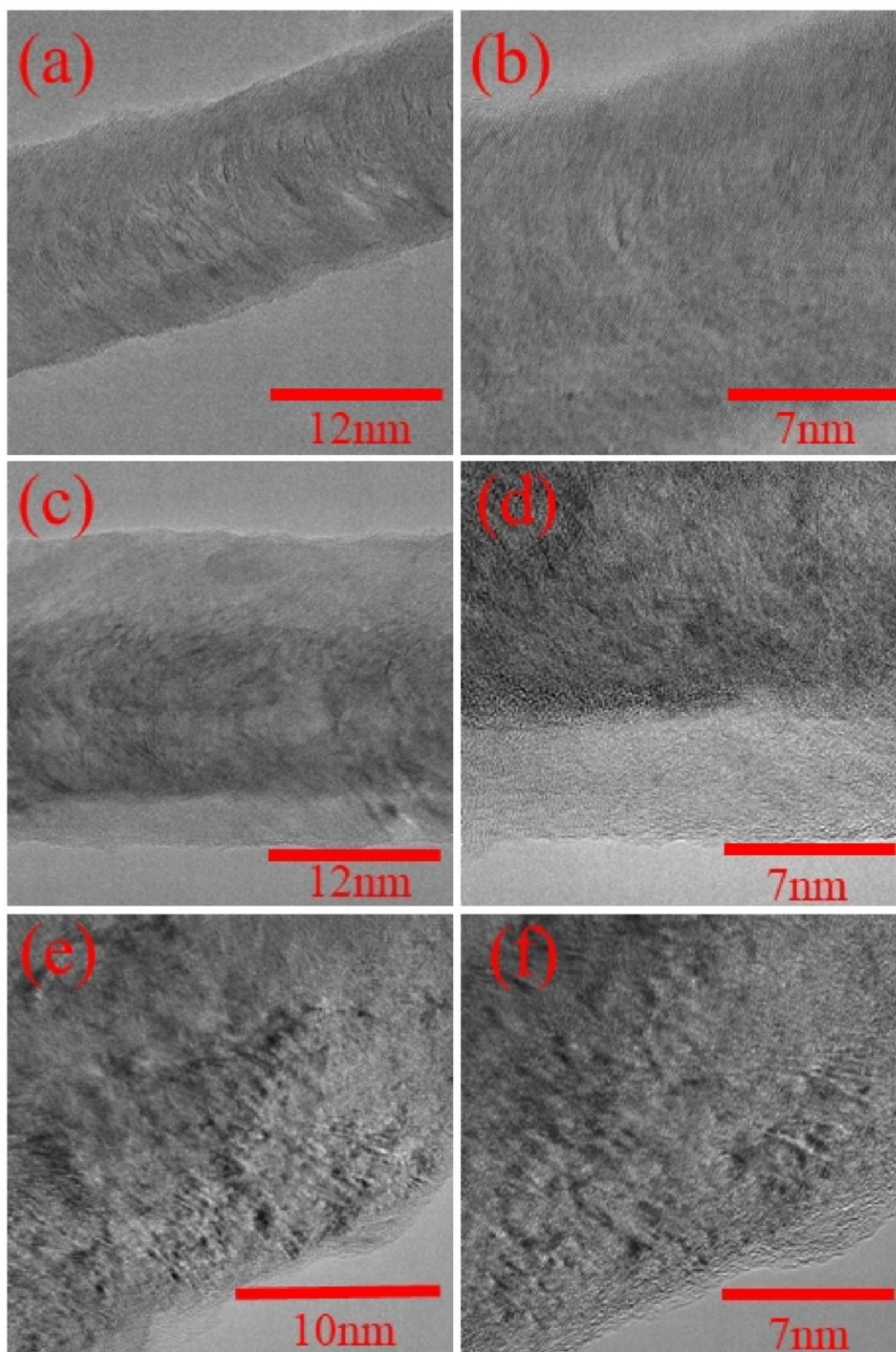


Figure 5.2. TEM images of (a)–(b) pure MWNTs, (c)–(d) the MWNT@PDA nanofillers, and (e)–(f) the MWNT@PDA-Ag-1.0 nanofillers.

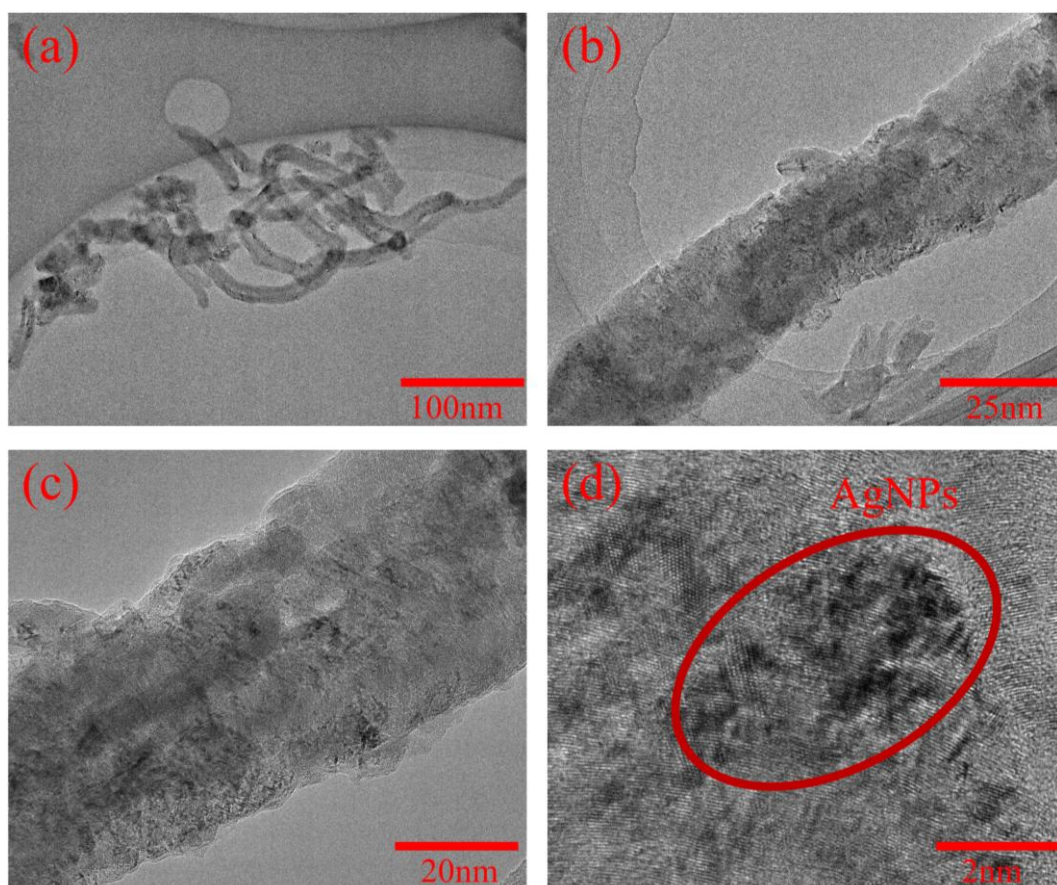


Figure 5.3. TEM images of the MWNT@PDA-Ag-1.5 nanofillers.

The possible mechanism of the oxidative self-polymerization of DA is demonstrated in **Fig. 5.4(a)** [216, 262, 263]. At first, DA was oxidized to DA-quinone, and DA-quinone then underwent intramolecular cyclization, through the Michael addition, to yield leucodopaminechrome. The oxidation and intramolecular rearrangement of leucodopaminechrome further produced 5,6-dihydroxyindole, and 5,6-dihydroxyindole was eventually polymerized to produce PDA. During the formation of PDA, the catechol groups retained the possibility to donate electrons to reduce silver ions into elemental silver.

Owing to their metal-binding ability, the catechol groups and the nitrogen-containing groups in PDA would have attracted $\text{Ag}(\text{NH}_3)_2^+$ ions. The silver ions would then have

been reduced to AgNPs according to the mechanism illustrated in **Fig. 5.4(b)**. The AgNPs were immobilized on PDA nanolayers, appearing as evenly distributed irregularly shaped black dots with diameters of a few nanometers (**Fig. 5.2(e)–(f) and 5.3**). The surfaces of the nanofillers became rougher, and the nanofillers seem as if they have lost their core-shell architecture.

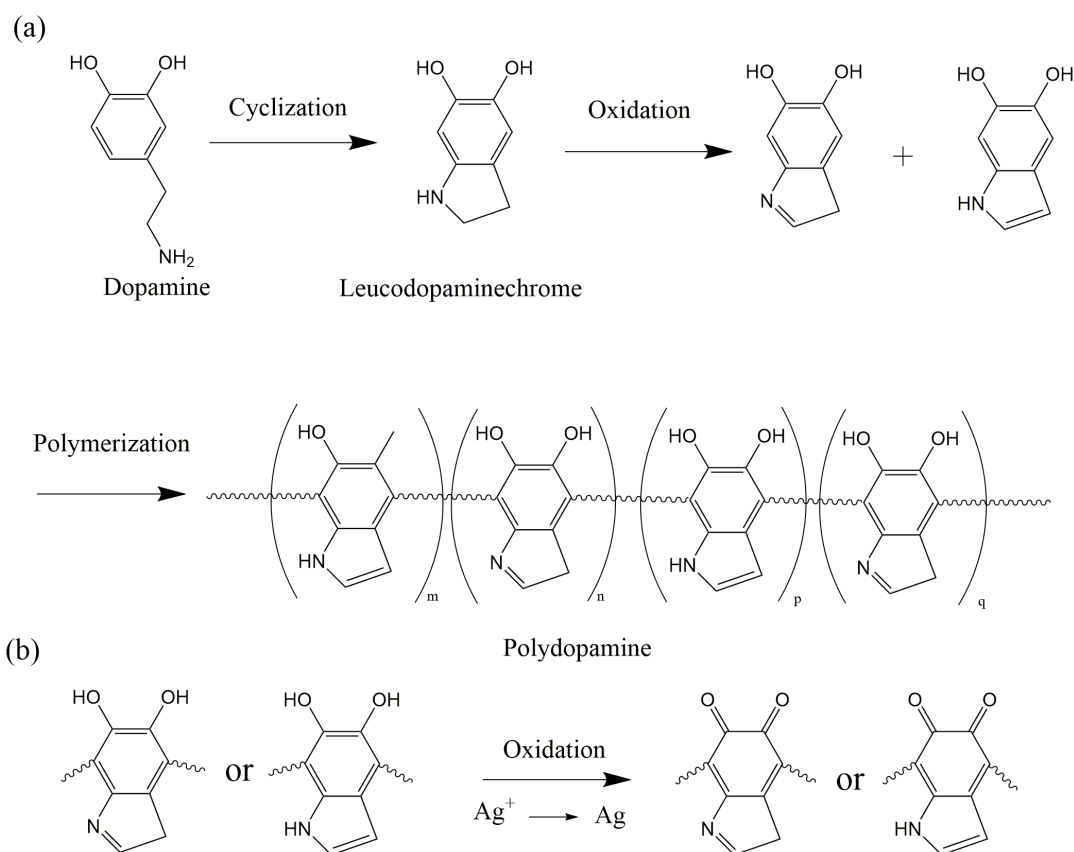


Figure 5.4. (a) Synthesis pathway of PDA. (b) Reduction of silver ions by PDA.

The MWNT@PDA-Ag-1.0 nanofillers were analyzed by a SEM-EDS characterization. As shown in **Fig. 5.5**, the observed oxygen-to-nitrogen ratio of the nanofillers, specifically at 6.2:3.8, demonstrates a notable correlation with the theoretical oxygen-to-nitrogen ratio of PDA at 16:7. This congruence serves as a strong indication affirming the presence of PDA nanolayers adhering to the MWNTs. Furthermore, the uniform and consistent distribution of AgNPs across the composite material closely mimicking the oxygen distribution pattern further underscores the successful

integration of AgNPs with the PDA matrix. This uniform dispersion of AgNPs alongside oxygen implies a thorough and effective compounding process, enhancing the overall structural integrity and potentially augmenting the desired electrical and mechanical properties of the PDA@MWNTs composite.

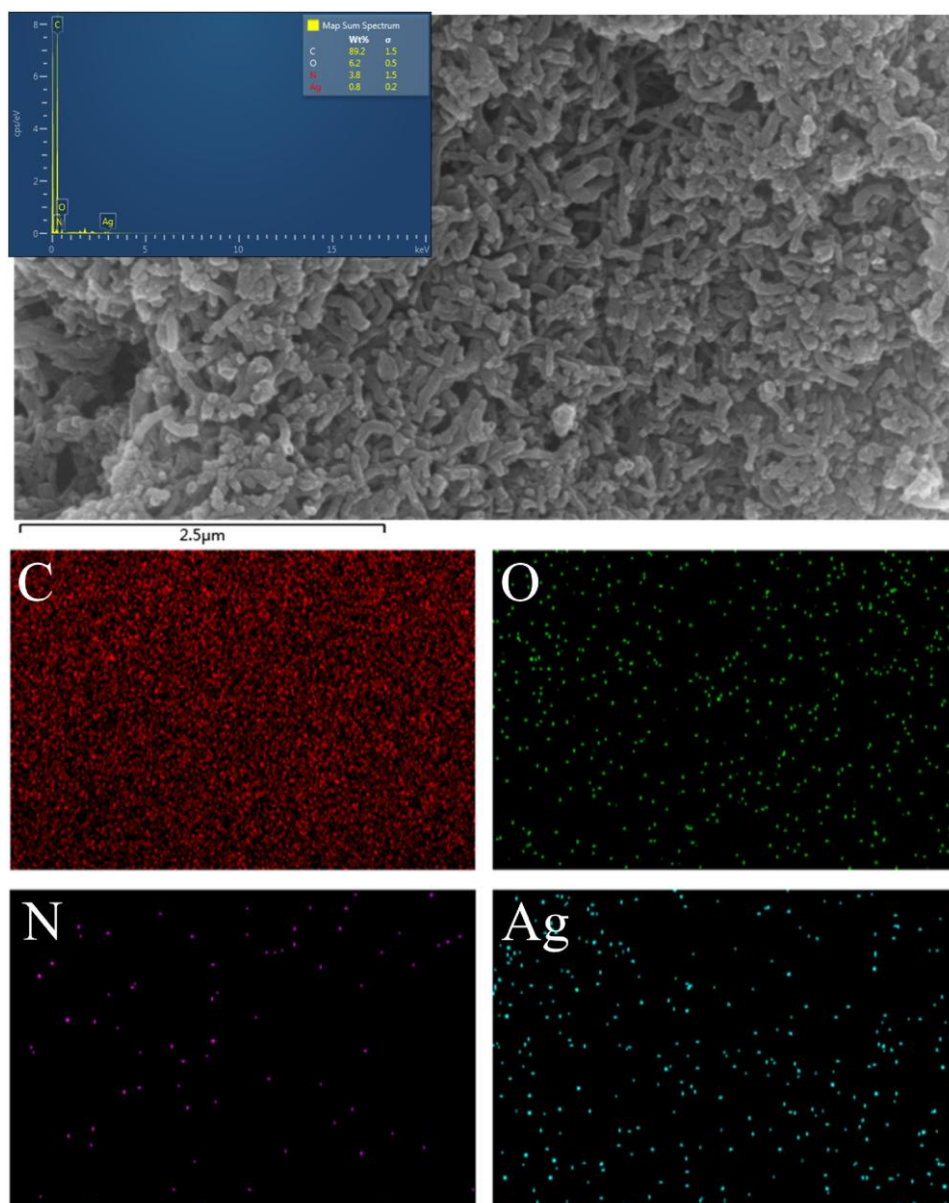


Figure 5.5. SEM image of the MWNT@PDA-Ag-1.0 nanofillers and the distributions of carbon, oxygen, nitrogen and AgNPs in the nanofillers.

To further verify the existence of AgNPs on PDA nanolayers, the XRD patterns of the MWNT@PDA-Ag-1.0 nanofillers at distinct stages of the fabrication process were acquired, as shown in **Fig. 5.6(a)**. The main peak of pure MWNTs occurs at around

26.6°, corresponding to the (0 0 2) face[243]. After MWNTs were coated with PDA nanolayers, the position of the main peak remained almost the same. The fact that no other major peaks appeared and only subpeaks emerged around the main peak.

The fact that no other major peaks appeared and only subpeaks emerged around the main peak indicates that the PDA nanolayers were tightly integrated with the MWNTs. The peaks of the MWNT@PDA-Ag nanofillers at 37 °, 44.5 °, 64.7° and 77° correspond to the (1 1 1), the (2 0 0), the (2 2 0) and the (3 1 1) face of silver crystals [264], respectively (**Fig. 5.6(a)**).

In order to clarify the chemical state of immobilized AgNPs, the MWNT@PDA-Ag-1.0 nanofillers were analyzed by XPS, as shown in **Fig. 5.6(b)**. The N1s peak at 403 eV binding energy (BE) is attributed to the nitrogen-containing groups in PDA, suggesting the existence of PDA. At around 370 eV BE, strong signals of silver are present, signifying the existence of silver. The energy spectrum of the Ag3d peak is contributed by both the Ag3d_{5/2} peak with 368.0 eV BE and the Ag3d_{3/2} peak with 374.0 eV BE. The fact that those two peaks are related to Ag (0) elements and that the peaks of ionic silver are not observed indicates that only zero-valence silver existed on PDA nanolayers [265].

The same conclusion can also be drawn from the Raman spectrum of a PVDF/MWNT@PDA-Ag-1.0 sensor specimen. In **Fig. 5.7**, only the peaks of MWNTs, i.e., a D peak at 1347 cm⁻¹, a G peak at 1587 cm⁻¹ and a 2D peak at 2689 cm⁻¹, can be found[245]. Since the peaks of ionic silver are not seen, it can be confirmed that only elemental silver was present.

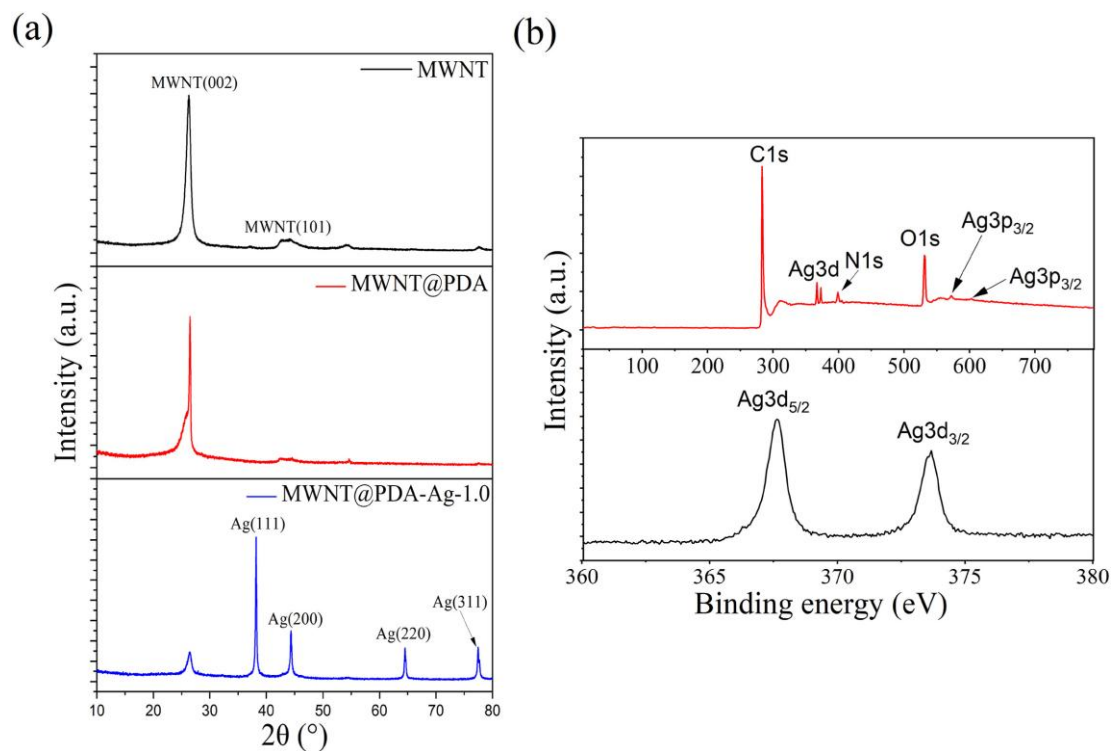


Figure 5.6. (a) XRD patterns of pure MWNTs, the MWNT@PDA nanofillers and the MWNT@PDA-Ag-1.0 nanofillers. (b) XPS spectrum of the MWNT@PDA-Ag-1.0 nanofillers.

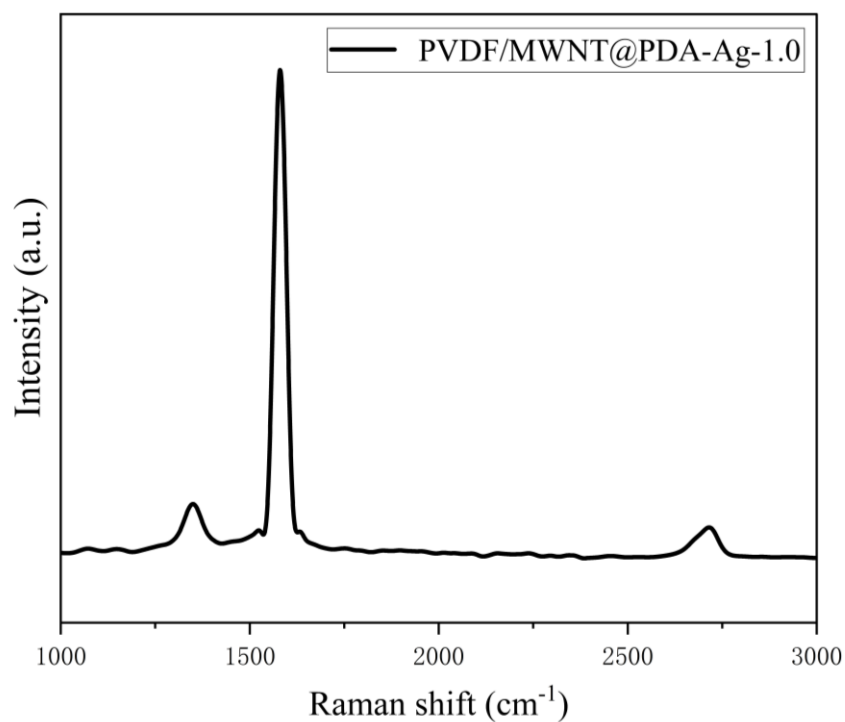


Figure 5.7. Raman spectrum of a PVDF/MWNT@PDA-Ag-1.0 sensor specimen.

Zeta potential is an electrostatic potential that exists remarkably close to the surface of a liquid-suspended particle. It is responsible for the repulsive forces among particles and can be used to evaluate the dispersion stability of nanoparticles. In this work, nanofillers were dispersed in water in order to measure their zeta potentials. Throughout a measurement process, the pH value of the solution would remain at 7. From **Fig. 5.8(a)** and **Table 5.1**, it is observed that the absolute zeta potentials of the PDA-coated nanofillers are higher than that of pure MWNTs. This improvement is attributed to the fact that the PDA nanolayers are rich in polar functional groups, which would have formed a large number of stable hydrogen bonds inside the solutions. A higher absolute zeta potential means that the surfaces of the nanofillers concerned have more charges and, hence, the nanofillers would have a higher tendency to repel each other. As a result, the nanofillers would be more stably dispersed inside a nanocomposite solution, and during blade coating, which is a liquid molding-based technique, the nanofillers would be more uniformly distributed. Furthermore, the conductivities of the nanofillers with immobilized AgNPs are 10% - 20% higher than that of the nanofillers with PDA nanolayers only. This is related to both the higher dispersion levels of the nanofillers with immobilized AgNPs, evident through their zeta potentials, and the high inherent conductivity of elemental silver.

The dispersion stability of the MWNT@PDA-Ag nanofillers is also demonstrated through a 24-h natural deposition process. The solutions used were prepared with a nanofiller content of 10 wt.%, and were mechanically stirred for 2 h and then ultrasonically dispersed for 0.5 h. As shown in **Fig. 5.9**, all of the nanofillers exhibited uniform dispersion within the first 6 h. After 24 h, deposition was clearly observed in the solution with pure MWNTs. The solutions with MWNT@PDA-Ag nanofillers, on the other hand, retained their initial dispersion states, proving the higher dispersion stability of the MWNT@PDA-Ag nanofillers in aqueous solutions.

To evaluate the difference between three types of MWNT@PDA-Ag nanofillers, each with a distinct AgNP content, UV–Vis spectra measurement was conducted. **Fig. 5.8(b)**

shows that all of the MWNT@PDA-Ag nanofillers exhibit a strong absorption peak near 428 nm which is corresponding to silver, but pure MWNTs and the MWNT@PDA nanofillers do not demonstrate any absorption behavior. This further proves that in the cases of the MWNT@PDA-Ag nanofillers, AgNPs were successfully immobilized on MWNTs. Moreover, the intensities of the absorption peaks of the MWNT@PDA-Ag nanofillers increase with the concentrations of the silver nitrate solutions used. This confirms that the use of a more concentrated silver nitrate solution would result in MWNT@PDA-Ag nanofillers with a higher AgNP content.

“In each PVDF monomer, owing to the presence of fluorine atoms, showcases a pronounced dipole moment, adding a layer of complexity to the material's behavior. Furthermore, at the molecular chain level, this effect is magnified, with each PVDF chain exhibiting a dipole moment oriented perpendicularly to its structural axis [271].

The process of crafting a nanocomposite solution, a critical step in the production of sensor specimens, involves a meticulous fusion of PVDF and a DMF solution. Through mechanical stirring, PVDF is gradually integrated into the DMF environment. Initially, as the stirring commences, the PVDF particles experience surface wetting—a phenomenon where DMF displaces any residual air clinging to the particle surfaces. Subsequently, the DMF solution infiltrates the interstitial spaces between the PVDF particles, initiating a process of particle swelling. This swelling effect is essential for the subsequent phases of the process[272]. Continual stirring action facilitates the dispersion of the swelled PVDF agglomerates, culminating in their complete dissolution within the DMF medium. This dissolution step is pivotal as it liberates the PVDF molecular chains from their lattice bonds, thereby enhancing their freedom of movement and mobility within the solution [272,273].

Consequently, in the context of the study at hand, the stage is set for the formation of predominantly α -phase PVDF crystals with inherent piezoresistive properties. To validate this hypothesis, an infrared characterization process is employed. Through this

analysis, distinct absorption peaks at 976 cm^{-1} and 796 cm^{-1} emerge as key identifiers [274], signaling the presence of the desired α -phase PVDF crystals within all examined nanocomposite sensor specimens[266]. This observation serves as a testament to the successful manipulation of PVDF within the DMF solution.

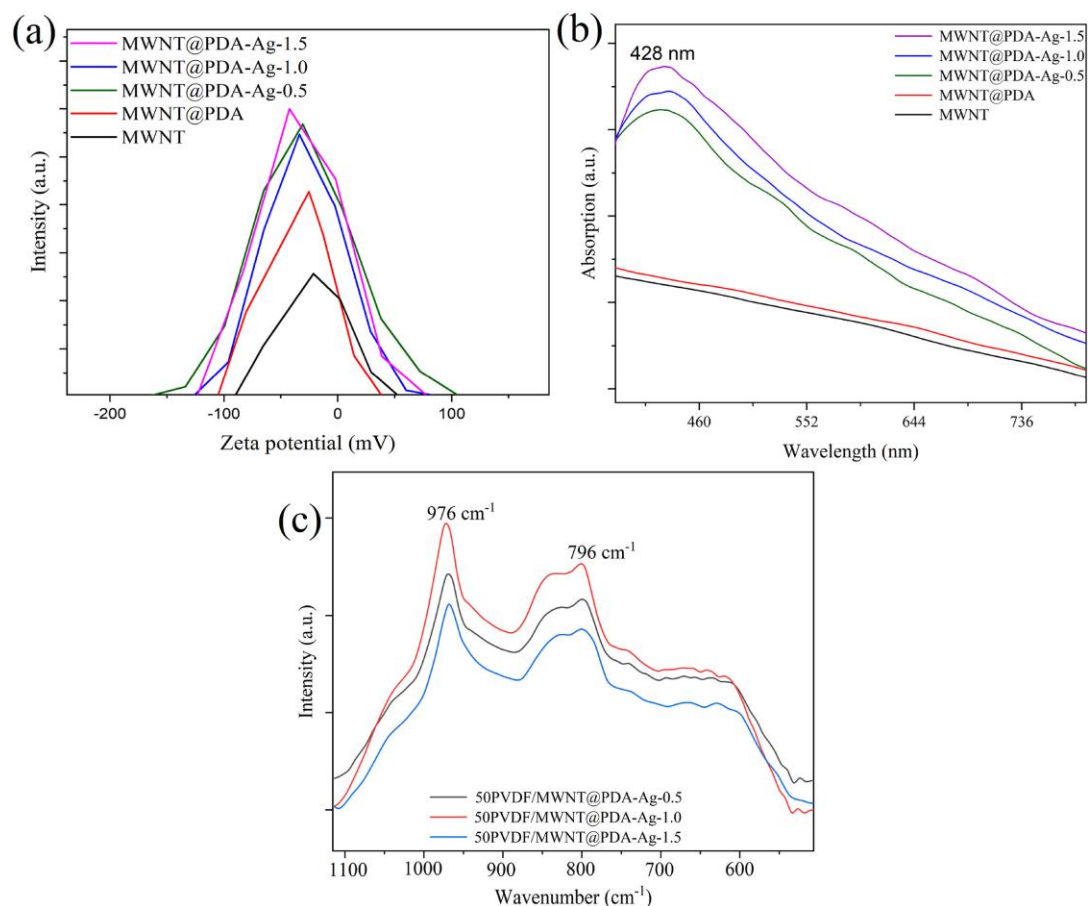


Figure 5.8. (a) Zeta potential distributions and (b) UV–Vis absorption spectra of pure MWNTs, the MWNT@PDA nanofillers and the MWNT@PDA-Ag nanofillers. (c) Infrared spectra of 50PVDF/MWNT@PDA-Ag sensor specimens.

Table 5.1. Zeta potential and conductivity of MWNT and MWNT@PDA-Ag fillers treated with different concentrations of silver nitrate

Zeta potential classes (mV)	Conductivity (mS/cm)
--------------------------------	-------------------------

MWNT	-10.04	0.00428
MWNT@PDA-Ag-0.5	-28.25	0.00507
MWNT@PDA-Ag-1	-33.95	0.00529
MWNT@PDA-Ag-1.5	-32.33	0.00538

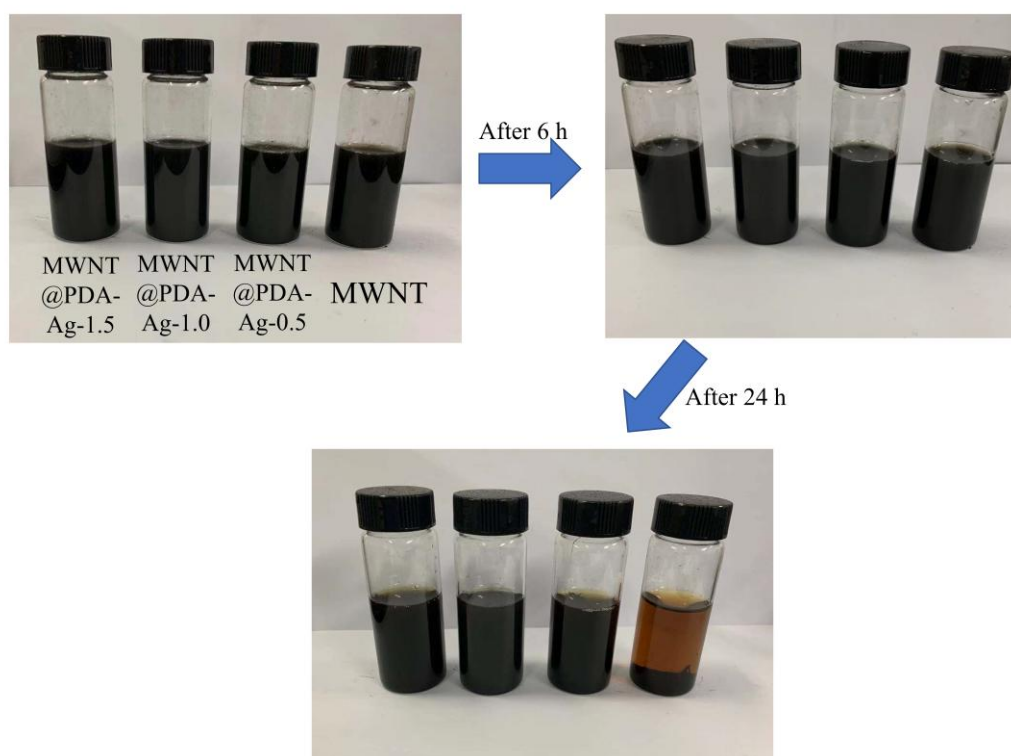


Figure 5.9. 24-hour natural deposition processes of pure MWNTs and the MWNT@PDA-Ag nanofillers with different AgNP contents.

5.3.2 Responses of AgNP-modified PDA-coated MWNTs nanocomposite sensors in sensing microscopic tensile deformations

The experimental setup for static low tensile tests is shown in **Fig. 5.10(a)** and the specific experimental process can be found in **Chapter 3 Section 3.3.2**.

The proposed nanocomposite sensor demonstrates the ability to capture resistance changes under low deformations (ϵ : <1%). As shown in **Fig. 5.10(b)**, all of the sensor specimens tested exhibit a reasonably linear resistance change vs. strain behaviour. It was noticed that the PVDF/MWNT@PDA sensor specimens (GF: 27.55) are more sensitive than the PVDF/MWNT sensor specimens (GF: 22.26). Considering the difference between the zeta potentials of the two types of nanofillers used and the difference between their conductivities (**Table 5.1**), the improvement in sensitivity is attributed to both the better dispersion of the MWNT@PDA nanofillers, which is the result of the viscosity of PDA. The fact that under low deformations, PDA nanolayers are conducive to the construction of tunneling junctions, which directly dictates the resistance changes across adjacent nanofillers. However, the improvement is still fairly limited, since the nonconductive PDA nanolayers on the MWNT@PDA nanofillers would not have electron transport, leading to high potential barriers between adjacent nanofillers.

The PVDF/MWNT@PDA-Ag-1.5 sensor specimens (GF: 37.87), on the other hand, are approximately 37% more sensitive than the PVDF/MWNT@PDA sensor specimens (GF: 27.55). This improvement is in line with the significant increase in nanofiller conductivity that was brought about by the AgNP-based surface modification. Immobilized AgNPs would have improved the electron transport ability of PDA nanolayers. As a result, under low deformations, the occurrence of the tunneling effect within the nanostructure of a sensor specimen would have been promoted.

Furthermore, as illustrated in **Fig. 5.10(c)**, a highly sensitive PVDF/ MWNT@PDA-Ag-1.5 sensor specimen shows a very stable voltage-current behaviour at constant strains. The gradients of the curves presented, which are effectively the resistances of the sensor specimen at the different strains applied, resemble the expected resistance change vs. strain behaviour of the proposed piezoresistive sensor, i.e., the resistance of a sensor specimen increases with tensile strain.

The tunneling resistance between two adjacent MWNTs can be represented by [267]

$$R_t = \frac{h^2 d}{\sqrt{2m\lambda} A e^2} \exp\left(\frac{4\pi d}{h} \sqrt{2m\lambda}\right) \quad 5.1$$

where A and d are the cross-sectional area and the distance of the tunneling junction, m and e are the mass and the quantum of charge, λ is the barrier height of the substrate, h is the Planck constant. On the other hand, the piezoresistivity of a single MWNT can be described by the heterogeneous fibrillar model proposed by Kaiser et al. [268, 269], i. e.,

$$R = \frac{L}{A} \exp\left(-\frac{\eta\omega_0}{K_B T}\right) \quad 5.2$$

where L and A are the effective length and the effective cross-sectional area of the MWNT, ω_0 is the electronic natural frequency, T is the temperature, K_B is the Boltzmann constant, and η is a constant that is related to the material properties of the MWNT. It can be inferred from equations (5.1) and (5.2) that the strain-induced resistance changes of a sensor specimen, underpinned by the tunneling effect, would present an exponential relationship with the distances between adjacent nano- fillers, whereas that underpinned by the piezoresistive effect would be linearly related to the deformations of the nanofillers.

By using PET molds with different thicknesses and set blade in different height, PVDF/MWNT@PDA-Ag-1.5 sensor specimens with different thicknesses were fabricated by blade coating method as shown in **Fig. 5.1**. As shown in **Fig. 5.10(d)**, the sensor specimens exhibit nearly the same linear resistance change vs. strain behaviour up to 0.6% strain. However, as the strain exceeds 0.6%, the resistance changes vs. strain behaviours of the sensor specimens begin to differ from each other. To be more specific, as the thicknesses of the sensor specimens increase from 25 μm to 150 μm , their GFs rise from 35.26 to 46.91. More importantly, the exponential levels of the resistance change vs. strain behaviours of the sensor specimens become greater. A possible explanation of this phenomenon is that within a small strain range, the piezoresistive

effect would also play an important role in determining the strain-induced resistance change of a sensor specimen, causing the resistance change vs. strain behaviours of the sensor specimen to appear relatively linear. At higher strains, the tunneling effect would dominate over the piezoresistive effect, adding exponentiality to the resistance change vs. strain behaviours of a sensor specimen. A thicker sensor specimen would naturally contain more nanofillers and, hence, more tunneling junctions, which would make the occurrence of electron tunneling more probable. Therefore, at higher strains, the resistance change vs. strain behaviours of a thicker sensor specimen would be more exponential than that of a thinner one.

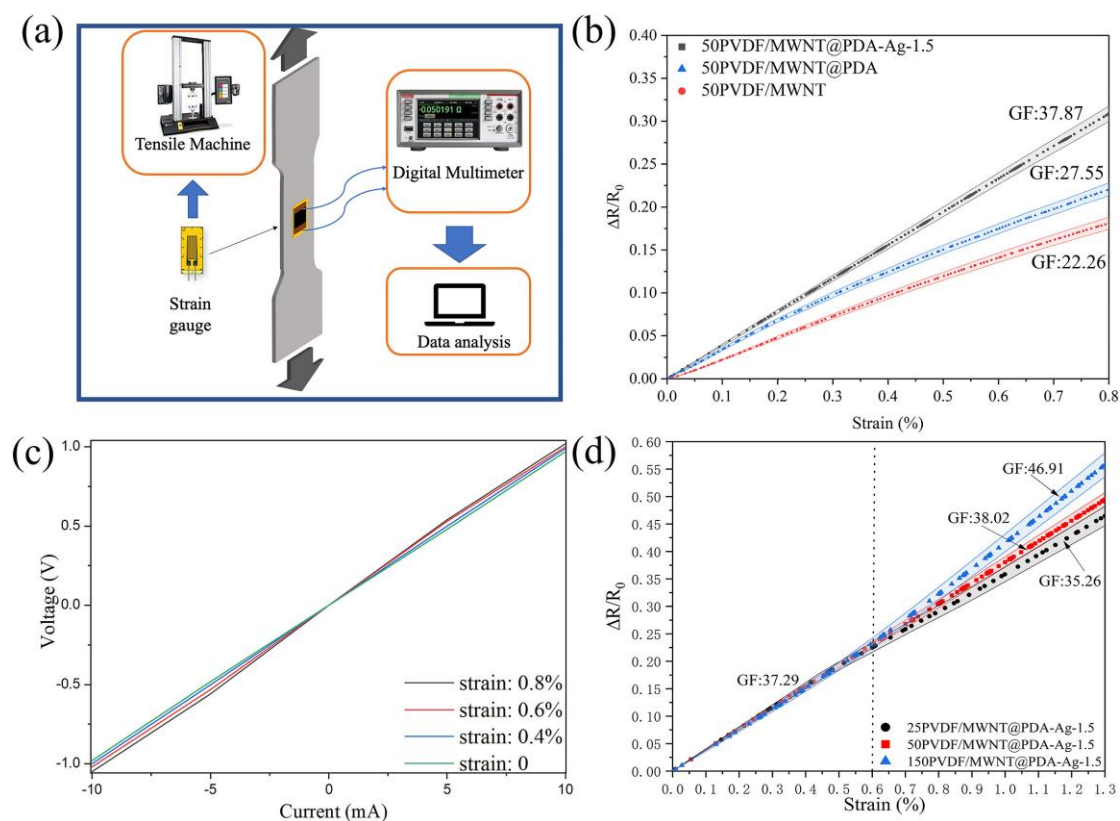


Figure 5.10. (a) Schematic diagram of static tensile experiments. (b) Relative resistance changes vs. strain curves of three 50PVDF/MWNT sensor specimens, three 50PVDF/MWNT@PDA sensor specimens and three 50PVDF/MWNT@PDA-Ag-1.5 sensor specimens (shaded areas: ± 1 standard deviation). (c) Voltage vs. current curves of a 50PVDF/MWNT@PDA-Ag-1.5 sensor specimen at different strains. (d) Relative resistance changes vs. strain curves of three groups of three PVDF/MWNT@PDA-Ag-1.5 sensor specimens.

1.5 sensor specimens, each group with a distinct thickness (shaded areas: ± 1 standard deviation).

5.3.3 Responses of AgNP-modified PDA-coated MWNTs nanocomposite sensors in sensing microscopic high-frequency vibrations

Fig. 11(a) shows the experimental setup for microscopic high-frequency vibration tests and the experimental process can be found in **Chapter 3 Section 3.3.1**.

From **Fig. 11(b)**, it is apparent that the performance of the proposed nanocomposite sensor in the ultrasonic regime is on par with that of commercial PZT sensors, capable of precisely capturing the two ultrasonic wave modes that propagate in plate-like structures, i.e., the fundamental symmetric Lamb wave mode (S_0) and the fundamental anti-symmetric Lamb wave mode (A_0). The observation that the responses of all of the nanocomposite sensor specimens tested are the strongest at the excitation frequency of 250 kHz, as shown in **Fig. 11(c)**, is consistent with the fact that the centre frequency of the PZT actuator that was used to excite ultrasonic waves is 250 kHz.

The PVDF/MWNT@PDA-Ag sensor specimens exhibit significantly higher sensitivities than the PVDF/MWNT sensor specimens across all of the excitation frequencies utilized. This is partially owing to the understanding that the PDA nanolayers on the PVDF/MWNT@PDA-Ag nanofillers would have improved the dispersion stability of the nano- fillers, as evident through the higher zeta potentials of the nanofillers (**Table 5.1**), such that the nanofillers would have been more uniformly distributed inside the blade-coated sensor specimens. Also, the PDA nanolayers, due to their elasticity, would have kept adjacent rod-like nanofillers in close proximity to each other. Both the uniform dispersion and the close contact of nanofillers are crucial to the construction of effective tunneling junctions, which underpin the sensing of low deformations.

Furthermore, among the PVDF/MWNT@PDA-Ag sensor specimens, those with higher AgNP contents always demonstrate higher sensitivities, regardless of the excitation

frequency utilized. For instance, at the excitation frequency of 250 kHz, the peak-to-peak amplitude of the S₀ mode captured by the PVDF/MWNT@PDA-Ag-1.5 sensor specimens (0.732 V) is approximately 40% and 12% higher than those of the S₀ modes captured by the PVDF/MWNT@PDA-Ag-0.5 sensor specimens (0.524 V) and the PVDF/MWNT@PDA-Ag-1.0 sensor specimens (0.654 V), respectively. This increase is attributed to the positive effect of AgNPs on electron tunneling. While the non-conductive PDA nanolayers on the PVDF/MWNT@PDA-Ag nanofillers would not have favored to electron transport, the AgNPs immobilized on the PDA nanolayers contributed to lowering the potential barriers of the layers, as evident through the enhanced conductivities of the nanofillers, in turn increasing the probability of occurrence of electron tunneling. Also, it is seen that the more AgNPs a nanofiller contains, the more conductive the nanofiller would be.

In order to ascertain the practicality of the proposed nanocomposite sensor in real-world scenarios, a long-term fatigue test was conducted using the experimental setup shown in **Fig. 5.11(a)**. In the test, a PZT actuator was used to excite the same ultrasonic wave for 1000 times, and both a nanocomposite sensor specimen and a PZT sensor were used to continuously capture the ultrasonic waves excited. As shown in **Fig. 5.11 (d)–(e)**, the level of degradation of the nanocomposite sensor specimen is minimal and well on par with that of the PZT sensor.

It is worth mentioning that while the proposed nanocomposite material itself is non-directional, when a piece of nanocomposite material is attached on by two electrodes, its directionality would depend on the configuration of the electrodes, because only resistance changes across the two electrodes would be measurable. To demonstrate the influence of electrode configuration on the directionality of the proposed nanocomposite material, two sensor specimens, each with a distinct electrode configuration, were used to capture the same ultrasonic wave, as illustrated in **Fig. 5.13(a)**. From **Fig. 5.13(b)**, it can be seen after a piece of nanocomposite material has been attached on by two electrodes, it would become most sensitive to ultrasonic wave components that

travel across its resistance measurement path (i.e., the path between its two electrodes) but insensitive to those that travel perpendicularly to it.

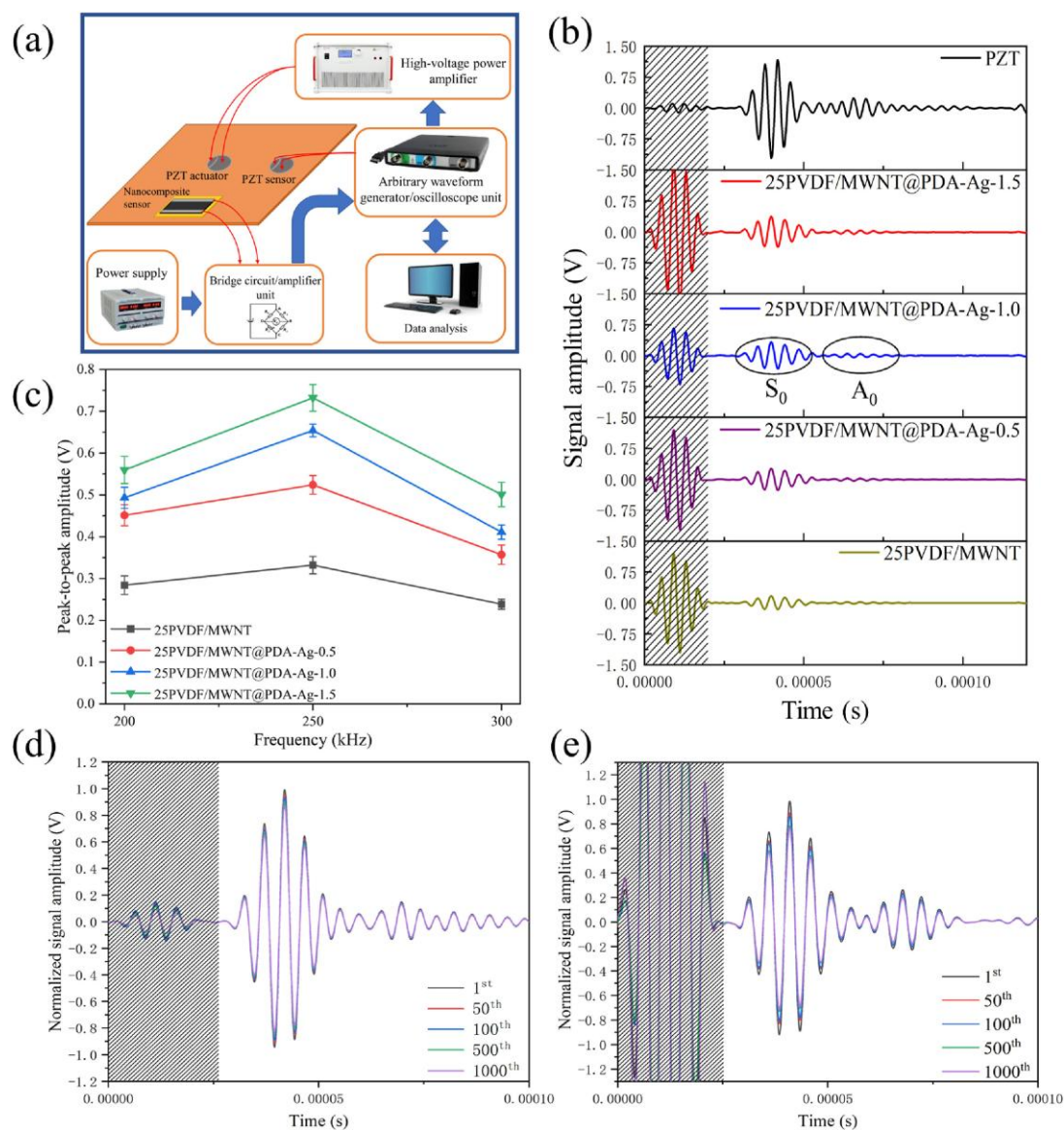


Figure 5.11. (a) Schematic diagram of ultrasound-based vibration experiments. (b) Ultrasonic signals that were captured by a PZT sensor, three 25PVDF/MWNT sensor specimens and three groups of three 25PVDF/MWNT@PDA-Ag sensor specimens, each group with a distinct AgNP content, under an excitation frequency of 250 kHz (shaded signals: crosstalk). The nanocomposite sensor signals were each obtained by taking the average of the signals captured by the three sensor specimens tested. (c) Peak-to-peak amplitudes of the ultrasonic signals that were captured by three 25PVDF/MWNT sensor specimens and three groups of three.

25PVDF/MWNT@PDA-Ag sensor specimens, each group with a distinct AgNP content, under various excitation frequencies (error bars: ± 1 standard deviation). The raw ultrasonic signals are provided in **Fig. 5.12**. Ultrasonic signals captured by a PZT sensor (**Fig. 5.11(d)**) and a 25PVDF/MWNT@PDA-Ag-1.0 sensor specimen (**Fig. 5.11(e)**) during a long-term fatigue test performed under an excitation frequency of 200 kHz (shaded signals: crosstalk).

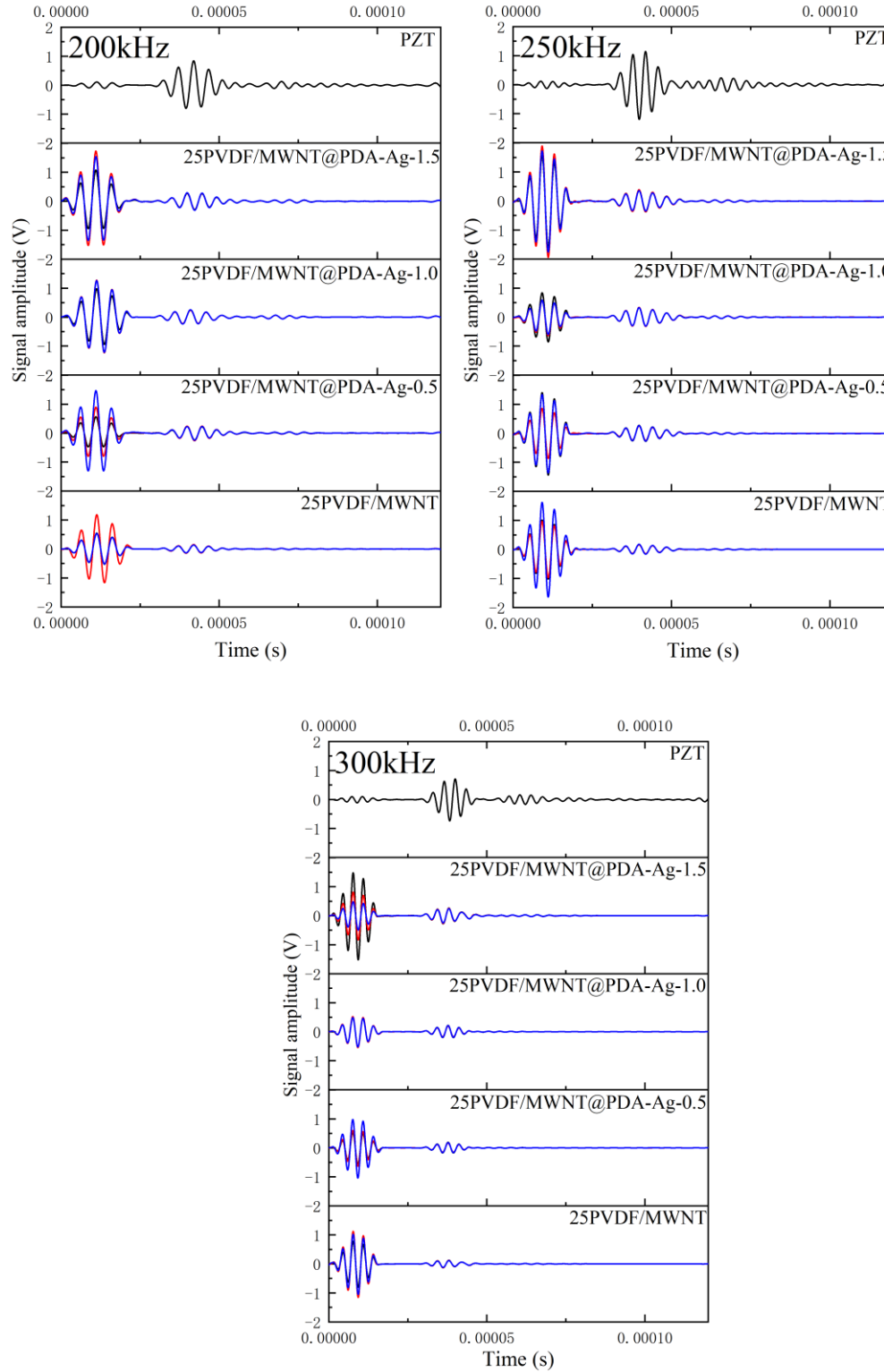


Figure 5.12. Ultrasonic signals that were captured by a PZT sensor, three 25PVDF/MWNT sensor specimens and three groups of three 25PVDF/MWNT@PDA-Ag sensor specimens, each group with a distinct AgNP content, under various excitation frequencies.

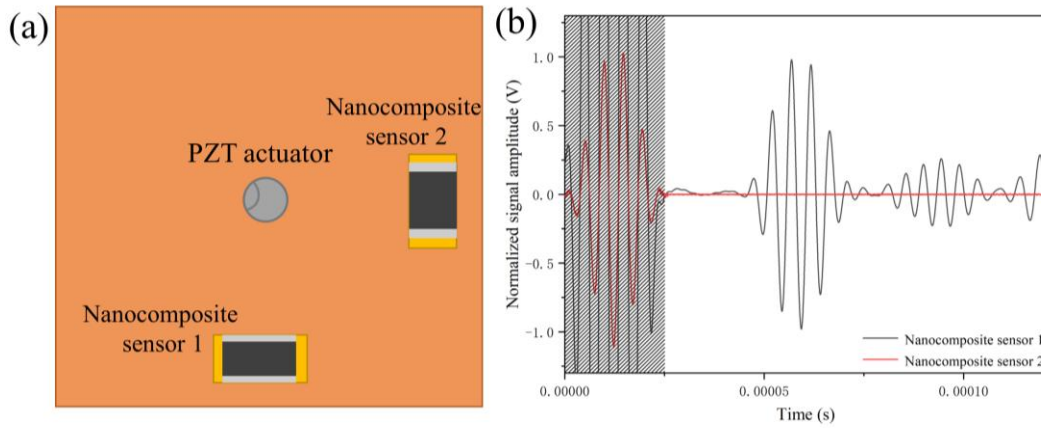


Figure 5.13. (a) Setup for the directionality test of the proposed nanocomposite material performed with two 25PVDF/MWNT@PDA-Ag-1.0 sensor specimens under an excitation frequency of 200 kHz. The ultrasonic wave excited by the PZT actuator travelled across the resistance measurement path (i.e., the path between the two electrodes) of Nanocomposite sensor 1 and perpendicularly to that of Nanocomposite sensor 2. (b) Ultrasonic signals that were captured by the two nanocomposite sensor specimens (shaded signals: crosstalk).

Inspired by the responses of the proposed nanocomposite sensor under the static tensile tests and the high-frequency vibration tests performed, we further speculate that the strain sensing mechanism of MWNT-based nanocomposite sensors would vary with strain level. Under a microscopic strain in the ultrasonic regime (ϵ : $<0.001\%$), the resistance change of a sensor specimen would be very much governed by the relative movements of the nanofillers, which change the distances between and, hence, the tunneling resistances across adjacent nano- fillers. As a result, we observe that the sensitivity of a sensor specimen to ultrasonic waves is directly proportional to its AgNP content (**Fig. 5.11(b)-(c)**), which determines the potential barriers between adjacent nano- fillers and, hence, the possibility of occurrence of electron tunneling. However, when a sensor specimen is subjected to a strain that is close to or even greater than the size of the nanofillers, the sensing mechanism would become different. Within a smaller strain range (ϵ : $<0.6\%$, in the case of this work), the nanofillers themselves

would undergo deformation or rearrangement, giving rise to noteworthy piezoresistive effect, in addition to the tunneling effect. At an even higher strain, the deformation and rearrangement of the nanofillers would drastically alter the tunneling paths inside the sensor specimen. Consequently, it is seen in this work that when the strain applied on a sensor specimen exceeds 0.6%, the exponential resistance changes vs. strain relationship that is associated with the tunneling effect would become much more apparent (**Fig. 5.10(d)**).

5.4 Conclusion

In this work, AgNPs were immobilized on the surfaces of MWNTs through a PDA-assisted process. The nanofillers synthesized were used to fabricate nanocomposite sensor specimens for acquiring microscopic static deformations and microscopic high-frequency vibrations. The results of the material characterizations performed prove that AgNPs were compounded, in their elemental form, with the PDA nanolayers on the surfaces of MWNTs. As a result, the electron transport ability of the PDA nanolayers was significantly improved, promoting the tunneling of electron across adjacent nanofillers. Through static tensile tests, it is shown that sensor specimens made from the nanofillers with immobilized AgNPs can be as much as 37% more sensitive than those made from the nanofillers with PDA nanolayers only. Also, by testing sensor specimens with different thicknesses, it is deduced that within 0.6% strain, the piezoresistive effect would also noticeably contribute to the strain-induced resistance change of a sensor specimen. Moreover, the results of high-frequency vibration tests demonstrate that the AgNP content of a sensor specimen influences positively its sensitivity over a wide frequency spectrum.

In summary, the PDA-assisted AgNP-based surface modification of MWNTs, presented in this work, offers a promising strategy for optimizing the sensitivities of carbon nanomaterial-based nanocomposite sensors to low deformations.

Chapter 6 Writable sensitive strain sensors fabricated by GO inks for multitype low deformation sensing

6.1 Introduction

In our previous study [248, 270], it was demonstrated that the PDA-coated strategy positively improved the sensitivity of prepared strain sensors by optimizing the dispersion ability of 1D MWNTs. Additionally, the Ag modification was found to further promote the tunneling of electrons across adjacent nanofillers, thus enhancing the GFs. On this basis, start from this chapter, similar strategies are being attempted to be applied to develop highly sensitive 2D graphene-based strain sensors.

The graphene family encompasses various members, including graphene flakes, GO, and rGO, each with unique properties relevant to strain sensing [105, 106, 271-273]. Graphene flakes exhibit high surface area and excellent conductivity, facilitating efficient strain transfer and enabling the sensitive detection of mechanical deformations. However, the aggregation tendency of graphene sheets presents a challenge as it gives rise to the formation of conductive pathways or clusters, thus compromising the electrical conductivity and overall sensitivity of strain sensing devices. GO is derived from graphene through the introduction of oxygen-containing functional groups such as hydroxyl, epoxy, and carboxyl groups, resulting in a layered structure with a significant oxygen functionality [274, 275]. This layered structure renders GO highly dispersible in solvents and offers convenient avenues for facile modification. The presence of oxygen-containing functional groups in GO provides additional sites for chemical modifications, making it a versatile material for enhancing sensitivity and tailoring the properties of strain sensors. However, GO exhibits lower sensitivity in strain sensing due to its reduced electrical conductivity as compared to pristine graphene. Conversely, rGO can be obtained from GO by reducing the oxygen functionalities, which restores graphene-like properties and enhances electrical

conductivity, endowing rGO with high conductivity. This conductivity enhancement in rGO contributes to improved strain sensing capabilities by facilitating efficient charge transport and facilitating the detection of mechanical deformations. In another word, rGO is given higher dispersibility but lower electrical conductivity compared to pristine graphene.

After comparing graphene, GO, and rGO, it can be observed that while GO may have lower electrical conductivity, its best dispersion ability and the abundance of functional groups offer greater potential for surface modification of nanofillers and sensitivity improvement, making it a suitable starting point for further research in strain sensing. Therefore, in this chapter, we aim to evaluate the performance of GO-based strain sensors in their unmodified state before any additional modifications or enhancements are applied.

The incorporation of oxygen-containing functional groups substantially enhances the hydrophilicity and dispersibility of GO. Those functional groups increase affinity of GO for polar solvents and its hydrophilic character, facilitating its dispersion in solution [276]. The improved hydrophilicity enables the formation of stable colloidal suspensions, preventing agglomeration and sedimentation of GO nanosheets, thus ensuring a more homogeneous and uniformly distributed solution. The better-dispersed state achieved through enhanced hydrophilicity and dispersibility of GO plays a vital role in achieving higher sensitivity [277]. When GO nanofillers are uniformly distributed within the sensor material, they can effectively interact with the applied strain, resulting in more accurate detection of deformations. Recently, using direct ink writing (DIW), Zhong et al. [278] successfully utilized the concept by formulating an aqueous nanocomposite ink comprising polydimethylsiloxane (PDMS) submicrobeads and electrochemically derived graphene oxide (EGO) nanofillers. This nanocomposite ink possesses a thixotropic, self-supporting viscoelasticity which can be easily extruded through very small nozzle openings (as small as 50 μm) allowing for excellent dispersed-state to achieve high gauge factor (GF: 20.3).

Beyond its excellent dispersion properties, the unique structure of GO, characterized by its intricate 3D-like folds and wrinkles, enables strain sensors to capture strain signals from multiple directions [279]. This capability empowers the sensor to detect various types of strains, including tensile, compression, and pressure. For instance, when pressure is applied to the GO-based sensors, the deformations in the folds and wrinkles of GO result in changes in its electrical conductivity. Monitoring those conductivity changes allows the sensor to accurately measure the intensity of the applied pressure.

Indeed, for broader real-world applications, such as electronic skins [97, 280, 281], health monitoring devices[3, 282], or intelligent robots [3, 282], considerations beyond the sensitivity and functionality of strain sensors are essential. The preparation process of the sensors plays a crucial role in ensuring their reliability and reproducibility. Factors such as fabrication techniques, material selection, and device integration need to be carefully addressed to achieve consistent and high-quality sensor performance [281, 283, 284]. Recently, the pen-on-paper (PoP) approach, a basic printing technique, shows significant advantage in meeting the installing requirements of flexible strain sensors by simply using patterning instruments like writable pen [285, 286]. For example, a commercial marker pen is able to adopt shape microfluidic channels on paper through directly writing hydrophobic ink. Those kind of writable paper-based strain sensors offer a flexible and cost-effective solution for strain sensing, allowing for easy fabrication and customizable sensing applications on paper substrates. Researchers have demonstrated the feasibility and convenience of fabricating strain sensors capable of detecting extremely low strains using the PoP approach[274, 285, 287-289]. For example, Yu et.al[274] prepared molybdenum carbide-graphene (MCG) composites with porous and stacking micro-structures on top of the paper substrate to act as piezoresistivity strain/pressure sensors. The modified graphene structure shows gauge factor as high as 73 and 43 for tensile and compressive strain ($\epsilon < 0.24\%$), respectively, with demonstration examples in detecting and recognizing human body motions.

Moreover, the microstructure of cellulose-conductive nanofillers within paper-based strain sensors is well-suited for converting microstructural deformations into electrical signals [290, 291], making it an ideal choice for sensing extremely small strains. The unique arrangement and alignment of cellulose fibres combined with the conductive nanofillers provide an effective pathway for strain transfer and electron conduction. As a result, even subtle deformations or microstructural changes in the paper-based sensor can be accurately detected and converted into measurable electrical signals. For example, Yu et al. [274] prepared molybdenum carbide-graphene (MCG) composites with porous and stacking micro-structures on top of the paper substrate to act as piezoresistivity strain/pressure sensors. The modified graphene structure shows gauge factor as high as 73 and 43 for tensile and compressive strain ($\varepsilon < 0.24\%$), respectively, with demonstration examples in detecting and recognizing human body motions. So far, many studies have demonstrated the feasibility and convenience in fabricating strain sensors to extremely low strain but the reliability and stability need further improvement.

In practical applications, the detection of complex multidirectional strains requires flexible strain sensors with high desirability. To achieve anisotropic sensing capability, one effective approach is to employ a nanofiller structure that incorporates wrinkles or cracks. The distinctive structure of GO, with its intricate 3D-like folds and wrinkles, endows strain sensors with the ability to detect strain signals from multiple directions³⁹. This unique characteristic enables the sensors to effectively capture various types of strains, including tensile, compression, and pressure. For example, when pressure is applied to GO-based sensors, the deformations of the folds and wrinkles of GO lead to alterations in its electrical conductivity. By monitoring these conductivity changes, the sensors can accurately measure the intensity of the applied pressure. This capability demonstrates the versatility and practicality of GO-based strain sensors in applications where the detection of multidirectional strains and precise pressure measurements are essential.

On this basis, to design a strain sensor prepared by PoP method to meet the installation requirements and use GO nanofillers to achieve both better dispersion state of inks and multidirectional strain sensing, this research represents the first attempt to explore the feasibility of using GO as nanofillers in the preparation highly sensitive strain sensors by PoP for multitype strains sensing. To investigate this concept, graphene was initially oxidized using the Hummer's method to achieve various degrees of oxidation. The resulting GO samples were then incorporated into a custom-made print pen along with polymer dispersants such as phenolic resin and amphoteric polyacrylamide. The morphology of the prepared GO nanofillers will be characterized using SEM. The degree of oxidation in the GO will be analyzed by using techniques such as Fourier-transform infrared spectroscopy (FTIR), XRD, and Raman spectroscopy.

To assess the performance of the strain sensors, the paper-based GO sensors themselves will be evaluated initially by subjecting the paper substrate to manual bending to measure the tensile and compression signals. Pressure signals will be evaluated by placing a pressure gauge on the paper substrate. Subsequently, the paper-based GO sensors will be mounted in a small-scale universal testing machines (UTMs) to conduct cyclic tests. Furthermore, the sensors will be attached to dog-bone tensile aluminum alloy substrates to simulate real-world scenarios involving multitype strain sensing using a larger-scale tensile machine. Following those evaluations, the study aims to simulate real-world applications for multitype strain sensing, such as wearable devices or engineering tests, by leveraging the advantages of GO-based paper strain sensors.

6.2 Experimental

6.2.1 Preparation of GO

GO was prepared by the oxidation of natural graphite powder according to Hummer's method. Typically, graphite powder (3.0 g) was added to concentrated sulphuric acid (H_2SO_4 98%, 70 mL) under stirring in an ice bath. Under vigorous agitation, Potassium permanganate (KMnO_4 , 4.5g-9g) was added slowly to keep the temperature of the

suspension lower than 20 °C. Successively, the reaction system was transferred to a 40 °C oil bath and vigorously stirred for about 2 h. Then, 150 mL water was added, and the solution was stirred for 15 min at 95 °C. Additional 500 mL water was added and followed by a slow addition of Hydrogen peroxide (H₂O₂ 30%, 10 mL - 30 mL), turning the colour of the solution from dark brown to yellow. The mixture was filtered and washed with 10% hydrogen chloride (HCl) aqueous solution to remove metal ions. The resulting solid was dried in air and diluted to 1000 mL, making a graphite oxide aqueous dispersion. Finally, it was purified by dialysis for one week using a dialysis membrane with a molecular cut-off weight of 10000–14000 g mol⁻¹ to remove the remaining metal species. The resultant graphite oxide aqueous dispersion was then diluted to 2 L, stirred overnight, and sonicated for 30 min to exfoliate it to GO. The GO dispersion was then centrifuged at 4500 rpm for at least 40 min to remove the unexfoliated graphite. It is expected to obtain GO fillers with different oxidation degrees by adding different oxidants and the GO products prepared by oxidants in different amounts (4.5g KMnO₄, 7g KMnO₄ and 9g KMnO₄) are nominated as GO-1, GO-2 and GO-3, respectively.

2.2 Preparation of GO-ink

0.1 g GO power were dispersed into 10 ml phenoxyethanol solution (including 10wt.% phenolic resin) and mixed with 0.02g methyl sodium naphthenate dispersed agent. The whole mixed solution conducted ultrasonic treatment for 4 h after being stirred for half an hour to prepare inks. The different group of GO inks made by power GO-1, GO-2 and GO-3, were named as GO-ink-1, GO-ink-2 and GO-ink-3 respectively.

6.2.3 Paper-based GO sensors fabrication

Component of Home-made print pen

The component of the home-made print pen is shown in **Fig. 6.1** and **Fig. 6.2(a)**. A home-made print pen consists of two parts: the barrel and the nib. The pen barrel stores dispersed GO ink and is equipped with two glass beads to help dispersion by shaking. Pen nib section includes storage foam, microporous membrane and PU foam as pen tip

(1 cm wide). Before going into the pen tip, the GO ink is absorbed in ink store foam, so that the writing process will be smoother and ensure the uniformity of writing. There is a micro-porous film to delete the agglomerated GO fillers before the pen tip and enter the pen tip, so as to ensure that only the dispersed ink can be on the paper. Similarly, the strain sensors made by GO-ink-1, GO-ink-2 and GO-ink-3 is named as S-GO-1, S-GO-2 and S-GO-3, respectively.

Device of GO paper-based sensors

A simple strain sensor film was prepared easily by writing a pen trace (4 cm ×1 cm) on the Xerox print paper with a home-made print pen, and then fixing the wires with silver glue and copper tape at both ends. Generally, the GO-containing ink were absorbed by the pulps and separated by the cellulose into different micro-bubbles. When the paper is suffered to different types of strain in either tensile, compression or pressure, those bubbles will be squeezed or stretched, resulting in the distance change or rearrangement in any direction of adjacent GO nanofillers inside the micro-bubbles as shown in **Fig. 6.2(b)**. Thus, a resistance change of the whole paper-based device can be observed by the multimeter.

Fig. 6.2(c) show a typical PoP trace by GO-ink-1 on the print paper and pasted on a curved object. The ink trace is evenly dispersed on the print paper, providing a promising start for the fabrication of a stable strain sensor. This study focuses on a more standard performance test so that all the strain sensors are made by home-made print pen with 1 cm wide pen tip.

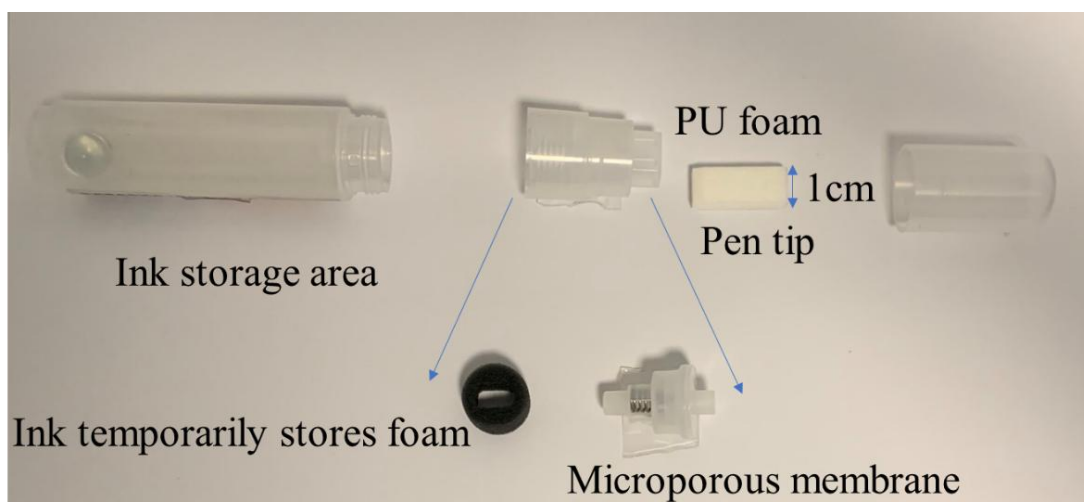


Figure 6.1. Component of the home-made print pen.

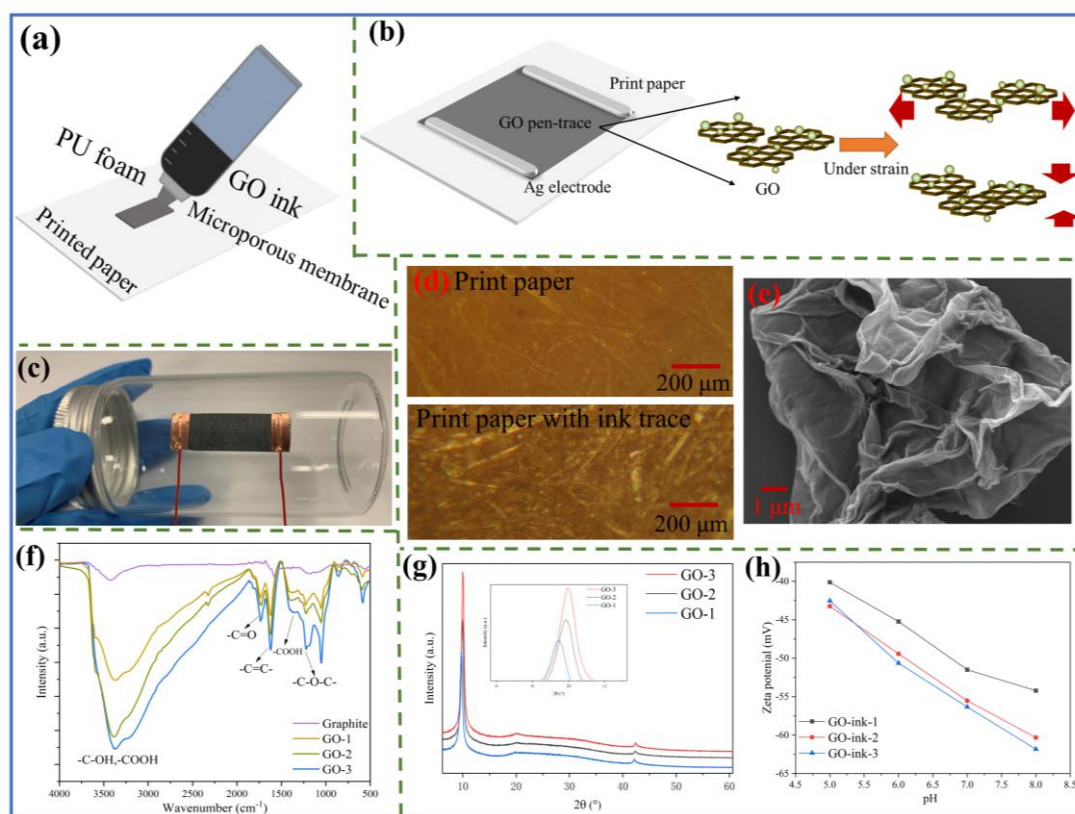


Figure 6.2. (a)Component of home-made print pen with GO ink; (b)Scheme of GO nanofillers to low deformation; (c) Typical ink trace on curved object; (d) Microscopy images of print paper trace without and with GO ink; (e) Typical SEM image of GO-1 nanofillers; (f) FTIR curves of graphite and GO nanofillers with different oxidation degree; (g) XRD patterns of GO nanofillers with different oxidation degree; (h) Zeta

potential values of GO inks with different oxidation degree under pH value varied from 5 to 8.

6.3 Results and discussion

6.3.1 Characterizations of GO nanofillers and GO-inks

Through the observation of microscopy, the microstructure of between paper and ink is shown as in **Fig. 6.2(d)**. Initially, the print paper is formed by the interlacing fibrous cellulose and pulp. After GO ink trace, the pulp is filled by the GO solution while the cellulose maintains its supporting network. This three-dimensional staggered structure separated the entire sensor into a large number of GO-pulp bubbles and connected by GO-cellulose staggered structure, providing a high-sensitivity potential to extremely small strain sensing.

The morphology of GO nanofillers is characterized by SEM. After oxidation, the graphene nanofiller lose its characterization of two-dimensional structure and become like three-dimensional as shown in **Fig. 6.2(e)**. SEM images of GO-1 to GO-3 can be found in **Fig. 6.3**. The crumpling was due to exfoliation of GO sheets and it was quite obvious that the exfoliated structure was several micrometers in size. It is also noticed that the surface of GO nanofillers become more rougher and the microdefects increase from GO-1 to GO-3. It is understood as that the oxidation process causes damage to the nanofiller surface and as the process continues, more nano-cracks appear due to more oxygen-containing functional groups generate.

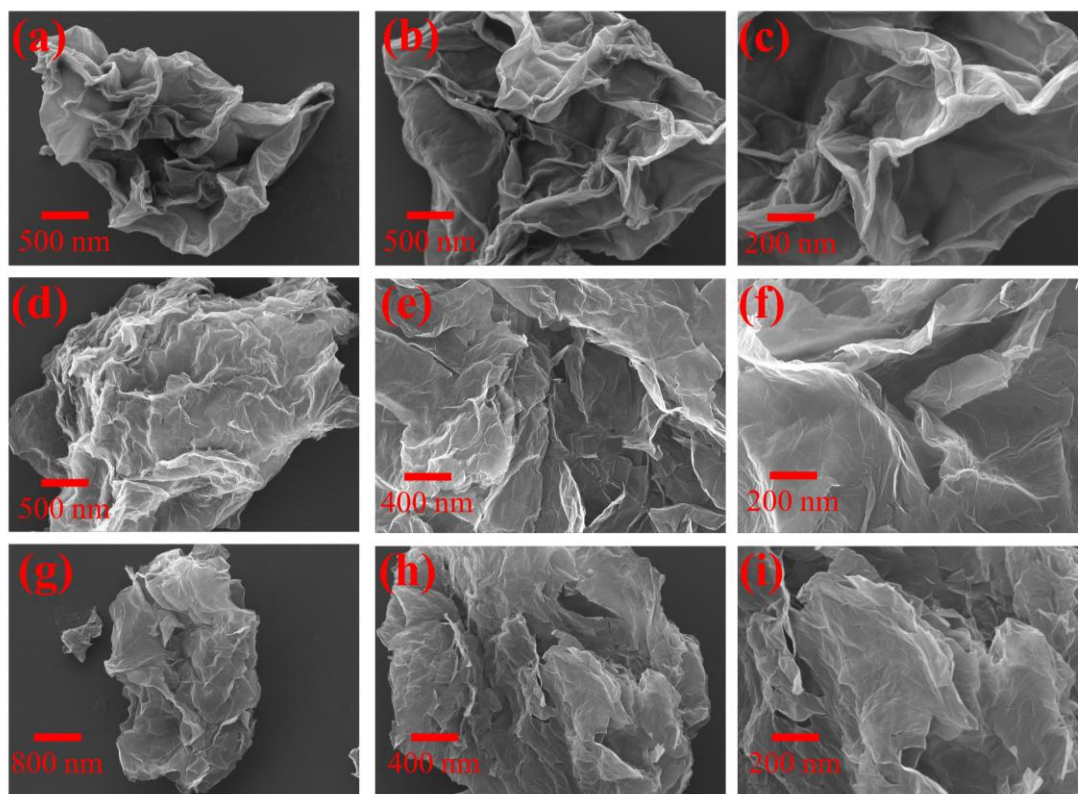


Figure 6.3. SEM images of GO-1 nanofiller (a)-(c), GO-2 (d)-(f) and GO-3 (g)-(h) nanofillers.

In this study, GO is prepared by Hummer's method and expected to be separated into three different degrees of oxidation levels by controlling the oxidizing agent concentration. The results can be demonstrated by the FTIR and XRD.

The FTIR spectra comparison of GO samples with different degree of oxidation and pure graphite are shown in **Fig. 6.2(f)**. When compared to the spectrum of graphite, the GO spectra exhibit additional peaks that provide insights into the oxidation process and the introduction of new functional groups. One significant difference is the appearance of a peak around 1620 cm^{-1} , which corresponds to the stretching vibrations of C=C bonds[271]. This peak is become small in the graphite spectrum but becomes prominent in the GO spectra. It indicates the exfoliation of graphite is the formation of sp² hybridized C=C bonds resulting from the oxidation process. Other peaks in the GO spectra represent oxygen-containing functional groups, such as the intense band at 3428 cm^{-1} indicating O-H stretching vibrations of -OH or -COOH groups. Additional peaks

include carbonyl C=O stretching vibrations (1732 cm^{-1}), C-O-OH (1335 cm^{-1}) stretching vibrations of epoxy groups (1305 cm^{-1}), and C-O stretching vibrations of alkoxy groups (1225 cm^{-1})[271]. It has been observed that the intensity of these oxygen-containing functional groups increases from GO-1 to GO-3, indicating varying degrees of oxidation of GO nanofillers.

The internal information of GO nanofillers can be study by the contrast of XRD patterns of GO nanofillers with different degree of oxidation as shown in **Fig. 6.2(g)**. Firstly, the missing peaks of pristine graphite at around 26° correspond to the complete oxidation result of graphite[243]. Due to (0 0 1) reflection of GO, the characteristic peaks of GO cantered at around 9.9° , corresponding to the interlayer spacing between the GO sheets. The presence of a minor shoulder peak near 2θ at 23° longitude in the XRD spectrum suggests the existence of defects in the graphene crystal structure and the occurrence of agglomeration between the graphene sheets. The inset figure shows the zoomed in area at around 9.9° and the small red shift of the characteristic peak of GO can be found. Theoretically, the increase of interlayer spacing is proportional to the degree of oxidation of GO nanofillers so that the small red shift is shown[292]. Together with the density of oxygen-containing functional group as shown in **Fig. 6.2(f)**, can be used to confirm the truth of GO with different degree of oxidation, so that the influence of degree of oxidation of GO nanofillers on the sensitivity of the obtained strain sensors can be found fairly in the below section.

Raman spectra (**Fig. 6.4**) were carried out for the samples of graphite and GO with different oxygen contents. The spectrum of graphite shows a strong G band at 1570 cm^{-1} due to first order scattering of the E_{2g} mode. It also contains a small band at 1354 cm^{-1} named the D band, which is evidence for the presence of defects in the graphite material such as bond-angle disorder, bond-length disorder, vacancies, edge defects, etc[245]. In GO group, the G band is shifted towards a higher wavenumber (1585 cm^{-1}) due to the oxidation of graphite and the D band has a higher intensity, which can be attributed to the formation of defects and disorder such as the presence of in-plane

hetero-atoms, grain boundaries, aliphatic chain, etc., It shows that the G band is shifted towards a higher wavenumber with the increase in oxidation level, associating with the formation of new sp^3 carbon atoms in the graphite lattice[293]. The overall Raman results show that as the oxidation degree of GO increase, the overall defects of the nanofillers are increasing.

The ink stability of GO-inks was assessed using zeta potential measurements, as depicted in **Fig. 6.2(h)**. Zeta potential is a fundamental property that characterizes the electrical properties and dispersion stability of materials. The results indicate that the values of zeta potential of GO-inks with the degree of oxidation keep high under different pH conditions. These elevated values can be attributed to the presence of oxygen-containing functional groups within the GO nanosheets, which contribute to the formation of electronegative sites. Additionally, a greater number of acidic groups on the surface of the GO nanosheets dissociate, further elevating the zeta potential. Significantly, it should be noted that the lowest zeta value of GO-ink-1 remains approximately 40 mV within the pH range of 4 to 8, which corresponds to the most commonly encountered usage environments. This indicates a high level of stability according to the standard for colloidal suspension stability[294]. Importantly, all the GO-inks investigated in this study comply with this stability standard, ensuring a fair competition in terms of strain sensing performance.

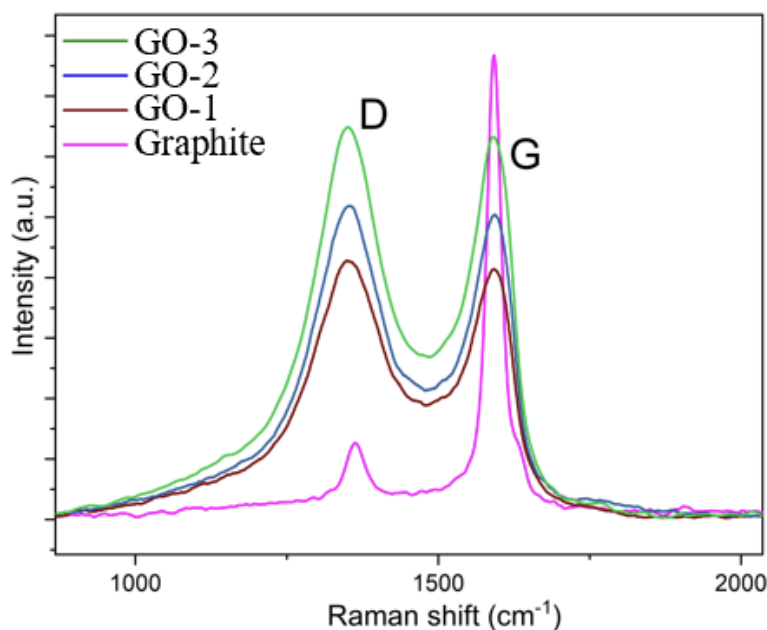


Figure 6.4. the Raman curves of graphite and GO nanofillers with different degree of oxidation.

6.3.2 Response of GO paper-based sensors in multitype strains

Here, we first evaluate the performance of GO paper sensors with three different levels of oxidation degree in term of tensile and compression strain by bending the GO paper-based sensors only first. In general, when ink is applied to print paper, it tends to penetrate only to a certain depth rather than saturating the entire print paper. As a result, the sensors can be subjected to tensile and compression strains by bending the outer surface (with ink traces on) or inner surface (without ink traces on) of the GO-based paper sensors. By bending the ink-trace-including surface of the GO-paper devices, the sensors are subjected to tensile stress, which induces an expansion of the cellulose-fibre network inside the paper and the stretch of the GO-pulps, resulting in the increase of the resistance. If the other surface of the GO-paper devices was bend, the opposite trend will appear as shown in **Fig. 6.5(a)**. In order to determine to sensitivity of GO sensors,

the applied strain (ε) can be calculated from the curvature of the sensor by the geometric relationships:

$$c = 2r \times \sin\left(\frac{l}{2r}\right) \quad 6.1$$

$$\varepsilon = \pm \frac{h}{2r} \quad 6.2$$

where c is the lateral distance between two electrodes; r is the radius of the curvature of the deformed sensor; l is the length of the arc after the deformation of the sensor; and h is the thickness of the paper-based sensors.

The relationship between average resistance changes and GFs of GO-based paper strain sensors with different degree of oxidation under tensile and compression can be found on the **Fig. 6.5(b)**. It can be seen from the figure that all the GO-based paper strain sensors are given the ability to capture the strain signals within applied strain of 0.8%. In this study, the sensitivity of strain sensors under tensile or compression strain was evaluated by gauge factor ($GF = (\Delta R/R_0)/\varepsilon$), where the ΔR is the resistance change, R_0 is the initial resistance and the ε is the applied or calculate strain. In the tensile group, the GFs of the sensors increased from 65.4 to 87.1 as the degree of oxidation decreased from S-GO-1 to S-GO-3. Similarly, in the compression group, the GFs increased from 59.4 to 77.4 with decreasing degrees of oxidation. Those results indicate that the sensors with higher degrees of oxidation exhibited lower GFs, suggesting lower sensitivity to strain.

In our precious characterizations, the FTIR suggests that the oxygen-containing functional groups is significantly increased from GO-1 to GO-3. Those functional groups disrupt the sp^2 carbon network of graphene and reduced its electrical conductivity[185], as a result there are less conductive electrical pass response to the applied strain, hinder the change in resistance.

As the degree of oxidation increases, the concentration of those functional groups also increases, leading to a higher density of defects in the graphene structure (Raman).

Those defects can act as scattering centers for charge carriers, leading to increased scattering and reduced carrier mobility[276, 293]. When strain is applied, the resistance change is influenced by the mobility of charge carriers. Higher defect density results in more scattering events, which hinder the movement of charge carriers and limit the resistance change. Also, defects can cause localized states within the GO material. Those localized states can trap charge carriers [295]. With a higher density of defects, more charge carriers may become trapped in localized states, reducing their contribution to the conductivity and resulting in a lower resistance change.

Additionally, the improved interfacial interactions of the graphene oxide may also contribute to the reduced sensitivity. The presence of oxygen-containing functional groups enhances the affinity of GO for various materials, leading to stronger interfacial bonding [295, 296]. This stronger interaction can restrict the movement or deformation of the graphene oxide layer under strain, resulting in a reduced response to strain. Overall, the increase in sensitivity of GO-based strain sensors with decreasing degrees of oxidation can indeed be attributed to the higher concentration of oxygen-containing functional groups, higher number of defects, and improved interfacial interactions.

Moreover, it is also found that the sensitivity of GO paper-based sensors under tensile is differed to those under compression at the same magnitude and this same phenomenon is also found in many paper-based strain sensors research [285, 297]. In this case, the observed differences can be attributed to the varying thicknesses of the printed paper, which affect the calculation of strain and the deformation of the nanofillers. The calculated strain values may differ from the actual strain experienced by the paper-based sensors due to the accumulation of ink primarily on the upper layer of the paper during the drawing process. Additionally, the nanofillers within the sensors undergo tensile and compressive forces, leading to different electron transport behaviours and resulting in distinct changes in resistance.

As discussed before, GO nanofillers, like-3D structure, is promised to high sensitivity in pressure sensing. In this study, a pressure gauge was used to determine the applied pressure and the same multimeter is used to record the resistance. The typical concluded result of S-GO-1 was show in **Fig. 6.5(c)**. The results of S-GO-2 and S-GO-3 are shown in **Fig. 6.6**. The sensors, constrained by the limited hardness of the print paper, are capable of detecting and distinguishing pressure signals within a specific range of 2 kPa to 8 kPa. Beyond this range, the sensors may not provide accurate or reliable measurements due to the limitations imposed by the paper's hardness. The sensitivity of GO sensors to pressure signal is calculate by pressure gauge factor ($S = (\Delta R/R_0)/\Delta P$), where the ΔP is the applied pressure change. From the pressure range of 2 kPa to 5.5 kPa, the sensitivity of all the paper-based sensors with different Degree of oxidation are around $3.6 \times 10^{-3} kPa^{-1}$, while those values are around $5.9 \times 10^{-4} kPa^{-1}$, when the pressure ranges from 5.5 kPa to 7.5 kPa. From the experiment results, a law of GO sensors of different oxidation degrees to different pressures is not observed. The reason may be when pressure hit on the paper-based sensors, only 10 μm thickness nanomaterials max response to the applied deformation. The slightness of the deformation change makes it difficult to discern the trend of GO nanofillers with varying degrees of oxidation. The subtle variations in deformation do not provide a clear indication of how the oxidation degree affects the behavior of GO nanofillers in the strain sensing application.

To further evaluate the stability of fabricated GO paper-based sensors, a tensile machine was used to bend the paper-based sensors. As shown in the **Fig. 6.5(d)**, both ends of prepared GO paper-based sensors is clamped by the clips of tensile machine. Bending and relaxing of the sensors were achieved by raising and lowering the clips and the applied strain can be calculated as the one in above session. A typical cyclic bending result of S-GO-1 in 1 Hz is shown in **Fig. 6.5(e)**. The sensors show satisfactory stability after tens of cyclic bending and the relative resistance change (about 0.082 for 0.2% strain, 0.193 for 0.4% strain) is similar to the result of bending by hands of the strain

range from 0.1% to 0.5% (average 0.0812 for 0.2 strain, 0.1983 for 0.4% strain). Overall, it is shown in this section that the strain sensing ability of GO inks paper-based sensors can be achieved by both human body and tensile machine.

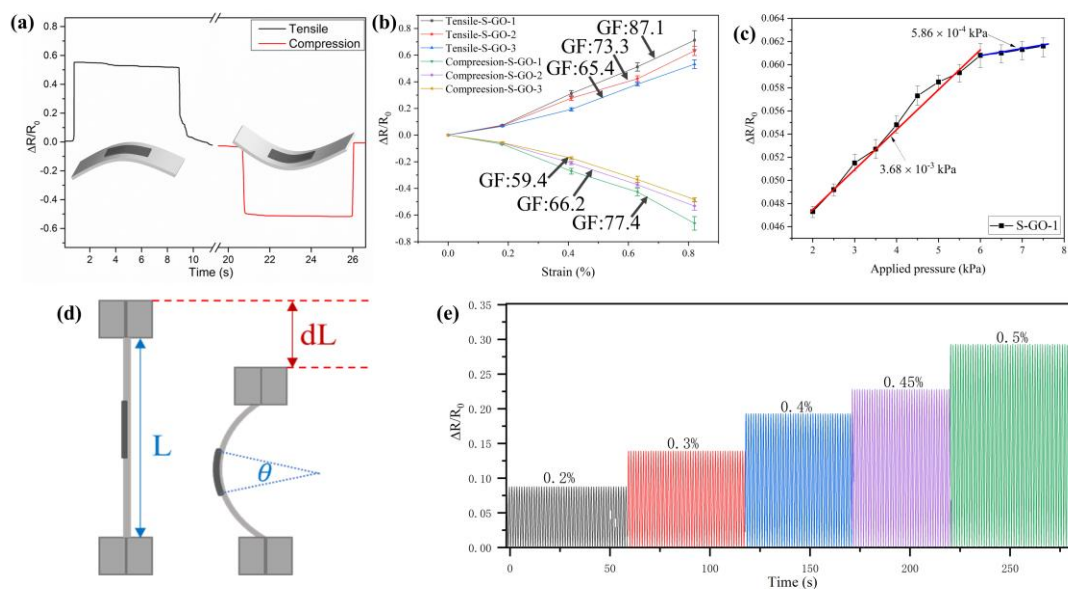


Figure 6.5. Typical tensile and compression signals of GO paper-based sensors achieved by bending(a); Concluded values of normalized resistance change of GO paper-based with different degree of oxidation under strain range from 0 to $\pm 0.85\%$ (b); Values of normalized resistance change of S-GO-1 under pressure range from 2 kPa to 7.5 kPa (c); (d) Schematic model of bending process of GO paper-based sensors by tensile machine; (e) Cyclic signals under strain range of S-GO-1.

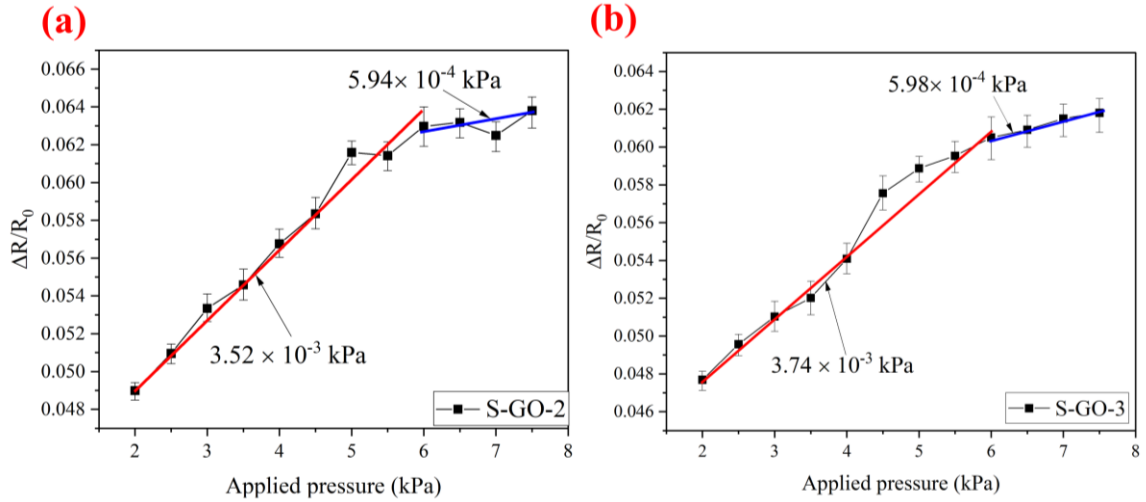


Figure 6.6. Concluded values of resistance change of S-GO-2 (a) and S-GO-3 (b) under pressure range from 2 kPa to 7.5 kPa.

6.3.3 Response of GO paper-based sensors placed on boards in multitype strains

In this section, the GO paper-based sensors were attached onto the surface of dog-bone aluminum alloy tensile specimen to further evaluate their multi-type sensing ability in a situation that is close to real scenario. The experimental process and experimental setup for sensing static tensile tests can be found in **Chapter 3 Section 3.3.2**. **Fig. 6.7(a)** demonstrate the experimental modes, including direct tensile, tensile achieved by 3-point bending and compression achieved by 4-point bending, and pressure sensing process.

Fig. 6.7(b) shows the resistance change-strain curves of GO paper-based sensors of different oxidation degrees under applied tensile. It is obvious that all the curves are smooth and the differences of those sensors become large as the strain range increases. The highest sensitive are achieved by S-GO-1 (GF:78.65), made by the lowest oxide group of GO nanofillers, under the strain range of 1%. Due to the limit of fixed axis of bending point, the max strain range is smaller than that of the biaxial tensile, which is about 0.7% and 0.3% for the 3-point and 4-point bending (**Fig. 6.7(c)-(d)**), respectively. However, the same palpable trend of sensitivity over the oxidation degree of GO nanofiller groups can be conclude, which is that the higher oxidation degree of GO nanofiller lead to the higher GFs.

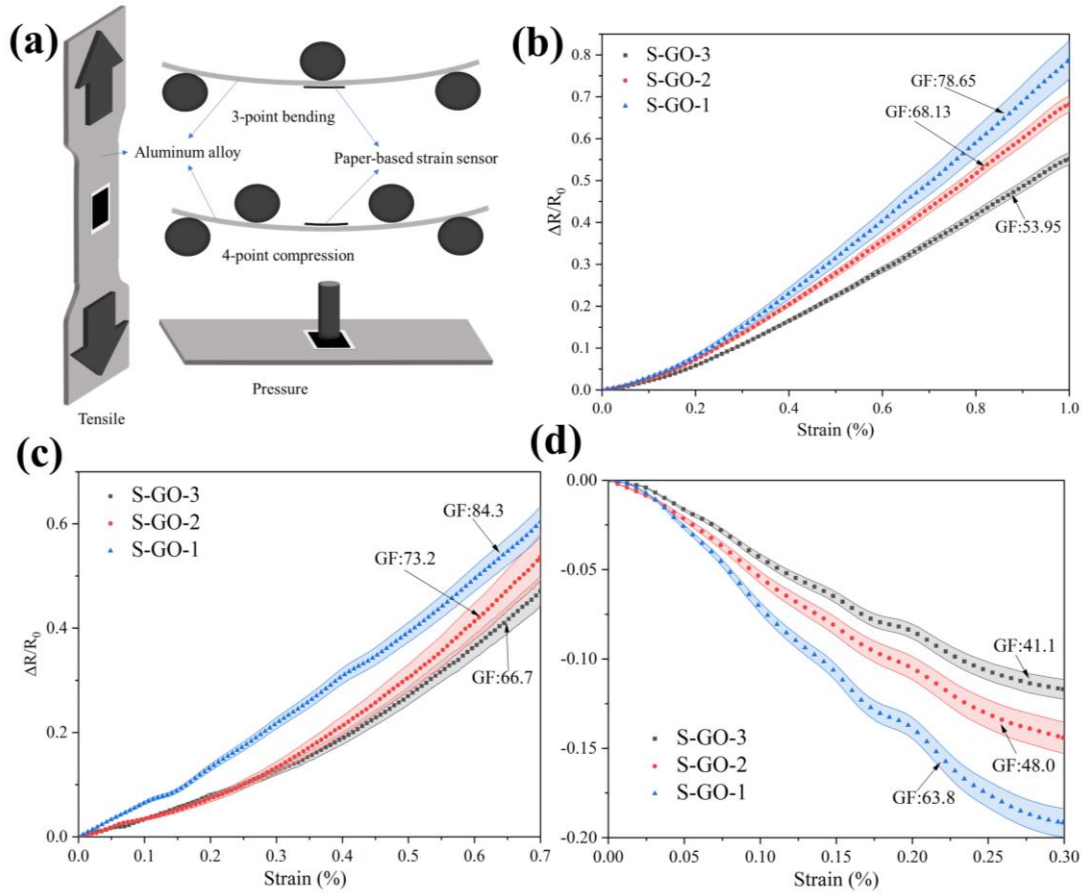


Figure 6.7. (a) Overall schematic models of biaxial tensile; 3-point bending; compression achieved by 4-point bending and pressure process of GO paper-based sensors on aluminum alloy specimens by tensile machine; Relative resistance changes vs applied strain of GO paper-based sensors with different oxidation degree under biaxial tensile test (b), 3-point bending test (c) and 4-point bending.

As for the pressure process, through the software setup of tensile machine, the applied force can be hold on a specific value for a moment, so that the step pressure curve can be obtained. As shown in **Fig. 6.8**, the response signal of S-GO paper-based sensors can be kept in a small change for the whole moment, proving the reliability of pressure results. It is also shown a decrease trend of the relative resistance change over the applied pressure, which is corresponding to same trend of S-GO paper-based sensor itself by the pressure gauge. By comparing the specific values of resistance change of the same type of sensor (S-GO-1) in the same applied pressure under those two different experiment setups, the difference is actually small. For instance, when subjected to a

pressure of 4 kPa, the response resistance signal recorded using a pressure gauge by hand is 0.0524, while the average value obtained from the tensile machine experiment is approximately 0.05263. Those small difference is strong enough to demonstrate the repeatability and reliability of GO paper-based sensors made by PoP method.

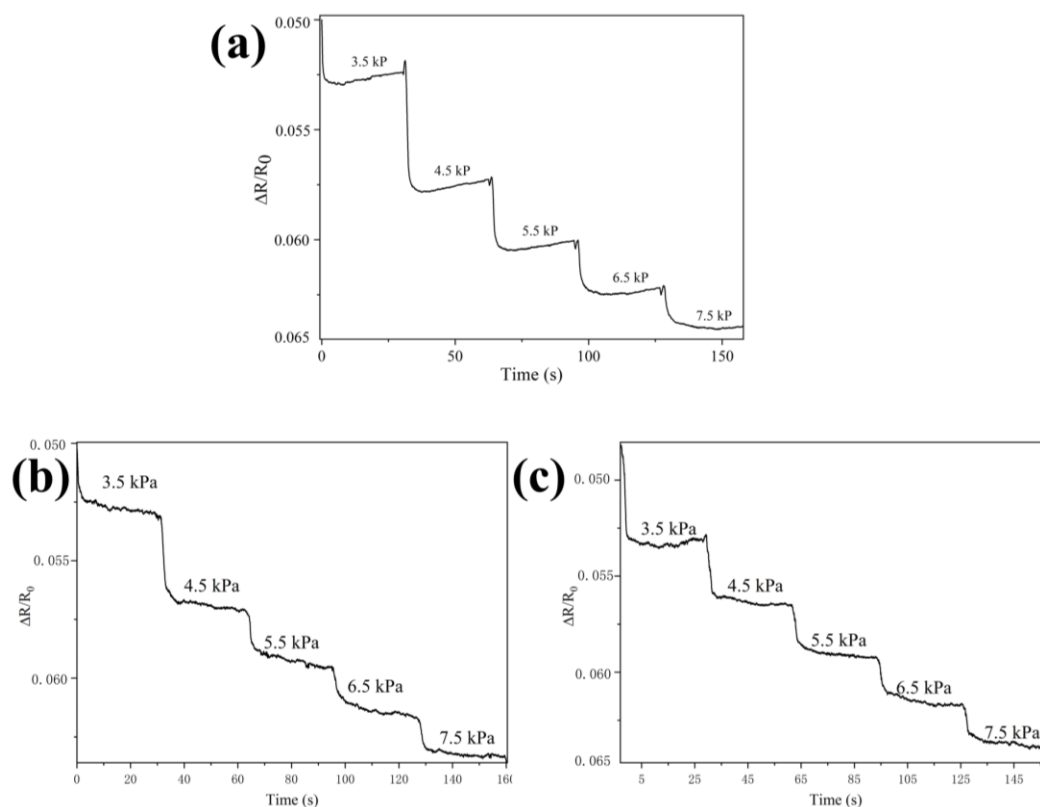


Figure 6.8. The step pressure signals of S-GO-1(a), S-GO-2 (b) and S-GO-3 (c) under pressure range from 2.5 kPa to 7.5 kPa.

In real applications, durability is also one of the important indicators for evaluating sensors. The **Fig. 6.9** compare the strain behavior of the same type of sensor made by the GO-ink-1, GO-ink-2 and GO-ink-3 within 3 month under tensile test. The difference of those sensors is that agglomeration of GO nanofillers inside the ink may increases as time goes by, resulting poor dispersion of nanofillers. As shown in the figure, the GFs decreases as the left time increases, meaning the sensitivity of 3-month-old ink is not as good as the one prepared immediately. So, it is observed that the sensitivity of GO paper-based sensors decreases to different degree after 3 months (12% for S-GO-1, 13% for S-GO-2 and 19% for S-GO-3).

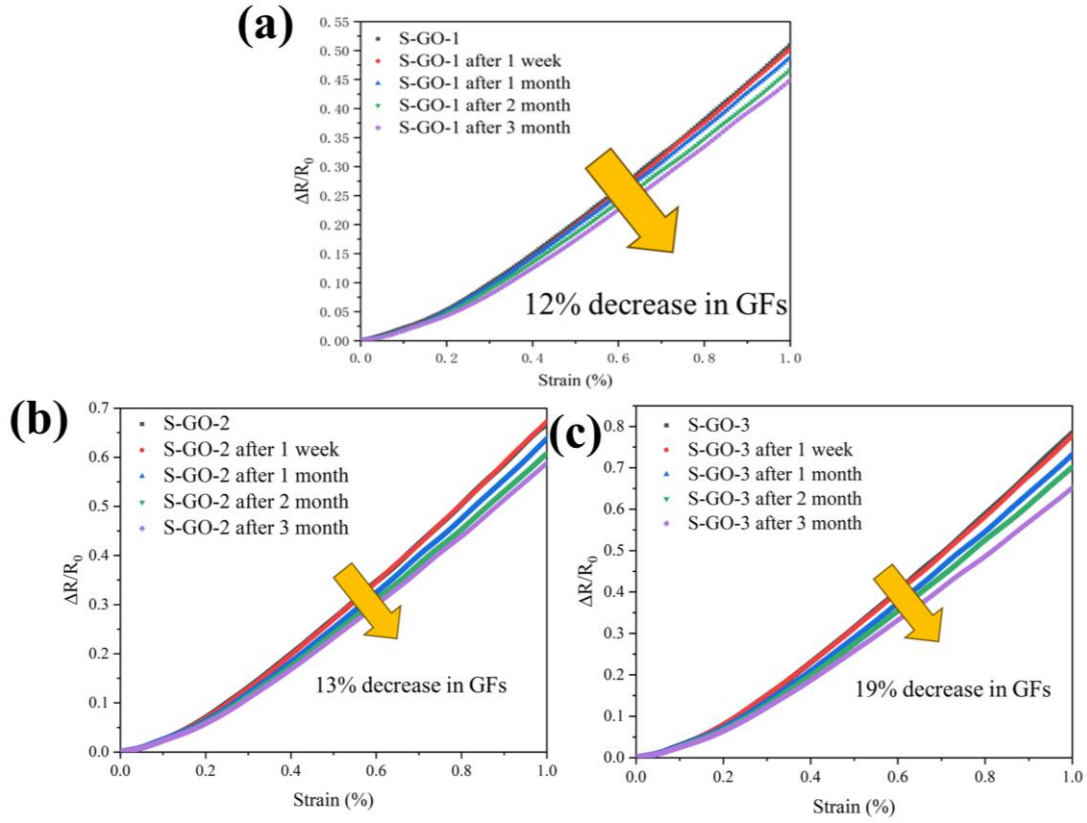


Figure 6.9. The strain behaviour of GO-based sensors made by inks GO-1(a), GO-2 (b) and GO-3 (c) among 3 months.

The experimental process and experimental setup for sensing vibration strain tests can be found in **Chapter 3 Section 3.3.3**. The data in **Fig. 6.10** indicated that as the S-GO-1 reaches the highest value of the vibration cycle, the strain gauge will reach the lowest value. It further demonstrates the responsiveness of those sensors, which can be comparable to that of commercial strain sensors within the studied vibration range. This finding suggests that the GO paper-based sensors effectively detect and respond to the applied vibrations, exhibiting performance similar to commercially available strain sensors. Additionally, it is worth noting that the strain range detected for the vibration experiment is exceptionally low. This implies that the GO paper-based sensors have the capability to accurately detect and measure very subtle changes in strain, even within this narrow range. This sensitivity to low strain levels is a valuable attribute for

applications that require precise monitoring and measurement of vibrations, especially in scenarios where the strain magnitudes are minimal.

The observation that all the GO paper-based strain sensors exhibit a similar resistance change under different frequencies (from **Fig. 6.10** to **Fig. 6.12**), consistent with the results from pressure tests, is an important finding. This consistency suggests that the response of the sensors is not significantly influenced by the frequency of the applied strain or pressure. It is also noted that the maximum applied strains in those tests are lower than those in previous tensile tests, with a value of $\varepsilon < 1$. This observation leads to the deduction that the GO paper-based strain sensors may not possess a high enough sensitivity to accurately detect and measure strains within such a low range.

Overall, the results indicate that the GO paper-based sensors exhibit excellent responsiveness and sensitivity within the tested vibration range, performing comparably to commercial strain sensors. The ability to detect such low strain levels further underscores the potential of those sensors for applications that demand high precision and sensitivity in vibration monitoring.

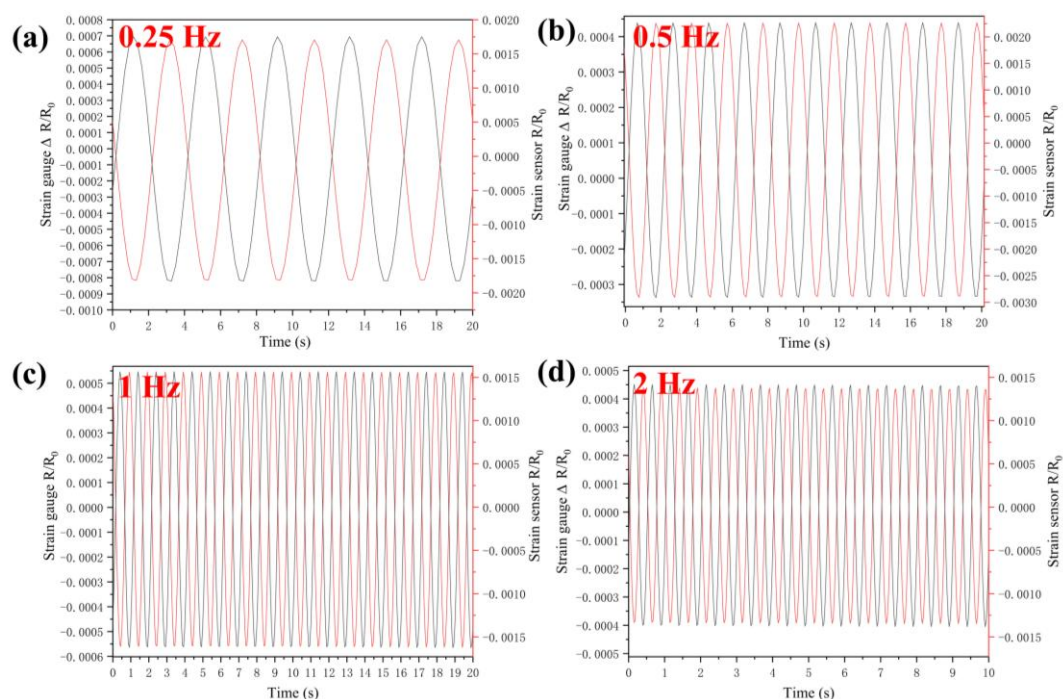


Figure 6.10. The vibration signal of S-GO-1 (black) and commercial strain gauge (red) under 0.25 Hz (a), 0.5 Hz (b), 1 Hz (c) and 2 Hz (d), respectively.

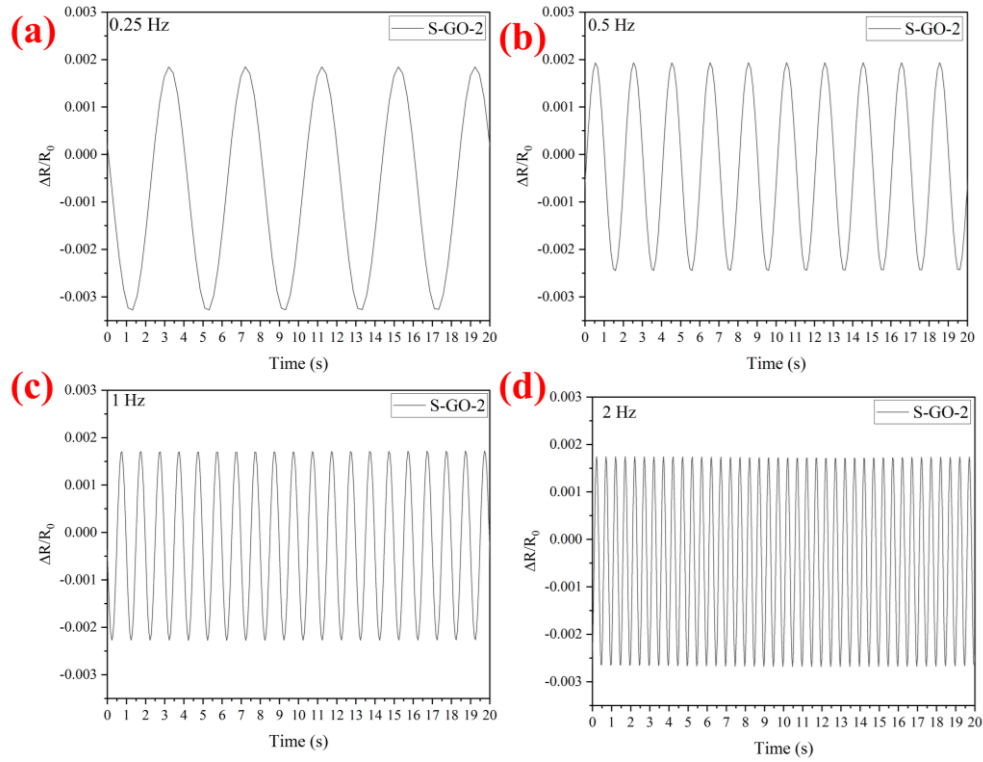


Figure 6.11. The vibration signal of S-GO-2 under 0.25 Hz (a), 0.5 Hz (b), 1 Hz (c) and 2 Hz (d), respectively.

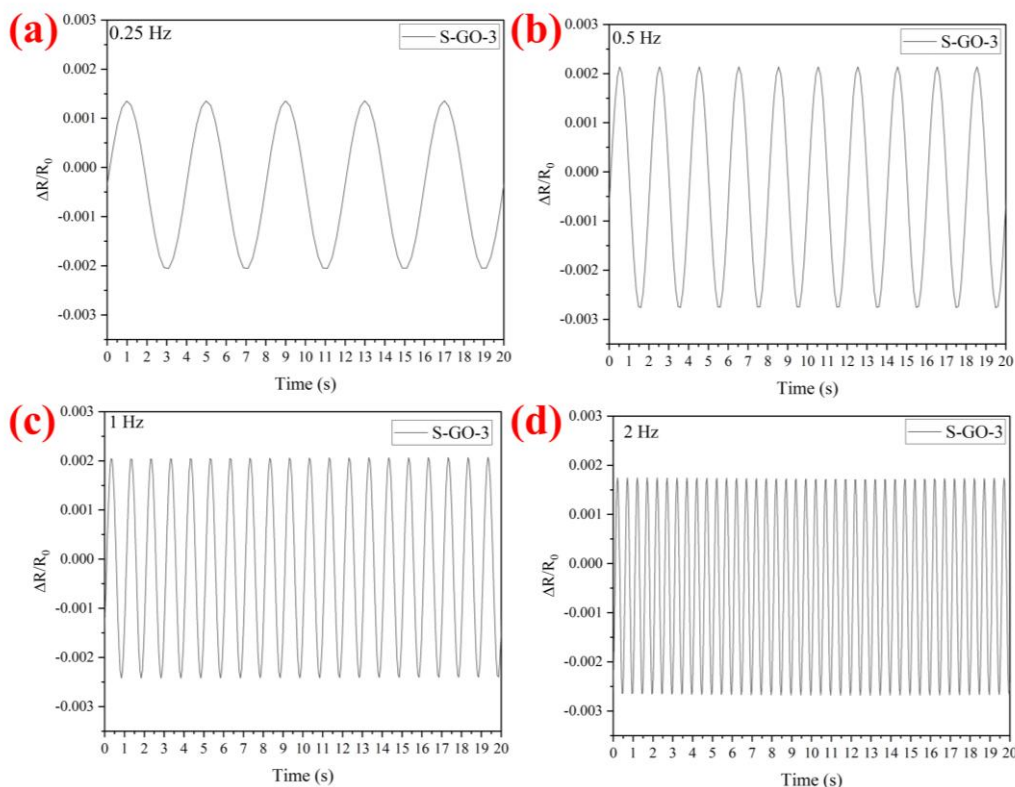


Figure 6.12. The vibration signal of S-GO-3 under 0.25 Hz (a), 0.5 Hz (b), 1 Hz (c) and 2 Hz (d), respectively.

6.3.4 Application examples of GO paper-based sensor for sensing multitype strains

In the above sections, we have demonstrated the performance of GO paper-based sensors in term of both sensor itself and as an applied sensor on different substrates. The results demonstrate the high sensitivity, stability, and responsiveness of the GO paper-based sensors. All those qualities indicate its possible real-world application as flexible strain sensors. Thus, in this section, we would further explore the performance of GO paper-based sensors in wearable device and engineering sensors to take advantage of its multitype strain sensing ability.

The preparation of the GO paper-based sensor for real applications follows a similar methodology as described in the previous experiment (**Chapter 6 Section 6.2.3**). There are a few differences in the setup. The backside of the sensor is coated with removable

double-sided tape, and a flexible PET thin film is used to cover the right side of the sensor. This ensures that the sensor is fixed in the correct position and provides protection against movement-related damage.

In Example 1, as illustrated in **Fig. 6.13(a)**, the sensor is attached to the arterial location of the pulse. Any changes caused by gestures or movements in that area can be detected and recorded. The signals captured represent the overall resistance difference when making a fist gesture or relaxing the hand. In Example 2, the high-resolution sensitivity of the paper-based sensors is utilized to record the position of a moving figure. As shown in **Fig. 6.13(b)**, the prepared sensor is attached to the middle side of the index finger. The different stopping positions of the finger can be determined by analysing the resistance recorded by the sensors. Furthermore, **Fig. 6.13(c)** demonstrates the ability of the sensors to detect quick bending signals of the finger when the bending cycle is approximately 1 Hz. This capability opens up possibilities for using gesture-based communication, as the recorded signals can be translated into readable language, facilitating communication for individuals who rely on body language.

Since the paper-based sensors show a great sensitivity in extremely low strain sensing and the non-toxicity of paper to human skin, it is possible to monitor some natural body signals. Take the eyelids as example, due to the natural expansion and contraction of the eyeballs at rest, the eyelid will produce pressure signals that are difficult to see by the naked eye, and this part of the signals play an important role in observing the health of the eye. We attached paper-based sensors to the upper part of the eyelids with removable adhesive tape and received resistance signals through a digital multimeter (DMM6500, Keithley Instruments, USA) as shown in **Fig. 6.13(d)**. The results showed that the signal of eye dilation was close to the respiratory rate (from about 0.1Hz to 1Hz). Additionally, the subject is instructed to rotate their eyeball every 30 seconds, resulting in observable deviations of the signal from the original curve at approximately 30-second. The comparison of signals from static and rotating eyeball conditions can be observed in **Fig. 6.13(e)**. Under static conditions, the signals remain smooth and

consistent. However, when the eyeball starts to rotate, there is always a disruption or distortion of the original curves, indicating the representation of the rotational results. This means that the simple paper-based sensor has the ability to simultaneously monitor the natural signal of the eye and the eye rotation signal. By further optimizing the sensor installation, it is possible to further identify the direction of eyeball rotation.

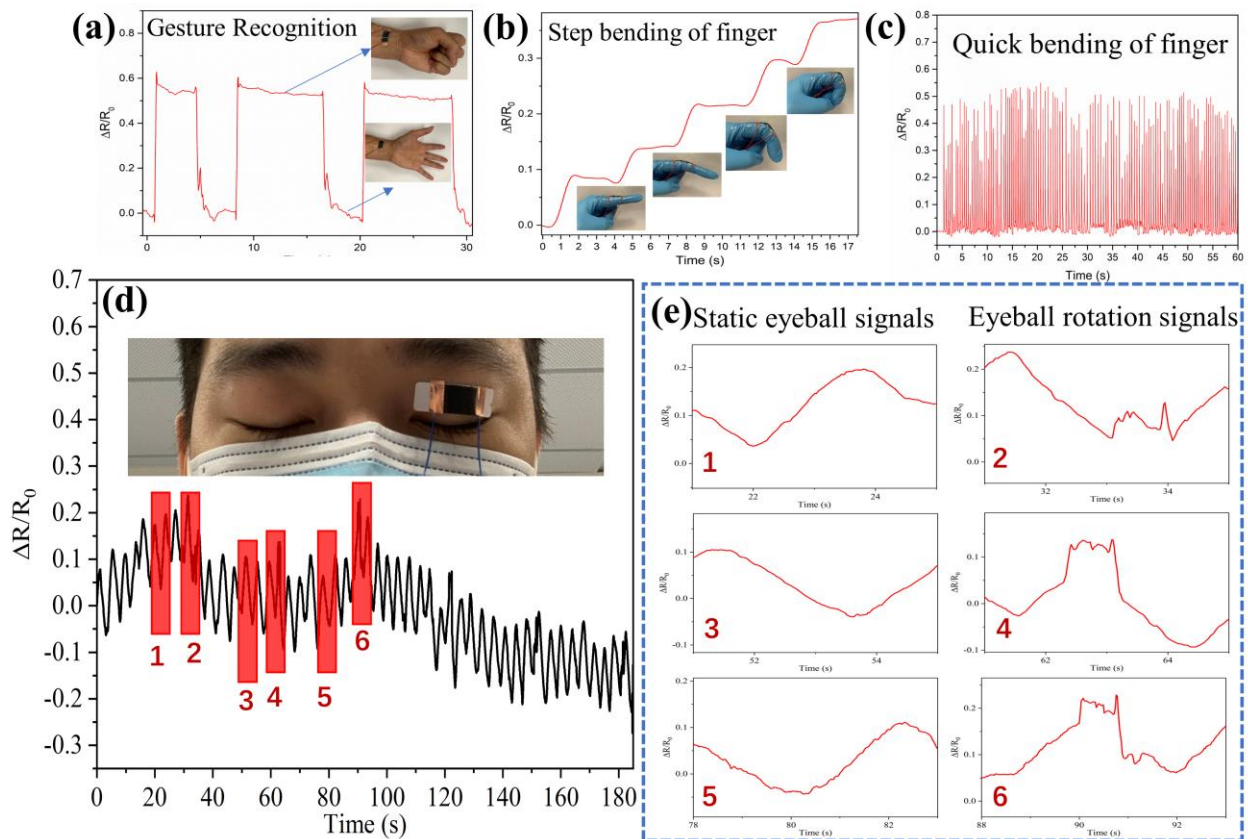


Figure 6.13. (a) gesture signal made by paper-based sensor; the step bending signal (b) and the quick bending signals (c) of paper-based sensor; (d) the natural eyelids signal and their enlarged figures.

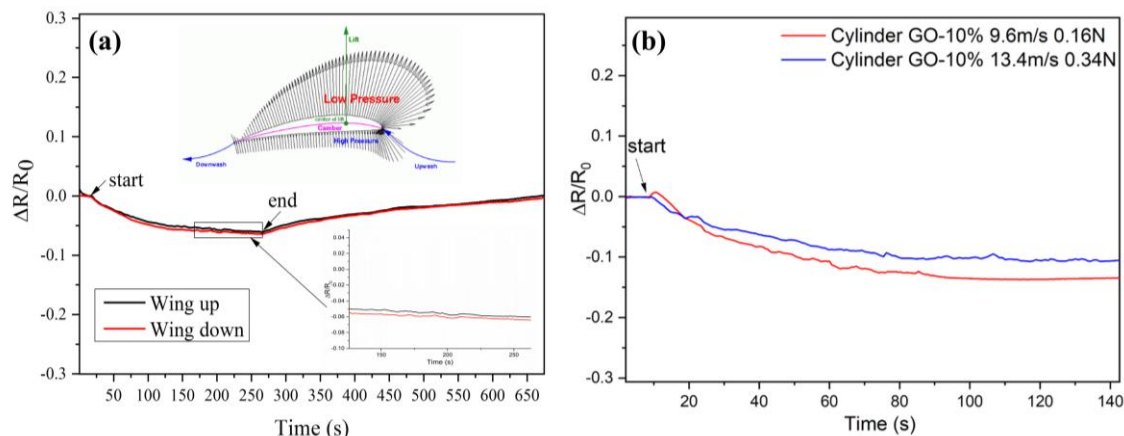


Figure 6.14. (a) The wind pressure signal on the different aspects of wing (The inserted figure shows the enlarge signals from 100 s to 280 s and the inserted images show pressure vectors and flow over a cambered section); (b) the different wind pressure signal of GO-based paper strain sensors under different wind speed.

In the field of engineering, various technologies have been employed to monitor different types of pressure. In this study, we explore the application of paper-based sensors for monitoring wind pressure in aerospace engineering. The resistance change of the sensors was recorded by attaching them to both ends of a wing model and using a digital multimeter (DMM6500, Keithley Instruments, USA).

As depicted in **Fig. 6.14(a)**, the pressure signal of the lower wing consistently exceeds that of the upper wing from the beginning. This is due to the inconsistent curvature at the ends of the wing. This observation highlights the sensor's ability to distinguish between different wind pressure states with clarity. In further experiments, the GO paper-based sensors were exposed to different frontal wind rates using a cylinder model, as shown in **Fig. 6.14(b)**. It is expected that higher wind speeds will result in higher wind pressures on the strain sensors. As a result, it is evident that the group subjected to a wind speed of 13.4 m/s exhibits a relatively significant resistance change.

Collectively, those experiments demonstrate that paper-based GO strain sensors are capable of detecting and differentiating applied pressure strain in engineering scenarios.

This finding underscores their potential for monitoring and assessing pressure variations in practical engineering applications.

6.4 Conclusion

In this study, graphene was first oxidized by the Hummer's method to different degree of oxidation and then put into the home-made print pen as the writable instruments for multitype strain sensing. The drawn trace of the prepared inks shows good writability in printed paper even when the paper substrate is in bent state. The FTIR, Raman and XRD confirm that the prepared GO have separated into 3 different degrees.

For the preformation, we first evaluate tensile and compression sensitivity of the GO-based paper strain sensors themselves by bending the paper substrate by hand. The resulted GF are as high as 87.1 and 77.4 in terms of tensile and compression strain sensing within range of 0.86%. Thanks to the 3D-like structure of GO, the GO-based paper strain sensors show the sensitivity of $3.6 \times 10^{-3} \text{ kPa}^{-1}$ in pressure sensing from the range of about 2 kPa to 5 kPa. Then, the GO-based paper strain sensors were attached to aluminum alloy substrate to simulate a real-world situation in tensile, compression and pressure sensing by a Instron tensile machine. The similar performance of the GO-based paper strain sensors shows great potential in meeting complicated real-world situation. GO sensors exhibited similar sensing ability even the GO inks were leave for over three months. Additionally, it is noted that the sensitivity of GO-based paper strain sensors reduces with an increase in the oxidation degree of GO. This can be attributed to several factors, including a higher concentration of oxygen-containing functional groups, an increased number of defects, and improved interfacial interactions within the GO material. Finally, the prepared sensors were applied to different actual applications including gesture recognition, eye movement and intraocular pressure signal measurement and wing wind pressure signal measurement.

To summary, this research give contribution to demonstrate the high performance of GO-based paper strain sensors in tensile, compression and pressure sensing by PoP approach. The prepared sensors also were utilized in actual applications in wearable device field and aerospace field.

Chapter 7 Evenly coating PDA nanolayers on graphene nanosheets through a novel two-step method: a new approach for optimizing the sensitivity of graphene-based strain sensors

7.1 Introduction

Due to the poor piezoresistive sensitivity of pure graphene, researchers around the world have been driven to increase the sensitivity of graphene-based strain sensors [31, 95, 96, 157]. So far, it can be separated into two different mechanisms-dominate types: over-connected dominate graphene-based strain sensors[97, 129] and tunneling effect dominate graphene-based strain sensors [98]. The first type relies on the over-connected graphene sheets, where the change in conductivity is determined by the contact resistance between adjacent sheets. When strain is applied to graphene, the overlapping area between neighboring sheets undergoes changes, resulting in resistance variations[298, 299]. For example, Hempel et al. [155] developed highly sensitive graphene-based thin film strain gauges through spray deposition. They explained the exceptional properties of these strain sensors by modeling the strain-induced changes in graphene flake-flake overlap. The latter type depends on the distance change between graphene sheets. According to the tunneling effect, there is a current flow from one isolated graphene sheet to another and it is predicted that the resistance will change exponentially with the increase of distance[300-302]. Zhang et al.[303] report a tunneling type of strain sensor based on graphene composite films with layered configuration. They found that GF is proportional to the initial tunneling distance of two nanographene flakes.

Normally, there are both types of mechanisms existing inside the strain sensors and playing different roles in contributing resistance change in different strain stages.

Limited by the scant over-connected area of graphene and the linear relationship between resistance change and applied strain by the over-connected theory model [98, 169], the GF of over-connected type strain sensors is restricted. On the other side, tunneling type strain sensors can achieve greater sensitivity by increasing the tunneling probability[166, 304]. By changing the over-connected type inside the graphene connecting system into tunneling type, theoretically higher GF can be obtained.

To explore and implement this concept, various research studies have been conducted. Inspired by our previous study[248, 270], PDA has shown as a suitable coating material in coating carbon nanomaterials to improve the sensitivity of 1 dimensional carbon nanotubes-based strain sensors. The use of PDA is due to its strong viscosity[305, 306], assisting in the dispersion of nanofillers[305, 307] and controllable forming process[308]. It is also possible to coating PDA nanolayers on 2-dimensional carbon nanomaterials to prepare layered structure and control the connection distance between nanofillers to dominate the tunneling resistance under strain. Among 2-dimensional carbon nanomaterials, GO has shown strong dispersion ability from solution forming and suitable for further surface modified, due to the presence of the oxygen-containing functional groups. By applying PDA nanolayers onto GO, the over-connected type within the graphene connectivity system can be transformed into a tunneling type, resulting in higher sensitivity. However, the existing coating research[309-311] show an unevenly enough distributed PDA nanolayer on the surface of graphene since the self-polymerization forming process of PDA is hard to keep sustainable due to the aggregation of DA monomer [312] and the competition between redox reactions of DA and GO and the self-polymerization of DA[310].

In our previous study [270], PDA has been shown as a suitable coating nanomaterial in coating carbon nanomaterials due to its strong viscosity and controllable forming process. GO have shown strong dispersion ability from solution forming and suitable for further surface modified, due to the presence of the oxygen-containing functional groups. Together, it is possible to coating PDA nanolayers on GO to prepare layered

structure and decrease the connection between graphene nanosheets. However, the existing coating research [309-311] show an unevenly enough distributed PDA nanolayer on the surface of graphene since the self-polymerization forming process of PDA is hard to keep sustainable due to the aggregation and conformity competition of DA monomer [312] and the competition between redox reactions of DA and GO and the self-polymerization of DA.

Firstly, to achieving evenly PDA coating on graphene for dispersion, it is theoretically possible to separate the PDA coating process into two steps. This strategy is underpinned by the premise that the chemical conditions required for the oxidation of DA differ from those conducive to the self-polymerization of DA. The proposed methodology entails first initiating redox reactions to anchor DA molecules onto GO. Subsequently, the formation of cohesive PDA nanolayers on the reduced GO takes place, wherein the self-polymerization of DA revolves around the anchored DA molecules. Also, the nanofillers are used to prepared full-filler film as strain sensors by the assistant of vacuum filtration process to make the nanoflakes contract with each other so the distance of graphene can be controlled by the coated PDA nanolayers.

Strain sensors containing PDA@rGO nanofillers with different PDA contents were prepared to achieve the best suitable distance between graphene flakes for tunnelling junctions. A full comparison of the PDA@rGO-based strain sensors with different PDA contents, to control the initial distance between adjusting graphene nanosheets, was obtained.

7.2 Experimental

Fig. 7.1 (a) outline the preparation process of PDA@rGO nanofillers. It starts with the oxidation of graphite to make GO, and the coating PDA nanolayers into GO nanoflakes by 2-step coating method.

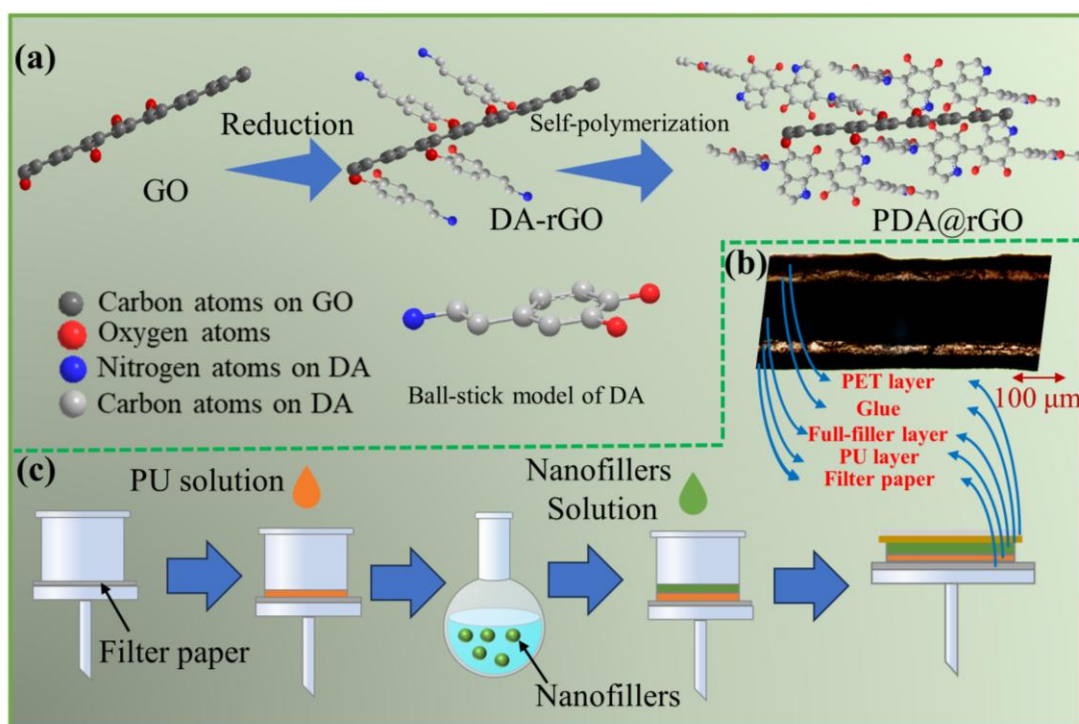


Figure 7.1. (a) Illustration of PDA 2-step coating process by ball-stick model; (b) Cross section images of full-filler sensors by optical microscope; (c) Fabrication process of full-fillers sensors.

7.2.1 Preparation of DA-rGO

Pure GO were prepared by traditional Hummer's method [99]. 1.5 g graphite and 0.85 g NaNO_3 were placed in a flask. Then, 75 mL H_2SO_4 was added in the flask with stirring in an ice-water bath and 8 -10 g KMnO_4 was slowly added over about 3 h. The mixture was stirred in the ice water bath for 6 h, following by a vigorously stirring for 2 days at room temperature to have the graphite oxidized. Then, the mixture was diluted with water (1000 mL) slowly, and the excess KMnO_4 was decomposed by hydrogen peroxide (H_2O_2 , 30 wt.%, 15 mL). The insoluble precipitations were removed by centrifugation several times. Then, the resulted GO solution was filtered and washed with HCl (10 wt.%, 1 L) and water for several times to remove the metal ions. The pristine brown GO solution was dialyzed with deionized water for 3 days before use to remove any residual salts and acids.

A certain amount of GO powder was placed in acetone solution and then suffer ultrasonic treatment for 8 h to form a 0.15 mg/ml solution. Then adding a small amount of 38% HCl to adjust the pH value of the solution between 2.8 - 4.8. 0.04 mg DA was then put into 100 ml acidic GO solution. Then the mixed solution was stirred rapidly and then stand for 12h. The electrostatic attraction between DA and the oxygen-containing functional group of GO will adsorb DA onto GO and then undergo a slow redox reaction, while the low concentration of DA can avoid the self-agglomeration of DA to the greatest extent and acidic conditions of solution can reduce the protonation of DA to form PDA. After that, the mixed solution was vacuum filtered and washed multiple times by deionized water, then dried at 80 °C to obtain DA-GO powders.

7.2.2 Preparation of PDA@rGO

A certain amount of DA-rGO power was put into phosphate buffer (pH 8-8.5, adjusted by NaOH) to prepared 0.15 mg/ml DA-rGO dispersion solution. 0.15 mg DA for preparation of PDA were adding into 100 ml DA-rGO dispersions and then treated by ultrasonic bath for 2 h at 20 °C to conduct the self-polymerization of DA. After that, the mixed solution was vacuum filtered and washed multiple times by deionized water, then dried at 80 °C to obtain PDA@rGO-1 powders.

To prepare higher PDA coating content nanofillers, repeated DA self-polymerization coating process were used in this study. For example, the twice coating cycle products were achieved by putting 0.15 mg DA into 100 ml PDA@rGO-1 dispersions (0.15 mg/ml) and then treated by ultrasonic bath for 0.5 h at 20 °C. After that, the mixed solution was vacuum filtered and washed multiple times by deionized water, then dried at 80 °C to obtain PDA@rGO-2 powders. To simplify, PDA@rGO-X were used to present the PDA@rGO with X coating cycles.

As blank control, PDA directly coated GO products were prepared and the process was as follows: 0.15 mg DA were putted into 100 ml GO phosphate buffer dispersions (0.15 mg/ml, pH:8 - 8.5) and then treated by ultrasonic bath for 0.5 h at 20 °C also to conduct

self-polymerization of DA. After that, the mixed solution was vacuum filtered and washed multiple times by deionized water, then dried at 80 °C to obtain PDA@rGO powders. To simplify, the PDA directly coat GO nanofillers is named by PDA@rGO-D.

7.2.3 Preparation of full-fillers sensors

The prepared nanofillers (including GO, DA-rGO PDA@rGO-D and PDA@rGO-X) were put into NMP solution to achieve 0.15 mg/ml nanofiller dispersed solutions. The dispersed solutions were magnetically stirred for half an hour and then sonicated for 2 hours to achieve better dispersed state. 0.05g porous polyurethane (PU) resin was also dispersed in 200 ml NMP solution to obtain PU dispersed solution through the same process.

To prepared full-filler strain sensors, vacuum filtration setup was used. Firstly, the filter paper is put on the filter inside the vacuum filtration setup. 2 ml porous PU/NMP dispersed solution were dropped into the mold inside the bush funnel. After vacuum treatment, the NMP liquid were gone, and the PU layer was left on the filter paper. Then, 5 ml nanofillers dispersed solution were dropped into the funnel and processed vacuum suction filtration treatment by several times so that a full-filler film can be form.

After fixed the electrodes by conductive silver glue at the ends of the full-filler layer and removed the PET mold, another flexible sticky ultra-thin PET polymer film used to protect the full-filler layer was covered. The optical image and fabrication process of the prepared full-filler sensors are shown in **Fig. 7.1(b)** and **Fig. 7.1(c)**. The thickness of the full-filler layer in sensors is about 200 μm . The fixed-shape full-fillers layer on filter paper are shown in **Fig. 7.2**.

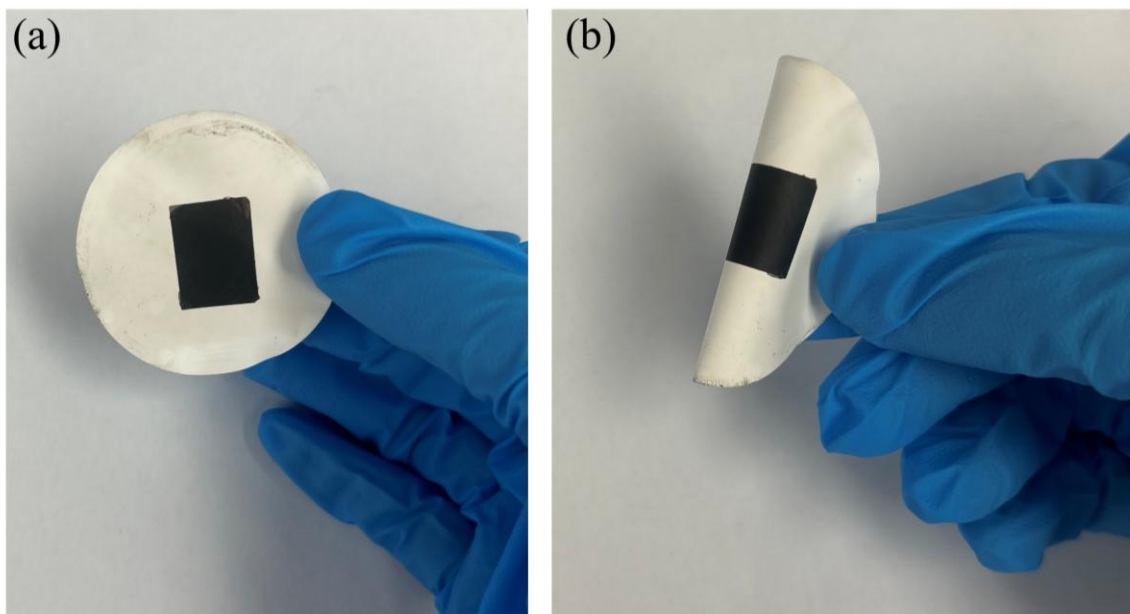


Figure 7.2. Actual images of full-fillers sensors.

In order to better distinguish between fillers and corresponding sensors in the following discussion section, the names of sensors prepared with corresponding fillers are prefixed with S. For example, S-PDA@rGO-1 represents the full-filler sensors that was prepared by PDA@rGO-1 nanofillers.

7.3 Results and discussion

7.3.1 Characterization of PDA@rGO by 2-step coating method

Fig. 7.3 and **Fig. 7.4** show the graphene framework and element mapping of C, O and N of PDA@rGO-1 and PDA@rGO-2 nanofillers prepared by 2-step coating method, respectively. The element distribution of C and O is overlapping with the graphene structure in both elements mapping, corresponding to the fact that oxygen-coating functional group is fixed on the surface of graphene. Since the N atoms only exist on the DA or PDA molecular structure, the N elements distribution in **Fig. 7.3** and **Fig. 7.4** can be used to prove the presence of DA or PDA on the surface of graphene.

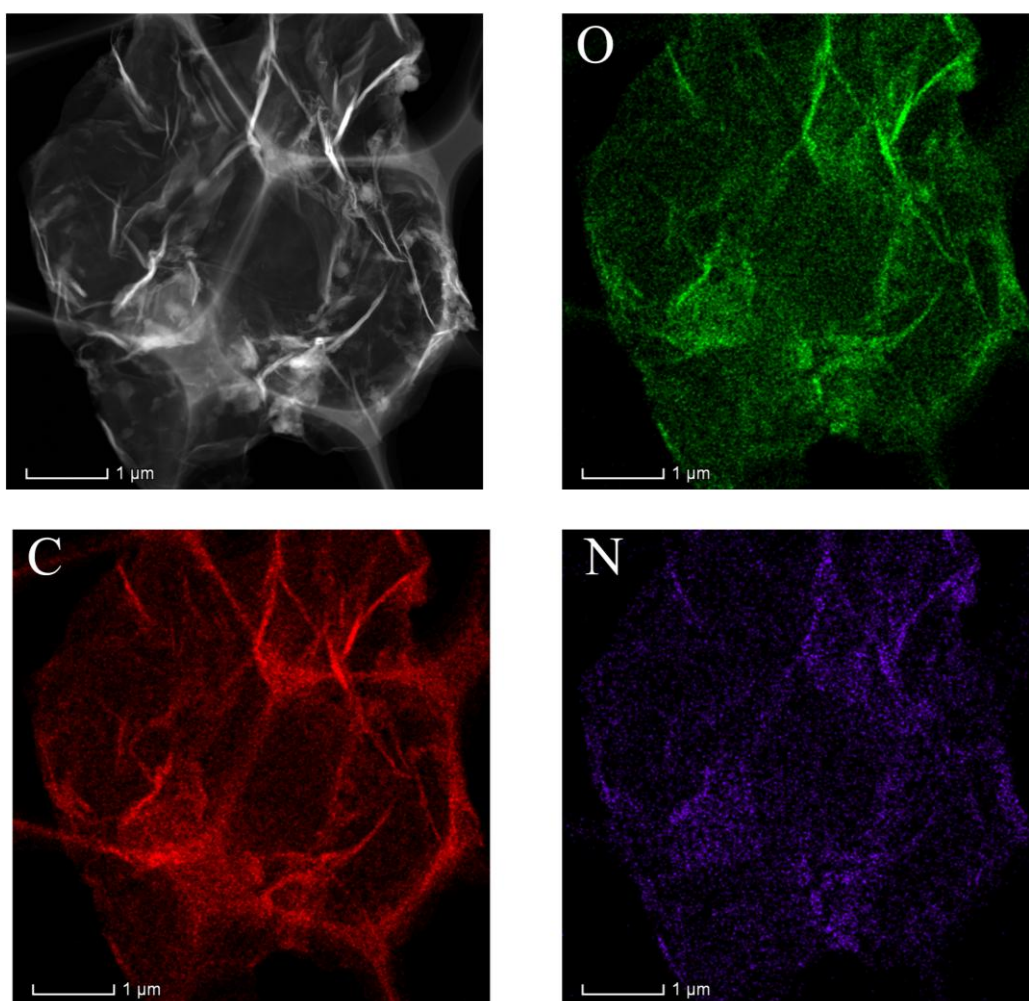


Figure 7.3. TEM image of PDA@rGO-1 nanofillers and the corresponding C, O and N element distribution mapping.

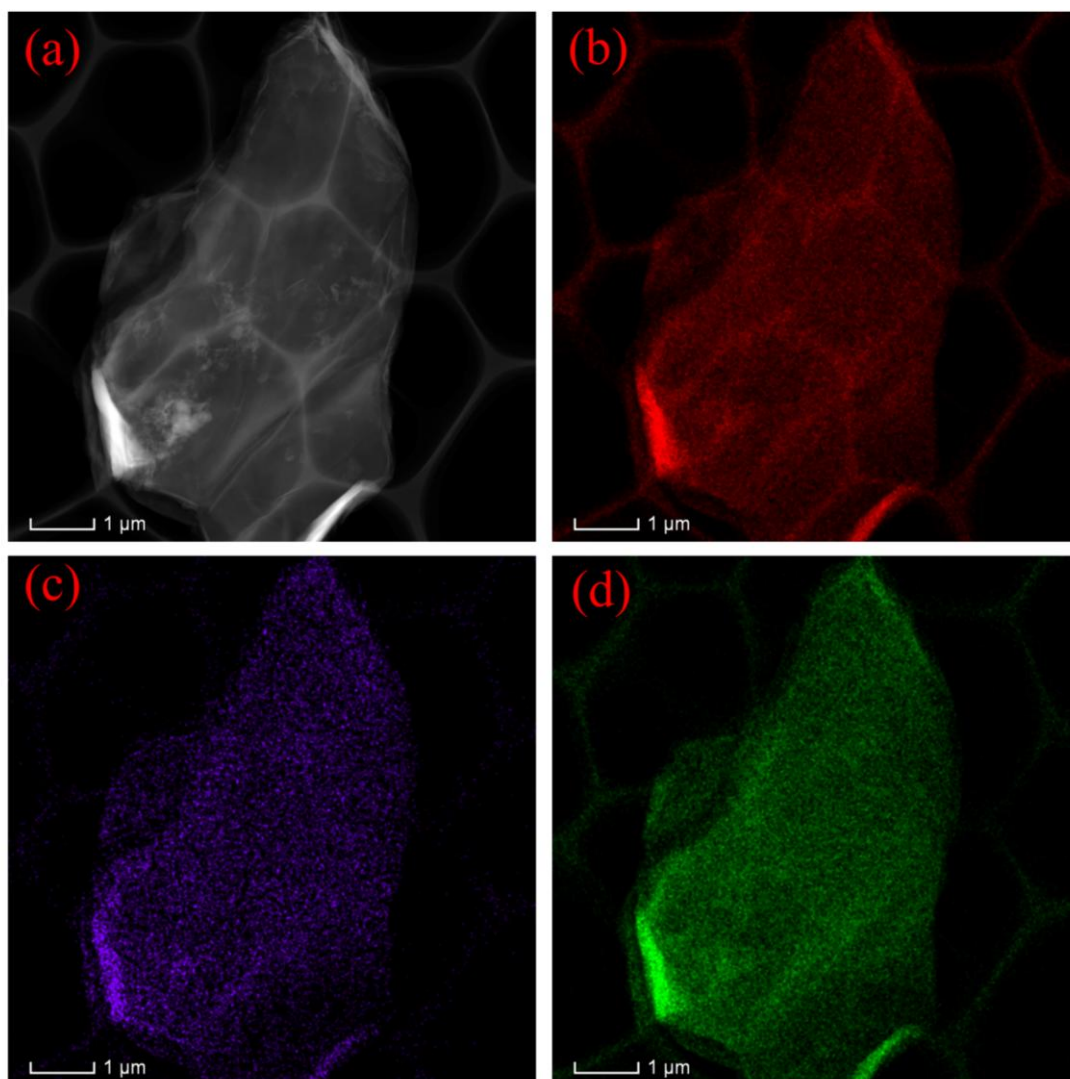


Figure 7.4. TEM image of PDA@rGO-3 nanofillers and the corresponding C, O and N element distribution mapping.

To further differentiate that if DA has been transformed into PDA or not, FTIR spectra were conducted for GO, DA-rGO, PDA, and PDA@rGO samples, as shown in **Fig. 7.5**. The distinctive peaks of pristine GO are observed at approximately 1092 cm^{-1} , 1276 cm^{-1} , 1620 cm^{-1} , and 1725 cm^{-1} , corresponding to the stretching vibration of C-O-H, C-O, C=C, and C=O, respectively[271]. The C=C peak, representing the graphene structure, is present in both DA-rGO and PDA@rGO, while the C=O peak, indicating the presence of oxygen-containing functional groups on GO, is reduced. This reduction suggests the occurrence of the first coating process of PDA and the preparation of rGO products. However, by adding more DA monomers and polymerizing, lactones are

formed on the structure of PDA, so peaks at similar positions (1735 cm^{-1}) reappear in PDA and PDA@rGO samples [313].

The N-H peak, associated with the shearing vibration of the amide II functional group in DA-related structures, can be utilized to confirm the presence of amide groups. Consequently, the N-H peak is observed in DA-rGO and PDA@rGO samples. After the polymerization of DA, the PDA molecular chain is formed through deprotonation and intermolecular Michael addition reactions of leukodopaminechrome, resulting in the appearance of a new characteristic peak at approximately 1692 cm^{-1} , corresponding to the C=N bond, in the PDA samples [314]. Finally, the FTIR spectrum of PDA@rGO exhibits combined characteristic peaks of N-H, C=C, and C=N, indicating the successful preparation and integration of PDA with rGO.

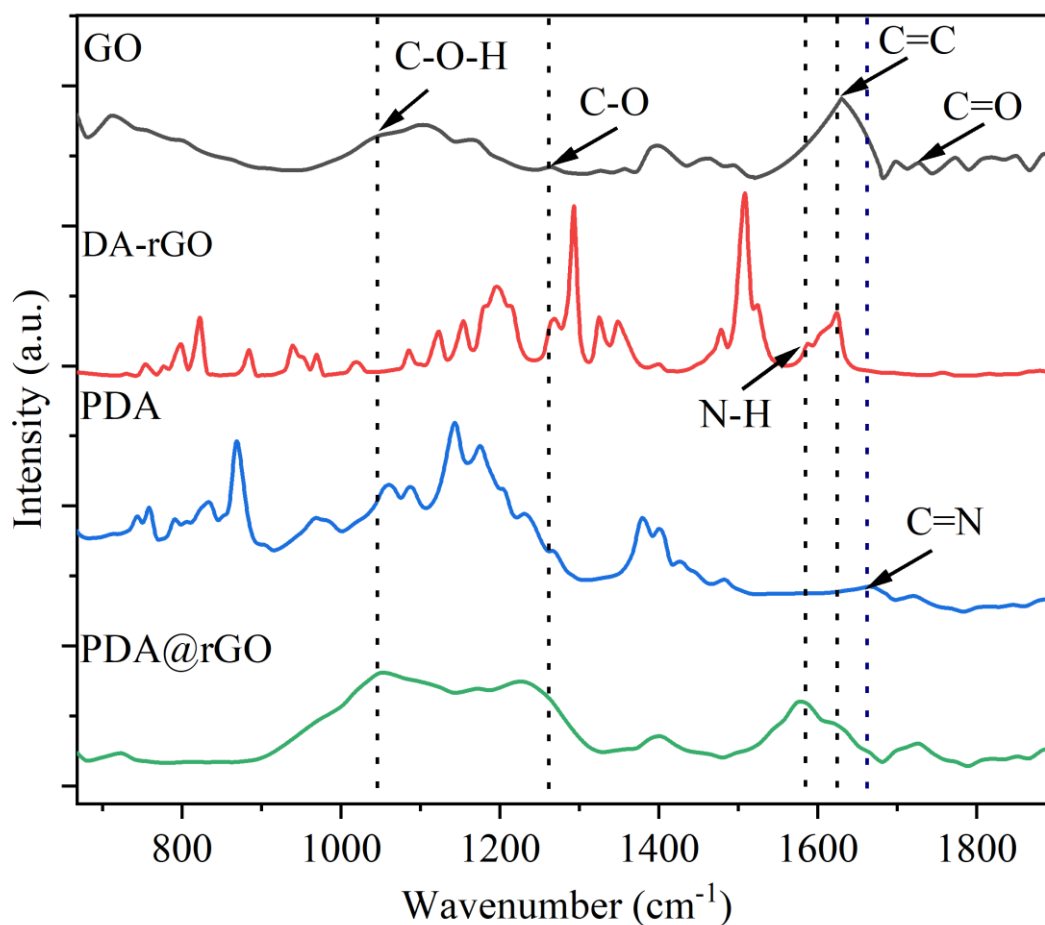


Figure 7.5. FTIR curves of pure GO, DA-rGO, PDA and PDA@rGO-1.

The morphology of PDA@rGO at different stages is conducted by TEM as shown in **Fig. 7.6**. The pristine GO is transparent with folds formed by the oxidation process of graphite and the size is about several micrometres (**Fig. 7.6(a)-(b)**). At smaller scales (20nm-50nm, **Fig. 7.6(a)-(b)**), pure GO exhibits fewer layered structure.

After the first stage of redox process, it is clear that many small nanoballs are formed on GO nanosheets (**Fig. 7.6(c)-(d)**) and the size is about several nanometres to twenty nanometres (**Fig. 7.7(c)-(d)**). Those nanoballs are understood as the redox products of DA and GO and the aggregate of DA. In this stage, the acid surrounding is not suitable for the DA molecules to react with each other to form the PDA long chains, thus they only stacked by π - π interaction or short DA chains to form nanoballs on GO.

By change the atmosphere alkaline buffer solution, the added DA starts to contact with the nanoballs and form PDA by self-polymerization, hence a PDA coating nanolayers can be obtained on the surface of GO. As shown in **Fig. 7.6(e)-(f)**, the colour of PDA@rGO-2 sample is darker than the pure GO nanofillers at the same scale.

Due to the competition between DA reduction process and self-polymerization, the resulted PDA in directly coating tend to aggregate with each other to form smaller layered structure at the surface of GO, unable to cover the whole surface area. As shown in TEM images (**Fig. 7.6(g)-(h)**) and, opaque PDA layers can be found, and in SEM images (**Fig. 7.8(a)-(c)**), the surface of GO is unevenly covered by the PDA aggregates. The unevenly distributed PDA aggregates might have a trouble in stacking graphene nanofillers and controlling the distance between nanosheets, which weakens the tunnelling effect.

On the other hand, it is shown that in TEM images (**Fig. 7.6(e)-(f)**) and SEM images (**Fig. 7.8(d)-(i)**), the surface of PDA@rGO samples by 2-steps coating is smoother and the aggregate of PDA is much less. Especially for PDA@rGO-1 shown in **Fig. 7.8(f)**, the folds of initial GO can be found, indicating that PDA is extremely thin and evenly

distributed. The smooth PDA nanolayer is considered to have a better result in controlling the distance between graphene nanosheet.

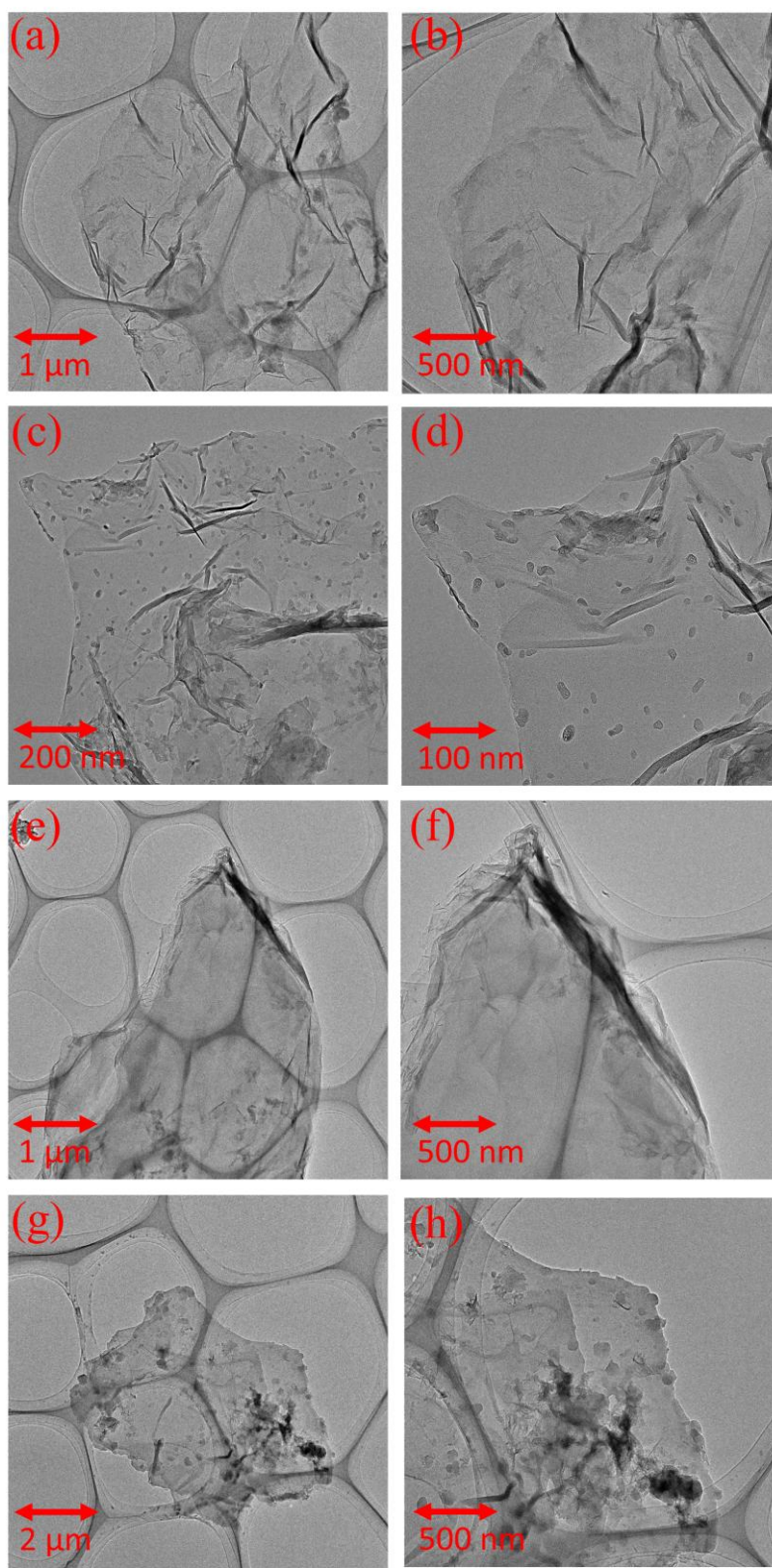


Figure 7.6. TEM images of (a)-(b) pure GO, (c)-(d) DA-rGO, (e)-(f) PDA@rGO-1 and (g)-(h) PDA@rGO-D.

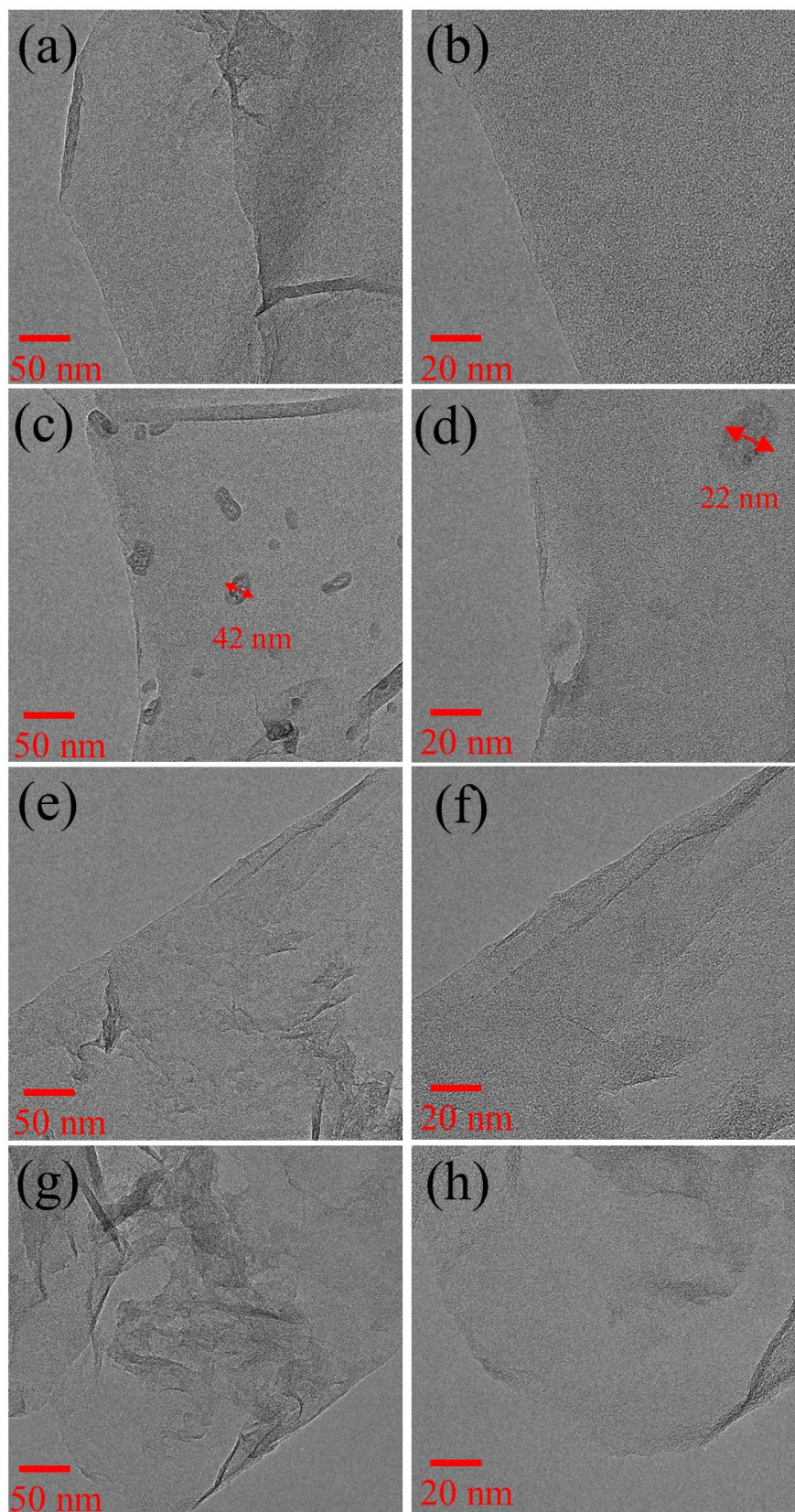


Figure 7.7. High resolution TEM images of (a)-(b) pure GO, (c)-(d) DA-rGO, (e)-(f) PDA@rGO-1 and (g)-(h) PDA@rGO-D.

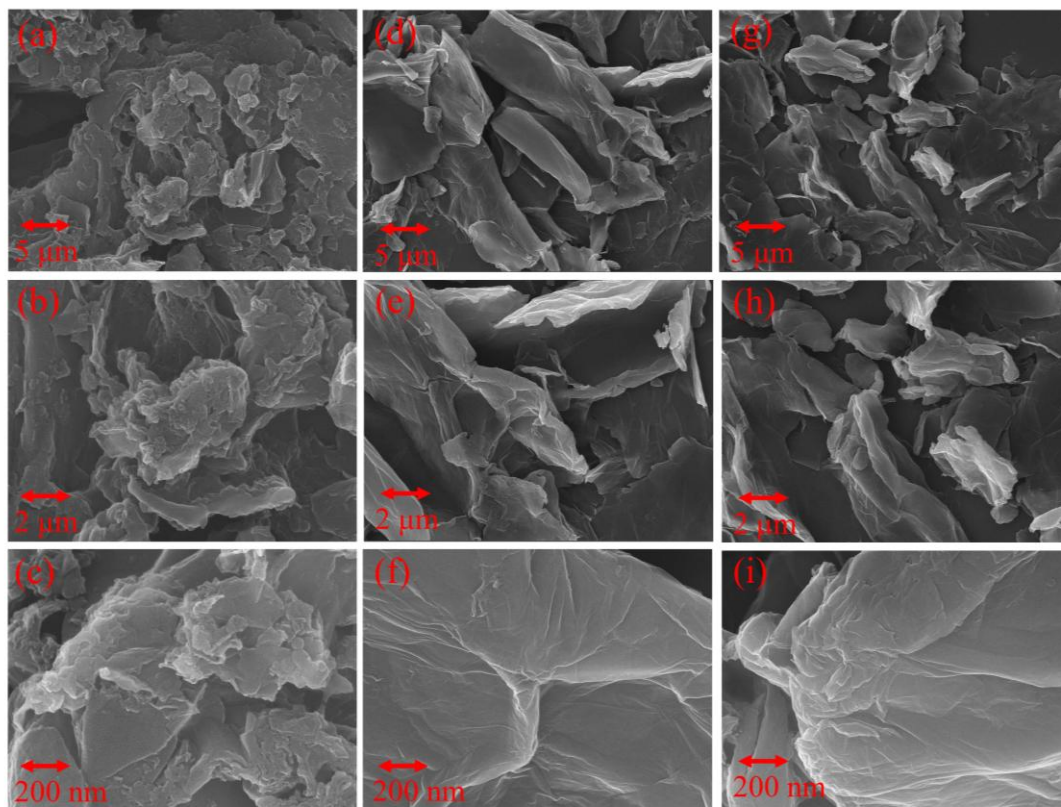


Figure 7.8. SEM images of (a)-(c) PDA@rGO-D, (d)-(f) PDA@rGO-1 and (g)-(i) PDA@rGO-2.

Moreover, from SEM-EDS characterization (**Fig. 7.9**), the PDA coverage on GO of PDA@rGO-1 sample is higher than the PDA@rGO-D by directly coating with same DA addition by nearly double, demonstrating that the coating efficiency of 2-step coating is higher than that for directly coating.

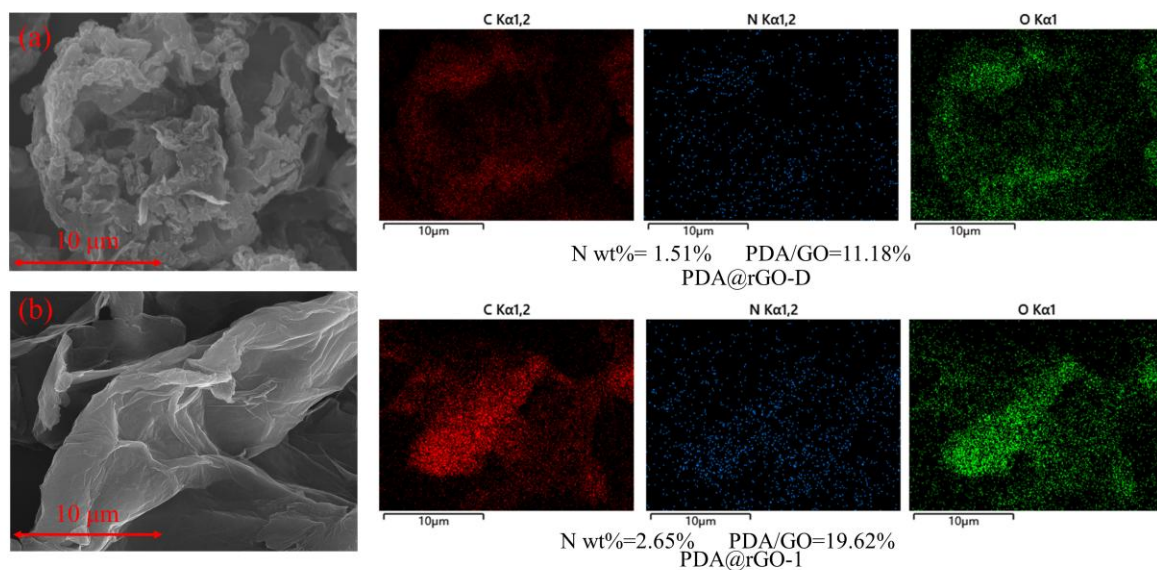


Figure 7.9. SEM images and the C, O and N elements mapping of (a) PDA@rGO-D and (b) PDA@rGO-1.

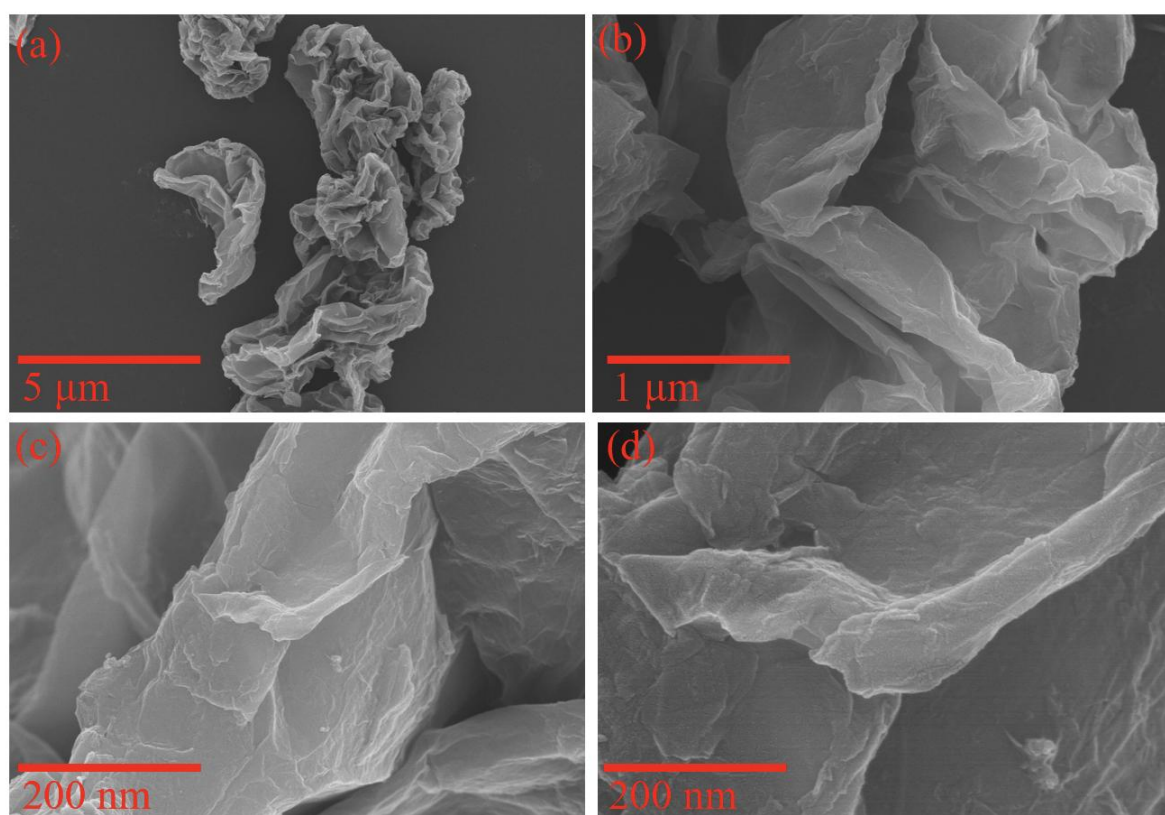


Figure 7.10. SEM images of PDA@rGO-3 nanofillers.

In our attempts, it is found that the PDA coating content can be controlled by cycle number of the second stage of 2-step coating method. **Fig 7.8(d)-(i)**, **Fig. 7.10** and **Fig 7.11** show the morphology of PDA@rGO groups samples with different second stage coating cycles from 1 to 6. In SEM images of PDA@rGO-1 as shown in **Fig. 7.8(d)-(f)**, the initial folds of GO can be clearly obtained and when the coating cycles reached 3, those folds in PDA@rGO-3 as shown in **Fig. 7.10** become flat. However, in PDA@rGO-5 and PDA@rGO-6 samples as shown in **Fig. 7.11(d)-(f)** and **Fig. 7.11(g)-(i)**, respectively, it is hard to tell GO characteristic structure from appearance, indicating that the coating thickness is increase with the second coating cycle number. It further demonstrates that the distance between the neighbouring graphene nanosheets increased with the second coating cycle number. It is shown that the influence of DA points on initial DA-rGO to help achieve smoother PDA layers becomes weaker as the coating cycle number increases.

Moreover, it is also noticed that in PDA@rGO-5 and PDA@rGO-6 samples as shown in **Fig. 7.11(f)** and **Fig. 7.11(i)**, the excess DA molecules tend to form a “brigade” between graphene nanosheets, which might further separate the neighbouring graphene to a certain extent and might resulting the aggregate of PDA@rGO nanofillers.

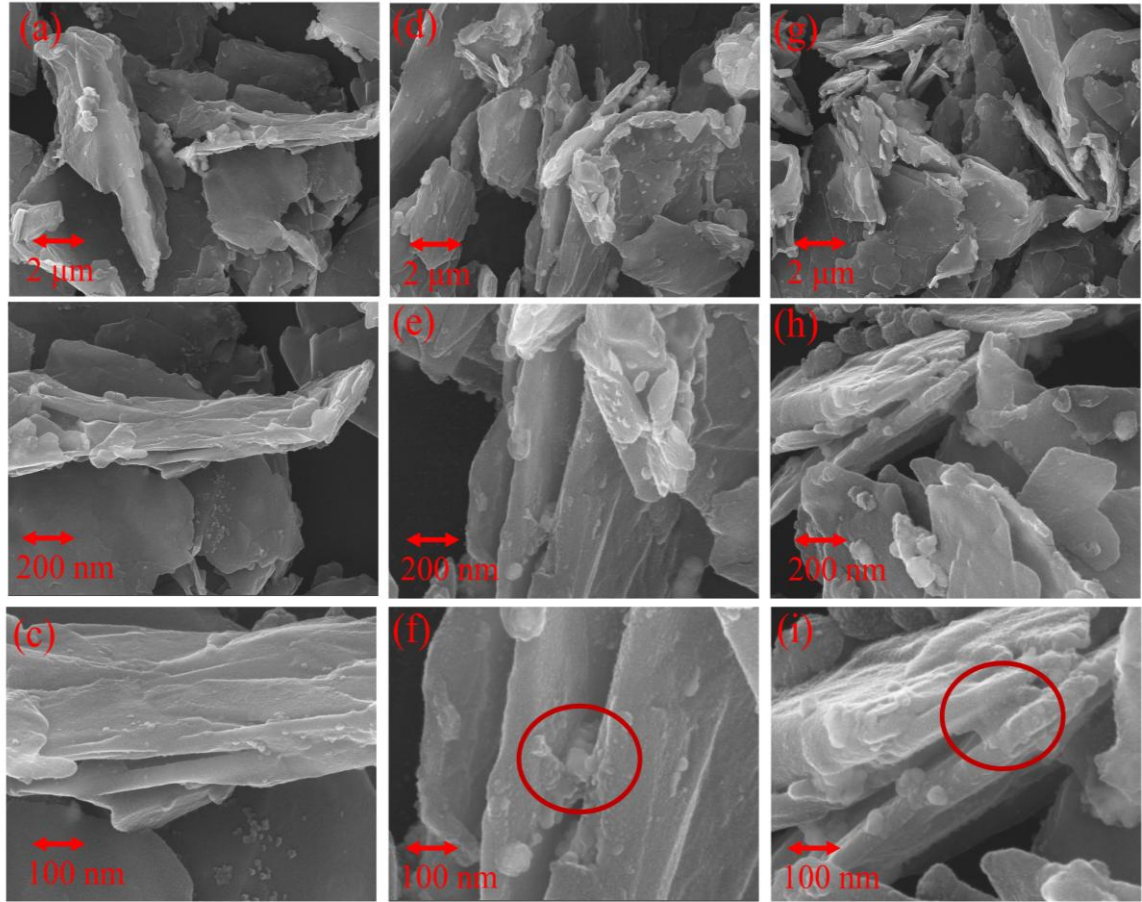


Figure 7.11. SEM images of (a)-(c) PDA@rGO-4, (d)-(f) PDA@rGO-5 and (g)-(i) PDA@rGO-6 (red circle refer to the PDA-formed bridge between graphene nanosheets).

7.3.2 Performance of PDA@rGO full-filler strain sensors by 2-step method

The experimental process and experimental setup for sensing low static tensile tests can be found in **Chapter 3 Section 3.3.2**. **Fig. 7.12** exhibit strain vs resistance changes of 5 parallel samples of PDA@rGO-1 sensors and its control groups (GO paper-based sensors, DA-rGO paper-based sensors and PDA@rGO-D sensors) within strain range of 1%. **Fig. 7.13** shows the average strain behaviours of PDA@rGO-1 sensors and its control groups (GO paper-based sensors, DA-rGO paper-based sensors and PDA@rGO-D sensors) within strain range of 1%.

On one hand, the curves can also be separated into 2 stages, corresponding to the mathematical model based on contacted principle ($\varepsilon \leq 0.3\%$) and the mathematical model based on tunnelling effect ($0.3\% \leq \varepsilon \leq 1\%$). The smooth increase area is referred to the contacted resistance change since the nanofillers are closed in this stage. According to the mathematical model based on contacted principle [155] that the resistance change should linearly increase with the applied strain, which consisting with obvious that the resistance change-strain curve shows approximatively linearly trend. The coated groups (PDA@rGO-1 sensors and PDA@rGO-D) is little more sensitive than uncoated group (GO paper-based sensors and DA-rGO paper-based sensors). This may be resulted by the possible higher dispersed state of nanofillers achieved by the PDA nanolayers on the graphene nanosheet and thus reduce the aggregation of nanofiller and then increase the effective contacted resistance change.

In the second stage ($0.3\% \leq \varepsilon \leq 1\%$), the resistance change of all the full-filler sensors shows an exponential increase with applied strain by the tunnelling effect, corresponding to the mathematical model [303, 315] as shown follow:

$$R_t = \left(\frac{8\pi h L}{3A^2 X d N} \right) e^{Xd} \quad 7.1$$

$$X = \frac{4\pi(2m\varphi)^{1/2}}{h} \quad 7.2$$

where L is the mean number of nanofillers forming to a single conducting path; N is the number of conduction paths; d is the mean distance between conductive particles; A is the mean effective cross section of nanofillers; h is Plank's constant; m is the mass of electron charge and φ is the mean height of potential barrier between adjacent nanofillers. In this stage, the coated groups still show a persistent higher sensitivity than the uncoated groups. It is referred to the fact that coating PDA nanolayers is able to change more contacted nanofiller into separated state in 10-20 nanometres, which contribute to more possible tunnel.

On the other hand, the GF trend that the coated groups are consistently higher than uncoated groups further confirm the better dispersed benefit bring by the PDA nanolayers on the surface of graphene.

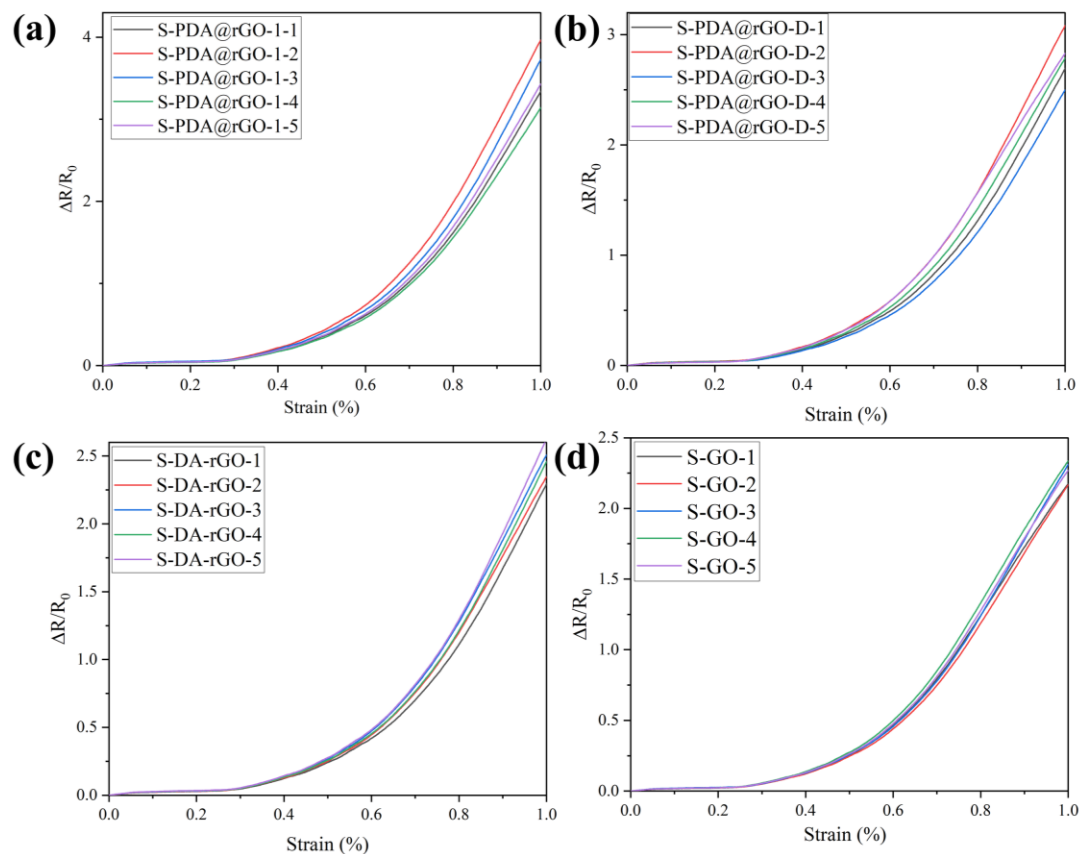


Figure 7.12. Repeated electrical resistance changes of GO, DA-rGO, PDA@rGO-1 and PDA@rGO-D sensors under 1% strain.

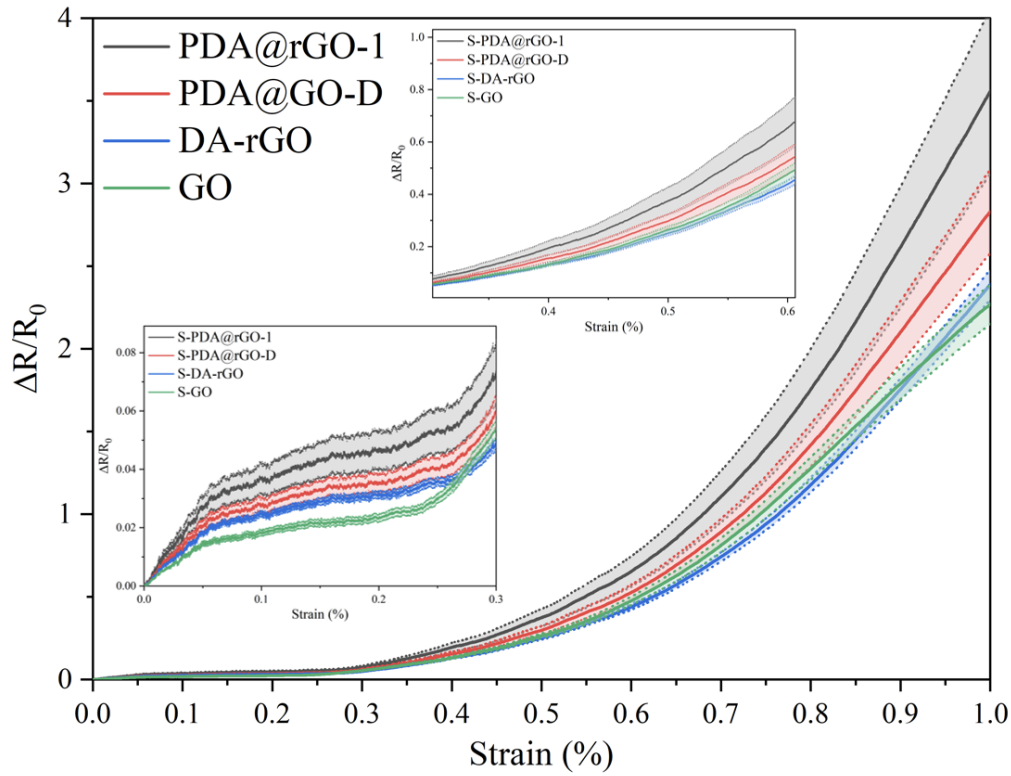


Figure 7.13. Electrical resistance curves of GO, DA-rGO, PDA@rGO-1 and PDA@rGO-D sensors pasted on the surface of aluminium alloy tensile specimens under 1% strain (shaded areas: ± 1 standard deviation).

To further confirm the conclusion as found in **Fig. 7.13**, the PDA@rGO full-fillers sensors were put into Dynamic Mechanical analysis (DMA, Discovery 850, TA instruments) machine to conduct the tensile test and the resistance change over applied strain curves can be found in **Fig. 7.14**. It is clear that all the sensors show a slight grow at the first stage ($\varepsilon \leq 0.3\%$) and then start to sharply increase at the second stage ($0.3\% \leq \varepsilon \leq 1\%$). In the first stage, it is also clear that the coated groups (GFs: around 103 for PDA@rGO-1 sensors and PDA@rGO-D sensors) is little more sensitive than uncoated group (GFs: around 92 GO paper-based sensors and DA-rGO paper-based sensors). In the second stage, the GFs of the sensors change from 223 to 273 at $0.3\% \leq \varepsilon \leq 0.6\%$ and 512 for GO paper-based sensors and 568 for DA-rGO paper-based sensors to 632 for PDA@rGO-D sensors and 765 for PDA@rGO-1 sensors at $0.6\% \leq \varepsilon \leq 0.9\%$. It is also noticed that the sensors made by 2-steps coating show a persistent higher resistance change than the other control groups, including the PDA@rGO-D

sensors in **Fig. 7.14**. In the previous section, it is shown that the surface of PDA coated nanofillers by 2-step process is smoother than the one that is made by directly coated PDA nanofillers. The higher evenly distributed PDA nanolayers have positive impact on the separating the nanofillers in a fixed value, which to achieve more effective tunnelling junctions between neighbouring nanofillers. Thus, higher GFs of PDA@rGO-1 sensors (GF:273 linear fitting from $0.3\% \leq \varepsilon \leq 0.6\%$; GF:765 linear fitting from $0.6\% \leq \varepsilon \leq 0.9\%$) are obtained.

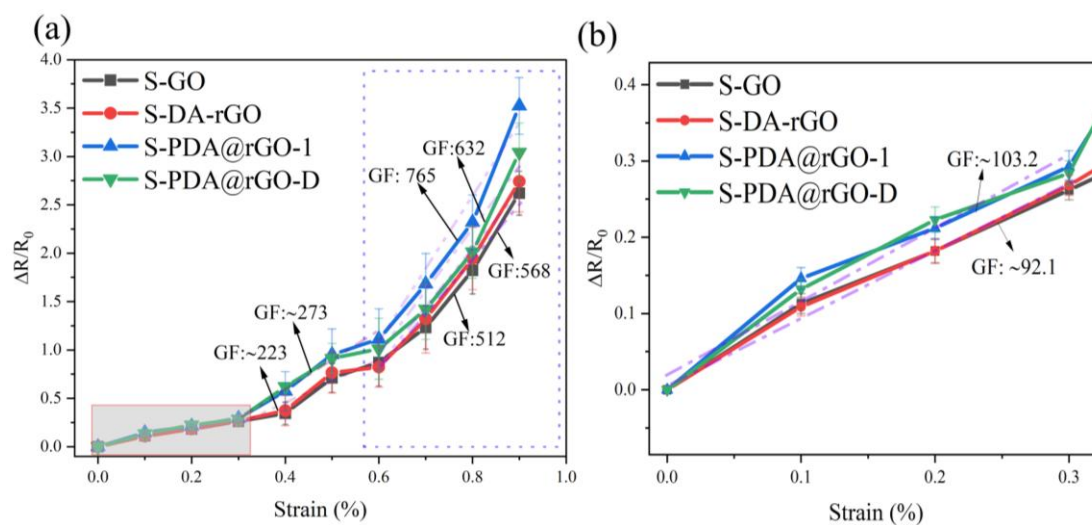


Figure 7.14. Electrical resistance changes of GO, DA-rGO, PDA@rGO-1 and PDA@rGO-D sensors under 1% strain and its enlarger area of applied strain from 0 to 0.3%.

7.3.3 Performance of PDA@rGO full-filler strain sensors with different PDA content

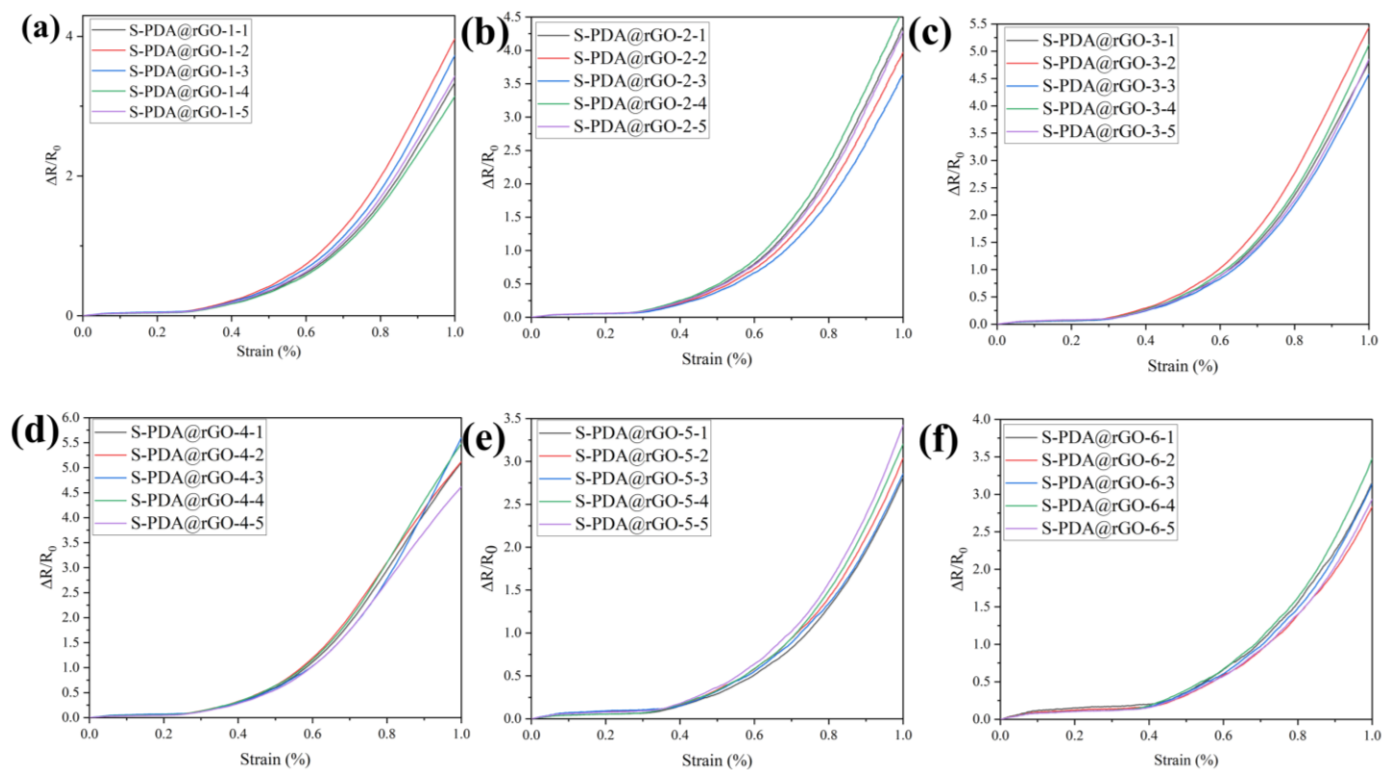


Figure 7.15. Repeated electrical resistance curves of PDA@rGO-X sensors with different PDA content under 1% strain.

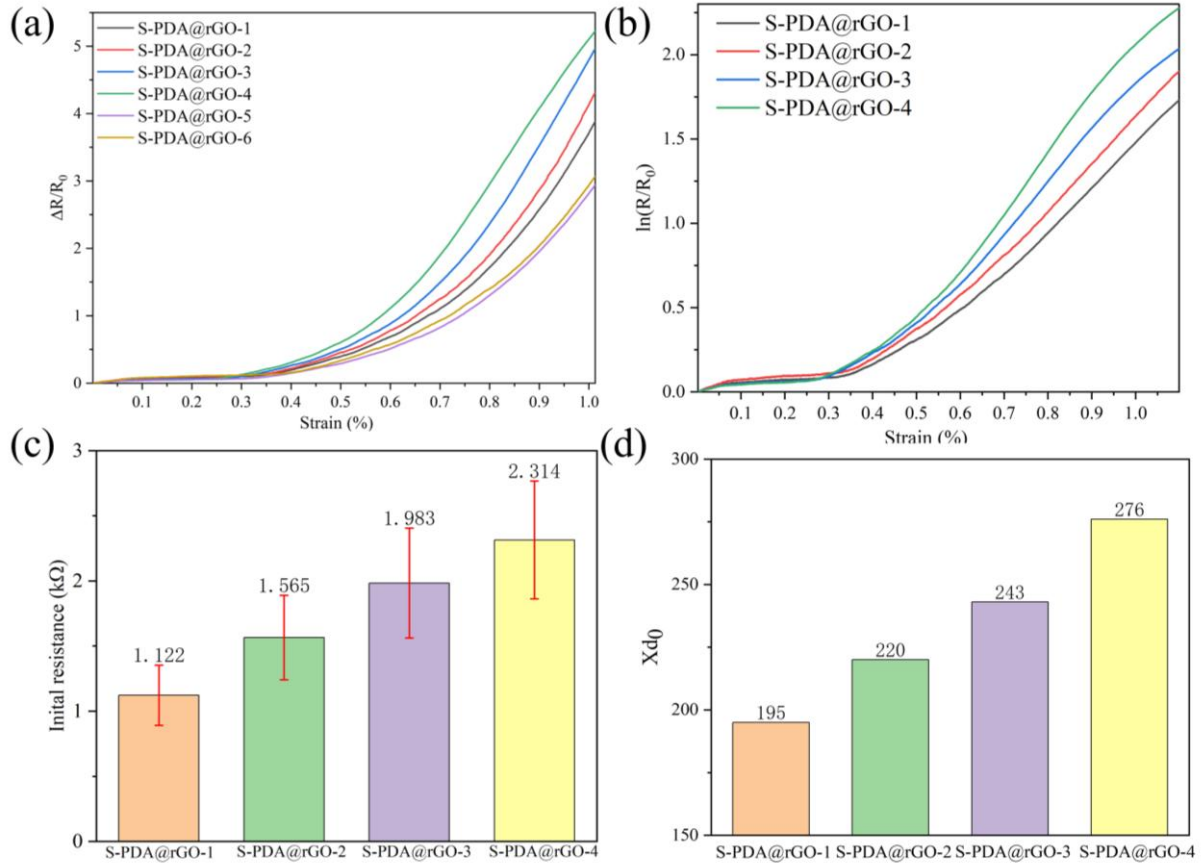


Figure 7.16. (a) Average electrical resistance curves of different PDA content PDA@rGO-X sensors pasted on the surface of aluminium alloy tensile specimens under 1% strain; (b) $\ln(R/R_0)$ value vs strain curves of different PDA content PDA@rGO-X sensors; (c) Initial resistance of different PDA content PDA@rGO-X sensors (1 cm wide); (d) The X_{d0} values of different PDA content PDA@rGO-X sensors.

In order to confirm the effectiveness influence of PDA nanolayers, PDA@rGO nanofillers and their corresponding sensors with different PDA content are obtained by increase the number of second steps in a 2-step coating process. It is expected to achieve a higher PDA content as the second coating cycle increase during the 2-step PDA coating process, reflecting as the X in PDA@rGO-X. **Fig. 7.15** exhibit strain vs resistance changes of 5 parallel samples of S-PDA@rGO-X within strain range of 1%. In **Fig. 7.16(a)**, the average resistance change-applied strain curves of those sensors are

presented. It is shown that all the PDA@rGO-X sensors show a similar increase trend. However, in the second stage ($0.3\% \leq \varepsilon \leq 1\%$), it is observed that the PDA content show a positive contribution to GFs from PDA@rGO-1 sensors to PDA@rGO-4 sensors. As the PDA content to increase, the GFs of PDA@rGO-5 sensors and PDA@rGO-6 sensors decrease suddenly and even lower than that of PDA@rGO-1 sensors. It can be deduced that the initial distance (d_0) of neighbouring nanofillers give contribution to tunnel resistance change when d_0 reach certain values. If the d_0 keep increasing, the contribution to GFs will decrease quickly as the further separation of nanofillers will achieve invalid tunnelling junctions.

To under the influence of d_0 to the sensitivity, we induce the strain change as follow:

$$\varepsilon = \frac{d - d_0}{d_0} \quad 7.3$$

where d_0 is the initial distance between neighboring graphene nanosheets, d is the distance between neighboring graphene flakes after the deformation. And the initial resistance of sensors contributed to tunneling effect can be rewrite as:

$$R_0 = \left(\frac{8\pi hL}{3A^2 X d_0 N} \right) e^{X d_0} \quad 7.4$$

Based on the equation 1, 3 and 4, the relationship between resistance changes and initial distance of nanofillers can be expressed as:

$$\ln \left(\frac{\Delta R}{R_0} \right) = X d_0 \varepsilon - \ln(\varepsilon + 1) \quad 7.5$$

Where the ΔR equally to $(R - R_0)$, represent the resistance change of strain sensors with the applied strain. Since the applied strain ($0 \leq \varepsilon \leq 1\%$) is extremely low, the value of $\ln(\varepsilon + 1)$ can be ignored so that the formula can be rewrite as:

$$\ln \left(\frac{\Delta R}{R_0} \right) = X d_0 \varepsilon \quad 7.6$$

In the expression of formula, the value of $\ln(R/R_0)$ show a linearly increase as the applied strain raise. To translate the data in **Fig. 7.16(a)** into above expression, **Fig. 7.16(b)** can be obtained. As shown in the figure, an approximatively linear curve of

PDA@rGO-1 sensors to PDA@rGO-4 sensors can be found which confirm the resistance change in $0.3\% \leq \varepsilon \leq 1\%$ is mostly contributed by the tunnelling effect.

In the second stage ($0.3\% \leq \varepsilon \leq 1\%$), the increase of PDA content is giving contribution to the initial distance of neighbouring nanofillers and the barrier between adjacent nanofillers (Xd_0), reflecting in the change in initial resistance (R_0) as shown in **Fig. 7.16(c)**. However, there is a limit for increase value of Xd_0 and in this study, the value is 276 (**Fig. 7.16(d)**). By further increase the content of PDA, it is difficult for charges to transport from one nanofiller to another since the tunnelling gap is too large, which may lead to the invalidation of tunneling effect.

On the other hand, it is obvious in the above SEM compared images that as the increase of PDA content on graphene coating process, there will be more aggregated nanofillers, which is believed to be adverse impact to control the d_0 , weaken the tunnelling effect to a certain extent. Thus, it is obvious that an even lower GF is obtained by further increase PDA content.

7.4 Conclusion

The tunnelling effect of graphene seems to be the most contributing factor for sensitivity within low strain range and to reach the limit of that, we proposed a 2-step PDA nanolayer coating method to separate the graphene flakes from each other to control tunnelling distance so that to control the probability of occurrence of tunnelling. The morphology results show that the surface of PDA@rGO prepared by 2-step is smoother than that prepared by directly PDA coating method. Also, the prepared nanofillers were used to form thin-film full-filler strain sensors by vacuum filtration to make the nanoflakes contract with each other so the distance of graphene can be controlled by the coated PDA nanolayers. Benefited from the higher evenly distributed PDA nanolayers to the separate the nanofillers in a fixed value, a 21% improvement in sensitivity is observed compared to the sensors that is obtained by directly PDA coating methods.

Moreover, by change the 2-step PDA coating cycle number, different thickness of PDA coating layer on graphene can be obtained. It is shown that the surface of PDA nanolayer become thicker but rough and even lead to the agglomeration of graphene nanofillers as the coating cycles increase. For performance comparison, it is found that the sensitivity of PDA@rGO-X sensors exhibited upper trend at first and the suddenly decline as the coating cycles increase, which means that there is a suitable distance between neighbouring graphene flakes for achieving the limit of tunnelling effect.

Chapter 8 Preparation of BP-PDA@rGO hybrid: dual mechanisms to enhance sensitivity of strain sensors to extremely low strain sensing

8.1 Introduction

The distance between neighbouring graphene response to tunnelling effect is limited by 10s nm [316]. If the value exceeds some certain, the probability to produce tunnelling junction will rapidly decline [303]. The further improvement in sensitivity may relies on inducing another matching nanofillers to have collaborative mechanism.

Another 2D nanomaterial, BP, has shown great potential in electronics and optoelectronics since its tuneable bandgap structure by layer number, high carrier mobility, and anisotropic electronic properties [317, 318]. Zhang et al. [319] observed a large piezoresistive effect in BP at room temperature. They attribute the large piezoresistance to strain modulated bandgap, which directly confirm with FTIR of strained black phosphorus specimen. The large piezoresistance of BP leads to sensitive transducers with large dynamic range that are useful in flexible electronics applications.

The mixing of BP and graphene have been tried by Liu et al. [320] firstly for lithium-ion battery. A typical BP/rGO hybrid nanofiller is synthesized by reduced GO into rGO which is linked to BP by P-O-C and P-C bonds. Later in 2020, the Chhetry et al. [321] group present a dual-parameter temperature-strain sensor based on a BP@laser-engraved graphene (LEG) heterostructure on polymer. The Passivated BP nanosheets were introduced into the 3D porous network of LEG, exhibiting positive temperature-dependent characteristics suitable for a thermosensitive sensor and resistive linear microcrack propagation mechanism in a tensile strain. Those study demonstrated the feasibility of connecting BP and graphene as a hybrid nanofillers.

Inspired by above research outcome, it is possible to prepare a PDA-functional graphene and BP hybrid nanofillers for higher sensitivity to low strain sensing. The graphene act as continuous phase for the conductive network and the PDA nanolayers help to achieve both better dispersion state and control the nm distance between graphene nanosheets, so that the tunnelling effect from graphene can achieve the best level. Then BP nanoflakes will be deposited on the PDA-functional graphene sheets by the P-O-C and P-C bonds to form sandwiched-like nanostructures [322]. It is hoped that the piezoresistivity from BP nanoflakes can help to generate more resistance change under strain to achieve better sensitivity.

8.2 Experimental

8.2.1 Preparation of BP nanofillers

Bulk black phosphorus crystal powder (200 mg) was added to the saturated NaOH/NMP solution (500 mL). The mixture was put in a sonicbath operated at 20 kHz frequency for 0.5 hour several times to conduct the preliminary liquid exfoliation of the bulk BP. After preliminary exfoliation, the solution was centrifuged at 5000-7000 rpm for 20-30 min at room temperature to remove any unexfoliated bulk BP crystal. The filtration precipitations obtained by preliminary exfoliation were redispersed in water (0.5mg/ml) and the solutions were washed by deionized water several times.

The black phosphorus solution (0.15 mg/ml in NMP) was then centrifuged at 10000 rpm - 18000 rpm for 20 min at -9 °C to separate the relatively thick BP. The prepared BP solutions centrifuged at 10000 rpm, 15000 rpm and 18000 rpm are named as BP-10000, BP-15000 and BP-18000, respectively.

8.2.2 Preparation of BP-PDA@rGO hybrid nanofillers

1ml BP solution (0.15 mg/ml, BP-10000, BP-15000 and BP-18000) was added into 50 ml PDA@rGO solution (0.15 mg/ml, including PDA@rGO-1 to PDA@rGO-4, the preparation process can be found in **Chapter 7 Section 7.2.2**). The mixture solutions were first sonicated for 0.5 h several time to have the fully mix and then stirred at 140

°C for 2 h to active the P-O-C and P-C connection. After that, the hybrid products were obtained by the filtration and dry at 80 °C. The schematic process of preparing hybrid nanofillers can be found in **Fig. 8.1**.

8.2.3 Preparation of full-fillers sensors

The BP-PDA@rGO strain sensors were fabricated by vacuum filtration assisted forming as same as described in **Chapter 7 Section 7.3**: first, the prepared BP-Y-PDA@rGO-X nanofiller was put into NMP solution to achieve 0.15 mg/ml nanofiller dispersed solutions. The dispersed solutions were magnetically stirred for half an hour and then sonicated for 2 h to achieve better dispersed state. 0.05g porous PU resin was also dispersed in 200ml NMP solution to obtain PU dispersed solution through the same process. To prepared full-filler sensors, vacuum filtration setup was used. Firstly, the filter paper is put on the filter inside the vacuum filtration setup. 2 ml porous PU/NMP dispersed solution were dropped into the mold inside the bush funnel. After vacuum treatment, the NMP liquid were gone, and the PU layer was left on the filter paper. Then, 5 ml nanofillers dispersed solution were dropped into the funnel and processed vacuum suction filtration treatment by several times so that a full-filler film can be form. After fixed the electrodes by conductive silver glue at the ends of the full-filler layer and removed the PET mold, a flexible sticky ultra-thin PET polymer film used to protect the full-filler layer was covered. The optical image and fabrication process of the prepared full-filler sensors are shown in **Fig. 8.1(b)** and **Fig. 8.1(c)**. The thickness of the full-filler layer in sensors is about 200 μm .

In order to better distinguish between fillers and corresponding sensors in the following discussion section, the names of sensors prepared with corresponding fillers are prefixed with S. For example, S-BP-18000-PDA@rGO-1 represents the full-filler sensors that was prepared by BP-18000 and PDA@rGO-1 hybrid nanofillers.

Fig. 8.1(d) shows the SEM image and element mapping of C, O, N and P of BP-PDA@rGO-1 nanofiller prepared by 2-step coating method, respectively. The O

element mapping represents to the oxygen-containing functional group on graphene, while the N element mapping and the concentrated P element mapping corresponds to the presence of DA or PDA molecules and the BP nanofillers. The overall elements can be used to confirm the presence of the hybrid nanofillers as shown in **Fig. 8.1(a)**.

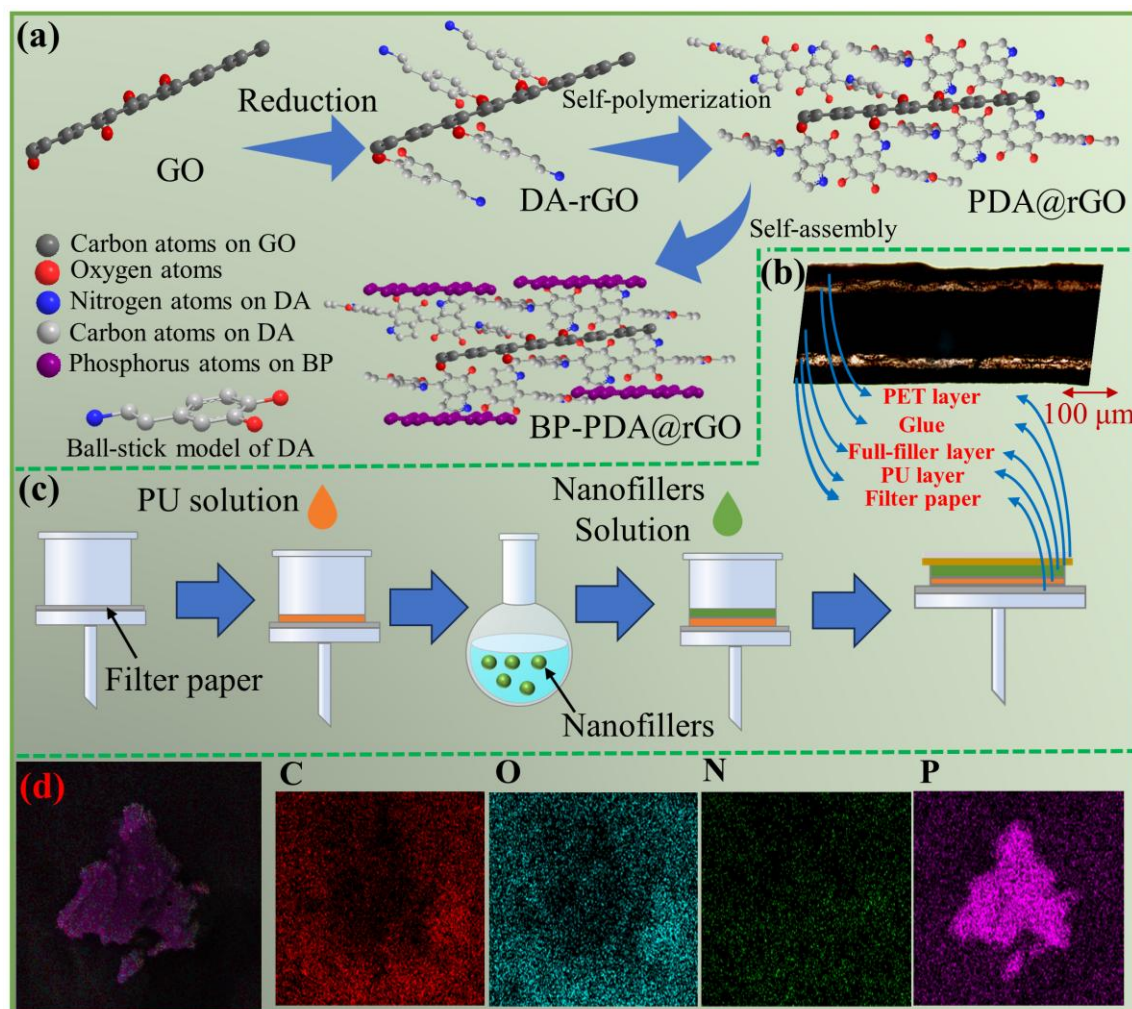


Figure 8.1. (a) Illustration of BP-PDA@rGO fabrication process by ball-stick model; (b) Cross section images of full-filler sensors by optical microscope; (c) Fabrication process of full-fillers sensors; (d) TEM-EDS mapping images of hybrid BP-PDA@rGO nanofillers.

8.3 Results and discussion

8.3.1 Characterization of BP nanofillers with different thickness

In this study, BP nanofillers were chosen as an extra nanofillers to active the dual mechanism due to its excellent piezoresistive property in low strain range and 2D size matching ability with graphene [321]. By applied the tunnelling effect between graphene nanosheets and the piezoresistivity of BP nanofillers, it is expected to prepare higher sensitive strain sensors to extremely low strain range.

First, BP nanofillers were peeled off from bulk BP through a liquid exfoliation process, which was conducted in an ultrahigh-speed centrifuge (The typical exfoliated BP nanoflake SEM and TEM image can be found in **Fig. 8.2** and **Fig. 8.3**, respectively). It is expected to obtain BP nanofillers with different layer numbers by centrifugal force at different speeds [323] and AFM images can used to evaluate the specific thickness of BP flakes.

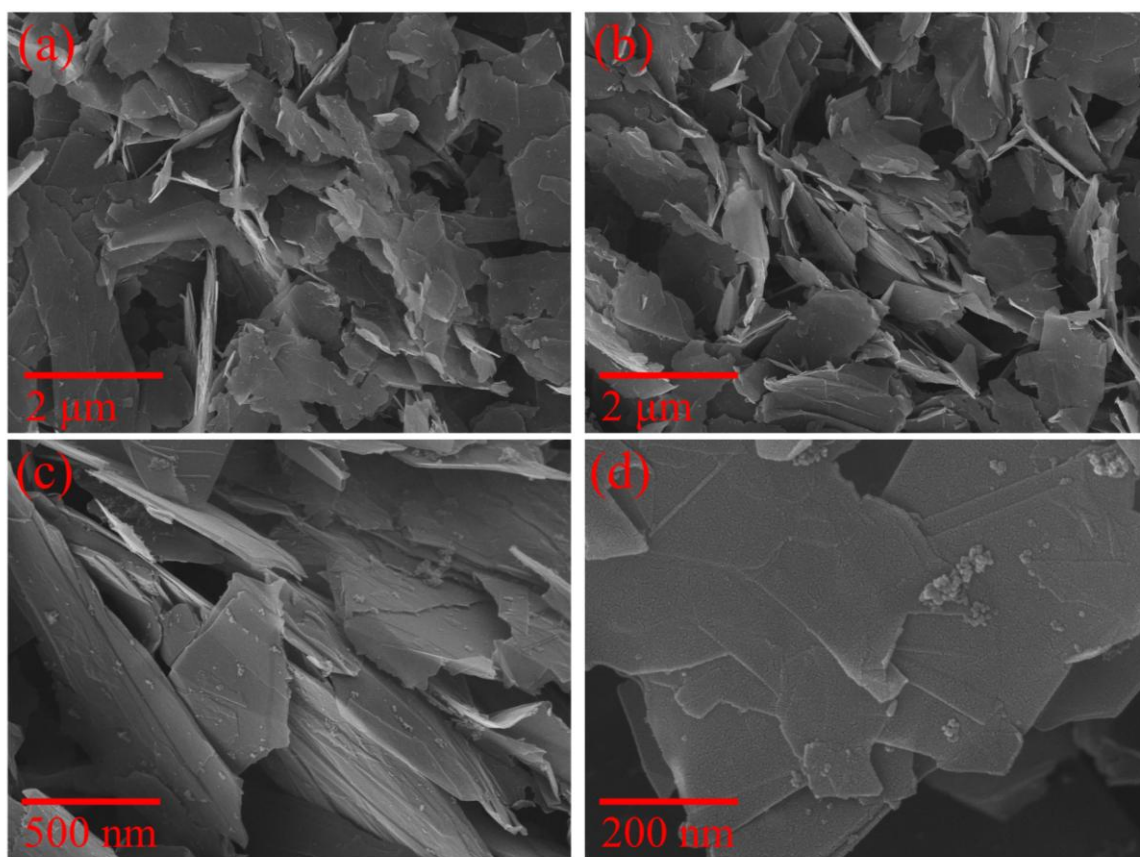


Figure 8.2. SEM images of BP-15000 nanofillers.

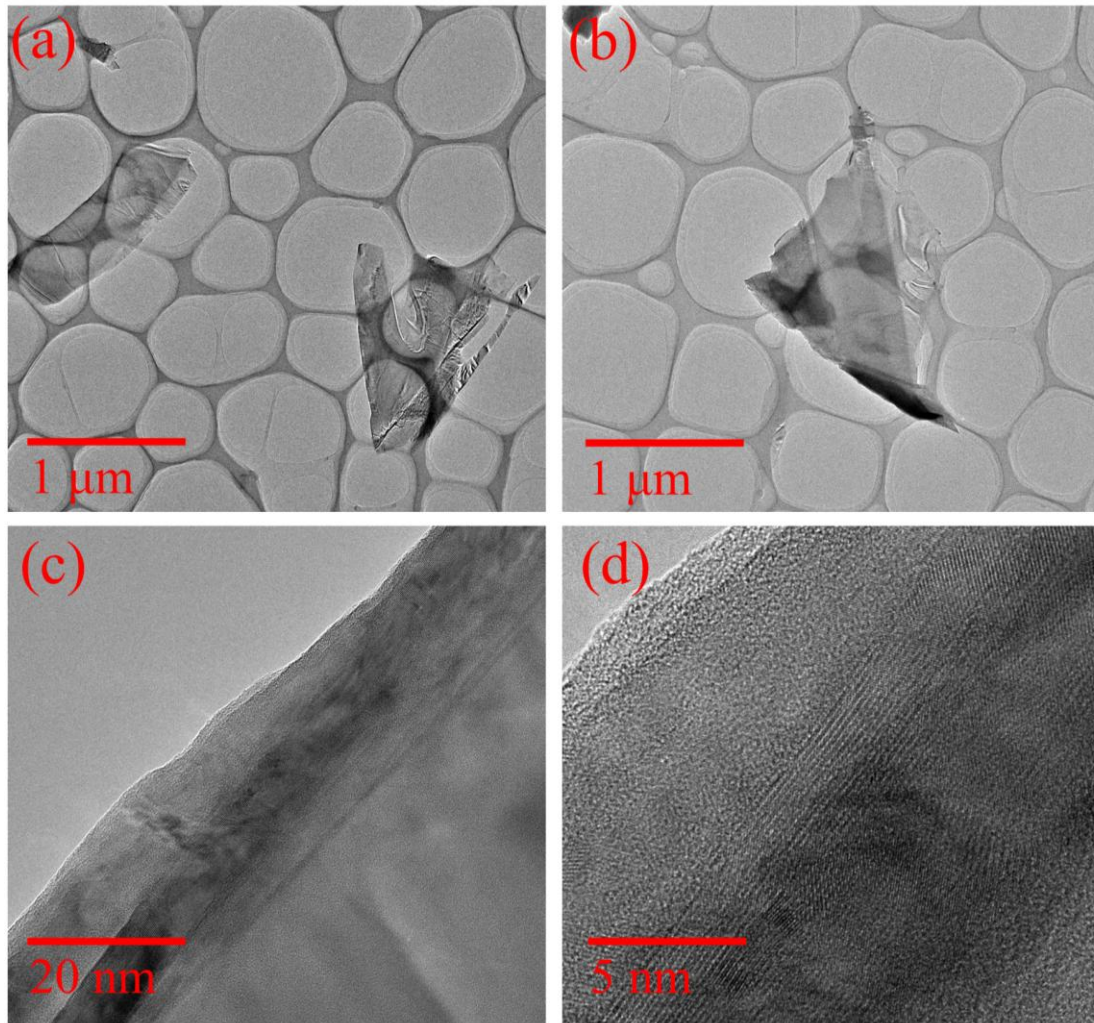


Figure 8.3. TEM images of BP-15000 nanofillers.

Fig. 8.4 shows the typical AFM images of BP nanofillers obtained by different centrifugal speed. The size of BP nanofillers at different centrifugal speeds are about 100 nm width. The BP-10000 nanofillers is about 100 nm thick while the thickness of BP-15000 nanofillers and BP-18000 nanofillers are over 10 nm and 1.5 nm, respectively. Considered the value of a theory thickness of single layer BP is about 0.6 nm [324], the layer numbers of obtained BP nanofillers is several, 10s and over 100 at 18000 rpm, 15000 rpm and 10000 rpm, respectively.

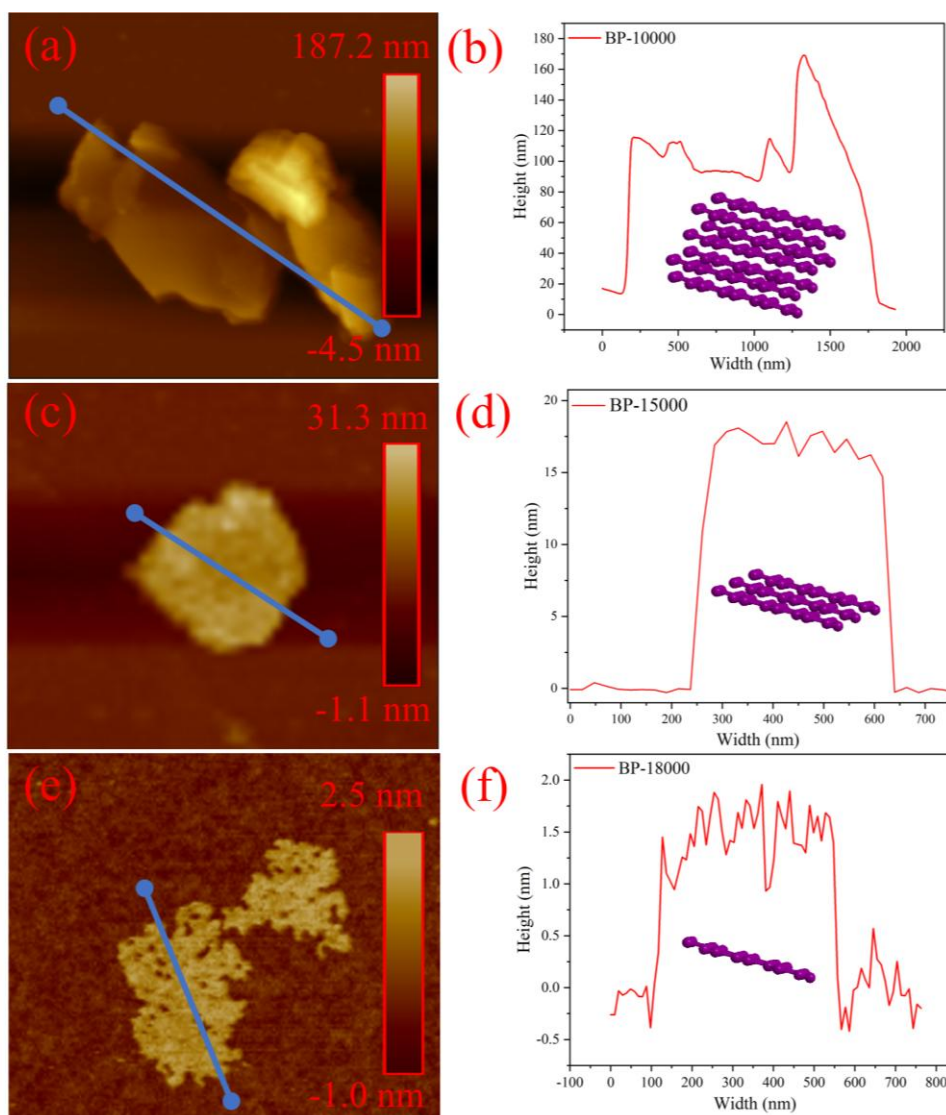


Figure 8.4. AFM images and the corresponding measured thickness curve of the BP-10000 nanofiller (a-b), BP-15000 nanofiller (c-d) and BP-18000 nanofiller (e-f).

BP-Bulk and BP-X nanofillers powders were dissolve in NMP standard solution. The absorption cures are shown in **Fig. 8.5**. There is a characted peaks of BP nanoflakes in about 245 nm^{-1} for BP-X nanoflakes, implying that the BP have been exfoliated into nano size. Moreover, it is observed that the intensity of the characted peaks become stronger as the centrifuging speed increase from 10000 rpm to 18000 rpm, which suggest that the size of BP flakes become smaller, corresponding to the results from AFM.

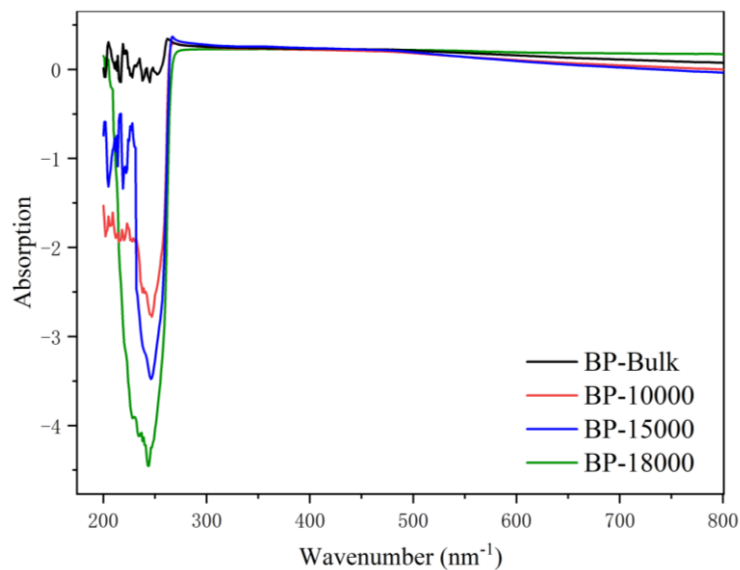


Figure 8.5. UV-Vis curves of BP bulk, BP-18000, BP-15000 and BP-10000 samples.

The Raman spectroscopy was used to further confirm the thickness difference of BP nanofillers obtained by different centrifuge speeds. As shown in **Fig. 8.6(a)**, the three different characterized peaks of BP can be found at around 362 cm^{-1} , 437 cm^{-1} and 466 cm^{-1} , which are assigned to the out-of-plane phonon vibrational mode (A_g^1) and in-plane phonon vibrational modes (B_{2g} and A_g^2) respectively[325].

As the centrifuge speeds to obtain BP nanofillers decrease from 18000 rmp to 15000 rmp, a small red shift by about 2.4 cm^{-1} , 1.8 cm^{-1} and 1.4 cm^{-1} can be found, while there is no more Raman shift observed as the centrifuge speeds continue to decrease. Due to the anisotropic structural change of phosphorene in fewer layers (especially in monolayer) may cause a higher anisotropic Raman scattering and this phenomenon may be weak or disappeared as the BP layer number increases [326], the difference between red shift and no shift in Raman spectroscopy can be used to tell the layer number of BP-18000 nanofillers is several and those of BP-15000 and BP-10000 is even more, which is consistent with the AFM results in **Fig. 8.4**.

Theoretically, when changing from bulk phosphorene crystals to monolayer phosphorene, the lattice parameters along the Z direction undergo obvious changes, while those along XY exhibit little changes. Thus, the intensity ratio of A_g^2 peak and A_g^1 peak in Raman spectroscopy can be used to determine the thickness range of BP nanofillers[331]. As shown in **Fig. 8.6(b)**, the ratio of A_g^2 peak and A_g^1 peak decrease from average 2.136 to 1.637 as the centrifuge speeds to obtain nanofillers decrease from 18000 rpm to 10000 rpm. The huge difference between those BP nanofillers can be used to confirm that the BP nanofillers are classified into different thickness levels[331], so that the effect of BP nanosize as hybrid nanofillers in BP-PDA@rGO system can be study by adding BP nanofillers obtained by 18000 rpm, 15000 rpm and 10000 rpm centrifuge speeds.

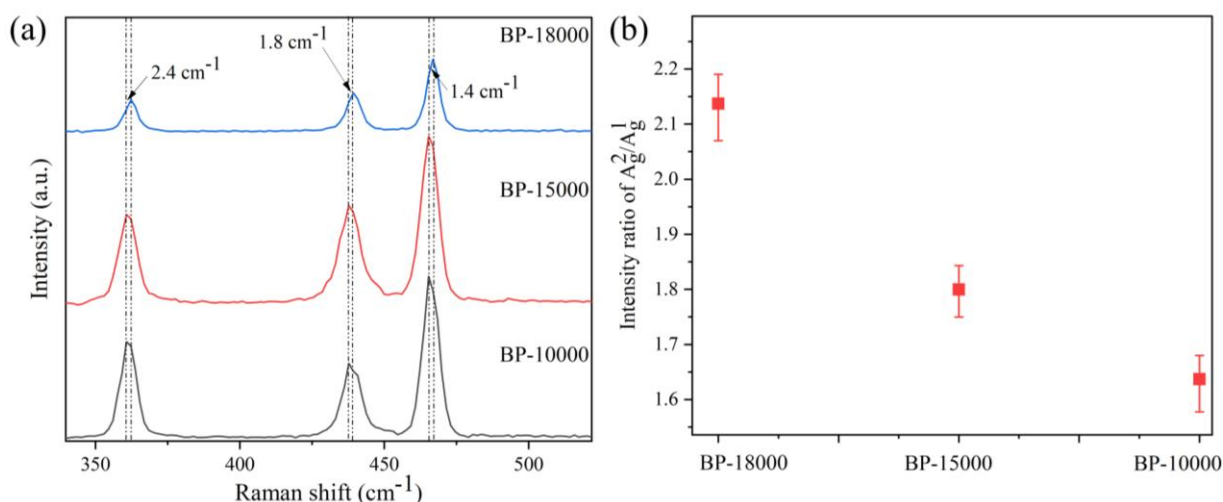


Figure 8.6. (a) Raman spectra of BP nanofillers with different thicknesses. (b) Curve of the intensity ratio of A_g^2 peak and A_g^1 peak.

8.3.2 Characterization of hybrid BP-PDA@rGO nanofillers

In this study, we expect to utilize the dual mechanisms to enhance the sensitivity by preparing the sandwiched-like hybrid nanostructure as shown in **Fig. 8.7(a)**. The basic sandwiched-like nanostructure is combined by larger-size PDA@rGO nanofillers (several μ ms) and smaller-size BP nanofillers (several hundred nms) in between. The self-assembly by electrostatic attraction of hybrid nanofillers in solution can be

activated by the chemical bonding connection between PDA polymer and BP nanofillers as shown in **Fig. 8.7(b)**.

Theoretically, phosphorene layer is covalently bonded by sp^3 hybridization of phosphorus atoms and there will be one lone pair of electrons left, thus BP is easily oxidized by air so that they are not stable enough for preparing actual devices. The usual solution is to consume the lone pair electrons of BP through passivation [327] and PDA is participated in this process. As shown in **Fig. 8.7(b)**, PDA molecular chains is able to passivate BP nanofillers through P-C bond and P-O-C bond.

XRD patterns are shown in **Fig. 8.7(c)**. A widely distributed strong diffraction peak at 24.8° , assigned to the (002) plane of hexagonal crystalline graphite, indicating the GO has been successfully reduced[243]. Besides, the sharp characterized peaks of BP nanofillers can be found at 16.6° , 34.4° and 51.2° , which consistent with the (002), (004), and (006) planes of orthorhombic black phosphorus structure[328].

The passivation process can be demonstrated by the FTIR curves of BP-PDA@rGO groups and PDA@rGO samples as shown in **Fig. 8.7(d)**. First, the characterized peak of C=C can be found at all curves illustrate that graphene structure is work as a base for the hybrid structure. Apart from that, the C=N peak (1692 cm^{-1}), N-H peak (1580 cm^{-1}) and C-N peak (1280 cm^{-1}), which are assigned to the unique PDA molecular structure[314], can be also found at BP-PDA@rGO groups, confirm with the coating structure that was obtained at **Chapter 7 Section 7.3.1**. The newly generated P element bonds at BP-PDA@rGO groups, including P-C (1429 cm^{-1}), P=O (1171 cm^{-1}) and P-O-C (998 cm^{-1}), confirm the bonding connection between BP and PDA nanolayers[329]. The FTIR patterns suggest that the BP nanolayers is successfully passivated by PDA nanolayer on rGO through P-C bond and P-O-C bond, which consistent with sandwich-like structure that was shown at **Fig. 8.1(a)**.

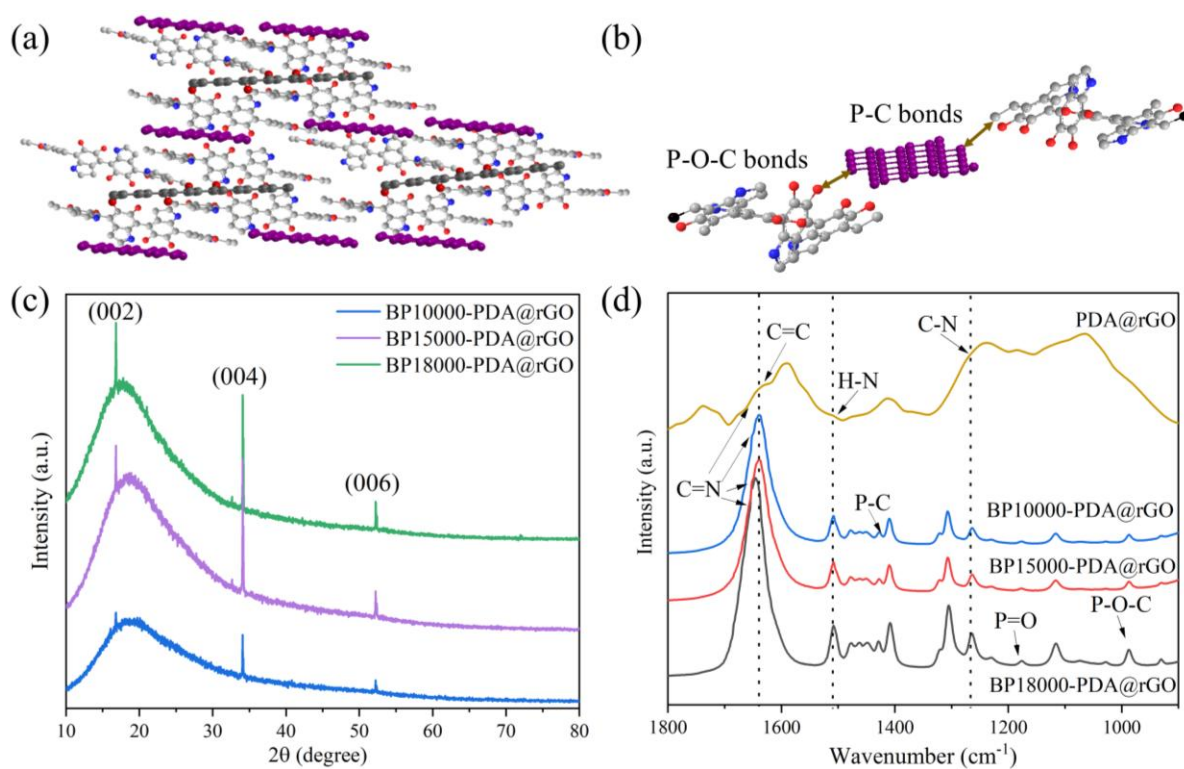


Figure 8.7. (a) The schematic diagram of hybrid BP-PDA@rGO nanofillers; (b) Chemical bonding between BP and PDA molecular; (c) XRD patterns of BP-PDA@rGO samples and (d) FTIR curves of BP-PDA@rGO groups and PDA@rGO nanofiller.

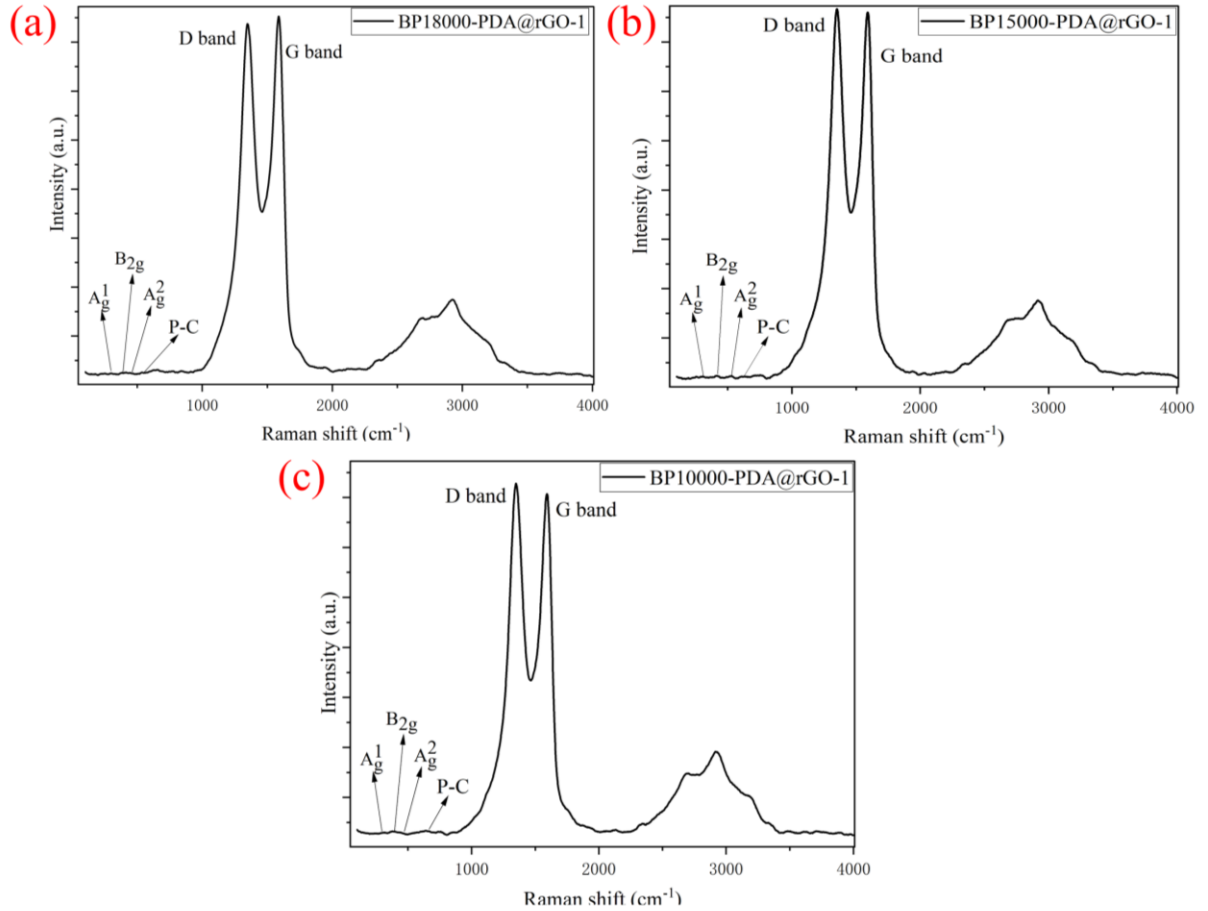


Figure 8.8. Raman curves of BP-18000-PDA@rGO-1 nanofiller (a), BP-15000-PDA@rGO-1 (b) and BP-10000-PDA@rGO-1 (c).

The Raman spectra (**Fig. 8.8**) show the typical characterized peaks of both BP (162 cm^{-1} , 437 cm^{-1} and 466 cm^{-1} , which assigned to the out-of-plane phonon vibrational mode (A_g^1) and in-plane phone vibrational modes (B_{2g} and A_g^2) respectively) [325] and graphene (1350 cm^{-1} and 1582 cm^{-1} , which assigned to the defects D band and the sp^2 plane vibration G band) [313]. Apart from that, a weak P-C band can be found in the samples, which suggest that the hybrid BP-PDA@rGO nanofillers are connected as integrate, consistent with the conclusion in FTIR.

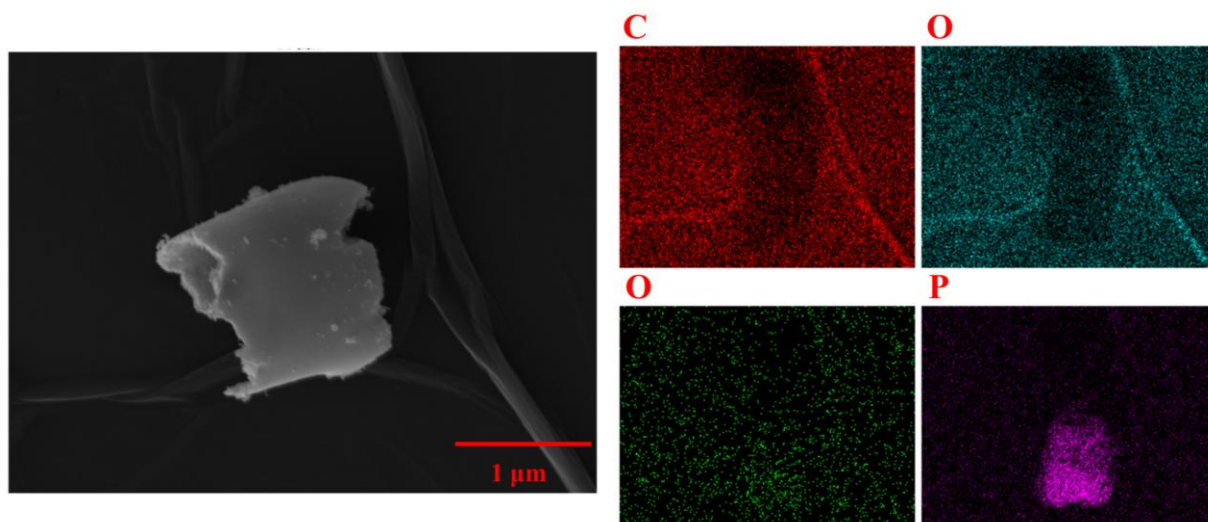


Figure 8.9. SEM image of BP-15000-PDA@rGO-1 nanofillers and the corresponding C, O, N and P elements distributed mapping.

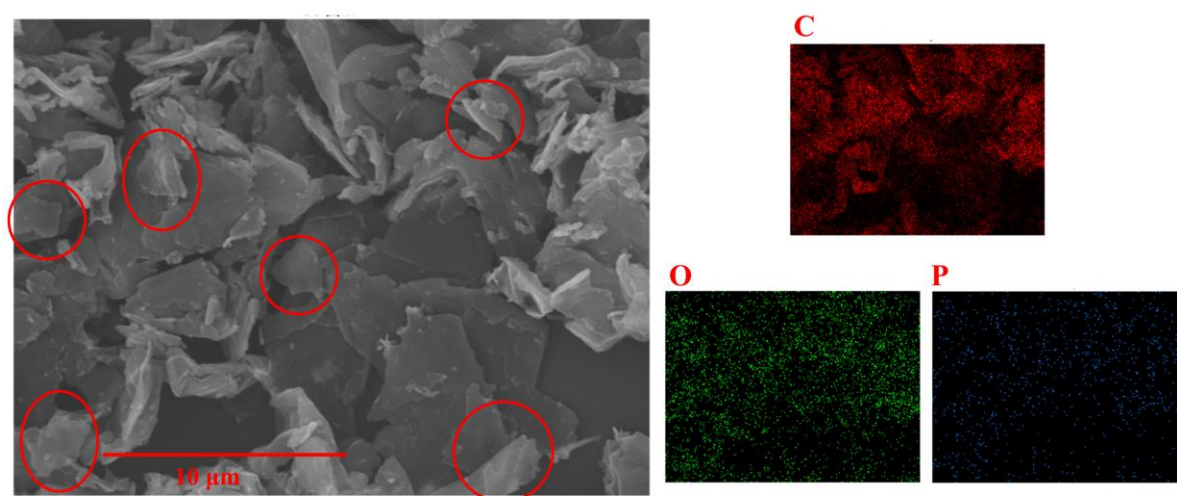


Figure 8.10. SEM image of BP-15000-PDA@rGO-1 hybrid nanofillers and the corresponding C, O and P elements distributed mapping.

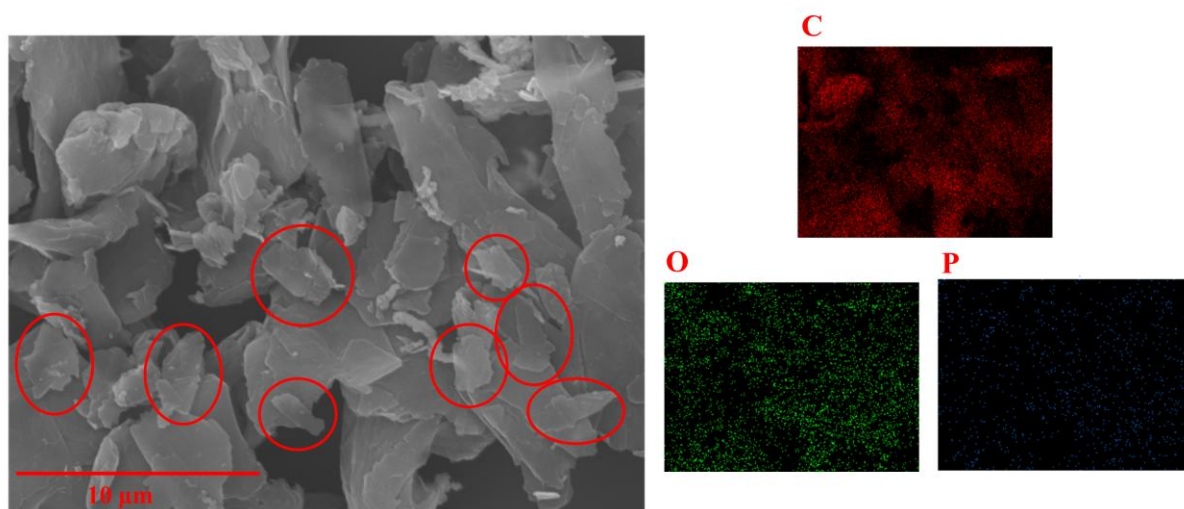


Figure 8.11. SEM image of BP-10000-PDA@rGO-1 hybrid nanofillers and the corresponding C, O and P elements distributed mapping.

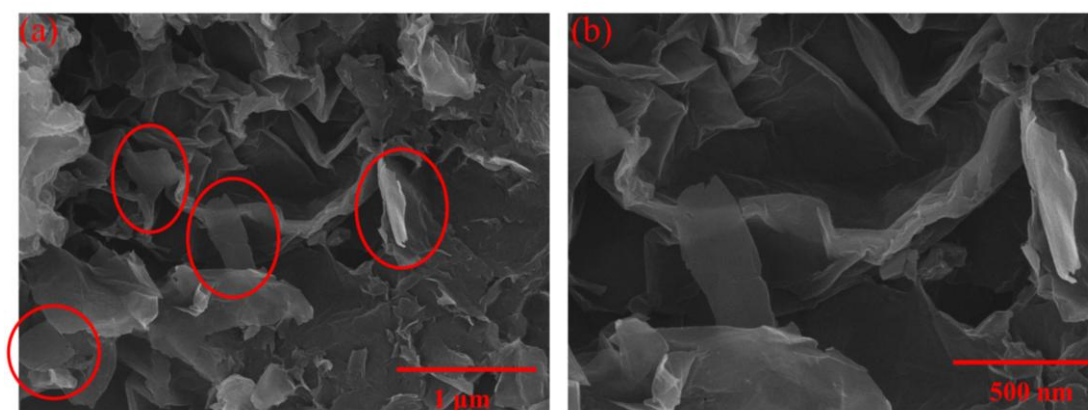


Figure 8.12. SEM image of BP-10000-PDA@rGO-1 hybrid nanofillers.

Fig. 8.9 shows a typical SEM image of deposited BP-PDA@rGO hybrid in dark field. It is clear that the folds of GO on the background and C, O and N elements distribute map suggest that the GO is referred to the PDA-coated rGO. It is shown that PDA-passivated BP flakes contacted on GO from the images.

Fig. 8.10, Fig. 8.11, and Fig. 8.12 shows the SEM images of specific hybrid nanofillers powders in bright field. The red cycle referred to the possible BP flakes on PDA@rGO sheets together with the elements mapping images. The hybrid images show that the BP flakes is insert on the GO sheets as hypothesis. Due to the size difference and the content used, there are only several BP flakes assembled with PDA@rGO nanofillers.

8.3.3 Performance of hybrid BP-PDA@rGO full-filler strain sensors

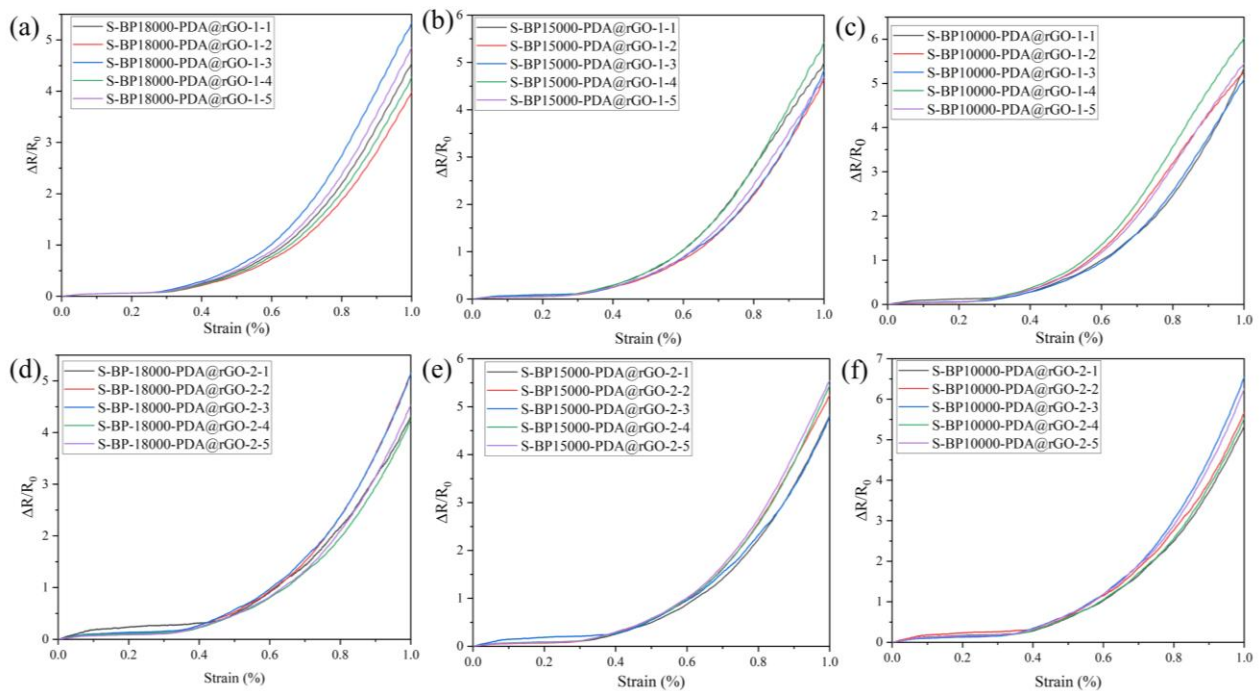


Figure 8.13. Repeated electrical resistance changes of BP-X-PDA@rGO-1 and s BP-X-PDA@rGO-2 sensors under 1% strain.

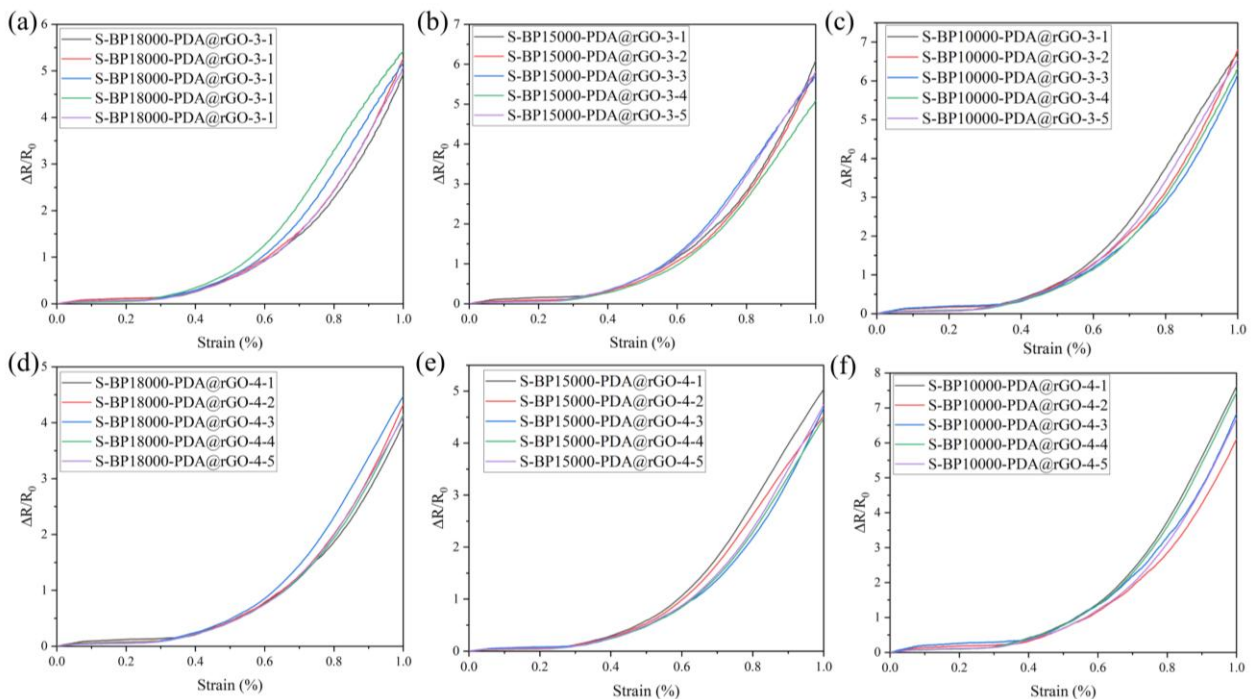


Figure 8.14. Repeated electrical resistance changes of BP-X-PDA@rGO-3 and BP-X-PDA@rGO-4 sensors under 1% strain.

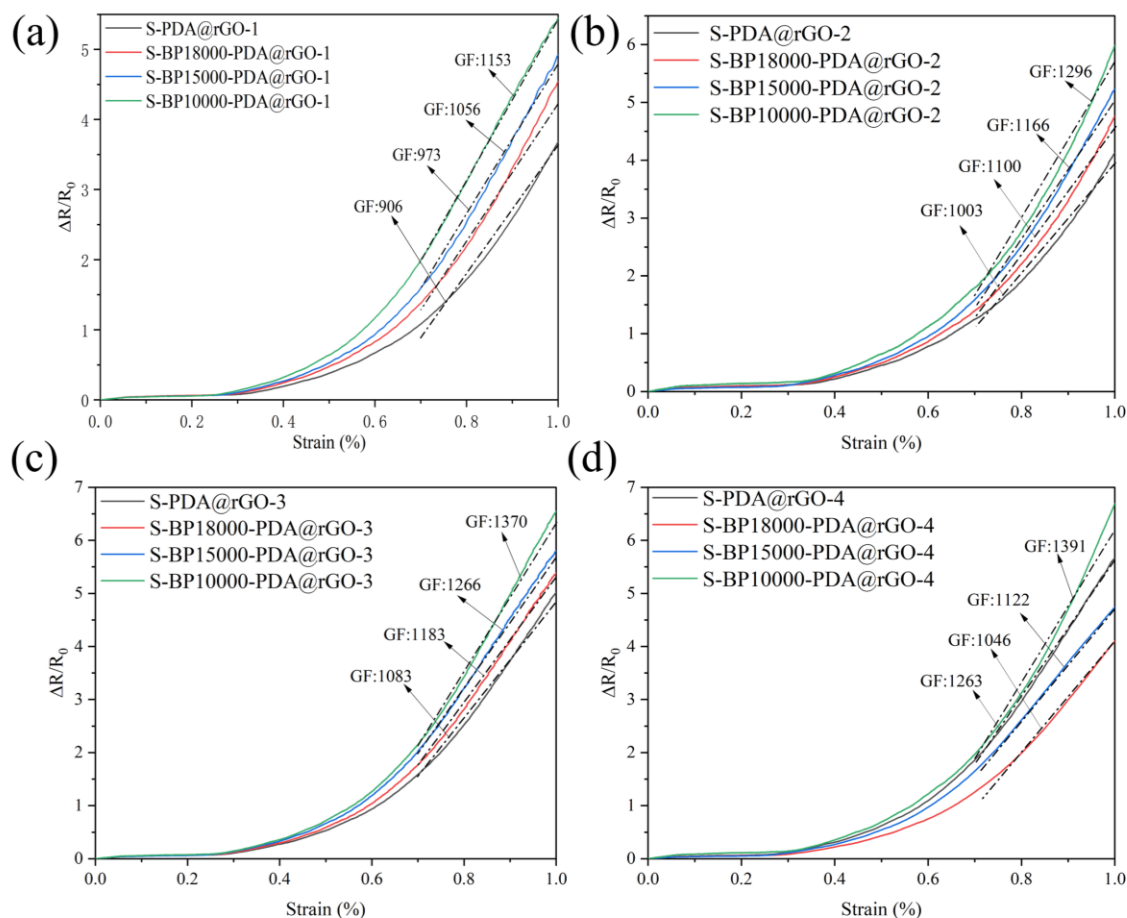


Figure 8.15. Average strain-resistance change curves of hybrid BP-PDA@rGO paper-based sensors with different thickness BP nanofillers changing from increased PDA coating contents (a)-(d) (GFs are calculated from linear line fitting by strain range of 0.7%-1.0%).

The hybrid BP-PDA@rGO strain sensors were attached to the surface of aluminium alloy tensile specimens to conduct tensile test within the strain range of 1% and the performance curves are shown in **Fig. 8.13** and **Fig. 8.14**. **Fig. 8.15** conclude the average the parallel curves. The specific experimental process and experimental setup for sensing low static tensile tests can be found in **Chapter 3 Section 3.3.2**.

The comparison are separated into 4 sets of PDA@rGO with different PDA coating content and each set including hybrid BP-PDA@rGO nanofillers with three different BP thickness so that the influence of BP thickness to the hybrid nanofillers can be study. As control group, the PDA@rGO strain sensors are added into for comparison and it is shown before that the sensitivity of PDA@rGO become higher as the PDA content increases.

As shown in the **Fig. 8.15**, all the hybrid BP-PDA@rGO nanofillers strain sensors exhibit similar resistance change trend as PDA@rGO nanofillers strain sensors, since the PDA@rGO nanofillers account for the majority of hybrid nanofillers. The major difference of hybrid nanofillers strain sensors with different BP thicknesses and to PDA@rGO nanofillers strain sensors are the resistance change trend after strain range of 0.3% and those range are considered as the tunnelling effect of PDA@rGO nanofillers become effective so it can be deduced that the resistance contribution of BP nanofillers to hybrid system is operating while the tunnelling effect of PDA@rGO nanofillers is working. In another word, it is the dual mechanism of hybrid system to the change of the sensitivity of BP-PDA@rGO strain sensors.

To better understand the influence of BP thickness to hybrid system qualitatively, the GFs were calculated from strain range of 0.7%-1.0% since the strain curves are suitable for linear fitting and it is the range when tunnelling effect of PDA@rGO reaches the limit. It is shows that the GFs of BP-PDA@rGO are increased as the BP thickness increases for BP-PDA@rGO-1 set to BP-PDA@rGO-3 set, while there is a sudden decline trend as the BP thickness increases for BP-PDA@rGO-4 set in **Fig. 11(d)**. However, the GF of S-BP10000-PDA@rGO-4 still higher than the blank control group S-PDA@rGO-4 and reach a similar value as S-BP10000-PDA@rGO-3, which can be used to illustrate that the hybrid system is efficacious.

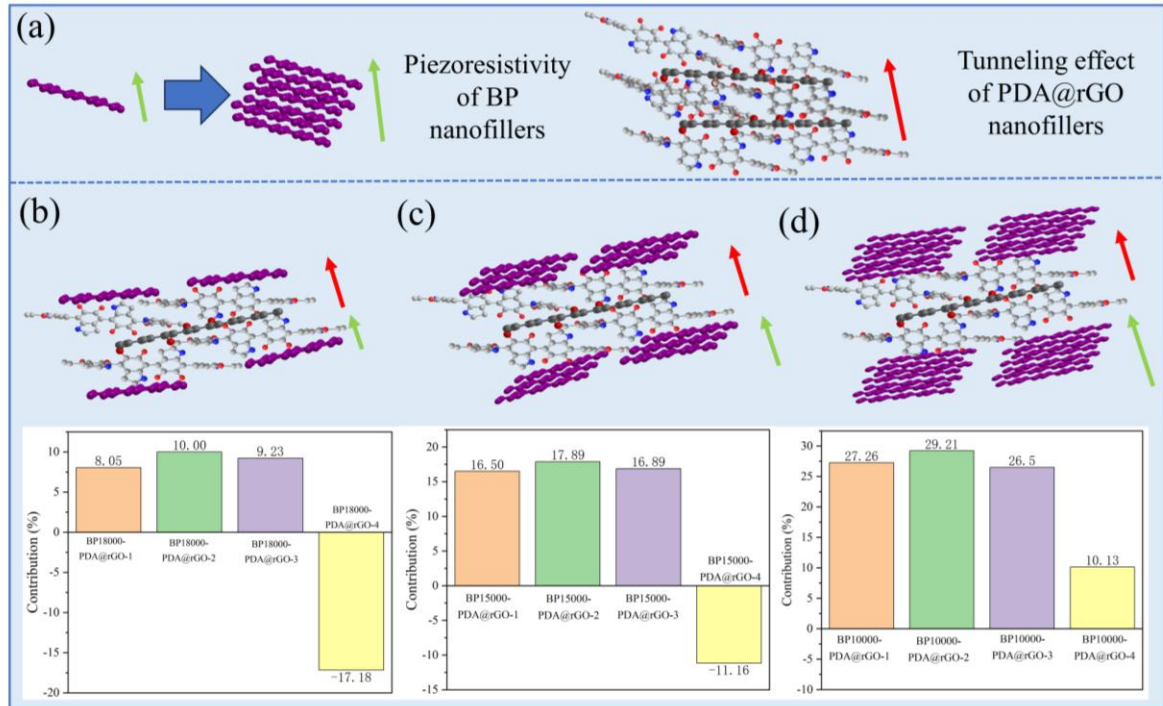


Figure 8.16. (a) Models of contribution by piezoresistivity of BP nanofillers and tunnelling effect from PDA@rGO nanofillers. (b) - (d) Compared GF contributions of hybrid BP-PDA@rGO-X sensors to their PDA@rGO-X sensors under different BP thickness.

The impact of BP thickness on the sensitivity of hybrid strain sensors is a critical aspect highlighted in the study. Notably, it is consistently observed that the BP-10000 nanofiller variants, characterized by their increased thickness, exhibit higher gauge factors (GFs). This trend underscores the positive influence of thicker BP layers on the hybrid sensor system, enhancing its overall performance.

The investigation delves into two key facts concerning BP nanofillers. Firstly, the study scrutinizes the piezoresistive properties of BP nanofillers. Research indicates that BP devices ranging from 10 to 30 nanometers, oriented in a zigzag configuration, exhibit a heightened piezoresistive effect. This effect intensifies with an incremental increase in the layer count of BP, achieved through minute asymmetric adjustments within a strain range of 1.2%. Essentially, thicker BP nanofillers are posited to bolster the

piezoresistive response, potentially enhancing sensor performance significantly, as reported in references.

Secondly, the research probes the impact of passivating BP with PDA. This passivation process involves the consumption of lone pairs of electrons present in the outer layer of BP. By doing so, it augments the surface barrier of BP, thereby diminishing the carrier mobility rate. This strategic alteration induced by passivation holds implications for fine-tuning the electronic properties of BP, showcasing a pathway to modulate carrier mobility and potentially enhance the overall performance of BP-based devices. [319, 330].

The sensitivity difference between hybrid strain sensors is understood as the dual mechanism of nanofillers, that is the piezoresistivity of BP nanofillers and tunnelling effect of PDA@rGO nanofillers as shown in **Fig. 8.16(a)**.

To distinguish the impact of BP thickness and the PDA coating content to the hybrid system, we further calculated the GF contribution of hybrid BP-PDA@rGO strain sensors to their blank control groups (e.g., PDA@rGO-X) and classified into three different BP thickness sets as shown in **Fig. 8.16(b)-(d)**. For example, the value of 8.05% was calculated by the growth part between S-BP18000-PDA@rGO-1 (GF:973) and its blank control S-PDA@rGO-1 (GF:906) within the strain range of 0.7%-1.0%.

For fixed BP thickness comparison, there is always a sudden decrease in GF contribution for the S-BP-PDA@rGO-4 hybrid strain sensors groups compared with the others regardless of which BP thickness levels. The results are referred to the outcome that BP nanofillers further expand the distance of PDA@rGO flakes and it is known that the limited tunnelling effect for PDA@rGO flakes is PDA@rGO-4 groups in the previous section. If the distance of neighbouring PDA@rGO flakes further increases by BP nanofillers in between, the sensitivity of sensors will suddenly decline as shown in **Chapter 7 Section 3, Fig. 7.16(a)**. Thus, it is shown that the GF contribution in S-BP-PDA@rGO-1 groups to S-BP-PDA@rGO-3 groups is positive.

The BP nanofillers here participate in enhancing the tunnelling effect of PDA@rGO nanofillers by separate the graphene from each other in the hybrid system.

For fixed BP content comparison, it is shown that the GF contribution of hybrid strain sensors always raise as the thickness of participated BP nanofillers improve. Especially for S-BP-PDA@rGO-4 groups, the GF contribution change from -17.8% to +10.13% as the BP nanofillers increase from several nms to 100s nms. The improvement is considered as the effective of the piezoresistive effect of the BP nanofillers in hybrid system since it shows the consistency that piezoresistive effect of the BP nanofillers is positively correlated with BP thickness. The role of PDA@rGO nanofillers in here is to fix the BP nanofillers in PDA@rGO flakes so that the piezoresistive effect of the BP nanofillers can happen when the tunnelling effect of PDA@rGO possibly reach its limit (as discussed in **Chapter 7 Section 7.3**).

To summary, we believe that it is the synergistic dual mechanisms of BP nanofillers and PDA@rGO nanofillers that help to achieve higher sensitivity in this study.

8.4 Conclusion

In this study, we tend to achieve high sensitivity by applying the dual mechanisms of two different 2D nanofillers (that is piezoresistivity of BP and tunnelling of graphene). By adding BP nanofillers with different thickness changing from several nms to over 100 nms, the sandwiched-like BP-PDA@rGO hybrid nanofillers can be prepared by connecting bond between P-C and P-O-C bonds. The performance results show that the BP thickness have a negative impact on the sensitivity of the hybrid strain sensors and it is always the thicker BP-containing sensors achieve the higher GFs. On the other hand, regardless of which BP thickness levels, there is always a sudden decrease in GFs as the PDA content reach the level that achieving the limit of tunnelling effect of graphene (PDA@rGO-4). Thus, it is both mechanisms (that is piezoresistivity of BP and tunnelling effect of graphene) synergistically contribute to varying sensitivity of

hybrid strain sensors. Overall, through a collaborative dual mechanism between BP and PDA@rGO, a hybrid nanofillers sensor with a sensitivity of up to 1300 was obtained.

Chapter 9 Conclusions and recommendations for future works

9.1 Conclusions

The demand for sensors with high sensitivity to low deformations has significantly increased in various high-value applications, including wearable electronics, human-machine interfaces, and condition monitoring of critical engineering structures. The emergence of advanced materials, such as low-dimensional nanomaterials, has enabled the development of more powerful, multifunctional, and intelligent sensors. Leveraging the unique properties of nanomaterials, strain sensors have been enhanced to be lightweight, physically flexible, and more sensitive compared to conventional counterparts. Those sensors are capable of detecting even minuscule deformations. It is now possible to fabricate strain sensors that can accurately capture and measure low strains. This advancement opens up opportunities for a wide range of applications where precise detection of low deformations is essential.

This thesis proposes strategies for optimizing sensitivity of strain sensors based on the following considerations. Firstly, from a mechanism-based perspective, the focus is on leveraging the tunneling effect to enhance sensitivity in detecting low strains. This involves creating nanoscale separations between the nanofillers to reduce the impact of disconnection mechanics and emphasize the tunneling effect, thereby improving the sensitivity of prepared strain sensors. Secondly, from the perspective of nanofiller modification and combination, several strategies are introduced. These include the application of viscous polymer nanolayers to enhance nanofiller dispersion and bonding with the polymer substrate. Surface modifications are employed to tailor the electronic properties of the nanofillers, while the use of hybrid nanofillers incorporates different materials to create more conductive pathways. Additionally, the design of sandwiched-like structures promotes stronger interactions between the nanofillers. By implementing

these strategies, the aim is to optimize sensitivity and enable more accurate and precise strain detection.

In Chapter 4, a PDA coating and hybrid carbon-based nanofillers were used to enhance the sensitivity of nanocomposite strain sensors to low strain. Characterizations such as XRD and XPS of PDA@MWNTs revealed that PDA precipitated onto the MWNTs surfaces as single-crystal layers with a thickness in the tens of nanometers range. Ultrasonic measurements demonstrated that the thickness of the PDA layers positively impacts sensor sensitivity, with a 40% improvement observed when the PDA addition was 15 wt.%. This suggests that PDA buffer layers enhance tunneling processes, which are more likely to occur when the distances between conductive nanofillers are at the nanometre level. Furthermore, nanocomposite sensors constructed from hybrid carbon nanofillers exhibited significantly enhanced ultrasonic signal acquisition, demonstrating a sensitivity that is at least ten times greater than that of MWNT-based sensors. Both types of nanofillers contribute significantly to the improved sensitivity of the proposed sensor, leading to increased geometrical contact between the nanofillers and thereby intensifying the tunneling effect. Additionally, as the mass fraction of graphene increased from 33% to 66%, the sensitivity of the proposed sensor increased by approximately 120%, surpassing the sensitivity of pure graphene sensors, even while using a lower graphene content.

In Chapter 5, AgNPs were immobilized on the surfaces of MWNTs through a PDA-assisted process. The resulting nanofillers were utilized to create nanocomposite sensor specimens capable of detecting minute static deformations and high-frequency vibrations. Material characterizations confirmed that AgNPs were effectively incorporated into the PDA nanolayers on the MWNTs surfaces, enhancing the electron transport ability of the PDA nanolayers and facilitating electron tunneling between adjacent nanofillers. Through static tensile tests, it was demonstrated that sensor specimens made from the nanofillers with immobilized AgNPs exhibited a sensitivity up to 37% higher than those made with PDA nanolayers alone. Additionally, by testing

sensor specimens of varying thicknesses, it was determined that the strain-induced resistance change in a sensor specimen was significantly influenced by the piezoresistive effect within a strain range of 0.6%. Furthermore, high-frequency vibration tests revealed that the AgNP content in a sensor specimen positively impacted its sensitivity across a wide frequency spectrum.

In Chapter 6, graphene was first oxidized by the Hummer's method to different degree of oxidation and then put into the home-made print pen as the writable instruments for multitype strain sensing. The drawn trace of the prepared inks shows good writability in printed paper even when the paper substrate is in bent state. The FTIR, Raman and XRD confirm that the prepared GO have separated into 3 different degrees. For the preformation, we first evaluate tensile and compression sensitivity of the GO-based paper strain sensors themselves by bending the paper substrate by hand. The resulted GF are as high as 87.1 and 77.4 in terms of tensile and compression strain sensing within range of 0.86%. Thanks to the 3D-like structure of GO, the GO-based paper strain sensors show the sensitivity of $3.6 \times 10^{-3} \text{ kPa}^{-1}$ in pressure sensing from the range of 2 kPa to 5 kPa. Then, the GO-based paper strain sensors were attached to aluminum alloy substrate to simulate a real-world situation in tensile, compression and pressure sensing by a Instron tensile machine. The similar performance of the GO-based paper strain sensors shows great potential in meeting complicated real-world situation. GO sensors exhibited similar sensing ability even the GO inks were leave for over three months. Additionally, it is noted that the sensitivity of GO-based paper strain sensors reduces with an increase in the oxidation degree of GO. This can be attributed to several factors, including a higher concentration of oxygen-containing functional groups, an increased number of defects, and improved interfacial interactions within the GO material. This research give contribution to demonstrate the high performance of GO-based paper strain sensors in tensile, compression and pressure sensing by PoP approach. The prepared sensors also were utilized in actual applications in wearable device field and aerospace field.

In Chapter 7, we have developed a two-step PDA nanolayer coating method to regulate the separation of graphene flakes, influencing the tunnelling distance and the probability of tunnelling occurrence. Morphological analysis demonstrates that the surface of the 2-step PDA@rGO samples is smoother compared to those prepared using a direct PDA coating method. Furthermore, the synthesized nanofillers were employed to fabricate thin-film strain sensors through vacuum filtration, enabling controlled contact between the graphene flakes by the PDA nanolayers. The even distribution of the PDA nanolayers effectively separated the nanofillers at a fixed distance, resulting in a 21% improvement in sensitivity compared to sensors prepared using direct PDA coating methods.

Additionally, by varying the number of cycles in the 2-step PDA coating process, different thicknesses of the PDA coating layer on graphene can be achieved. It was observed that as the coating cycles increased, the PDA nanolayer became thicker but rougher, potentially leading to agglomeration of the graphene nanofillers. In terms of performance comparison, it was found that the sensitivity of the PDA@rGO-X sensors initially increased with the coating cycles and then abruptly declined. This indicates that there exists an optimal distance between neighbouring graphene flakes to achieve the maximum tunnelling effect.

In Chapter 8, it is shown to achieve high sensitivity by applying the dual mechanisms of two different 2D nanofillers (that is piezoresistivity of BP and tunnelling of graphene). To create the hybrid nanofillers, we incorporated BP nanofillers with varying thicknesses ranging from a few nanometers to over 100 nanometers. Through the formation of P-C and P-O-C bonds, the resulting sandwiched-like BP-PDA@rGO hybrid nanofillers were obtained. Performance evaluations revealed that the thickness of BP had a negative impact on the sensitivity of the hybrid strain sensors. Interestingly, the sensors containing thicker BP layers consistently exhibited higher GFs. Regardless of the thickness of BP, there was always a sudden decrease in GFs when the PDA content reached a level that achieved the tunnelling limit of graphene (PDA@rGO-4).

Hence, both mechanisms, the piezoresistivity of BP and the tunnelling effect of graphene, synergistically contributed to the varying sensitivity observed in the hybrid strain sensors. By harnessing the collaborative dual mechanism between BP and PDA@rGO, we successfully developed hybrid nanofillers that yielded a remarkable sensitivity of up to 1300.

9.2 Recommendations for future work

Building upon the insights and methodologies outlined in this thesis, the trajectory for future research in strain sensor technology is characterized by a multifaceted approach aimed at refining sensor sensitivity, broadening application horizons, and addressing existing research constraints. Firstly, an in-depth exploration of the tunneling effect stands as a paramount avenue for enhancing sensor performance. Delving deeper into this pivotal mechanism entails scrutinizing the impact of various nanomaterials and nanoscale separations on tunneling dynamics. By experimenting with an array of nanofillers, researchers can assess the influence of factors like size, shape, and composition on sensor sensitivity, thereby paving the way for tailored sensor designs optimized for heightened accuracy and responsiveness.

Secondly, the development of 3D nanomaterials emerges as a promising frontier for advancing strain sensor capabilities beyond the confines of 1D and 2D structures. Embracing the unique properties of 3D nanomaterials, such as nanostructured metals or ceramics, holds the potential to revolutionize sensor technology. Explorations into diverse synthesis methods for 3D nanomaterials and their integration into strain sensors can unlock novel avenues for enhancing sensitivity and performance. Concurrently, the exploration of alternative dual mechanisms beyond the proven combination of BP and graphene offers a fertile ground for innovation in sensor design. By investigating new synergistic pairs of nanomaterials, researchers can uncover novel avenues for crafting highly sensitive strain sensors tailored to specific application requirements. Lastly, the translation of advanced strain sensors from theoretical constructs to practical

applications in real-world scenarios holds immense promise. Testing these sensors across varied environments and conditions, alongside exploring seamless integration strategies into existing systems, marks a crucial step towards realizing the full potential of these cutting-edge technologies. Collaborative efforts with industry partners to identify specific use cases and refine sensor functionalities further solidify the bridge between theoretical advancements and practical implementations in the realm of strain sensor technology.

Moreover, the integration of simulation technology and artificial intelligence (AI) presents a transformative opportunity in advancing the field of strain sensor technology. Leveraging simulation tools allows researchers to model and simulate complex sensor behaviours under varying conditions, enabling the prediction of sensor performance with high accuracy. AI algorithms, such as machine learning and neural networks, can assist in optimizing sensor designs, analysing large datasets to identify patterns, and enhancing sensor capabilities through intelligent data processing. By harnessing the power of simulation technology and AI, future research endeavours can expedite the development of highly efficient and adaptive strain sensors, pushing the boundaries of sensor technology towards unprecedented levels of precision and functionality.

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