Application of three-dimensional graphene in sound generation via thermoacoustics

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**APPLICATION OF THREE-DIMENSIONAL GRAPHENE IN
SOUND GENERATION *via* THERMOACOUSTICS**

NGOH ZHI LIN

SCHOOL OF ELECTRICAL & ELECTRONIC ENGINEERING

2021

**APPLICATION OF THREE-DIMENSIONAL GRAPHENE
IN SOUND GENERATION *via* THERMOACOUSTICS**

NGOH ZHI LIN

School of Electrical & Electronic Engineering

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

2021

Statement of Originality

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

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A handwritten signature in black ink, appearing to read 'Zhi Lin', with a horizontal line underneath.

[Ngoh Zhi Lin]

Supervisor Declaration Statement

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

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Assoc Prof Teo Hang Tong Edwin

Authorship Attribution Statement

This thesis contains material from 1 paper(s) published in the following peer-reviewed journal(s) where I was the first and/or corresponding author.

Chapters 3 and 4 are published as Z. L. Ngoh, P. Guiraud, D.Tan, S. Giordano, O. Bou-Matar, E. H. T. Teo, P. Pernod, P.Coquet, R. Lardat. Experimental characterization of three-dimensional Graphene's thermoacoustic response and its theoretical modelling. *Carbon* **169**, 382-394 (2020). DOI: 10.1016/j.carbon.2020.06.045.

The contributions of the co-authors are as follows:

- A/Prof Teo and Prof Pernod provided the initial project direction and edited the manuscript drafts.
- Pierre and I prepared the manuscript drafts with equal contribution.
- The manuscript was revised by Pierre, Dr Tan, Dr Giordano, Dr Bou-Matar, A/Prof Teo, Prof Pernod, Prof Coquet, Dr Lardat and I.
- I co-designed the study with Pierre and performed all the laboratory work at CNRS International NTU Thales Research Alliance (CINTRA).
- Pierre, Dr Tan, Dr Giordano, Dr Bou-Matar and I analyzed the data.
- All material characterization, including sample preparation, was conducted by me in Nanoelectronics I and Nanoelectronics II.

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[Ngoh Zhi Lin]

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Abstract

Piezoelectric transducers are currently being used in sound generation applications such as medical ultrasound, ultrasound cleaners, microwave imaging and Sound Navigation and Ranging (SONAR). However, piezoelectric transducers have a small operating frequency band and large material size is required for low frequency sound generation. Thermoacoustics, on the other hand, is a non-mechanical sound generation method with a broad operating frequency band with potential to be an alternative sound transmitter. Its size independent acoustic frequency allows for utilization of small-size materials at low frequencies. Similar to piezoelectric transducers, material selection is important for effective utilization of sound generation. A good material candidate for such acoustic technique needs to have low electrical resistance for electrical current to pass through and Joule heating to occur, large surface area to maximize interactions with its surrounding medium, high thermal conductivity (κ) for uniform heat distribution and fast heat dissipation, and low specific heat capacity (C_p) for minimum heat storage.

Carbon is a good base material due to its properties. Especially carbon nanostructured materials, which possess many favorable properties (electrical resistance of 2 – 2200 Ω , thermal conductivity of 200 – 5000 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, specific heat capacity of 0.71 – 0.74 $\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$). Among various carbon nanostructured materials, three-dimensional graphene (3D-C) has interesting properties which provide it the potential to emit sound most efficiently. Its high porosity provides more surface contact with its surrounding medium allowing for fast thermal dissipation, and steep temperature gradients. At present, most studies have only investigated the effect of power input, output acoustic frequency and receiver-sample distance on measured sound pressure levels (SPLs) of 3D-C. Other key critical factors pertaining to the physical and chemical properties of 3D-C, such as connection method, acoustical backing, length, width, height, pore per inch (ppi) and

macro-density, as well as the addition of reduced graphene oxide (rGO) and hexagonal boron nitride (h-BN), which can potentially impact 3D-C's generated SPLs and operating temperatures warrants a study. The effect of these properties were hence investigated in this thesis.

The initial part of the thesis covers 3D-C synthesized on nickel foams via thermal chemical vapor deposition (TCVD), with their crystal quality verified by Raman spectroscopy. With a Modulated Differential Scanning Calorimeter (MDSC), C_p was measured to be $0.68 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$, lower than reported values of CNTs ($0.72 - 0.75 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$) and graphite ($0.72 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$). This indicates its potential to emit sound with greater efficiency than its predecessors. A lab-based acoustic set-up was built to conduct experiments for validation of various hypothesis and acoustical measurement standards were established to ensure consistency during inter-experimental comparison.

Influence of acoustic frequency and electrical input power were also investigated. Increasing the acoustic frequency and electrical input power of 3D-C increases the generated SPLs as increasing these parameters result in faster oscillations of 3D-C's surrounding medium. These results were validated by previous conducted studies with the same linear relationship observed.

Changes were also made to 3D-C's physical properties to understand their effect on emitted SPL. The dimensions of 3D-C as a whole material, namely length and width, do not affect SPL. An increase in material size by 50 % and 150 % increases electrical resistance by 30 % and 95 % respectively, which would theoretically induce more Joule heating. This increase, however, resulted in increased material volume, and hence not result in a higher SPL generation. Increasing material contact surface with its medium by increasing porosity by 20 pores per inch (ppi) would, in theory, cause an increase in contact surface area by 40 %, improving thermal dissipation and sound generation. This

increase, however, was negated by an increase in material thickness by 3 mm, resulting in a similar amount of material present per millimeter. Increase in contact surface area induced by ppi change however does increase 3D-C's cooling rate by 200 %. Increasing 3D-C's growth time doubled material density, resulting in an increase in C_p by 27 times. This indicates an increase in the material's heat storage capacity, causing a decrease in induced temperature gradient, leading to a decrease in SPL generation by ~30 dB. Increasing material density by compressing 3D-C to half its height, on the contrary, results in a ~5 dB increase in SPL at acoustical frequencies above 20 kHz due to additional constructive interference induced by compression. Therefore, to achieve maximum thermoacoustic sound generation, 3D-C has to have high porosity and low density and thickness.

The effect of the addition of rGO and h-BN on 3D-C's thermoacoustic effect were investigated concurrently. Random deposition of rGO sheets covered 3D-C's pores, reducing its contact surface area with its surroundings and thermal dissipation, thereby reduced its sound generation by ~10 dB as compared to pure 3D-C. h-BN, an electrically insulating material with similar crystal structure to graphite, was coated on the surface of 3D-C to improve thermal dissipation. However, the deposition of h-BN resulted in a SPL reduction of ~5 dB due to the graphene being defective after h-BN deposition. The hybridization of h-BN with 3D-C (3D-BNC), allowed for the changing of the material electrical resistance based on material composition. For example, $30 \times 20 \times 2 \text{ mm}^3$ 3D-C had an electrical resistance of 2.5Ω , while $30 \times 20 \times 2 \text{ mm}^3$ 3D-C with a chemical composition of 75 % 3D-BN and 25 % 3D-C had an electrical resistance of 85Ω and $30 \times 20 \times 2 \text{ mm}^3$ 3D-C with a chemical composition of 50 % 3D-BN and 50 % 3D-C has an electrical resistance of 100Ω for 3D-BNC. This resulted in more effective Joule heating and decreased the electrical input current required to generate sound by 55.6 %

and 66.7 % respectively.

A systematic study, varying test configuration and physical parameters of 3D-C and addition of h-BN and rGO sheets, had been conducted for optimization of 3D-C's thermoacoustic performance. Additional studies, such as bending 3D-C during applicational use and increasing the range of acoustic frequency and input power, are recommended to be conducted to improve 3D-C's efficiency for applicational use. 3D-BNC can be utilized in sound generation applications where impedance matching is required. A proof of concept of 3D-C's ability to generate sound underwater was also demonstrated, which exhibits its potential to be utilized in SONAR with a broad frequency operation band.

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1. Introduction

1.1 Background

Sound generators are vibrating objects that can produce sounds have attracted considerable research interest due to their broad range of applications such as communications, navigation, tracking and ultrasound [1]. The overall efficiency and quality of these applications are highly dependent on the performance of the sound generators. To achieve optimum acoustic performance, acoustic impedance of the sound generator has to match its surrounding medium to minimize scattering, reflections, refractions and thermal absorption of the generated acoustic signal [2]. An optimized sound generator not only needs to possess a large operating frequency band for the user to have a wide frequency bandwidth, but also should be able to produce high sound generation at low power with high power efficiency to minimize operating expenses [1].

In general, there are two common methods have been used for sound generation, namely moving-coil and piezoelectricity. The former generates sound by utilizing moving coils while the later produces sound by piezoelectric transducers. As illustrated in Figure 1, the main components of a traditional speaker required for moving-coil sound generation consist of a permanent magnet and a metal wire coiled around the smaller end of a paper cone [3]. This paper cone is supported by elastic suspensions at its both ends to allow for regular forward and backward movements. When oscillating electric current flows into the metal coil, an oscillating magnetic field will be induced. This oscillating magnetic field interacts with the magnetic fields produced by the permanent magnet to produce alternating magnetic attractive and repulsive forces. These magnetic forces cause the paper cone to move forward and backward proportionately to the electrical current, hence generating sound [3]. On the other hand, piezoelectric

transducers which were first synthesized in 1949 utilize an alternating current (AC) as its power source for sound generation [4]. When AC is conducted across a piezoelectric transducer, the material undergoes mechanical expansions and contractions in a sequential pulsating manner. This sequential pulsating movement brought about by the AC induces a similarly pulsating movement in its surrounding medium [5] and thereby generating sound. As piezoelectric transducers have a higher electrical impedance than moving coil speakers, they can perform at a higher efficiency and generate higher SPLs than traditional speakers at the same input power [6]. This brings about the use of piezoelectric transducers in a wide range of acoustic applications, including medical ultrasound, ultrasonic cleaners, microwave imaging and Sound Navigation and Ranging (SONAR) [7-9].

Figure 1. Schematics of components in a traditional speaker [3].

The abovementioned sound generation techniques are able to generate high amplitudes of SPLs through their direct mechanical interaction with the surrounding medium. However, frequency of sound generation by such mechanical movements is

highly dependent on the material resonant frequency, which is generally characterized by a narrow frequency band, limiting its effective operating frequency bandwidth [10]. Furthermore, large piezoelectric transducers are necessary for sound generation at low frequencies of kHz range and below. This is because optimization of the utility of piezoelectric transducer's resonant frequency, otherwise known as fundamental frequency, requires the material thickness to be at either half or odd multiples of the frequency of sound generation [11, 12], resulting in the frequency of sound generation to be inversely proportional to the dimensions of piezoelectric transducers. These two aspects limit the practical applications of piezoelectric transducer, where low frequencies of sound generation are required.

To address the abovementioned issues, thermoacoustic, which can generate acoustic waves by utilizing thermal energy gradients, has been considered as another alternative technique for sound generation [13]. When thermoacoustic sound generators are utilized, the induced thermal energy is transmitted to their surrounding medium. This thermal energy dissipation results in a gain in the surrounding medium's kinetic energy and thereby induce faster movements. The induced temperature gradient would result in an orderly movement of the surrounding medium, hence generating sound. Without the use of physical movements, the operating frequency of materials utilized for thermoacoustic sound generation is independent of material resonant frequency [13], resulting in the material having a broader frequency band of operation and its frequency of sound generation being independent of material dimensions.

Generally, a good material used for thermoacoustic sound generation needs to have a high thermal conductivity (κ) and low specific heat capacity (C_p). High thermal conductivity is required for efficient dissipation of the induced thermal energy into its surrounding medium, while a low specific heat capacity is needed to decrease the

amount of thermal energy required to increase the material temperature [14, 15]. Low thickness is also desired to minimize the heat capacitance per unit area (*HCPUA*) of the material [14, 15]. Among the various materials, metals are a class of materials, which possess the required thermal properties ($\kappa = 10.7 - 418 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, $C_p = 0.015 - 1.885 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$ [16]) for thermoacoustic sound generation, have been used as an initial proof of concept of thermoacoustic sound generation in the early 1900s. However, only a low measured amplitude of SPL was obtained due to the low electrical resistance and high thickness of the platinum sheet (0.7 μm thick) [17, 18]. As demonstrated previously, the *HCPUA* of the metal materials can be further decreased by reducing their dimensions to nanometer-scale. For example, metal nanowires deposited on substrates with nanometer-scale thicknesses have been developed in recent years [19-21]. Despite these improvements in efficiency of the thermoacoustic sound generation, the obtained SPLs were still unable to meet market demands. Therefore, it is still highly desirable to develop other alternative material which not only possesses all the required material properties including high electrical resistance, excellent thermal conductivity and low specific heat capacity, but also can generate high SPLs and achieve superior efficiency when used for thermoacoustic sound generation [17, 18].

1.2 Motivation

Carbon nanostructured materials (e.g., graphene, CNTs) with high thermal conductivity (200 – 5000 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ [22, 23]), low specific heat capacity (0.71–0.74 $\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$ [24, 25]) and relatively low density (2 – 2100 $\text{mg}\cdot\text{cm}^{-3}$ [26-28]) can meet most of the abovementioned requirements and have been considered as promising candidates for thermoacoustic sound generation [29-31]. To date, multiple efforts have been devoted to the design and synthesis of various carbon nanostructured materials for

thermoacoustic sound generation [32-36]. However, most of the previously reported carbon nanostructured materials are limited to fabrication at small dimensions (up to 2 x 2 cm) and are only able to achieve low levels of thermoacoustic sound generation efficiency, which hinder their further practical industrial applications [32-36]. On the other hand, three-dimensional graphene (3D-C) not only has the desired material properties, but also has high contact surface area with its surrounding medium due to its highly interconnected porous microstructure, which is expected to result in increased interactions between the material and its surrounding medium [13], thereby potentially increasing generated SPLs and thermoacoustic sound generation efficiency. Unlike other carbon nanostructured materials, the dimensions of 3D-C are easily scalable with the variation of the utilized furnace and template, hence allowing for its easy large-scale synthesis.

3D-C with an increased contact surface area is expected to increase its interactions with its surrounding medium, possibly improving its thermoacoustic sound generation capabilities. At present, most studies have only investigated the effect of power input, output acoustic frequency and receiver-sample distance on measured SPLs of 3D-C [34, 37]. Other key critical factors pertaining to the physical properties of 3D-C, both at macro and micro scales, which can potentially impact the *HCPUA* of 3D-C and hence its thermoacoustic sound generation efficiencies warrant a study. In commercial applications, the implementation and design of the 3D-C for integration into the application is also critical in ensuring its feasibility to function. The limited work done on the effects of electrical connection and acoustical backing on 3D-C's thermoacoustic sound generation efficiencies [34, 37] hence justifies an investigation.

Moreover, limited studies have been conducted on the effect of hybridizing carbon nanostructured materials on thermoacoustic sound generation. Leveraging on 3D-C's

high contact surface area, surface modifications can be conducted to 3D-C to further increase its contact surface area with its surrounding medium, which is likely to increase its SPL and deserves further study.

Furthermore, electrical resistance of the material utilized can be increased to improve the efficiency of thermoacoustic sound generation [11,12]. Majority of research conducted on thermoacoustic sound generation focused on carbon nanostructured materials and metal sheets [32-36]. Research on the incorporation of materials that possess suitable thermal properties while having higher electrical resistance for more effective Joule heating into carbon nanostructured materials and higher thermoacoustic sound generation levels have yet to be conducted.

1.3 Objectives and scope

Based on the discussed background and motivation, the main objectives and scope of this thesis are shown below:

- 1) Tuning synthesis parameters to obtain defect-free 3D-C. The microstructure, morphology and properties of the obtained free-standing 3D-C will be characterized to verify the absence of defects in the final product.
- 2) 3D-C will be connected to an acoustic measurement set-up to measure its generated SPLs when electrical input frequency and input power are varied. The obtained results are to be analyzed and compared with previously reported carbon nanostructured materials to corroborate the thermoacoustic characteristics of 3D-C. The effect of connection and acoustical backing on the generated SPLs and operating temperatures of 3D-C will be investigated to gain an understanding of their effects on thermoacoustic sound generation.
- 3) 3D-C with variable parameters will be fabricated to investigate the effect of

macroscale size, porosity, thickness as well as density on the generated SPL and operating temperature of the 3D-C. The obtained experimental results are to be compared against simulation results to further validate the various hypotheses.

4) Various materials including reduced graphene oxide (rGO) and hexagonal-boron nitride (h-BN) will be incorporated with 3D-C to investigate their ability to improve thermoacoustic sound generation.

5) Demonstrate the ability of 3D-C to generate sound in air and underwater.

1.4 Major contribution of the thesis

This thesis focuses on how changes in material parameters and composition will affect the thermoacoustic performance of the 3D-C. After verification of 3D-C's quality, a series of critical parameters involved in the fabrication process and the acoustic measurements have been systematically investigated, and a summary of the identified relationships are as follows:

1) Defect-free 3D-C has been synthesized and the effect of electrical input frequency, input power, connection and acoustic backing on SPL and operating temperature of the 3D-C have been investigated. Both frequency and electrical input power have direct relationships with SPL. While the length of connection path does not affect the generated SPL, the rise in power density causes the sample to thermally decompose at lower input powers. Adding volumetric amounts of conductive silver (Ag) paint decreases amount of material available for thermoacoustics, thereby reducing SPLs. Adding minimal amounts of conductive Ag paint, which functions only as an electrical connection between sample and electrical source, increases power density. This renders the sample more susceptible to thermal decomposition. The addition of an acoustical backing reflects sound back into the receiver, resulting in constructive interference,

which in turn increases the SPL.

2) The effects of various parameters, including macroscale size, porosity, thickness and macro-density of the 3D-C, on its SPL and operating temperature have been studied. Increasing the original dimensions of 3D-C ($20 \times 20 \times 2 \text{ mm}^3$) by 50 % and 150 % does not affect SPL despite changes to sample electrical sheet resistivity and surface area. This is attributed to the effect of impedance matching, which negates the effects on thermoacoustic sound generation. An increase in porosity increases contact surface area and hence thermal dissipation, improving thermoacoustic sound generation. An increase in material thickness increases heat capacitance per unit area of 3D-C, resulting in more thermal energy stored in the material instead of dissipating into its surroundings and decreasing thermoacoustic efficiency. Increasing porosity by 20 pores per inch (ppi) on generated SPL causes an increase in contact surface by 40 %, which in turn increases sample cooling rate by 200 %. Any possible improvements on SPLs are negated by an increase in thickness by 3 mm. Increasing material growth time doubled material density, which in turn leads to an increase in *HCPUA* by 27 times and a reduction in sound generation by ~30 dB. Densification, by physical compression of 3D-C to half its original height, does not result in reduction in SPL.

3) The generated SPLs of 3D-BNC are less than those of the 3D-C. Electrical current induced into the 3D-BNC only flows through electrically conductive 3D-C and avoids h-BN layers. In addition, the increase in heat capacitance results in poorer heat dissipation, leading to the poorer thermoacoustic performance of the hybrid material. Deposition of h-BN layers onto 3D-C via High Power Impulse Magnetron Sputtering not only results in chemical bonding between the two layers, but also introduces defects onto 3D-C, resulting in a reduction in SPL generation by ~5 dB. Deposition of rGO sheets onto 3D-C covers the pores of 3D-C, decreasing its contact surface area with its

surrounding medium, resulting in deterioration in SPL by ~10 dB.

4) An analysis of 3D-C's capabilities in thermoacoustic sound generation against other carbon nanostructured materials as well as traditional piezoelectric transducers has been conducted. Demonstrations of 3D-C's potential to play music akin to a loudspeaker and transmit sound in underwater conditions have also been accomplished.

1.5 Organization of thesis

Chapter 1 introduces this thesis, providing the background, motivation, objectives and scope, and main contributions of this thesis. Chapter 2 provides the literature review. This includes the mechanism of piezoelectricity and the various types of piezoelectric transducers, which are the current state-of-the-art mechanism and materials for sound generation in the market. Next, the mechanism of thermoacoustics is explained, along with its material requirements and actuation means. Previous studies on thermoacoustics, as well as properties and synthesis methods of 3D-C are summarized and discussed. Chapter 3 elaborates on the experimental and theoretical methodologies for 3D-C and material characterization. The microstructure and quality of the synthesized 3D-C, as well as the parameters critical to electro-thermoacoustic efficiency were also examined. Chapter 4 elaborates the effect of external parameters, namely the effect of acoustic frequency, input power, connection path and acoustic backing on the generated SPLs of the 3D-C. Chapter 5 discusses the effects of physical parameters of the 3D-C including size, porosity, thickness and density, on their generated SPL and operating temperature. The experimental results were also compared with simulation results to validate the corresponding hypotheses. Chapter 6 examines the influences of the incorporation of rGO and h-BN with 3D-C on their generated SPLs. Finally, Chapter 7 concludes this thesis, with demonstrations of 3D-C generating sound in air and

underwater as well as suggestions for future work and 3D-C as a sound generator.

2. Literature review

2.1 Piezoelectric transducers

The current state of the art in sound generation uses piezoelectric transducers, which generates sound using the piezoelectric effect.

2.1.1 Piezoelectric effect

Piezoelectric transducers utilize the piezoelectric effect to generate sound. For a material to utilize the piezoelectric effect, it has to possess a flexible crystal structure which allows the central atom to move away from the center of the unit cell, resulting in spontaneous polarization and causing the crystal structure to expand in the same direction as the migration of the central atom as seen in Figure 2 [38]. Methods to polarize materials are covered in their relevant sections in section 2.1.2.

Figure 2. Schematic of the central atom moving from its original position. A, O and B represent the large cations, oxygen anions and small cations present in the unit cell respectively. (a) Original cubic crystal structure, and (b) polarized asymmetric crystal structure with the central atom having moved in the direction of the arrow, with the small blue sphere representing the central position of the tetragonal unit cell, and the black sphere represents the actual location of the cation in the tetragonal unit cell [38].

Next, poling is conducted for piezoelectric ceramics and single crystals. Domains, which are small areas of dipoles with similar orientations, exists within each grain of the piezoelectric crystal. The spontaneous polarization of the domains are of opposing directions to each other, resulting in a cancellation of material spontaneous polarization and its piezoelectric capabilities. Poling is hence conducted at temperatures below T_c and above room temperature, where a large electric field is injected to the material to orientate the dipoles in the same direction and induce piezoelectricity characteristic into the material Figure 3 [39].

Figure 3. Orientation of dipoles (a) before, and (b) after poling.

After material polarization, an electric field larger than the critical coercive field (E_c) [40] is introduced. This electric field reverses the generated polarization present in the piezoelectric transducer, allowing the central atom to relocate along the direction of the electric field should orientation of the crystal structure allow. In the process of polarization reversal, the material's crystal structure expands in the direction of the applied electric field, and the extent of the expansion is directly proportional to the amplitude of the electric field [38]. Applying an AC, which has controlled fluctuations, would cause the material to constantly expand and contract. This orderly expansion and contraction of the bulk material induces a longitudinal movement of the surrounding medium, which causes a pressure gradient and hence generates sound (Figure 4).

Figure 4. Longitudinal motion of particles due to expansion and contraction of piezoelectric transducer.

2.1.2 Types of piezoelectric transducers

There are several types of piezoelectric transducers, namely piezoelectric ceramics, piezoelectric single crystals and piezoelectric polymers [38, 41-44].

2.1.2.1 Piezoelectric ceramics

Piezoelectric ceramics were the first type of piezoelectric transducer to be utilized for sound generation, with the demonstration on the use of quartz in SONAR in early 1918. With research and development, barium titanate was later demonstrated in 1944 to have better piezoelectric performance than quartz. Further research and development resulted in lead zirconium titanates (PZT) outperforming barium titanate in 1954 [45]. Since then, PZTs have been the preferred choice of piezoelectric ceramic for sound generation. Both barium titanate and PZTs are inorganic solid solutions. Barium titanate comprises of barium cations (Ba^{4+}), titanium cations (Ti^{2+}) and oxygen anions (O^{2-}) (BaTiO_3), while PZTs are made of lead cations (Pb^{4+}), oxygen anions (O^{2-}) and varying compositions of zirconium (Zr^{2+}) and titanium (Ti^{2+}) cations ($\text{Pb}[\text{Zr}_x\text{Ti}_{1-x}]\text{O}_3$). Both of their cubic unit cell comprises of one O^{2-} located at the center of each face, one large cation (Ba^{4+} or Pb^{4+} for BaTiO_3 and PZT respectively) at each corner of the unit cell and a central smaller cation (Ti^{2+} for BaTiO_3 and a distribution Zr^{2+} and Ti^{2+} between PZT) located in the middle of the unit cell (Figure 5a) [38].

Figure 5. Schematic of the central atom moving from its original position. A, O and B represent the large cations, oxygen anions and small cations present in the unit cell respectively. (a) Original cubic crystal structure, and (b) polarized asymmetric crystal structure with the central atom having moved in the direction of the arrow, with the small blue sphere representing the central position of the tetragonal unit cell, and the black sphere represents the actual location of the cation in the tetragonal unit cell [38].

For piezoelectric ceramics to achieve spontaneous polarization, their cubic crystal structure needs to be altered to become asymmetric. This can be achieved by ensuring that operating temperatures are below the Curie point (T_c , above 200 °C [46, 47]) [38, 41-44]. Above T_c , piezoelectric ceramics have a cubic crystal structure. Below T_c , the central cation moves out of its original central position in the unit cell, resulting in an expansion of the unit cell in the same direction of cation shift. The movement of the central cation also causes an imbalance of charges, inducing a positive charge in the upper section of the tetragonal unit cell with the central cation and a negative charge in the other section. This difference in charges result in a spontaneous polarization in the direction from the negatively charged section to the positively charged section (Figure 5b).

Piezoelectric ceramics consist of multiple crystalline structures in a single piece of material. The presence of multiple crystalline structures in piezoelectric ceramics results in the presence of grain boundaries in the material. When an electric field is applied, these grain boundaries pin crystalline structures in a piezoelectric ceramic and prevent the unit cell from distorting [48, 49]. This causes piezoelectric ceramics to have a high E_c (PZT-5H, $5 - 7 \text{ kV}\cdot\text{cm}^{-1}$), and hence require high electrical currents for polarization [50].

2.1.2.2 Piezoelectric single crystals

Piezoelectric single crystals are mainly made of lead magnesium niobate-lead titanate (PMN-PT, $\text{Pb}[\text{Mg}_{1/3}\text{Nb}_{2/3}]\text{O}_3\text{-PbTiO}_3$) or lead zinc niobate-lead titanate (PZN-PT, $\text{Pb}[\text{Zn}_{1/3}\text{Nb}_{2/3}]\text{O}_3\text{-PbTiO}_3$) [51, 52]. Individual pieces of piezoelectric single crystals have unique whole, single grain crystal structures consisting of multiple domains, unlike piezoelectric ceramics which are made of multiple grains. As a result, after poling, the domains in the piezoelectric single crystals are able to orientate in the same direction as the electric field, while the domains in the piezoelectric ceramics are unable to orientate in the same direction as the electric field due to the grain boundaries pinning them in their original orientation (Figure 6) [53]. This difference in orientation when the electric field passes through results in piezoelectric single crystals having a lower E_c (PMN-PT, $1.8 - 2.8 \text{ kV}\cdot\text{cm}^{-1}$) than piezoelectric ceramics (PZT-5H, $5 - 7 \text{ kV}\cdot\text{cm}^{-1}$) [50]. Piezoelectric single crystals hence require lower electrical currents to depolarize and polarize, which could increase cost effectiveness.

Figure 6. Orientation of (a) piezoelectric single crystals, and (b) piezoelectric ceramics after poling.

Polarization of piezoelectric single crystals is achieved using the same method as piezoelectric ceramics (section 2.1.1) [38, 41-44]. Unlike piezoelectric ceramics, the highest operating temperature of piezoelectric single crystals are defined by the temperature (T_d) which the material transitions from its polarized rhombohedral crystal structure to its depolarized tetragonal crystal structure (70 – 95 °C) [54]. The lower operating temperature as compared to piezoelectric ceramics (above 200 °C) indicates that it would depolarize at lower temperatures and not be able to generate sound at higher temperatures. In addition, due to their mechanical anisotropic property, single crystals need to be mechanically compressed during operation to prevent device failure.

While the discovery of the Bridgman method has been able to grow larger piezoelectric single crystals, the limited available crystal dimensions limits its ability to generate sound at lower frequencies. In addition, the cost of piezoelectric single crystal synthesis is relatively higher than piezoelectric ceramics. Piezoelectric single crystals will hence only be preferred to be used in applications where the cost of design of piezoelectric ceramics outweigh the fabrication costs of piezoelectric single crystal [52].

2.1.2.3 Piezoelectric polymers

A critical parameter for a material to have optimum acoustic transmission is acoustic impedance matching. Acoustic impedance of a material is calculated using

$$Z = \rho \times v, \quad (1)$$

where Z represents acoustic impedance ($\text{Pa}\cdot\text{s}\cdot\text{m}^{-1}$), and ρ and v represent the density ($\text{kg}\cdot\text{m}^{-3}$) and speed of sound ($\text{m}\cdot\text{s}^{-1}$) in the material respectively. For underwater sound generation, due to the high speeds of sound and densities of piezoelectric ceramics and single crystals ($7.8 - 8.12 \text{ g}\cdot\text{cm}^{-3}$) [55], their acoustic impedances (more than 30 MRayls) of sea water is more than twenty times that of seawater (1.5 MRayls, speed of sound = $\sim 1500 \text{ m}\cdot\text{s}^{-1}$, $\rho = 1.0273 \text{ g}\cdot\text{cm}^{-3}$) [38]. In addition, piezoelectric ceramics and single crystals are not flexible. Material flexibility is a required property for applications which require the material to conform to curved surfaces, such as autonomous underwater vehicles. Such applications are hence unable to utilize piezoelectric ceramics and single crystals. Piezoelectric polymers, are hence used for niche applications which require high material flexibility and acoustic impedance matching [38].

Polyvinylidene fluoride (PVDF) is the most commonly used piezoelectric polymer in acoustic wave generation. It is made of interconnected repeating units of $[\text{C}_2\text{H}_2\text{F}_2]$, with a default non-polar crystal structure (Figure 7, Form II). Upon physical distortion *via* mechanical rolling or stretching the material, the carbon atoms move out of their original positions, resulting in a polar crystal structure (Figure 7, Form I) [56]. In the polar crystal structure, the dipoles present in PVDF can then be poled to align along the same direction. Poling the dipoles of PVDF polarizes the material, hence allowing for piezoelectric sound generation to occur when an electrical current higher than E_c is introduced [38, 41, 57].

Figure 7. Forms I and II of PVDF. The small and big circles represent the carbon and fluorine atoms respectively [41].

While piezoelectric polymers have increased flexibility and superior acoustic impedance matching over piezoelectric ceramics and piezoelectric single crystals, it has a lower melting point of 177 °C, which is lower than the operating temperatures of piezoelectric ceramics (above 200 °C, [46, 47]). Its lower operating temperatures indicate that it would not be able to withstand high levels of electrical input power prior to thermal decomposition. This indicates that it would hence have a lower amplitudes of sound emission levels as compared to piezoelectric ceramics, and hence cannot be utilized for high power applications.

2.1.3 Issues of piezoelectricity

Utilization of piezoelectric mechanism in sound generation has a few design considerations. Firstly, there are two factors to consider when designing a sample utilizing piezoelectric materials: resonant frequency of the material, which is dependent on its physical parameters [58] and; its method of mechanical vibration [59]. Utilization of a mechanical method of sound generation results in the frequency of generated acoustic waves being limited to material resonant frequency. Piezoelectric sound transducers hence have a narrow operating frequency band. Secondly, the frequency at

which the piezoelectric material is able to generate sound efficiently is inversely proportional to its density and grain size [60]. This indicates that large piezoelectric materials are required for sound generation at low frequencies. Large bulky materials will require more design considerations as well as increase transportation costs. Lastly, synthesis of piezoelectric ceramics and piezoelectric single crystals require expensive and tedious processes at high temperatures. Post synthesis, additional refinements are required to remove impurities present in the materials, further increasing process costs [38].

2.2 Mechanism of thermoacoustics

Thermoacoustics involves the generation of sound using a thermal source. When a material is heated, due to the law of conservation of energy [61], the induced thermal energy is transferred into its surrounding medium when the neighboring particles collide with the material and gain the kinetic energy of the heated material. These particles transmit the transferred kinetic energy to their surrounding particles away from the heat source. Concurrent transmission of kinetic energy in a controlled fashion construct acoustic waves (Figure 8).

Figure 8. Vibrating particles oscillating longitudinally after gaining kinetic energy.

This acoustic transmission process can be described by thermodynamics. The first

law of thermodynamics states that the change in the internal energy, $\Delta\check{U}$ (J), present in the system is given by

$$\Delta\check{U} = \Delta Q + \Delta W, \quad (2)$$

where ΔQ represents the thermal energy supplied to the closed system (J) and ΔW represents the work done on the system (J) [13]. ΔQ is define by [11]

$$\Delta Q = m \times C_p \times \Delta T, \quad (3)$$

where m , C_p and ΔT represent the mass (kg), specific heat capacity ($\text{J}\cdot\text{kg}^{-1}\cdot^\circ\text{C}^{-1}$) and change in temperature of the system respectively ($^\circ\text{C}$).

ΔW is related to the pressure inside a sound wave, p (Pa), with

$$\Delta W = p \times \Delta V, \quad (4)$$

where ΔV represents the change in the volume of the closed system (m^3). p is also representative of the average internal energy density as follows:

$$p \equiv \frac{\check{U}}{V}, \quad (5)$$

where $\check{U}$ and V represent the internal energy (J) and finite volume (m^3) of the system respectively.

When work is done by the system, Eq. (4) and (5) can be substituted into Eq. (2) to give

$$\Delta\check{U} = \Delta Q - (p \times \Delta V). \quad (6)$$

Due to the absence of physical movements in thermoacoustics, there is no mechanical volume-work done, i.e. $\Delta V = 0$, and $\Delta W = 0$. This means that only ΔQ is generated, which is equivalent to $\Delta\check{U}$ based on Eq. (6).

Manipulating Eq. (4) gives [13]

$$\Delta p = \frac{\Delta\check{U}}{V}, \quad (7)$$

where Δp represents the change in system pressure. Thermoacoustics is hence an isochoric process with a constant volume V [62] and a variation in the system internal

energy, $\Delta\tilde{U}$, results in a change in system pressure Δp . When a controlled variation of thermal energy source, such as an alternating current (AC) with a sinusoidal voltage, is provided, the internal energy of the system at a point of time is

$$U_{el}(t) = \Delta\tilde{U} \times \sin(\omega \times t), \quad (8)$$

where $\Delta\tilde{U}$, ω and t represent the internal energy input into the system (J), angular frequency ($\text{rad}\cdot\text{s}^{-1}$) and time (s) respectively. Since $\Delta W = 0$, the change in internal energy, which is internal energy input into the system is equivalent to the thermal energy supplied to the system (Eq. (6)). Eq. (3) can hence be substituted into Eq. (6) to give

$$\Delta\tilde{U} = m \times C_p \times \Delta T \quad (9)$$

and be substituted into Eq. (8) to give

$$U_{el}(t) = m \times C_p \times \Delta T \times \sin(\omega \times t). \quad (10)$$

The sinusoidal electrical input current is defined by

$$I_{el}(t) = I \times \sin(\omega \times t) = \frac{U}{R} \times \sin(\omega \times t), \quad (11)$$

where I and R represent the electric current (A) and resistance (Ω) respectively.

Electric input power is calculated by multiplying the sinusoidal voltage with its corresponding electrical input current, hence giving rise to

$$P_{el}(t) = \Delta\tilde{U} \times \sin(\omega \times t) \times I \times \sin(\omega \times t). \quad (12)$$

Since the original input energy is the product of I and R , Eq. (9) can be simplified to

$$P_{el}(t) = I \times m \times C_p \times \Delta T \times \frac{[1 - \cos(2 \times \omega \times t)]}{2}. \quad (13)$$

As seen in Eq. (7), Δp varies with different amounts of $\Delta\tilde{U}$, which is varied by the changing sinusoidal AC input. It can hence be deduced that any point of time t , the pressure, $p(t)$, is approximately equivalent to the outward heat flux, $\dot{Q}(t)$, and hence the function of the supplied electric power $P_{el}(t)$. With a periodic sinusoidal change in $P_{el}(t)$, there would be an equivalent sinusoidal $\dot{Q}(t)$, hence inducing a pressure gradient and

generating sound [13].

Unlike piezoelectric materials, materials utilizing thermoacoustics do not use mechanical movements to generate sound. The lack of dependence on mechanical movement for sound generation allows thermoacoustic materials to have a wide frequency band of operation independent of the dimensions of the sample. This indicates its potential to be a single material solution for multiple applications.

2.3 Methods for actuation of thermoacoustics

There are two approaches to inducing the thermoacoustic effect.

2.3.1 Photo-thermoacoustics

Photo-thermoacoustics is a mechanism which was discovered 20 years ago and utilizes high energy electromagnetic (EM) waves, such as light or microwaves as the energy source. This mechanism can be split into two steps. The first step is known as the photo-thermal mechanism. Pulses of high energy EM waves are emitted into the photo-thermoacoustic material, which absorbs the electromagnetic wave as it passes through. When these EM waves interact with the photo-thermoacoustic material, the photo-thermoacoustic material absorbs the wave energy. The absorbed wave energy excites electrons in the valence band to jump into the conduction band. This phenomenon results in the generation of free carriers – holes are generated in the valence band while the electrons function as free carriers in the conduction band (Figure 9a). When the excited electrons in the conduction band return to the valence band, photons are released (Figure 9b) [63, 64]. These photons have energy amplitudes equal to the difference between the conduction and valence band. The second step of photo-

thermoacoustics then occurs – thermoacoustics. The photons then interact with its surrounding medium through collisions and scattering. At large amounts of photon energy, these interactions result in heating and movement of the material’s crystal lattice, creating phonons. These phonons function as heat transfer packets of energy vibrating in the lattice structure, hence allowing for heat transfer. This heat transference through the material then generates a thermal energy change in the surrounding medium. Utilization of pulses of a programmed EM wave source, a temperature gradient can be induced with increasing and decreasing thermal energy transference. This agitation of the surrounding medium in a cyclical longitudinal motion hence results in the generation of acoustic waves [65-70].

Figure 9. (a) Excitation of electron from its valence band (blue sphere) into the conduction band (red sphere), leaving behind a hole in the valence band (white sphere). (b) Excited electron from conduction band (red sphere) returns to the position of the hole in the valence band (white sphere), emitting a photon in the process.

Much research has been conducted on the potential of photo-thermoacoustics to replace ultrasounds in the tomography of human tissue, with a huge interest in the identification of breast cancer in individuals [71-74]. Application of a 3D graphene

sponge as a loudspeaker had also been demonstrated by Giorgianni *et al.* in 2018, with efficiency of photo-thermoacoustics boosted with the use of modulation [75]. While this novel method of sound generation does not involve direct contact between the sample and power source, it also indicates that external impediments materializing between the sample and power source would render this technique unfeasible. In addition, passing through a different surrounding medium, the changes in the index of refraction would alter the travelling path of the light source, hence increasing difficulty in directing the light source at the material for photo-thermoacoustic sound generation.

2.3.2 Electro-thermoacoustics

The mechanism of electro-thermoacoustics was first realized in 1917 [17], and utilizes a programmed electrical current as its energy source. Like photo-thermoacoustics, electro-thermoacoustics can be split into two steps. Firstly, Joule heating occurs. Application of a large enough potential difference to overcome the material's electrical resistance will result in a potential difference induction at the opposite ends of the material. This potential difference will serve as a driving force for the electrons within the material. As electrons flow due to the potential difference, a current within the boundaries of the material is generated and can be used to elicit different effects with different load types placed across the potential difference. As the electrical current overcomes the electrical resistance of the material, the energy required to overcome the electrical resistance is emitted into its surrounding medium as phonons. Next, thermoacoustics occurs. The emitted phonons collide with their surrounding medium, causing vibrations. With high levels of phonon energy, these phonon collisions would result in the surrounding medium heating up and moving. The induction of a

programmed electric field, such as an alternating current (AC), would result in an induced temperature gradient in the material due to the varying amounts of Joule heating induced by the AC. At a microscopic level, this temperature gradient induces vibration of the particles in the surrounding medium, i.e. expansions and contractions as a whole. The patterns of these rapid movements follow that of the temperature gradient, which was induced by the programmed AC input. This vibration couples into the surrounding medium as longitudinal waves and hence the generation of sound [13, 14, 19, 76, 77]. In this actuation method, the frequency and sound amplitude is dependent on the parameters of the input electrical signal, which will be discussed in depth in section 2.4 [77-80].

Unlike photo-thermoacoustics, the energy source of electro-thermoacoustics directly injects the power into the material in use. This direct injection of the power source reduces physical interferences between the power source and electro-thermoacoustic material, hence increasing mechanism reliability. The direct injection of the power source used in this mechanism also reduces power losses, hence resulting in a larger frequency band of operation ranging from Hz to MHz [81]. Its operational frequency range includes that for sound generation, hence allowing it to be suitable for sound generation.

2.4 Factors affecting electro-thermoacoustics

There are several factors which affect thermoacoustic sound generation. The relationship between these factors and SPL can be summarized in [34]

$$p_{rms} = \frac{R_0 \gamma - 1}{r_0 v_{gas}} \frac{e_{gas}}{M(e_{electro-thermoacoustic\ material} + e_{glass}) + e_{gas}} q_0 e^{-j \frac{\omega x}{v_{gas}}}, \quad (14)$$

where p_{rms} represents SPL (Pa), R_0 and r_0 represent Rayleigh distance (m) and distance

between thermoacoustic material and sound receiver (m) respectively, γ represents heat capacity ratio of gas, v_{gas} represents speed of sound of the surrounding medium ($\text{m}\cdot\text{s}^{-1}$), e_i represents thermal effusivity of material i , q_0 represents input power density ($\text{W}\cdot\text{m}^{-3}$), and M represents the frequency related factor which can be estimated to be 1 at high frequencies. Acoustic frequency is considered high when acoustic frequency exceeds $\frac{4\pi\alpha_{\text{GF}}}{L_{\text{GF}}^2}$, where α_{GF} represents thermal diffusivity of the thermoacoustic material ($\text{m}^2\cdot\text{s}^{-1}$) and L_{GF} represents effective thickness of the thermoacoustic material (m) [34].

Heat capacity ratio is calculated using [34]

$$\gamma = \frac{C_p}{C_v}, \quad (15)$$

where C_p and C_v represent the specific thermal capacity ($\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$) at constant pressure and volume respectively.

Rayleigh distance is calculated using equation (16) [34]

$$R_0 = \frac{A}{\lambda}, \quad (16)$$

where A represents area of thermoacoustic material (m^2) and λ represents acoustic wavelength (m).

Material effusivity is calculated using [34]

$$e_i = \sqrt{\kappa_i \rho_i C_{p,i}}, \quad (17)$$

where κ_i , ρ_i , $C_{p,i}$ represent the thermal conductivity ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$), density ($\text{kg}\cdot\text{m}^{-3}$) and specific thermal capacity ($\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$) at constant pressure of material i respectively.

Acoustic frequency (Hz), f , and acoustic wavelength (m), λ , are related to speed of sound via

$$v_{\text{gas}} = f \cdot \lambda. \quad (18)$$

Input power density is related to electrical resistance *via*

$$q_0 = \frac{I^2 \cdot R}{V}, \quad (19)$$

where I and R represent input electrical current (A) and sample resistance (R) respectively and V represents volume of material utilized (m^3).

Substituting Eqs. (15) – (19) into Eq. (11),

$$p_{rms} = \frac{A \cdot f}{r_0 v_{gas}} \frac{\gamma - 1}{v_{gas}} \frac{\sqrt{\kappa_{gas} \rho_{gas} c_{p,gas}}}{M(\sqrt{\kappa_{GF} \rho_{GF} c_{p,GF}} + \sqrt{\kappa_{glass} \rho_{glass} c_{p,glass}}) + \sqrt{\kappa_{gas} \rho_{gas} c_{p,gas}}} \frac{I^2 \cdot R}{V} e^{-j \frac{\omega x}{v_{gas}}} \quad (20)$$

is obtained.

From Eq. (20), several relations can be derived. Firstly, SPL has a linear relationship with acoustic frequency, thermoacoustic material surface area, gas heat capacity ratio and input power density. Secondly, SPL is inversely proportional to distance between thermoacoustic material and acoustic receiver, and square of the surrounding medium's speed of sound. Thirdly, SPL is inversely proportional to the square root of the thermal conductivity, density and specific heat capacity of the thermoacoustic material in use. These relationships show that material properties have a significant impact on electro-thermoacoustic sound generation. It is hence critical to select a material with appropriate properties based on the observed relationships to optimize electro-thermoacoustic sound generation.

2.5 Choice of materials for electro-thermoacoustics

Efficient utilization of electro-thermoacoustics will require the material to have high thermal conductivity and low heat capacity per unit area ($HCPUA$) [13, 15, 33-35, 37, 78, 79, 82-94]. Thermoacoustics involves the utilization of a sharp temperature gradient to generate sound. Efficient use of thermal energy being injected into the system would require the material to rapidly and efficiently transmit maximal amounts of thermal energy into its surrounding medium with minimal loss. High thermal conductivity would

allow the material to dissipate the injected heat spontaneously [95] and a low *HCPUA* indicates that little energy is required to change the material's temperature by one K per unit area [96], which signifies that low amounts of thermal energy is stored by the material during heat transmission. The material also requires a minimal electrical resistance of 1 Ω for electrical current to be able to conduct through the material and induce Joule heating without causing the system to short circuit.

The theory of using electro-thermoacoustics to generate sound was established in the early 1900s and the initial proof of concepts shown by applying an AC to a thin strip of platinum (Figure 10), whereby the emitted acoustic frequency would be double of the electrical input signal [17, 18]. However, high costs of both raw material and its production to thin strips resulted in minimal continued research on the potential of sound generation *via* thermoacoustics.

Figure 10. Initial proof of concept of thermoacoustics using a thin strip of platinum [17].

In 1999, Shionda *et al.* demonstrated the ability of silicon, a more economical material, to generate sound using electrothermoacoustics. While the porous silicon has low heat capacity, it also has a low thermal conductivity [97], indicating that the material does not require a lot of thermal energy to raise its temperature. However, the material does not dissipate heat quickly into its surroundings. This results in the inefficient use of thermoacoustics to generate sound, and minimal effort was done to continue the study.

2.5.1 Introduction to the carbon element

Carbon is a chemical element in Group IV of the periodic table which is able to form many allotropes. The properties of carbon depend on its physical forms and types of bonds present in the material. Graphite is an allotrope of carbon bonded by covalent bonds. These C-C covalent bonds induce sp^2 hybridization with 0.142 nm C-C bond lengths [98]. Each carbon atom of graphite shares its electrons with three other carbon atoms, forming a hexagonal planar layer, and each hexagonal planar layer is bonded with each other utilizing van der Waals forces (Figure 11). These weak van der Waals forces allow for the graphite layers to be able to slide over each other, causing the material to be slippery and be utilized in applications such as pencil lead and lubricants [99]. The unique bonding in graphite also results in graphite having vastly different out-of-plane and in-plane maximum thermal conductivities of $5750 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ and $21 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ respectively [100]. Furthermore, each carbon atom in graphite has a non-bonded electron [98]. These electrons become delocalized and is able to travel between the hexagonal layers, resulting in an electrically conducting material ($40,000 - 170,000 \text{ S}\cdot\text{m}^{-1}$) [101].

The high thermal conductivity of graphite is a critical parameter for electro-thermoacoustic sound generation for rapid transmission of heat generated by Joule heating into the surrounding medium of the material. There is hence interest in the utilization of carbon for electro-thermoacoustic sound generation.

Figure 11. Hexagonal crystal structure of graphite with weak van der Waals (dotted lines) between its layers [98].

2.5.2 Carbon nanostructured materials

The understanding that carbon is a material capable of a multitude of physical forms resulted in an increased interest and research in it. This brought about the synthesis of carbon nanostructured materials. A multitude of different carbon nanostructured materials have been discovered over the past 30 years CNTs, graphene and 3D-C were synthesized in 1991 [29], 2004 [30] and 2011 [31] respectively. The high thermal conductivity ($200 - 5000 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$) [22, 23] and low electrical resistance ($2 - 2200 \Omega$) [33-35, 81, 86, 92, 94, 102, 103] of these carbon nanostructured materials sparked much interest and research on their potential in multiple applications, such as conducting films, conducting fillers, transistors, energy storage, adsorption, photocatalysts, membranes, electrodes, biotechnology and electromagnetic interference (EMI) shields [26, 104-114]. These carbon nanostructured materials also have a low fabricable material thickness (micrometer to nanometer), indicating a large surface contact area with their surrounding medium. In addition, most of the recently discovered carbon

nanostructured materials have reported low C_p ($0.71 - 0.74 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$) [24, 25], making them ideal candidates for thermoacoustics. Their low densities of less than 200 mgcm^{-3} [31, 115, 116] also reduces transportation costs, providing them an economic edge over dense piezoelectric materials ($8.12 \text{ g}\cdot\text{cm}^{-3} - 7800 \text{ kg}\cdot\text{m}^{-3}$ [117]). Research on the efficiency of thermoacoustics for sound generation using carbon nanostructured materials hence resumed.

2.6 Reported literature for electro-thermoacoustics

There are numerous materials which have been experimented on to determine the potential utilization of electro-thermoacoustics mechanism as a substitute for speakers namely nanometer thin metal sheets and various carbon nanostructured materials.

2.6.1 Nanometer thick metal sheets

Thin metal sheets were first considered for electro-thermoacoustics [17]. Due to material thickness being in the range of hundreds of nanometers, the initial thin metal sheets have a high heat capacity. This results in the material storing heat instead of quickly dissipating it into its surroundings when heat is introduced to the material, resulting in poor electro-thermoacoustic sound generation [19]. Hence, minimal studies were conducted on the potential of these materials for sound generation. In the recent decade, increased ease and economical value of the processes have rekindled such studies and research.

La Toracca and Bobinger *et al.* conducted thorough investigations on the simulation and application of Ag nanowires (NWs), copper (Cu) NWs and gold (Au) films on glass and polyimide (PI) substrates for electro-thermoacoustic sound generation [19-21, 118]. Comparing the properties of Ag NWs and Au films, Ag NWs have a slightly higher

electrical resistance of $3.5 \, \Omega$ indicating the potential for Ag NWs to generate sound more efficiently than Au films. Experimental results show that the slight difference in their electrical resistance do not have a huge impact on the electro-thermoacoustic performance of the samples. Comparing the acoustic performance of Ag NW on glass and PI substrate, Ag NW performed better on the glass substrate by 20 dB due to its higher electrical resistance. This reinforces the hypothesis reflected in Eq. (20) (section 2.4) that a higher electrical resistance would improve acoustic performance [118]. On a PI substrate, the Ag NW was able to generate similar SPLs below 1.5 kHz while the sample was bent, with deviations at higher frequencies due to constructive and destructive acoustic interferences [21]. Comparing the 3 materials, Cu NWs had the lowest cost of manufacturing [119] while exhibiting the same acoustic performance at the low frequency with lower input power [90].

Daschewski *et al.* investigated both the theoretical and experimental electro-thermoacoustic properties of several nanometer thin sheets: titanium and indium-tin-oxide (ITO) [77, 80]. These materials have lower *HCPUA* and higher electrical resistances than gold and aluminum [13], hence making them more desirable for electro-thermoacoustics. In his studies, Daschewski *et al.* elaborated on the relationships between *HCPUA*, electrical resistivity, distance of material from microphone, electrical input power and the acoustic performance of the samples theoretically as shared in Eq. (20) (section 2.4) and proved them to be true experimentally [77, 80].

2.6.2 Carbon nanostructured materials

The discovery of carbon nanostructured materials resulted in the continued research on the potential of the use of electro-thermoacoustics to replace piezoelectric transducers.

2.6.2.1 Graphene

Once such investigated carbon nanostructured material is graphene. Graphene is a single layer of 2D sheet comprising of chemically bonded carbon atoms (Figure 12) [120]. In addition to the nanometer thin metal strips, La Toracca and Bobinger *et al.* also investigated the ability of graphene on PI substrate to generate sound electro-thermoacoustically [121]. Normalized to an input power of 1 W and a 1 m distance between the microphone and material, graphene generated an increased 5 dB of sound pressure level (SPL) as compared to Ag NW and Au film, indicating an improved efficiency in the utilization of electro-thermoacoustics [121].

Figure 12. Schematic of graphene's microstructure [120].

Studies were also conducted by other researchers on the performance of free-standing graphene as well its performance on different substrates, namely paper, glass, polyethylene terephthalate (PET), polydimethylsiloxane (PDMS) as well as additional studies on the PI substrate.

Tian *et al.* investigated the effect of layer number on the electro-thermoacoustic performance of graphene on a paper substrate [35]. With an increasing number of

graphene sheets, the *HCPUA* of the material increases, resulting in poorer electro-thermoacoustic performance [35]. This was also supported by Xing *et al.* [15]. In addition, Xing *et al.* demonstrated that high substrate thermal effusivity, low thermal conductivity of the surrounding medium and high *HCPUA* of the thermoacoustic material reduces thermal dissipation, resulting in poorer electro-thermoacoustic performance (Figure 13 and Figure 14) [15]. Tian *et al.* proceeded to transfer graphene on flexible PET encased in an earphone to study its potential as an earphone. As with his previous study [35], increasing the number of graphene layers increases its *HCPUA*, decreasing its electro-thermoacoustic efficiency. Unlike commercial earphones which utilize piezoelectricity, sound generation *via* electro-thermoacoustics allows a wider operating frequency range with a flatter acoustic performance. Additionally, graphene is optically transparent, which could grant it the possibility to be a multi-functional material [87].

Material	PDMS	PET	Glass	Graphene	Air
Density ρ ($\text{kg}\cdot\text{m}^{-3}$)	970	1390	2600	2100	1.16
Thermal conductivity κ ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)	0.15	0.15	1.1	130	0.0263
Specific heat c_p ($\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$)	1460	1172	840	710	1007

Figure 13. Density, thermal conductivity and specific heat capacity of polydimethylsiloxane (PDMS), polyethylene terephthalate (PET), glass, graphene and air [15].

Figure 14. Theoretical and experimental sound pressure levels (SPLs) of graphene mounted on PET, PDMS and glass with an input power of 0.6 W and receiver-sample distance of 1 cm [15].

Studies on PI substrate demonstrated the flexibility of the electro-thermoacoustic sample [122, 123]. In addition, when a direct current (DC) offset is added to the AC, it improves the acoustic performance and the acoustic frequency becomes the same as the input signal [123]. Suk *et al.* demonstrated the sound generation of graphene on glass, PDMS and PET substrates, with the acoustic performance of the samples being in the same order due to their thermal conductivities [33]. Increasing porosity of the substrate introduces atmospheric air into the bulk material, decreasing the amplitude of properties of the bulk material, such as density, thermal conductivity and *HCPUA*. With properties more suitable for electro-thermoacoustic actuation, the sample's efficiency improved.

Subsequently, Kim *et al.* investigated the electro-thermoacoustic properties of graphene on a patterned PI substrate [32]. As observed by Suk *et al.*, with an increased porosity of the substrate, SPL increases due to less heat being transferred to the

substrate, as well as an increased proportion of the properties of atmospheric air being a part of the bulk material. The unique structure of the patterned PI substrate also allowed increased exposure of the material to its surrounding fluid medium instead of trapping thermal energy within the confines of the substrate, hence resulting in an improved acoustic performance over the previous studies of graphene on paper, PDMS, and PET substrates.

In 2019, Tu *et al.* explored the use of vertical graphene in electro-thermoacoustics [91]. The previous studies of graphene had a sheet-like structure with the height in nanometers and the material grew along the x and y axis. The vertical graphene examined by Tu *et al.* however, was of high porosity with height in micrometer scale, and the material grew along the z axis. Despite the presence of defects (D peak present in Raman spectroscopy at 1350 cm^{-1} Raman shift) in the investigated graphene (Figure 15) and increased *HCPUA* due to increased material, the drastic increase in exposure of graphene to its surrounding medium resulted in an enhanced acoustic performance compared to the nanometer thick graphene studied prior.

Figure 15. Raman spectrum of graphene investigated by Tu *et al.* [91].

All studies concluded the linear relation between the frequency of signal input and SPL [15, 32, 33, 35, 87, 122, 123], the relation between input power and SPL [15, 35, 122, 123], the inverse relation between measurement distance and SPL [15, 35, 123] and the linear relation between number of electrodes and SPL [87, 123].

2.6.2.2 Reduced Graphene Oxide

Other than graphene, Tian *et al.* also investigated the ability of reduced graphene oxide (rGO) film for electro-thermoacoustic sound generation. rGO has properties similar to graphene and the potential to grow at a larger scale than the latter. The studies showed that rGO films have flexibility similar to graphene, as well as a linear relation between acoustic frequency and SPL [36, 84, 124], which is similar to studies done for graphene (section 2.6.2.1).

Subsequently, Kim *et al.* chemically functionalized rGO with nitrogen (N-rGO) to reduce material electrical resistance from 491 to 71 Ω and investigated its electro-thermoacoustic performance [85]. With the addition of a substrate, constructive interference occurs, and sample performance improves. A thermally conductive substrate is optimal for fast heat transfer into its surrounding and hence, ideal for electro-thermoacoustic application. The choice of substrate as well as an increased surface contact with the surrounding medium resulted in an improvement in sample performance as compared to pure graphene and rGO.

2.6.2.3 CNTs

Another carbon nanostructured material which was considered for electro-thermoacoustics is CNT. CNTs comprise of graphene sheets rolled into 1D tubes of

carbon atoms (Figure 16) [125], unlike the single layered graphene sheets in Figure 12. The CNT yarns are pulled from their arrays to be aligned and suspended between the electrodes connecting the sample to the acoustics set-up [126, 127].

Figure 16. Schematic of CNT's micro-structure [125].

In 2008, Xiao *et al.* demonstrated the ability of CNTs to generate sound electro-thermoacoustically [17]. They modified the electro-thermoacoustic relation by Arnold and Crandall to include heat exchanges occurring in the sample, depicting the mechanism more accurately for carbon nanostructured materials. The effect of parameters on CNTs are the same as studied for other materials: input power having a direct correlation with SPL, frequency having a linear relationship with SPL, and that increasing the number of material layers decreasing $HCPUA$, hence decreasing the SPL of the sample [86]. Subsequently, Xiao *et al.* investigated the effect of varying gaseous mediums on electro-thermoacoustic efficiency. Due to its low specific heat capacity, high thermal conductivity and high density, electro-thermoacoustic performance for CNT films in Argon (Ar) gas was the highest. This is followed by air and helium (He) gas, which have surrounding medium properties not as desirable for electro-

thermoacoustics (Table I) [128].

Table I. Specific heat capacity, thermal conductivity and density of Ar, air and He gaseous mediums investigated in Xiao *et al.*'s study at 26.85 °C and 1 atm [128].

Gaseous medium	C_p (J·g ⁻¹ ·K ⁻¹)	κ (W·m ⁻¹ ·K ⁻¹)	ρ (kg·m ⁻³)
Ar	0.52034	0.0178	1.6225
Air	1.00643	0.0262	1.1764
He	5.1931	0.156	0.1624

After Xiao *et al.*'s revision of the electro-thermoacoustic relation, many studies ensued on improving the sound generation efficiency of CNTs. Kozlov *et al.* demonstrated that sound generation *via* electro-thermoacoustics is more efficient than photo-thermoacoustics due to its more direct energy conversion methods [103]. Dense multi-walled (MW) CNT forests were discovered to have lower efficiencies than the MWCNT sheets, which is attributed by the decreased contact surface with the surrounding medium [103]. This caused lower heat transfer rates, inducing less efficient electro-thermoacoustics [103]. Suzuki *et al.* discovered that MWCNT webs perform better electro-thermoacoustically than MWCNT films, attributed by the inclusion of air in MWCNT webs, allowing for rapid thermal cooling and hence a steep temperature gradient during operations [93].

Later in 2013, Lim *et al.* added on to Xiao *et al.*'s calculations for electro-thermoacoustics [129]. They presented the calculations for near-field performances, which had not been included in Xiao *et al.*'s work [86]. The inverse relation between distance of microphone and sample had also been observed [129].

With developments of the ability of CNTs for sound generation *via* electro-

thermoacoustics, Wei *et al.* demonstrated the potential of CNT to be used in earphones by attaching MWCNT fibers across patterned silicon wafers [94]. By increasing the groove depth, air gaps are introduced between MWCNT fibers and silicon substrate, hence allowing for rapid cooling of the material and inducing a steep temperature gradient for efficient electro-thermoacoustic sound generation. The synthesized MWCNT earphone was designed with a Universal Serial Bus (USB) connection, which encompasses a DC bias for amplification of generated sound, for ease of use. This can be integrated into semiconductor packages for scalability of mass manufacturing.

Aliev *et al.* conducted thorough studies on the potential of CNTs potential for electro-thermoacoustic sound generation. In 2010, they demonstrated the ability of CNTs to generate sound electro-thermoacoustically underwater and in ethanol, of which the former medium provided better performance results due to the hydrophobic nature of CNTs, which produced air bubbles in water and reduced thermal inertia between CNTs and their surrounding medium [81]. CNTs encapsulated in cellulose tissue exhibited a broad band of operating frequency from 8 Hz to 100 kHz, with a flat frequency response in ethanol from 50 to 100 kHz. This is in contrast with the lead zirconate titanate (PZT) compared in the study, which only generated sound at its resonance frequency at specific peaks. The graph comparing underwater sound generation abilities of the samples are as seen in Figure 17. When enclosed between plastic plates, which have a resonance frequency, and filled with Ar gas, CNTs exhibited a resonant acoustic peak with increased SPL instead of a broad operating frequency range when generating sound without an enclosure. Comparing aligned CNTs and randomly deposited CNTs, aligned CNTs exhibit better electro-thermoacoustic performance due to the anisotropic thermal properties of CNTs.

Figure 17. Underwater sound generation normalized to input power of 1 W and surface area of 1 cm² by PZT in water (red) and CNTs in ethanol (green) and water (blue) [84].

After preliminary proofing of the ability of CNTs to generate sound underwater, Aliev et al. improved the efficiency of the set-up by comparing effects of various gases functioning as the surrounding medium in the test chamber [133]. MWCNT generated sound with the highest SPL in Xenon (Xe), which is the surrounding medium with the lowest heat capacity in this work (Table II). At low pressures whereby gas density is low and particles are able to rapidly move for fast heat transfer for electrothermoacoustics, a linear relationship between SPL and pressure was observed. However, at high pressures, particles are unable to move as swiftly as before, resulting in SPL plateauing and being independent of the pressure of the test chamber. In a closed system within an enclosure filled with Ar gas, a resonant peak is observed at the resonant frequency of the closed at a higher SPL as compared to an open system. Varying volume of the enclosure, an inverse relation between SPL and enclosure volume was observed, which is in agreement with theoretical hypothesis. A small enclosure, with walls larger than the thermal diffusion length of the gaseous medium to prevent poor thermal

performances due to thermal diffusion into the thermally insulative enclosure, was highly recommended. Later in 2014, Aliev *et al.* further investigated the observations in the enclosures [130]. The frequency of the sample's resonance peak was affected by several factors. Firstly, the surrounding medium, which in this study was air and underwater, which was attributed by differences in the interactions between the sample and its surrounding particles. Secondly, thickness of the enclosure also affects SPL. The higher the thickness of the enclosure, the higher the frequency of the resonant peak and the lower the SPL is. Thirdly, water depth, which would have mass loading on the membranes of the enclosure, would decrease the frequency of the resonant peak. However, should the membranes be flexible and not rigid like glass, the increase in pressure when the water depth increases would increase internal pressure of the enclosure, thereby inducing an increase in the frequency of the resonant peak instead of a decrease in the glass membranes.

Table II. C_p of gaseous medium in Aliev *et al.*'s study at 25 °C and 1 atm [125].

Gaseous medium	C_p (J·kg ⁻¹ ·K ⁻¹)
Xe	158.3
Ar	521.5
Freon, R134A	851
Sulfur hexafluoride (SF ₆)	664
Nitrogen gas (N ₂)	1041
Air	1006.3
He	5193

Aliev *et al.* also investigated the effect of number of electrodes and surface area of MWCNTs exposed to the surrounding medium on SPL [92]. Experimental results show that neither factor have an effect on SPL, but surface area determines the maximum input power which MWCNTs are able to handle prior to thermal decomposition. While the input power density of a material remains unchanged, increasing the surface area of MWCNTs increases total power capacity of the sample, hence allowing for increased input power and increased SPL. The addition of DC to the electrical signal was also observed to result in acoustic frequency to be equal to that of the input power signal [92, 102]. Aliev *et al.* also investigated use of electrical pulses instead of continuous electrical signals to improve efficiency, which works better underwater than in air due to interactions with surrounding particles. Signal processing was also utilized to minimize signal distortion caused by the use of pulse excitations. Finally, Aliev *et al.* demonstrated the ability of free-standing single-walled (SW) CNTs to generate sound in air, which is higher than the previous studies on MWCNTs due to their lower $HCPUA$, resulting in lower heat retention and hence more efficient electro-thermoacoustic

performance [89]. Due to the small size of the tested material, SWCNTs exhibited anisotropic sound generation at high frequencies of 32kHz and above, which will be useful for applications which require directional sound generation such as SONAR.

Bouman *et al.* then investigated the effect of input power-frequency, amount of DC injected and percentage of signal modulation to its signal carrier on the efficiency of MWCNTs varying frequency [131]. As input power-frequency increases, the power efficiency increases, which is in agreement with previous studies that SPL increases with input power-frequency. With input power normalized, the ideal amount of DC for maximum efficient use of the input power is at ~62 % of the signal amplitude. Taking into account the signal distortion caused by its harmonics, which increases with more signal modulation, the ideal percentage of signal modulation to its signal carrier is 100 %.

All studies showed an inverse relationship between number of material layer and SPL [86, 128, 129], that DC biasing increasing sample SPL [93, 103, 131]. There was a linear relationship between input power and SPL [81, 86, 89, 92, 130, 132], as well as acoustic frequency and SPL [81, 86, 93, 94, 102, 103, 128, 129, 131, 132].

2.6.2.2 Hybrid materials

With multiple studies conducted on the electro-thermoacoustic effect of graphene and CNTs, there was a developing interest for the effect of graphene and CNTs hybrids. Yeklangi *et al.* synthesized CNTs drop-casted onto rGO on PET substrate, with the CNTs increasing contact surface area for faster thermal dissipation [76]. The sample had an electrical resistance of 321 Ω , which is lower than that of pure graphene (436 Ω). This results in a lower input power required for electro-thermoacoustic sound generation, and hence higher sound generation efficiency. Like previous studies, a linear

relationship between frequency and SPL was observed.

2.6.3 3D-C

The final carbon nanostructured material which was studied for its use in electro-thermoacoustics is 3D-C which are made of stacked layers of graphene sheets. 3D-C retains the properties present in graphene while providing a macroscale dimension to its microstructure. 3D-C is hence able to exhibit the properties of graphene on a macro level, increasing its utilization in applications [113].

2.6.3.1 Fabrication methods of 3D-C

The fabrication methods of 3D-C can be mainly categorized into two different classes: the self-assembly and template-assisted methods [133].

Self-assembly methods of synthesis are template-free. There are two main fabrication methods under self-assembly, namely hydrothermal and solvothermal. Both methods utilize solutions of graphene oxide (GO) of their desired concentration.

Hydrothermal fabrication utilizes aqueous solutions of GO, where water is the solvent in the GO solution. The GO solutions are first sonicated to ensure uniform distributed prior to pouring them into autoclaves, which maintains the high pressures required for hydrothermal to occur [134]. These autoclaves are then placed in ovens at high temperatures [135] for long periods of time (12 h). At high pressures and temperatures (above 100 °C), the GO solution agglomerates and is reduced, producing a condensed free-standing 3D-C (Figure 18) [136].

Figure 18. 3D-C fabricated via hydrothermal fabrication. (a) GO solution before hydrothermal synthesis and 3D-C after hydrothermal synthesis, and (b) free-standing 3D-C [136].

Solvothermal fabrication utilizes solutions of GO with non-aqueous solvents, such as acetone, ethanol and isopropanol, instead of water, as the medium of GO dispersion. Firstly, the water in aqueous GO solution is replaced with the non-aqueous solvent by repeatedly replacing the water solvent to ensure complete exchange. The non-aqueous GO solution is then placed in an autoclave at high temperatures to allow for reduction and agglomeration of the graphene layers. After removal from the autoclave, water is added to the ethanol-filled 3D-C and the solution carefully drained. This step is repeated at least 15 times to ensure that all ethanol present in 3D-C is fully replaced with water. The water-filled 3D-C is then freeze-dried to remove the water trapped in its pores and obtain the free-standing 3D-C (Figure 19) [137-139].

Figure 19. 3D-C fabricated via solvothermal fabrication [137].

Template-assisted methods of fabrication require the use of templates for graphene layers to deposit on to produce 3D-C. There are two main ways of synthesis under template-assisted methods, namely template-assisted assembly method and template-assisted chemical vapor deposition (CVD) [133].

The template-assisted assembly method involves the deposition of GO or graphene sheets at low temperatures. There are several templates which can be used for template-assisted assembly, namely ice crystals and polystyrene (PS) balls [133]. Ice crystal templates are made from GO or partially reduced GO uniform aqueous solutions. The solution is then freeze casted and the solutions further reduced to form 3D-C. Next, the solution-soaked 3D-C is rinsed with DI water to remove the water-soluble solvents. Finally, water is removed *via* freeze drying and annealed to obtain the free-standing 3D-C [140]. PS ball templates are fabricated by first polymerizing PS microspheres prior to being dispersed and sonicated in DI water. GO solution is then dripped into the homogeneous aqueous PS microsphere solution and the solution vacuum filtrated to remove water. Sheets of GO and PS microspheres are then peeled off the filter and air dried. Free-standing 3D-C is finally obtained by annealing the sheets of GO and PS microspheres, where the PS microspheres are removed and GO sheets are reduced to graphene (Figure 20) [141].

Figure 20. Template-assisted assembly of 3D-C using PS microspheres [141].

In template-assisted CVD, a 3D interconnected porous nickel (Ni) foam is used as the template due to their ability to function as a catalyst for graphene synthesis. Under

atmospheric pressure, 3D interconnected porous Ni foams are thermally annealed at 1000 °C and the carbon precursor, methane gas (CH_4) is passed through the furnace. At high temperatures and with a decreased activation energy brought about by the metal catalyst, CH_4 dehydrogenates and deposits graphene layers onto the 3D interconnected porous metal foam. The 3D-C coated interconnected porous Ni foam is then dip-coated with a protective layer of poly(methyl methacrylate) (PMMA). Wet etching is next conducted to remove the interconnected porous metal foam, followed by removal of PMMA to obtain the final product of free-standing 3D-C (Figure 21) [31].

Figure 21. Template-assisted CVD of 3D-C using 3D interconnected porous Ni foam [31].

In this thesis, good control over the microstructure of 3D-C is required for a repeatable controlled study on the electro-thermoacoustic sound generation performance of 3D-C. Comparing the various fabrication methods, template-assisted synthesis would provide the best control as the final microstructure of 3D-C is a copy of the template used. Comparing template-assisted assembly and template-assisted CVD, template-assisted assembly required the utilization of GO sheets. The final product of 3D-C could possess dangling oxygen bonds should GO not be fully reduced to rGO. Template-assisted CVD

is hence the chosen 3D-C fabrication method for this thesis.

2.6.3.2 Reported literature of 3D-C in electro-thermoacoustics

3D-C was discovered in 2011 [31], two decades and half decade later than CNTs and graphene respectively. Research on its ability to generate sound electro-thermoacoustically was hence not as extensive as the latter two carbon nanostructured materials.

The ability of 3D-C to generate sound electro-thermoacoustically was first demonstrated in 2015 [34]. 3D-C has electrical resistances in the range of $10\ \Omega$, which is significantly lower than graphene ($30\ \Omega$ to $k\Omega$), rGO ($77\ \Omega$ to $500\ \Omega$), CNTs ($k\Omega$) and hybridized CNT on rGO ($321\ \Omega$). The trends observed by varying frequency, input power and distance between microphone and sample were the same as those observed in previous sections 2.6.1, 2.6.2.1, and 2.6.2.3. Comparing samples dried *via* natural drying and freeze drying, the microstructure of natural-dried 3D-C collapsed, while the microstructure of freeze-dried 3D-C retained, resulting in freeze-dried 3D-C having higher SPLs than natural-dried 3D-C (Figure 22). The acoustic results also outperformed several reported graphene results (Table III), which is attributed by the high porosity of 3D-C providing the material with additional exposure to its surrounding medium, atmospheric air. However, 3D-C synthesized in these works are defective, as evidenced by the presence of the D peak at 1350cm^{-1} Raman shift in Raman spectroscopy (Figure 23). Presence of defects in 3D-C could result in phonons being unable to travel within a material as efficiently. A less efficient phonon movement would result in less efficient

heat dissipation of the material, and decrease electro-thermoacoustic sound generation.

Figure 22. SEM micrographs of (a) natural-dried 3D-C and (b) freeze-dried 3D-C [34].

Table III. Comparison of sound generation levels of 3D-C synthesized by Fei *et al.* with previously reported graphene materials. All results are normalized with a driving voltage of 3.16V, input power of 1W, acoustic frequency of 10 kHz and 3 cm distance between microphone and sample [34].

Material	Sound Pressure Level (dB)
Freeze-dried 3D-C	72
Natural-dried 3D-C	65
Graphene on PDMS	23
Graphene sheet on paper	42

Figure 23. Raman spectra of natural-dried and freeze-dried 3D-C [34].

In 2018, Lee *et al.* compared the electro-thermoacoustic performance of graphene and 3D-C [37]. Raman spectroscopy of both materials reflected an absence of the D peak, indicating pristine crystalline structures. The first harmonics of sound generation of 3D-C was observed to consistently be at least 20 dB more than of graphene, attributed by increased surface contact with the surrounding medium due to its high porosity. The SPLs of the following harmonics decreased, which was as expected in acoustical theory. As observed in the previously studied materials (sections 2.6.1, 2.6.2.1 and 2.6.2.3), increases in input power would induce a higher SPL generated by the materials.

2.6.3.3 Comparison with carbon nanostructured materials

While CNTs have been heavily studied for their application as an electro-thermoacoustic speaker, strands of CNT yarns require a nano-manipulator to be pulled out from their forests [126] prior to encircling them around the copper electrodes for use, making it a tedious process for upscale manufacturing (Figure 24). Material size of 3D-C, on the other hand, is only limited by the catalyst and furnace size, hence allowing for easier large-scale fabrication [142].

Figure 24. Schematics of using nano-manipulator to extract CNTs from their forests [126].

3D-C has the potential to further increase the efficiency of electro-thermoacoustics,

due to the large contact surface it has with its surrounding medium as compared to other carbon nanostructured materials. Figure 25 shows the scanning electron microscopy (SEM) micrographs of CNTs, graphene and 3D-C. CNTs are 1D materials, with its contact surface area with its surroundings only around its strands (Figure 25a [86]). Graphene is a 2D material, where its contact surface area with its surroundings along a planar axis (Figure 25b [35]). 3D-C, on other hand, is an interconnected 3D material with contact surface area along its interconnecting struts (Figure 25c [26]). This shows that it has the largest contact surface area with its surroundings, leading to increased interactions with its surrounding medium and hence has the potential for increased electro-thermoacoustic sound generation.

Figure 25. SEM micrographs of (a) CNTs [89], (b) graphene [35] and (c) 3D-C [23].

In previous 3D-C electro-thermoacoustic sound generation studies [14, 34], protective poly(methyl methacrylate) (PMMA) were removed using acetone. This means that free-standing 3D-Cs were directly retrieved from the acetone bath, which could fracture easily due to the hydrophobicity of 3D-C and its lightweight properties. An alternative method of PMMA removal needs to be considered for easier handling and scaling up of 3D-C production.

In addition, there are numerous synthesis and material parameter variations which have yet to be investigated. Firstly, the pores per inch (ppi) can be increased to boost the air flow and improve the contact surface area of 3D-C with its surrounding medium.

Secondly, the optimized number of graphene layers for efficient electro-thermoacoustics has yet to be investigated. In graphene and CNTs, it had been investigated that for less than ten layers of material, increasing the number of material layers would increase its *HCPUA*, thereby decreasing their electro-thermoacoustic efficiencies. However, 3D-C is more layered than previously studied carbon nanostructured materials (by an order of magnitude). There has yet to be a study on the optimum trade-off for a decrease in *HCPUA* and electrical resistance for optimal electro-thermoacoustic efficiency. Thirdly, past studies used the same method of connecting carbon nanostructured materials to the electrodes, namely, application of a line of conductive Ag paint along the edge of the carbon nanostructured material. There were no thorough investigations on the effect of electrical paths on electro-thermoacoustic efficiency. An investigation of the electrical paths would be beneficial for commercial design of electro-thermoacoustic speakers. In addition, the effect of material macroscale size has yet to be studied. While material size has been proven to have no effect on its operating frequency, its effect on sample SPL has yet to be investigated as well. An increase in material utilized would increase total surface area of material exposed to its surrounding medium, and hence potentially improve sample efficiency. Finally, only nanostructured materials which consist of purely carbon materials have been investigated. An increase in material electrical resistance is desired to fully utilize energy conversion from electrical to thermal energy *via* Joule heating. The addition of electrically insulating materials to these carbon nanostructured materials would allow those materials to utilize Joule heating with higher efficacy and could improve the electro-thermoacoustic efficiency of the sample.

3 Experimental methodology

3.1 3D-C Synthesis

In this work, 3D-C was synthesized using thermal chemical vapor deposition (TCVD) as described in [105] and [143]. The sacrificial catalytic Ni template foam (110 ppi, 2 mm thickness, Latech Scientific Supply Pte. Ltd.) was placed in at midpoint of the split-tube furnace as seen in Figure 26. Ar and hydrogen (H_2) gases were flown into the furnace as the inert carrier gas and reducing agent respectively. At 1000 °C, methane (CH_4) gas, the precursor for carbon growth, is flown into the system. With decreased activation energy arising from sacrificial catalytic Ni template foam, H_2 dehydrogenated CH_4 into carbon and H_2 . Carbon was deposited onto the sacrificial catalytic Ni template foam as graphene layers, and H_2 [144] was released back into the system. Post synthesis, the flow of CH_4 was halted, and the split-tube furnace opened to allow for rapid air cooling.

Figure 26. Schematics of TCVD growth set-up of 3D-C.

The 3D-C coated sacrificial catalytic Ni template foam was then dip-coated with a protective layer of PMMA and heated at 100 °C for 60 min for polymer curing. The

material was next chemically etched in hydrochloric acid (HCl) at 85 °C for 4 h to remove the sacrificial catalytic Ni template foam. After chemical etching had been completed, HCl was rinsed off by immersing PMMA coated 3D-C in deionized (DI) water for thorough rinsing of HCl and the samples left at room temperature and pressure overnight for evaporation of DI water. PMMA was next removed by annealing the material in an annealing boat in a split-tube furnace at 700 °C for 60 min with Ar and H₂ gas flow, which serve as the inert carrier gas and reducing agent respectively, to obtain free-standing 3D-C. The schematics of the fabrication of free-standing 3D-C is as seen in Figure 27.

Figure 27. Schematics of fabrication of free-standing 3D-C.

3.2 Material characterization

Several characterizations are required to determine the quality of 3D-C post synthesis.

Firstly, a Scanning Electron Microscope (SEM, JEOL JSM-IT100) was utilized for

better visualization and understanding of material microstructure. SEM-Energy Dispersive X-Ray Spectroscopy (EDX, FEI Nova NanoLab™ 600 DualBeam, Oxford XMAX Detector) was conducted on BN coated 3D-C to analyze the BN coating on 3D-C. X-ray Photoelectron Spectroscopy (XPS, PHI Quantera II) was also carried out to verify the types of chemical bonds present between the h-BN coat and 3D-C.

A Raman spectroscope (WITec CRM200 Raman, utilizing Nd:YAG 532 nm laser as excitation source) was used to determine crystallinity of graphene layers in 3D-C. During characterization, a laser with wavelength of 532 nm is directed at the material. Upon contact with the material, photons from the laser interact with the electron clouds of the material in contact. This results in excitation of the electrons in the material from its original energy state (ground state) to a separate excited energy state. This excited energy state is at an energy level higher than the ground state. As the electron naturally transits back into its ground state, it releases the excess energy in the form of a photon which continues interacting with the remainder of the bulk material. This re-emission of photons could contain the same energy level as the original incident laser, otherwise known as Rayleigh scattering. Photon re-emission could also contain different energy levels from the original incident laser due to the electron transiting downwards to a different spin as compared to previously. As a result, the energy of the photon post emission will have minor differences from the incident photon. loses a portion of its energy. This phenomenon is known as Raman scattering (Figure 28). A detector detects these emitted photons and sends the data to a computer, which correlates the energy levels of these photons with their wavelengths (Raman shift). The wavenumbers of the peaks of these Raman shifts (Raman peaks) differ based on the interaction of the material with the laser photons, and can hence be used to infer the characterized material and its quality [145].

Figure 28. After a laser source excites the material, photons are re-emitted due to electrons returning to their ground state and producing Rayleigh scattered and Raman scattered photons.

In graphene, the presence of the D peak at 1350 cm^{-1} indicates the presence of defects, while the presence of the G and 2D peaks at 1580 cm^{-1} and 2705 cm^{-1} indicates the presence of graphene. The combination of these results signifies the presence of crystalline graphene in 3D-C [26, 31, 34, 105, 145-147]. Intensities of the G and 2D peak can also be utilized to infer the number of graphene layers present in the material. The ratio of 2D to G peak ($\frac{I_{2D}}{I_G}$) has an inverse relationship with the number of graphene layers present in the material. As the number of graphene layers present increases, $\frac{I_{2D}}{I_G}$ decreases, and hence can be used as an approximate comparison of graphene layers present [148, 149].

Macro-density was calculated by dividing the weight of the samples by their macro-dimensions. Weights of the materials were obtained from an electronic weighing scale (Analytical Balance ME204E, Mettler Toledo). Next the macro-dimensions of the materials (Figure 29) were measured, and calculations were done to obtain macro-density. The method of obtaining sample weight and volume includes the weight and volume of atmospheric air present in the sample and is hence not representative of the weight and volume of the material respectively.

Figure 29. Macro dimensions of material.

A thermogravimetric analyzer (TGA, Shimadzu DTG-60) was utilized to determine decomposition temperature of the material. An alumina crucible containing a minimum of 5 mg of sample, which had been crushed into powder, were loaded into the chamber and measured against an empty reference alumina crucible. The temperature of the chamber was first equilibrated at 30 °C prior to heating to 1100 °C at a rate of 10 °C·min⁻¹ with an atmospheric air flow rate of 50 mL·min⁻¹. The percentage of sample mass in the loaded crucible as compared to the initial sample mass was measured and recorded throughout the experiment. Material decomposition temperature was characterized by a sharp drop in mass percentage measurements.

A modulated differential scanning calorimeter (MDSC, TA Instruments MDSC 2920) was used to determine C_p of the material, which is representative of how much the material stores heat per unit volume. A reference alumina crucible and another alumina crucible containing a minimum of 4 mg of sample, which had been crushed into powder, were loaded into the chamber. The chamber was then equilibrated at 30 °C before being heated to 300 °C at a rate of 2 °C·min⁻¹ with a maximum “heat only” amplitude of ±0.318 °C for 60 seconds to modulate maximum temperature of the system. Throughout the heating process, the heat flow of the sample was recorded. $C_p = \frac{\text{Heat flow}}{\text{Ramp rate}}$, with heat flow

obtained from the measurements of MDSC and ramp rate being $2\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ as described.

3.3 Electrical characterization

To understand the electrical properties, two different electrical characterizations were conducted.

Firstly, the electrical sheet resistance of the material was measured using a four-point probe (Karl SUSS 200 Micro-Prober) with the Van der Pauw (VDP) method. The VDP method allows for the user to probe the sample at any 4 arbitrary points [150]. Upon initialization, current will be flown through an edge and voltage will be flown through the opposite edge. This process is repeated till all 4 probes have been utilized and the measurement results are tabulated with the electrical sheet resistance of the material derived.

Secondly, the electrical resistance of the sample post mounting was measured by probing two ends of the complete sample and taking the reading from a multimeter (Fluke 83 III).

3.4 Analysis of 3D-C quality

3.4.1 Visual images

Post PMMA annealing, the obtained free-standing 3D-C was as seen in Figure 30a. Under SEM microscopy, the porous microstructure of the material was obtained as seen in Figure 30b, with a further magnified image in Figure 30c. Comparing the porous microstructure of (Figure 30b) with pure Ni foam used as its sacrificial template (Figure 30d), it is revealed that the material's microstructure remains undamaged from the accelerated drying at 80°C in air and PMMA annealing *via* thermal decomposition.

Figure 30. Images of 3D-C. (a) Visual image of 3D-C, (b) SEM micrograph of 3D-C under $\times 100$ magnification, (c) SEM micrograph of 3D-C under $\times 500$ magnification and (d) SEM micrograph of Ni foam under $\times 100$ magnification.

3.4.2 Material properties

Density of the in-house synthesized 3D-C were first calculated. The obtained density of the in-house synthesized 3D-C is $3 \text{ mg} \cdot \text{cm}^{-3}$, which is consistent with previous studies [26, 106, 142, 143].

Decomposition temperature of 3D-C was obtained *via* TGA to ensure the absence of contaminants such as HCl and Ni. Below 515°C , sample weight percentage remained relatively constant. Above 515°C , 3D-C began decomposing with significant reduction in sample weight percentage from 605 to 915°C . Majority of 3D-C had completely decomposed above 915°C (Figure 31). These obtained results indicate the pristine

quality of synthesized graphene in 3D-C [151].

Figure 31. Weight percentage of 3D-C against temperature during TGA.

Next, C_p of 3D-C was determined using MDSC as an indication to its ability to transmit heat effectively when electrical power is input into the sample for Joule heating. The results are as seen in Figure 32. At room temperature and pressure, the C_p of 3D-C's ($0.68 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$) is lower than CNTs [24] and graphite [25] (Table IV), indicating that 3D-C stores less heat when heated. This allows more heat to be transmitted, indicating that 3D-C stores less heat when heated. With increased heat transmission, there is better potential for 3D-C to generate sound *via* electro-thermoacoustics more efficiently.

Figure 32. C_p of 3D-C's against temperature.

Table IV. Literature C_p values of CNTs and graphene at 25°C.

Material	C_p ($\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$)	Reference
Aligned MWCNT	0.74	[24]
Random MWCNT	0.75	[24]
Random SWCNT	0.72	[24]
Graphite	0.71	[25]
3D-C	0.68	This work

Finally, synthesized 3D-C was probed with the four-point probe to determine its electrical sheet resistance. Post-characterization, it was analyzed that 3D-C sample has an electrical sheet resistance of $0.4 \Omega\cdot\Box^{-1}$. This signifies that 3D-C has a high electrical conductivity to allow electrical current to flow through it, such that Joule heating and hence electro-thermoacoustics can occur.

3.4.3 Material quality

Quality of the material was also verified using Raman spectroscopy and the obtained spectrum is as seen in Figure 33. Both G and 2D peaks are present in the Raman spectrum at wavenumbers 1580 cm^{-1} and 2705 cm^{-1} respectively. The D peak at wavenumber 1350 cm^{-1} was absent, indicating the absence of defects. These hence indicates that the graphene present in 3D-C were of pristine crystalline quality [26, 31, 34, 105, 145-147], unlike previous studies which utilized defective 3D-C (section 3.2). The intensity of the 2D peak was 0.79 of the G peak ($\frac{I_{2D}}{I_G} \approx 0.79$), indicating the presence of few layers of graphene in 3D-C [148, 149].

Figure 33. Raman spectrum of in-house fabricated 3D-C.

3.5 Design of the simulation model

Simulations were also conducted to validate the impact of the material variation on electro-thermoacoustic sound generation. These parameters include input electrical frequency, input power, connection pathways, the addition of an acoustical backing and

material size, thickness and macro-density. These simulations were conducted by the Aiman-fims group from Institut d'Electronique de Microélectronique et de Nanotechnologie (IEMN) as part of on-going collaboration works.

Simulations were conducted using the Matlab programming language, which allows for numerical computing of the potential electro-thermoacoustic sound generation of 3D-C. Viewing the cross-section of 3D-C from its SEM micrograph and taking a slice of it (Figure 34), both 3D-C and its surrounding medium are coexisting in every slice. Each slice can be deemed as a distinct layer of the material, with z_j representing layer number and N as the number of distinct layers used for the simulation. These slices are utilized as the “thermophone” section in the simulations. The “back medium” section illustrates where 3D-C begins, while the “front medium” illustrates the front of 3D-C. Simulations were conducted in the acoustic frequency range of 0.5 – 50 kHz, with the input parameters as listed in Table V and Table VI.

Figure 34. Cross-section of 3D-C in simulations coexisting with its surrounding medium.

Table V. Parameters of samples used in experiments.

Sample Name	A	B	C	D	E	F	G	H	I	J
L_x (mm)	30	20	20	20	20	20	20	20	30	50
L_y (mm)	20	20	20	20	20	20	20	20	20	20
L_z (mm)	2	2	2	2	2	2	2	2	2	2
N (simulations)	28	x	x	x	x	28	x	x	x	28
Ppi	110	110	110	110	110	110	110	110	110	110
Macro-density (mg·cm ⁻³)	3	3	3	3	3	3	3	3	3	3
Connection (see Table V)	Point	Same Side	Across	Diagonal	All across	Point	Line	Volume	Point	Point
Electrical Resistance (Ω)	3.7	2.0	2.2	2.5	2.2	2.9	2.1	1.7	3.8	5.1

Sample Name	K	L	M	N	O	P	Q	R
L_x (mm)	30	30	20	20	30	30	30	30
L_y (mm)	20	20	20	20	20	20	20	20
L_z (mm)	5	2	0.5	1	2	2	2	2
N (simulations)	70	28	x	28	x	x	x	x
Ppi	130	110	110	220	x	110	110	110
Macro-density	3	9	44	6	11	3	3	3
(mg·cm⁻³)								
Connection (see	Point	Point	Line	Point	Point	Point	Point	Point
Table V)								
Electrical	1.8	1.1	2.7	3.7	2.4	8.5	85	100
Resistance (Ω)								

Table VI. Parameters of the various mediums used in simulations.

	ρ (kg/m ⁻³)	C_p (J.kg ⁻¹ .K ⁻¹)	C_v (J.kg ⁻¹ .K ⁻¹)	B (Pa)
Air	1.20	9.96×10^2	7.17×10^2	1.01×10^5
3D-C	3.0	660	660	1.44×10^8
	α_T (K ⁻¹)	κ (W.K ⁻¹ .m ⁻¹)	λ (N.s.m ⁻²)	μ (N.s.m ⁻²)
Air	3.33×10^{-3}	26.2×10^{-3}	16.82×10^{-6}	5.61×10^{-6}
3D-C	2.6×10^{-6}	160	0	0

In the simulation, a “two temperature” model was utilized as the unique microstructure of 3D-C with more than 90 % porosity renders other simulation models not applicable [78, 79]. In this 1D simulation, the acoustic waves are simulated to be radiated as planar waves with harmonic time dependency. The energy, linear momentum and mass conservation equations in a fluid, which is the surrounding medium (atmospheric air) were written as:

$$i\omega\rho C_{p,f}T = \kappa_f \frac{d^2T}{dz^2} + i\omega\alpha_T T_0 \rho_f, \quad (21)$$

$$\omega\rho_f v = -\frac{dp}{dz} + (\lambda + 2\mu) \frac{dv}{dz}, \quad (22)$$

$$\frac{i\omega}{B_0} \rho_f - i\omega\alpha_T T + \frac{dv}{dz} = 0, \quad (23)$$

where i represents the imaginary units, ω represents radial frequency ($\text{rad}\cdot\text{s}^{-1}$), ρ_f represents density of the surrounding medium ($\text{kg}\cdot\text{m}^{-3}$), $C_{p,f}$ represents specific heat at constant pressure of the fluid ($\text{J}\cdot\text{kg}\cdot\text{K}^{-1}$), T and T_0 represents the temperatures of the fluid and ambient temperature (K) respectively, κ_f represents fluid thermal conductivity ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$), z_j represents layer number, α_T represents coefficient of volumetric expansion (K^{-1}), p represents acoustic pressure (Pa), v represents velocity ($\text{m}\cdot\text{s}^{-1}$), λ and μ represent the first and second viscosity coefficients respectively ($\text{Pa}\cdot\text{s}$) and B_0 represents bulk modulus (Pa).

The energy conversion equation for the solid phase (3D-C), which has a different temperature from its fluid phase, was written as

$$i\omega\rho_s C_{v,s} T_s = \kappa_s \frac{d^2T_s}{dz^2} + S_0, \quad (24)$$

where ρ_s represents density of the solid ($\text{kg}\cdot\text{m}^{-3}$), $C_{v,s}$ represents specific heat of at constant volume of the solid ($\text{J}\cdot\text{kg}\cdot\text{K}^{-1}$), κ_s represents thermal conductivity of the solid ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$), T_s represents the temperature of the solid (K) and S_0 represents input power density ($\text{W}\cdot\text{m}^{-3}$).

At the interfaces between 3D-C and atmospheric air, normal surface tension, velocity and temperatures have been assumed to be continuous. To simulate the difference in temperature between the two mediums, a coupling parameter, g ($\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$), was introduced, where g is proportional to the difference in temperature between the two mediums. The boundary conditions at the layer interfaces can hence be written as

$$T_{s,j-1}(z_j) = T_{s,j}(z_j), \quad (25)$$

$$T_{j-1}(z_j) = T_j(z_j), \quad (26)$$

$$v_{j-1}(z_j) = v_j(z_j), \quad (27)$$

$$\tilde{p}_{j-1}(z_j) = \tilde{p}_j(z_j), \quad (28)$$

with normal surface tension present in the fluid defined by

$$\tilde{p} = p - (\lambda + 2\mu) \frac{dv}{dz}. \quad (29)$$

The transfer of thermal energy from 3D-C to atmospheric air was defined by

$$q_{s,j}(z_j) = q_{s,j-1}(z_j) - g(T_{s,j}(z_j) - T_j(z_j)), \quad (30)$$

and

$$q_{f,j}(z_j) = q_{f,j-1}(z_j) + g(T_{s,j}(z_j) - T_j(z_j)), \quad (31)$$

where $q_{s,1}(z_1) = q_{s,N+1}(z_{N+1}) = 0$. The heat flux in 3D-C and atmospheric air were calculated using

$$q_s = -\kappa_s \frac{dT_s}{dz}, \quad (32)$$

$$q_f = -\kappa_f \frac{dT}{dz}, \quad (33)$$

respectively. The normal surface tension, velocity and temperatures in atmospheric air were derived using

$$\tilde{p} = \alpha_T B_0 T - \left(\lambda + 2\mu + \frac{B_0}{i\omega} \right) \frac{dv}{dz}, \quad (34)$$

$$v = -\frac{1}{i\omega\rho_f} \left(\alpha_T B_0 + \frac{i\omega\rho_f C_V}{\alpha_T T_0 B_0} \left(\lambda + 2\mu + \frac{B_0}{i\omega} \right) \right) \frac{dT}{dz} + \left(\lambda + 2\mu + \frac{B_0}{i\omega} \right) \frac{\kappa_f}{i\omega\rho_f \alpha_T T_0 B_0} \frac{d^3 T}{dz^3}, \quad (35)$$

and

$$T = Ae^{-ik_{ac}z} + Be^{+ik_{ac}z} + Ce^{-\theta_{th}z} + De^{+\theta_{th}z}, \quad (36)$$

respectively, where A, B, C and D are unknowns and k_{ac} and θ_{th} are asymptotic solutions of the associated fourth order differential equation. More thorough explanations of the simulation can be found in [78, 79].

3.6 Sample configuration and parameters

Post-fabrication, the materials were mounted onto their respective holders using conductive Ag paint (Leitsilber 200, Ted Pella) for electrical, acoustical and thermal characterization. Table VII shows the front and back views of 3D-C adhered to their holders as a visual representation of their electrical connection configuration. The length (L_x), width (L_y), height (L_z), number of layers used in simulation (N), pores per inch (ppi), macro-density, connection types and DC resistance of the samples are elaborated in Table VIII.

The density (ρ), specific heat capacity at constant pressure (C_p), specific heat capacity at constant volume (C_v), bulk modulus, coefficient of volumetric expansion (B), thermal conductivity (κ) and the first (λ) and second (μ) viscosity coefficients for 3D-C and atmospheric air in the simulations are elaborated in Table IX.

Table VII. Front and back views of samples with different connection types and holders.

Sample type	Front view	Back view
3D-C on microscope glass slide with point connection
3D-C on microscope glass slide with line connection
3D-C on microscope glass slide with volume connection
3D-C on microscope glass slide with 4 connection paths
3D-C on microscope glass slide with 4 connection paths merged into 2
3D-C on customised acrylic holder slide with point connection

Table VIII. Parameters of samples used in experiments.

Sample Name	A	B	C	D	E	F	G	H	I	J
L_x (mm)	30	20	20	20	20	20	20	20	30	50
L_y (mm)	20	20	20	20	20	20	20	20	20	20
L_z (mm)	2	2	2	2	2	2	2	2	2	2
N (simulations)	28	x	x	x	x	28	x	x	x	28
Ppi	110	110	110	110	110	110	110	110	110	110
Macro-density (mg·cm ⁻³)	3	3	3	3	3	3	3	3	3	3
Connection (see Table V)	Point	Same Side	Across	Diagonal	All across	Point	Line	Volume	Point	Point
Electrical Resistance (Ω)	3.7	2.0	2.2	2.5	2.2	2.9	2.1	1.7	3.8	5.1

Sample Name	K	L	M	N	O	P	Q	R
L_x (mm)	30	30	20	20	30	30	30	30
L_y (mm)	20	20	20	20	20	20	20	20
L_z (mm)	5	2	0.5	1	2	2	2	2
N (simulations)	70	28	x	28	x	x	x	x
Ppi	130	110	110	220	x	110	110	110
Macro-density	3	9	44	6	11	3	3	3
(mg·cm⁻³)								
Connection (see	Point	Point	Line	Point	Point	Point	Point	Point
Table V)								
Electrical	1.8	1.1	2.7	3.7	2.4	8.5	85	100
Resistance (Ω)								

Table IX. Parameters the various mediums used in simulations.

	ρ	C_p	C_v	B
	(kg/m ⁻³)	(J.kg ⁻¹ .K ⁻¹)	(J.kg ⁻¹ .K ⁻¹)	(Pa)
Air	1.20	9.96×10^2	7.17×10^2	1.01×10^5
3D-C	3.0	660	660	1.44×10^8
	α_T	κ	λ	μ
	(K ⁻¹)	(W.K ⁻¹ .m ⁻¹)	(N.s.m ⁻²)	(N.s.m ⁻²)
Air	3.33×10^{-3}	26.2×10^{-3}	16.82×10^{-6}	5.61×10^{-6}
3D-C	2.6×10^{-6}	160	0	0

3.7 Acoustic, input power and thermal characterization

The acoustic measurement set-up (Figure 35) was established with reference to the set-up by Aliev *et al.* [81]. The output generator module (Brüel & Kjær Type 3160-A-022) transmits the input data from the lap-top to the power amplifier (Brüel & Kjær Type 2735). The power amplifier amplifies AC signal from the output generator, which is applied to the mounted sample. A microphone (Brüel & Kjær Type 4138), which is 3 cm from the mounted sample, receives the acoustic signal generated from the sample. The pre-amplifier (Brüel & Kjær Type 2670) and the conditioning amplifier (Brüel & Kjær Type 2690), with sensitivity of 100 mV/Pa, amplifies the output signal of the microphone. The output generator module receives this amplified signal and transmits to the lap-top for conversion and data logging of sample SPLs. The operating power and temperature measurements were recorded captured by a power meter (Hioki PW335) and infrared thermal camera (Fluke Ti480) respectively. With the frequency of transmission for maritime radio and navigation to be approximately 3 to 30 kHz, the experimental acoustic frequency has been limited to the range of 1 to 40 kHz. The operating temperatures have also been limited to 200 °C as a feasible safety limit.

Figure 35. Acoustic, input power and thermal characterization of sample in operation. (a) Schematics of measurement set-up. 1 Lap-top, 2 output generator module, 3 power amplifier, 4 3D-C mounted on substrate on retort stand, 5 microphone, 6 microphone preamplifier, 7 conditioning amplifier, 8 power meter and 9 infrared thermal camera. (b) Visual image of measurement set-up. (c) Visual image of 3D-C mounted on substrate in measurement set-up.

Prior to 3D-C acoustic measurements, the acoustic set-up was calibrated to ensure the system was functioning as planned. A known moving-coil loudspeaker (Visaton K 28 WP (8 Ω)) functioning as the sample was attached to the power amplifier prior to operation. At an input frequency of 5 kHz, input voltage of 1 V_{rms} and measuring distance of 3 cm, the microphone received a SPL of 86.6 dB. The obtained acoustic spectrum is as seen in Figure 36. The obtained SPL is normalized to an input power of 1 W and a measuring distance of 1 m using

$$\begin{aligned} \text{Normalized SPL} = & \text{Measured SPL (dB)} + 20 \cdot \log_{10}(\text{Measuring distance}) \\ & + 20 \cdot \log_{10}\left(\frac{1 \text{ W}}{\text{Input power}}\right) \end{aligned} \quad (37)$$

to obtain 74.2 dB, which is in agreement with the datasheet of the speaker.

Figure 36. Acoustic (in green) and voltage (in blue) spectra of moving-coil loudspeaker.

The obtained SPL values were normalized to two different conditions. In acoustic spectra with varying acoustic frequencies, the obtained SPLs were normalized to an input power of 1 W and a measurement distance of 1 m using Eq. (37). In acoustic spectra with varying input powers, the obtained SPLs were normalized to a measurement distance of 1 m using Eq. (37).

4 Influence of electrical input frequency, input power, connection and acoustical backing

After attaching 3D-C samples to specifically designed holders, the acoustic frequency and input power was varied on Sample A to understand their fundamental effects on the electro-thermoacoustic performance of 3D-C. Next, samples of different configurations (Table VII, section 3.6) were connected to the acoustic system and the measurements taken.

4.1 Influence of electrical input frequency

In this thesis, sinusoidal AC, which utilizes both positive and negative input power, is used as the input power source (section 3.4). The amplitudes of the positive and negative input power are the same, except the current flows in opposite directions. Hence, during the phase of negative input power being injected into the sample (red portion in Figure 37a), the magnitude of Joule heating is the same as its positive counterpart, resulting in a same temperature reading and the acoustic frequency to be double of the input power-frequency (red portion in Figure 37b).

Figure 37. Transition from electrical input power to temperature via Joule heating when an AC sinusoidal wave is injected into the sample, where f represents the frequency of input power. Positive and negative input power are represented in black and red respectively. (a) Input power against time, (b) Temperature of 3D-C induced by Joule heating against time. Transition from electrical input power to temperature gradient via Joule heating when an AC sinusoidal wave is injected into the sample, where f represents the frequency of input power. Positive and negative input power gradients are represented in blue and orange respectively. (c) Input power against time, (d) Input power gradient against time, (e) Temperature gradient against time.

Since electro-thermoacoustics utilizes an input power gradient to induce a temperature gradient for sound generation (section 2.3.2), the described phenomenon above is also reflected in the orange portions of Figure 37c-e. This occurrence of acoustic frequency doubling that of signal frequency is also substantiated by

$$P_{input} = I_{input}^2 \times R = I^2 \times \sin^2(\omega \times t) \times R = I^2 \times R \times \frac{1 - \cos(2 \times \omega \times t)}{2}, \quad (38)$$

where P_{input} represents input electrical power (W), I_{input} represents input electrical current (A), R represents sample resistance (Ω), ω represents angular frequency ($\text{rad} \cdot \text{s}^{-1}$) and t represents the time which the set-up is in operation (s).

A 3D-C sample of macro-dimensions $30 \times 20 \times 2 \text{ mm}^3$ was mounted on a microscope glass slide with point connection (Sample A). This sample was injected with a 1 kHz AC sinusoidal wave with 2 W input power and the experimental results as seen in Figure 38. The acoustic

peak was received at 2 kHz, twice that of the frequency of AC input, which is in agreement with previous studies [13, 93, 147, 152-154].

Figure 38. Acoustic signal received by microphone and input AC voltage of acoustic set-up into Sample A against input AC frequency of acoustic set-up.

Next, Sample A was injected with electrical input frequency varying from 0.5 to 30 kHz while maintaining input power at 2 W to determine the effect of frequency on SPL (Figure 39). At the acoustic frequencies between 0.5 and 15 kHz, acoustic frequency has a linear relationship with SPL. As input power-frequency increases, input power gradient increases, inducing a higher temperature gradient and hence better electro-thermoacoustic performance. From 16 to 30 kHz, the neighboring particles of 3D-C approach their speed limit of oscillation. At a constant oscillation speed, the kinetic energy of the surrounding medium in 3D-C generates similar levels of thermal energy, resulting in the stagnation of the temperature gradient and causing a plateau in the generated SPL. This is in good agreement with the previous studies conducted on carbon nanostructured materials (graphene, rGO and CNTs in sections 2.6.2.1, 2.6.2.2 and 2.6.2.3 respectively) and Eq. (20) (section 2.4) [34, 37, 81]. The plateau in electro-thermoacoustic performance suggests the potential for 3D-C to have a broad

operating frequency band at higher frequencies, which is beyond the operating frequency of the equipment in use.

Figure 39. Normalized SPL against acoustic frequency of Sample A at a constant input power of 2 W. The red and yellow dashed lines represent the linear relationship and plateau of normalized SPL with acoustic frequency respectively.

4.2 Influence of input power

Next, the effect of input power on electro-thermoacoustic performance was investigated. When input power is increased, the amplitude of the temperature difference between 3D-C and its surrounding medium increases proportionately, resulting in an increase in temperature gradient and electro-thermoacoustic sound generation. To verify this, Sample A was mounted onto the acoustical measurement set-up. At a constant acoustic frequency of 10 kHz, the input power was varied from 0.1 to 10 W, and the normalized SPL as tabulated in Figure 40a. The input power has a linear relationship with normalized SPL with a standard deviation of 1.91 dB, which supports Eq. (20) (section 2.4) and is in agreement with previous literature results

(nanometer thick metal sheets, graphene, rGO, CNTs and 3D-C, section 2.6). The anomaly at an input power of 7.3 W (circled in red) has a normalized SPL of 39 dB, which is within the error of 5 dB indicated by the error bars, and is hence acceptable.

Next, operating temperature was taken at the input power range between 0.1 and 10 W, and the results are as tabulated in Figure 40b. The graph shows a linear relationship between operating temperature and input power, whereby the operating temperature of the sample begins to rise at a faster rate. At lower input powers (less than 0.3 W), the surrounding medium is able to assist in air cooling the medium rapidly and minimize increases in operating temperature. As input power increases, more Joule heating occurs and thermal energy of the sample increases, dissipating more heat into its surroundings. Since the air flow through the pores of 3D-C pores remains the same, less effective cooling of the sample is achieved, resulting in the linear increase in operating temperature, which is in good agreement with previous studies (nanometer thick metal sheets, graphene, rGO and CNTs) [35, 36, 84, 85, 155, 156]. A high input power would induce a high operating temperature, which would result in device failure should the sample holder be unable to operate at the operating temperature of desired input power. The high operating temperature of 3D-C at high input powers hence needs to be taken into consideration while designing the prototype.

Figure 40. (a) Normalized SPL and (b) operating temperature against input power of Sample A at a constant acoustic frequency of 10 kHz.

4.3 Influence of connection

Next, the effect of how 3D-C is connected to the acoustic system on SPL is investigated using Samples B, C, D and E. The acoustical measurement set-up was connected to the samples at different locations of conductive Ag paint as seen in Table VII (section 3.6), hence varying the length of the connection pathway and sample electrical resistance as seen in Table VIII (section 3.6). “Same side” denotes alligator clips on paths 1 and 2 (Sample B), “across” denotes alligator clips on paths 1 and 3 (Sample C) and “diagonal” denotes alligator clips on paths 1 and 4 (Sample D). Next, Sample E was made by the addition of two Ag paint paths used to link up paths 1 with 2 and 3 with 4 such that all four paths are utilized at the same time. “All across” denotes alligator clips on paths 5 and 6.

The acoustic measurements of the samples from acoustic frequencies of 0.5 to 50 kHz were measured and tabulated in Figure 41a. Below 20 kHz, the samples showed a linear relation between acoustic frequency and normalized SPL, which is consistent with previous results (section 4.1). Across Samples D, C and E, and B, while electrical resistance of the samples decreases by $0.3\ \Omega$ and $0.2\ \Omega$ respectively with shorter connection paths (Table VIII, section 3.6), the high thermal conductivity of 3D-C allows for not only the electrical pathway (red and orange areas of the infrared thermal images in Figure 42a – d), but also the entire material to generate sound *via* electro-thermoacoustics. This signifies that below 20 kHz, the location of Ag paint connection on 3D-C does not affect electro-thermoacoustic sound generation performance. Sample E, however, generated ~5 dB lower SPL as compared to the other samples. This is attributed by the pathway which the electrical currents travel in Sample E. The electrical configuration of Sample E has paths 1 with 2 and 3 with 4 (Table VII, section 3.6) merged. These mergers involve connecting the electrical paths in a parallel manner, resulting in equal electrical power being injected into the sample through all four paths. The increased

sources of electrical input power resulted in Sample E having a much larger radiating surface area (Figure 42d) than the other three samples. With a larger radiating surface area, Sample E experienced far field acoustic diffractions at lower acoustic frequencies, resulting in lower SPLs. For far field acoustic diffraction to occur, the distance between 3D-C and the microphone is governed by

$$r = \sqrt{(z - L_{th})^2 + (y - y')^2 + (x - x')^2},$$

where L_{th} (x , y , z) is the coordinates of the microphone's location (m) and (x' , y' , L_{th}) is the coordinates of 3D-C (m). Sample E having the largest radiating surface area results in it having the largest coordinates, and was hence impacted by the effect of acoustic diffractions at lower acoustic frequencies. The effect of acoustic diffractions on SPL is further emphasized above an acoustic frequency of 20 kHz, where the difference in normalized SPL between Sample E and the other three samples was increased by an additional ~5 dB. Samples B, C and D have very similar SPL performance with a negligible difference of ~4 dB.

Figure 41. Acoustic and temperature measurements of Sample B, Sample C, Sample D and Sample E. (a) Measurements of normalized SPL against acoustic frequency, (b) Measured temperature against varying input power at a constant acoustic frequency of 10 kHz

Figure 42. Thermal images of (a) Sample B, (b) Sample C, (c) Sample D and (d) Sample E in operation at a constant input power of 3 W at acoustic frequency of 10 kHz.

Next, operating temperatures of the samples from input powers of 0.25 to 15 W were measured at a constant acoustic frequency of 10 kHz and tabulated in Figure 41b. An increase in input power increases sample temperature due to increased utilization of Joule heating, with all samples showing the same trend in Figure 41b. This result is in agreement with previous results (section 4.2). Comparing temperatures of the samples, it can be observed that the operating temperatures of the samples are relatively similar with a maximum difference of 5 °C at low input powers (below 1 W). As input power increases, the temperatures diverge and are in the ascending order of Sample E, Sample D, Sample C and Sample B, with Sample C and Sample D having similar temperature profiles. At an input power of 5 W, the temperatures of Sample E, Sample D, Sample C and Sample B are 64 °C, 90 °C, 64 °C and 164 °C respectively. This relation in sample temperature is related to amount of 3D-C heated up along

the area of the electrical connection path, as seen in the infrared thermal images in Figure 42. The area of electrical connection path (red and orange areas in red circles) decreases in the order of Sample E, Sample D, Sample C and Sample B, with Sample C and Sample D having similar areas of electrical connection path. This area signifies the amount of material where thermal energy is congregated. With increasing uniform distribution of thermal energy throughout the material, the ability of concentrated thermal energy to dissipate into its surroundings is increased. This results in samples with larger electrical connection paths having lower operating temperatures to ascend in the order of Sample E, Sample D, Sample C and Sample B.

Following, the impact of the amount of conductive Ag paint added to connect the sample to the acoustic measurement set-up was studied. Firstly, one drop of conductive Ag paint with a surface area of $0.2 \times 0.2 \text{ cm}^2$ was applied onto the middle of the bottom edges of 3D-C to adhere it to the microscope glass slide (Sample F). Next, a strip of conductive Ag paint with a surface area of $2.0 \times 0.2 \text{ cm}^2$ was applied along the bottom edges of another piece of 3D-C for adhesion to the microscope glass slide (Sample G). Finally, a strip of conductive Ag paint with a surface volume of $2.0 \times 0.2 \times 0.2 \text{ cm}^3$ was applied through the edges of the 3D-C for adhesion to the microscope glass slide (Sample H). A clear depiction of conductive Ag paint on the microscope slides can be seen in Table VII (section 3.6).

The acoustic performances of the samples from acoustic frequencies of 0.5 to 50 kHz were measured and tabulated in Figure 43a. In Figure 43a, the normalized SPLs of all samples have a linear relation with acoustic frequency, which agrees with the previous results in section 4.1. Samples F and G have very similar SPL performance with a negligible difference of ~2 dB. Sample H has the lowest performance among the three samples, consistently generating sound ~5 dB lower than Samples F and G. This is attributed by the coating of conductive Ag paint on

3D-C. Conductive Ag paint is a highly electrically conducting material with a low electrical sheet resistance of $0.02 - 0.04 \Omega \cdot \square^{-1}$. Coating 3D-C with conductive Ag paint resulted in the electrical currents only conducting through the conductive Ag paint without passing through 3D-C. This resulted in insignificant power losses into its surroundings when an electrical power is injected into its surroundings. This inefficient Joule heating is hence unable to induce large pressure gradients in its surrounding medium, resulting in less efficient electro-thermoacoustic sound generation.

Figure 43. Acoustic measurements of Sample F, Sample G and Sample H. (a) Normalized SPL against acoustic frequency, and (b) normalized SPL against input power at a constant acoustic frequency of 10 kHz.

Next, the acoustic performances of the samples from input powers of 0.2 to 13 W were measured at a constant acoustic frequency of 10 kHz. The normalized SPL values were tabulated and plotted against input power as seen in Figure 43b. In Figure 43b, normalized SPLs of all samples were having a linear relationship with input power, which agrees with the previous results in section 4.2. Samples F and G have very similar SPL performance with a negligible difference of ~ 2 dB. Sample H has the lowest performance among the three samples, consistently generating sound ~ 5 dB lower than Samples F and G. These observations are in agreement with Figure 43a, supporting the hypothesis of DC resistance having an impact on electro-thermoacoustic sound generation.

Thereafter, the operating temperatures of the samples at a constant acoustic frequency of 10 kHz from input powers of 0.2 to 13 W were measured and tabulated in Figure 44a. At low input powers below 2 W, the temperatures of the samples were similar to room temperature, resulting in negligible temperature differences of 5 °C. As input power increases, the difference in operating temperatures increase. At an input power of 5 W, the temperatures of Sample H, Sample G and Sample F were 77 °C, 90 °C and 127 °C respectively. This order of sample operating temperature is inversely related to the amount of conductive Ag paint utilized to connect the sample to the acoustic system. While the addition of conductive Ag paint reduces the electrical resistance of Samples G and H by 27.6 % and 41.4% respectively (Table VIII, section 3.6), causing a reduction in the amount of Joule heating and hence effective SPL generated *via* electro-thermoacoustics, it also reduces the power density of the material. The increased amounts of conductive Ag paint functions as an added electrical contact surface area, hence reducing the amount of 3D-C available for electro-thermoacoustic sound generation. This results in a decrease in sample power density, resulting in less localized Joule heating and lower operating temperatures. These results are supported by infrared thermal images taken while Samples G and H were operating at 3 W input power and acoustic frequency of 10 kHz (Figure 45). In Figure 45a, the entirety of 3D-C present in Sample G is shown to be operating at above 50 °C (in red and orange). However, in Figure 45b, the portion of 3D-C present in Sample H which had been coated with conductive Ag paint is shown to be operating below 40 °C (in purple and blue in red rectangles). This signifies that Sample H has a smaller area of material irradiating heat, leading to less electro-thermoacoustically available 3D-C to generate sound *via* electro-thermoacoustics, hence resulting in lower SPL generation.

Figure 44. Relationship between temperature and SPL for Sample F, Sample G and Sample H. (a) Operating temperature against input power, and (b) SPL against operating temperature.

Figure 45. Thermal images of (a) Sample G and (b) Sample H in operation with input power of 3 W and acoustic frequency of 10 kHz.

On the other hand, normalized SPLs of the samples were plotted against their corresponding operating temperatures of the samples to understand their electro-thermoacoustic sound generation performance against their operating temperatures (Figure 44b). Although Sample H had generated lower normalized SPLs than Sample F in Figure 43a, Sample H operates at lower temperatures to generate the same SPLs as Sample F. To generate a normalized SPL of 40 dB, Sample H had an operating temperature of 80 °C, while Sample F had an operating temperature of 110 °C. This implies that Sample F has a larger range of SPL generation than Sample H before thermal decomposition and device failure occurs. Taking into account both operating

temperature and SPL, Sample G with a line type application of conductive Ag paint would be the ideal way of conductive Ag paint application.

4.4 Influence of acoustical backing

Subsequently, the effect of an acoustical backing on electro-thermoacoustic performance was investigated.

The use and configuration of holders are critical in an electro-thermoacoustic set-up.

Firstly, it functions to provide the electro-thermoacoustic material mechanical robustness and support. Secondly, the distance at which the substrate is located from the electro-thermoacoustic material would affect its SPLs. When the electro-thermoacoustic material is located too close to its holder, a portion of the thermal energy emitted during Joule heating would be transferred to the holder *via* heat conduction. Thermal energy transferred to the holder would hence not be able to be utilized for electro-thermoacoustic sound generation, resulting in lower SPLs and efficiency. To prevent thermal losses, the distance between the electro-thermoacoustic material and holder has to be larger than the thermal layer, which is defined by [19, 78, 157]

$$L_{th} = \sqrt{\frac{2\kappa_f}{\rho_f C_{p,f} \omega}}, \quad (40)$$

where κ_f , ρ_f , and $C_{p,f}$ represent the thermal conductivity ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$), macro-density ($\text{kg}\cdot\text{m}^{-3}$) and specific heat capacity ($\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$) of the surrounding medium while ω represents angular frequency ($\text{rad}\cdot\text{s}^{-1}$). At room temperature and pressure, the thermal layer ranges from 0.23 to 6.81 μm at the acoustic frequency range of 1 to 30 kHz. The minimum pore size of in-house fabricated 3D-C is 100 μm (Figure 30b), hence allowing for electro-thermoacoustic sound generation within the material.

3D-C was adhered on an acrylic holder with a hole in the middle as a sample generating

sound in free-field (Sample I). After measurements have been made, an acoustical backing (3.8 mm thick, Plexiglas, Dama Trading Pte Ltd) was added to cover the hole of 3.8mm depth and the measurements repeated. The hole depth far exceeds that of the thermal layer and should hence enhance 3D-C electro-thermoacoustic sound generation.

The acoustic measurements of the samples from acoustic frequencies of 0.5 to 30 kHz were measured and the normalized SPL values tabulated in Figure 46a. Comparing the normalized SPLs prior and post addition of an acoustical backing, the addition of an acoustical backing increased electro-thermoacoustic sound generation of Sample I by ~6 dB at the acoustic frequency between 1 and 6 kHz. This is attributed by constructive interference, where the distance between 3D-C and the acoustical backing is a multiple of the acoustic wavelength. The acoustical backing 3 mm from 3D-C functioned as a wall, allowing for acoustic waves generated by 3D-C to reflect off the surface of the acoustical backing. These reflected acoustic waves constructively interfere with the acoustic waves generated by 3D-C *via* electro-thermoacoustics, hence enhancing electro-thermoacoustic performance.

Figure 46. SPL and operating temperature measurements of Sample I without and with its acoustical backing. (a) Normalized SPL against acoustic frequency, and (b) Temperature against input power at a constant acoustic frequency of 10 kHz.

At the acoustic frequency between 6 and 16 kHz, the SPL of Sample I with the added acoustical backing started to decrease, and eventually generated lower SPLs than without the

acoustical backing from 12 to 16 kHz. This decrease in electro-thermoacoustic sound generation is attributed by the presence of the acoustic backing. The acoustical backing functioned as a wall, reflecting the acoustic waves generated by 3D-C electro-thermoacoustically. The 3.8 mm distance between 3D-C and the acoustical backing resulted the reflected acoustic waves interacted with the electro-thermoacoustic waves generated by 3D-C. As the distance between 3D-C and the acoustical backing is a sum of a multiple of the acoustic wavelength and half of the acoustic wavelength, destructive interferences occurs and measured SPL decreases. Above 16 kHz, the SPL of Sample I with acoustical backing increases and surpasses the sample without an acoustical backing at 30 kHz. The increased SPLs are attributed to constructive interference, as discussed earlier in this section.

Next, the operating temperatures of Sample I with and without acoustical backing were measured at a constant acoustic frequency of 10 kHz while input power was varied from 0.2 to 10 W and the results tabulated in Figure 46b. The operating temperatures of Sample I with and without the acoustical backing are very similar, with a negligible operating temperature difference of 5 °C. The similar operating temperatures shows that the electro-thermoacoustic sound generation of Sample I with and without its acoustical backing were of similar levels, with the difference in captured SPLs due to the interferences between the generated and reflected acoustic waves. The similar operating temperatures also indicate that the distance between 3D-C and the acoustical backing was sufficient. Sufficient distance between 3D-C and acoustical backing ensures minimal thermal losses from 3D-C to the acoustical backing, hence maximizing Joule heating utilization in electro-thermoacoustic sound generation. The distance also allowed for sufficient air cooling between 3D-C and the acoustical backing during electro-thermoacoustic sound generation, hence ensuring minimal overheating of 3D-C and prevent undesired thermal decomposition.

4.5 Conclusion

The impact of electrical input frequency, input power, connection and acoustical backing on electro-thermoacoustic sound generation have been investigated. As reported in literature, electrical input frequency and input power have a linear relationship with SPL due to an increased temperature gradient induced in 3D-C, of which signifies that the basis of electro-thermoacoustic sound generation is consistent with previous studies. On the other hand, lower operating temperatures were achieved with the use of a “line” type electrical connection. The addition of an acoustic backing also encourages acoustic constructive interferences, improving electro-thermoacoustic sound generation SPLs of 3D-C by ~6 dB at acoustic frequencies between 1 and 6 kHz. These factors should be taken into consideration during prototype design of 3D-C as a sound generator to maximize its electro-thermoacoustic sound generation.

5 Variation of material properties

Physical properties of 3D-C, e.g., physical macro-dimensions, *ppi*, material thickness and density, of various 3D-C pieces were modified prior to Ag paint adhesion to microscope glass slides (Table VIII, section 3.6). The samples were then linked to the acoustic system and the measurements taken. The results of the measurements were tabulated and analyzed in this chapter. These results were also compared with a simulation model for validation. After which, the efficiency of 3D-C was calculated and benchmarked.

5.1 Variation of physical macro-dimensions

The fabrication method of 3D-C, which is only limited by the furnace and sacrificial catalytic Ni template foam size, has the potential for large-scale manufacturing. It is hypothesized that large pieces of 3D-C would increase the amount of material for the electrical current to conduct through, thereby having a higher DC resistance and Joule heating, increasing its electro-thermoacoustic performance. Samples F, A and J, which are made with different lengths of 3D-C (Table VIII, section 3.6), were mounted onto the acoustic measurement set-up for measurements and the normalized results are as tabulated in Figure 47.

Figure 47. Experimental and theoretical simulated acoustic performance of Sample F, Sample A and Sample J. (a) Normalized SPL against acoustic frequency. (b) Normalized SPL against input power at a constant acoustic frequency of 10 kHz.

Figure 47a shows the graph of normalized SPLs against an acoustic frequency range of 0.5 to 50 kHz. At an acoustic frequency between 0.5 and 10 kHz, the normalized SPLs of the samples increased in a linear manner with acoustic frequency, which is in agreement with previous results (section 4.1) and simulation results. The three samples, Samples A, F and J, have similar electro-thermoacoustic performances with a negligible normalized SPL difference of ~4 dB. This is due to the electro-thermoacoustic sound generation being driven by electrical input power instead of the electrical potential difference present in the material. As described earlier, the graph in Figure 47a has SPL normalized to input power of 1 W. Samples F, A and J have different lengths of 3D-C, resulting in DC resistance increasing in the same order (Table VIII, section 3.6). This normalization to input power of 1 W hence resulted in the effect of DC resistance on electro-thermoacoustic sound generation to be accounted for. The effect of normalization was also substantiated by the experimental results having good matching with simulations.

From the acoustic frequency of 10 to 20 kHz, the SPLs of all three samples began plateauing. From the acoustic frequency of 20 to 50 kHz, the SPLs of Samples A and J decreased, with

Sample J decreasing at a faster rate than Sample A. This observation of SPLs plateauing, and eventually decreasing, are attributed by acoustic diffractions in the far field. Far field acoustic diffractions were simulated to generate SPLs using

$$p_{FF}(x, y, z) = \frac{i\omega\rho_f}{4\pi} \int_{-L_x/2}^{L_x/2} \int_{-L_y/2}^{L_y/2} v(x', y') \frac{e^{-ikr}}{r} dx' dy', \quad (41)$$

where $v(x', y', z)$ represents the velocity of the surrounding medium ($\text{m}\cdot\text{s}^{-1}$) at $L_{th}(x, y, z)$, the coordinates of the microphone's location (m), ρ_f represents the density of the surrounding medium ($\text{kg}\cdot\text{m}^{-3}$), ω represents angular frequency ($\text{rad}\cdot\text{s}^{-1}$) and r represents the distance between 3D-C and the microphone (m). The distance between 3D-C and the microphone required for far field acoustic diffraction is governed by Eq. (39) (section 4.3). Due to Sample J having the largest L_y among the three samples (Table VIII, section 3.6), it would hence undergo far field acoustic diffraction at lower acoustic frequencies. This results in Sample J experiencing far field acoustic diffractions first, which decreases the acoustic signal received by the microphone and hence recorded SPL, followed by SPLs of Sample A decreasing at a lower rate and SPLs of Sample F plateauing. The experimental results of far field acoustic diffraction phenomena were also well predicted by simulations (Figure 47a), as supported by the close matching of the simulated results with the measurements.

Next, the acoustic performances of the samples from input powers of 0.1 to 10 W were measured at a constant acoustic frequency of 10 kHz and the normalized SPLs tabulated as seen in Figure 47b. All three samples exhibited a linear relationship between input power and normalized SPL, which is in agreement with previous results (section 4.2) and simulations. In addition, all samples have similar SPLs generated with a negligible SPL difference of ~4 dB. Unlike the relationship between normalized SPLs and acoustic frequencies, the relationship between normalized SPL and input power was not influenced by sample size. This is due to the input power and normalized SPL relation being a direct influence of only electro-thermoacoustic sound generation and not acoustic diffractions. This hypothesis is also

supported by simulations, which were a good match with the experimental results.

While majority of acoustic applications are focused on having a low input power, the purpose of the investigation of varying physical macro dimensions is to investigate the potential of 3D-C to up-scale its ability to generate sound caused by the increase in DC resistance. Figure 48 shows the graph of measured SPLs against an electrical input current range of 0.1 to 2 A at a constant acoustic frequency of 10 kHz. Despite the differences in length and hence DC resistance, all three samples generated similar SPLs at the same input current. This is attributed to the effect of material volume utilized for electro-thermoacoustics. From Eq. (20) (section 2.4), it can be seen that SPL is directly proportional to input power but inversely proportional to material volume. The increase in DC resistance by 28 % and 76 % was accompanied by an increase in material volume by 50 % and 150 % for Samples A Sample J respectively, resulting in a negation of the effect of DC resistance and the samples having similar electro-thermoacoustic sound generation performances.

Figure 48. Measured SPL of Samples F, A and J against an input current range of 0.1 to 2 A.

5.2 Variation of ppi and thickness

Next, the effect of sample thickness and porosity on electro-thermoacoustic performance was investigated.

Samples A and K, which consist of 3D-Cs of different porosities and sample thicknesses (Table VIII, section 3.6) due to their different sacrificial catalytic Ni foam templates, were mounted onto the acoustic measurement set-up for measurements and the normalized results tabulated in Figure 49.

Figure 49a shows the graph of normalized SPL against an acoustic frequency range of 0.5 to 50 kHz. From 0.5 to 12 kHz, the normalized SPLs of Samples A and K have a linear relationship with acoustic frequency, which is in agreement with previous results (section 4.1) and simulation results. In addition, Samples A and K have similar electro-thermoacoustic sound generation performance with negligible SPL difference of 3 dB. This is attributed by their similar contact surface area with their surrounding medium. Sample K has a pore per inch (ppi) value of 130, which is 20 more than that of Sample A. An increase in ppi in Sample K results in an increase in porosity of 3D-C, and hence contact surface area with its surrounding medium. An increased contact surface area with the surrounding medium increases the interaction of the 3D-C with its surrounding medium, hence inducing more electro-thermoacoustic sound generation. This increase in contact surface area is reflected in the simulations by increasing the specific surface area of Sample K to be 140 % more than Sample A. In addition, Sample K is also thicker than Sample A by 3mm. The 250 % increase in material thickness in Sample K resulted in an increase in the L_{th} coordinate of 3D-C, hence inducing far field acoustic diffractions (Eq. (39), section 4.3) and negating the SPL improvements which an increase in ppi could bring about. This effect negation is reflected in the simulations by having a similar number of layers per millimeter for Sample A and Sample K, which agrees with the

experimental results.

Figure 49. Experimental and theoretical simulated acoustic performance of Sample A and Sample K. (a) Normalized against acoustic frequency, and (b) operating temperature against input power at a constant acoustic frequency of 10 kHz.

At the acoustic frequency between 12 and 50 kHz, the normalized SPLs of both Samples A and K decrease. This is attributed to far field acoustic diffractions occurring at higher acoustic frequencies, as discussed in section 4.3. However, the simulated results for Samples A and K differ, with Sample K hypothesized to have its decrease in normalized SPL to be at 20 kHz instead of 30 kHz. This is attributed by the utilization of cross-section slices of 3D-C in the simulation model and the increased material thickness of Sample K. Each slice of 3D-C would produce acoustic waves which would constructively interfere with a small delay

$$\sum_{n=0}^N \cos \left(kx_0 + nk \frac{L_z}{N} \right) = \cos \left(kx_0 + k \frac{N}{2} \frac{L_z}{N} \right) \frac{\sin \left((N+1) \frac{kL_z}{2N} \right)}{\sin \left(\frac{kL_z}{2N} \right)} \quad (42)$$

which would result in anti-resonances happening at every acoustic frequency where

$$f = \frac{c_0}{L_z \frac{N+1}{N}} k \quad (43)$$

is fulfilled, where k represents an integer, N and n represent the total number of slices which 3D-C has been sliced into and the slice number of 3D-C respectively, x_0 and L_z represent the thickness of the n_0 slice of 3D-C and macro-thickness of the 3D-C sample respectively (m) and C_0 represents the speed of sound of the surrounding medium (m·s⁻¹).

Next, the operating temperatures of the samples from input powers of 0.15 to 15 W were measured at a constant acoustic frequency of 10 kHz and the results tabulated in Figure 49b. The operating temperatures of Sample A and Sample K are very similar, with a negligible operating temperature difference of 5 °C. The similar operating temperatures of the two samples substantiates that they have similar electro-thermoacoustic sound generation performances, as discussed for the acoustic frequency spectra. While they have similar operating temperatures, the higher porosity and hence contact surface area of Sample K allows it to cool thrice as fast as Sample A after switching off the AC source (supplementary videos S1 and S2, <https://tinyurl.com/SupportingVideos>).

5.3 Variation of density

Next, the effect of density on its electro-thermoacoustic performance was investigated. There are several methods to changing the density of 3D-C.

The first method of changing material density is to increase the thickness of the struts in 3D-C. The growth time of graphene on the sacrificial catalytic Ni template foam was lengthened to increase the number of graphene layers being deposited on Ni (Sample L). Comparing the macro-densities of Sample A and Sample L, the increase in growth time resulted in the macro-density of Sample L to be 300 % that of Sample A. This increase in macro-density is representative of the number of graphene layers present in 3D-C. Both Sample A and Sample L were grown using the same sacrificial catalytic Ni template foam. The sacrificial catalytic Ni template foam would hence have similar surface contact area with the methane precursor and have similar rates of graphene layer growth. With the increased graphene growth time, it can hence be hypothesized that more graphene layers were grown on the sacrificial catalytic Ni template of Sample L, resulting in increased material and macro-density.

Next, SEM was conducted on Sample A and Sample L to understand the effect of increased

material density on material microstructure (Figure 50). Figure 50a and Figure 50c shows the SEM micrographs for Samples A and L respectively at a magnification of 100 times. At this magnification level, it can be observed that the overall microstructure of Sample A and Sample L remains similar. While the surface of Sample A appears smooth (Figure 33a), the surface of Sample L appears undulating (Figure 50c). This was confirmed with increased SEM magnification. Figure 50b and Figure 50d shows the SEM micrographs for Samples A and L respectively at a magnification of 500 times. The surface of Sample A appears slightly undulated, with the cross-section cut made exhibiting thin layers of stacked graphene (Figure 50b). The undulated surface of Sample L was revealed to be caused by the random agglomeration of graphene layers. The cross-section cut of a strut of Sample L strut revealed thick, randomly agglomerated graphene layers. These thick, randomly agglomerated graphene layers could result in the material being classified as a graphite instead of few or multi-layered graphene. In addition, the increased stacking of graphene layers could also induce defects to the material, which would further reduce electro-thermoacoustic sound generation. The presence of defects in a material function as a roadblock to phonon movement, which are packets of vibrational kinetic energy. Phonons move within a material to transmit vibrational kinetic energy, which is translated to thermal energy at high levels of vibrational kinetic energy. Less efficient phonon movement would result in less efficient heat dissipation of the material, hence reducing electro-thermoacoustic sound generation.

Figure 50. SEM micrographs of (a) Sample A at 100 and (b) 500 times magnification respectively, Sample L at 100 and (d) 500 times magnification respectively.

Next, Raman spectroscopy (Figure 51) conducted on Sample L to verify the presence of defects and the amount of graphene layers present in the material. The Raman spectrum of Sample L showed the absence of D peak at wavenumber 1350 cm^{-1} and the presence of G and 2D peaks at wavenumbers 1580 cm^{-1} and 2705 cm^{-1} respectively. The wavenumbers of the peaks present in the Raman spectrum of Sample L is the same as Sample A, indicating that Sample L was of pristine quality [26, 31, 34, 105, 145-147]. Comparing the intensities of the 2D and G peaks, the intensity of the 2D peak was approximately 0.45 of the G peak ($\frac{I_{2D}}{I_G} \approx 0.45$), suggesting the presence of multiple layers of graphene in 3D-C [148, 149]. This ratio is also lower than that of Sample A ($\frac{I_{2D}}{I_G} \approx 0.80$), which signifies the presence of more graphene layers in Sample L. These results substantiate the findings from the SEM micrographs that

denser Sample L has thicker struts due to random graphene agglomeration.

Figure 51. Raman spectra of Sample A (black) and Sample L (red).

After adhesion to its glass microscope slide *via* conductive Ag paint, Sample L was mounted onto the acoustic measurement system and its measurements were taken (Figure 52).

Figure 52. Experimental and theoretical simulated acoustic performance of Sample A compared with Sample L. (a) Normalized SPL against acoustic frequency, (b) Normalized SPL against input power at a constant acoustic frequency of 10 kHz.

Figure 52a shows the graph of normalized SPL plotted against an acoustic frequency range of 0.5 to 50 kHz. Throughout the full acoustic frequency spectrum, Sample L exhibits a similar linear relation between acoustic frequency and SPL as Sample A. This similar electro-thermoacoustic sound generation trend implies that the basis of electro-thermoacoustic sound generation for Sample L is similar to Sample A, with an increase in material density not affecting the trend of electro-thermoacoustic sound generation. This similar trend was also reflected in the simulation results, which have good agreement with the experimental results. Comparing the generated SPLs of Sample A with Sample L, Sample L experienced a ~25 dB decrease in SPLs. The large decrease in electro-thermoacoustic sound performance in Sample L is attributed by an increased strut thickness brought about by increased material density. For optimal electro-thermoacoustic sound generation to occur, a material is required to have a low heat capacity per unit area (*HCPUA*) [14, 15]. A low *HCPUA* means that when heat is induced in the material, most of the induced heat along its contact surface is dissipated into its surroundings instead of being stored within the material. *HCPUA* of a material is defined by

$$HCPUA = t_s \times \rho_s \times C_{p,s}, \quad (44)$$

where t_s , ρ_s and $C_{p,s}$ represent the thickness of the struts of 3D-C (m), density of the struts of 3D-C ($\text{kg}\cdot\text{m}^{-3}$) and the specific heat capacity of 3D-C ($\text{J}\cdot\text{kg}\cdot\text{K}^{-1}$) respectively, is a critical parameter for optimal electro-thermoacoustic sound generation [14, 15]. A low *HCPUA* indicates minimal heat storage by the material along its contact surface when thermal energy is induced in it. This signifies that a majority of the induced thermal energy would be dissipated into its surrounding medium, hence resulting in optimal electro-thermoacoustic sound generation. Tripling macro-density resulted in an increase in the ability of the material to store heat along its contact surface when a heat source is introduced, hence reducing electro-thermoacoustic sound generation. The increased *HCPUA* is reflected in the simulations with a factor of 27 for good fitting between experimental results and simulations (Figure 52a).

Next, the acoustic performances of the samples from input powers of 0.1 to 10 W were measured at a constant acoustic frequency of 10 kHz. The obtained SPL values were normalized and tabulated as seen in Figure 52b. Both samples exhibited a linear relationship between input power and normalized SPL, which is in agreement with previous results (section 4.2) and simulations. This 25 dB difference in SPL generation reflected in the acoustic frequency spectra (Figure 52a) is also seen in this power spectra. This similar difference, coupled with the good match with simulations, reinforces the hypothesis of the impact of material density of electro-thermoacoustic sound generation performance.

Next, a commercial 0.5 mm thick 3D-C was procured from ACS Material (Sample M) to compare its electro-thermoacoustic sound generation with in-house fabricated 3D-C and verify the effect of material density and thickness.

The macro-density of Sample M was calculated to be $44 \text{ mg}\cdot\text{cm}^{-3}$, which is 22 times that of in-house fabricated 3D-C. The high macro-density of Sample M signifies a high material density, which implies that the $HCPUA$, which is the product of t_s , ρ_s and $C_{p,s}$, would increase. While the thickness of Sample M is a quarter of in-house fabricated 3D-C (Sample A, Table VIII), its much higher material density would result in an increased $HCPUA$, which is a crucial factor for electro-thermoacoustic sound generation [14, 15]. A high $HCPUA$ signifies that when heat is injected into the material, it would store more heat instead of dissipating it into its surroundings. Decreased heat dissipation results in a smaller temperature gradient, and hence lower electro-thermoacoustic sound generation performance.

The microstructure and indication of number of graphene layers present in Sample M was then evaluated *via* SEM, with the micrographs depicted in Figure 53. Figure 53a and Figure 53c shows the SEM micrographs for Samples A and M respectively at a magnification of 100 times. The overall microstructure of Sample A and Sample M can be observed to be similar at this magnification level. Figure 53a shows that the surface of Sample A appears smooth, while

Figure 53c shows that the surface of Sample M appears uneven. This surface morphology was confirmed upon increasing SEM magnification. Figure 53b and Figure 53d shows the SEM micrographs for Samples A and L respectively at a magnification of 500 times. In Figure 53b, the surface of Sample A appears slightly uneven. The cross-section of a cut made on a strut of Sample A reveals thin layers of stacked graphene, revealing that Sample A consists of few layers of stacking graphene. In Figure 53d, the surface of Sample M appears more undulated. The cross-section of a cut made on a strut of Sample M reveals wrinkled graphene layers stacked to a higher thickness than Sample A. The undulated surface of Sample M was revealed to be caused by the wrinkling of graphene layers. The wrinkling of the graphene layers in Sample M, coupled with increased graphene deposition, could potentially bring about defects to the material. Defects present in a material would impede the movement of phonons. With impeded phonon movement, kinetic energy is not as easily transferred within the material, resulting in less efficient heat dissipation and electro-thermoacoustic sound generation. This increase in graphene layers could also result in Sample M's properties to trend towards graphite. Graphite has a thermal conductivity of $5750 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, which is less than graphene (more than $10000 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) [100]. The potential decrease in thermal conductivity could result in less thermal energy being dissipated into the surrounding medium, and hence a smaller temperature gradient and lower electro-thermoacoustic sound generation.

Figure 53. SEM micrographs of (a) in-house grown 3D-C at 100 and (b) 500 times magnification respectively, (c) 3D-C procured from ACS Material at 100 and (d) 500 times magnification respectively.

Next, Raman spectroscopy was conducted on Sample M (Figure 54) to verify the amount of graphene layers and presence of defects in the material. The Raman spectrum of Sample M reveals the absence of D peak at wavenumber 1350 cm^{-1} and the presence of G and 2D peaks at wavenumbers 1580 cm^{-1} and 2705 cm^{-1} respectively. This Raman spectrum is similar to 3D-C synthesized in-house (Sample A), indicating that procured 3D-C (Sample M) was of pristine quality [26, 31, 34, 105, 145-147]. Examination of the intensity of the 2D and G peaks of Sample M shows that the intensity of the 2D peak was approximately 0.64 of the G peak ($\frac{I_{2D}}{I_G} \approx 0.64$), verifying the presence of few layers of graphene in the commercially procured 3D-C (Sample M) [148, 149]. The 2D to G peak ratio of Sample M is lower than that of Sample A ($\frac{I_{2D}}{I_G} \approx 0.79$), implying that Sample M has more graphene layers than Sample A. Sample M

can hence be hypothesized to have lower electro-thermoacoustic sound generation due to the thicker graphene layer stacking, and hence less heat dissipation into its surroundings.

Figure 54. Raman spectra of Sample A (black) and Sample M (red).

Sample M was then mounted onto a microscope glass slide using conductive Ag paint and its acoustic performances measured (Figure 55). Figure 55a shows the graph of normalized SPL plotted against an acoustic frequency range of 1 to 14 kHz. Throughout the full acoustic frequency spectrum, Sample M exhibits a linear increase in SPL with a linear increase in acoustic frequency. This observation of Sample G and Sample M having similar electro-thermoacoustic sound generation trends shows that the method of electro-thermoacoustic sound generation of Sample M is similar to Sample G. This signifies that a difference in sample macro-density and thickness does not affect how electro-thermoacoustic transducers generates sound. Examining the generated SPLs of Sample G and Sample M, Sample M generated SPLs

~15 dB less than Sample G. This is attributed by the decrease in the *HCPUA* of Sample M. Comparing Sample M physical properties with *HCPUA* with Sample G, while the C_p of both materials remain the same ($0.68 \text{ J}\cdot\text{g}\cdot\text{K}^{-1}$), Sample M has a quarter of Sample G's material thickness and 220 % of Sample G's material density. This results Sample M having a *HCPUA* 155 % times of Sample G. When heat is injected into Sample M, this increased *HCPUA* resulted in Sample M storing thermal energy along its contact surface instead of rapidly dissipating it into the surrounding medium of the material. Decreased thermal dissipation resulted in a lower temperature gradient and hence, decreased electro-thermoacoustic sound generation.

Figure 55. Acoustic performance of Sample G compared with Sample M. (a) Normalized SPL against acoustic frequency, and (b) normalized SPL against input power at a constant acoustic frequency of 10 kHz.

Next, the acoustic performances of the samples from input powers of 0.25 to 10 W were measured at a constant acoustic frequency of 10 kHz. Figure 55b shows the plot of normalized SPL values against input power. The normalized SPLs of samples G and M increased linearly with input power and normalized SPL. This trend is in line with previous results (section 4.2), verifying a similar electro-thermoacoustic mechanism. Comparing the normalized SPL values of Samples G and M, there is a ~15 dB difference, which is the same magnitude as the acoustic frequency spectra (Figure 55a). This same magnitude of difference reinforces the hypothesis on the effect of sample thickness and density, which affects *HCPUA* and hence electro-

thermoacoustic sound generation.

Another method of changing material density is by physically compressing of 3D-C. Spacers of 1 mm height were placed next to 3D-C to prevent over-compression of 3D-C. An acrylic sheet was then placed on the spacers and 3D-C and a 0.5 kg weight placed on the acrylic sheet to compress 3D-C (Figure 56) to obtain compressed 3D-C (Sample N). Due to the compression of 3D-C to half its original height, Sample N has double the material density of its original 3D-C.

Figure 56. Schematic of 3D-C being compressed. (a) Before compression, and (b) after compression.

Next, SEM was conducted on Sample N to identify microstructure changes caused by the physical compression (Figure 57). Figure 57a and Figure 57c show the SEM micrographs at 100 times magnification of Sample A and Sample N respectively. Comparing the SEM micrographs, both Samples A and Sample N have the same hexagonal structure, while Sample N has more material present in the same area of SEM micrograph. This implies that the physical compression of 3D-C only increased the amount of material present within the same unit volume, and did not alter the general microstructure of the material. Next, the SEM micrographs were taken at 500 times magnification to ensure that the struts of 3D-C were not compromised (Figure 57b and Figure 57d for Sample A and Sample N respectively). Examining the Figure 57b and Figure 57d, it can be observed that minimal changes had occurred to 3D-C post compression, enforcing the minimal effect of mechanical compression

on the struts of 3D-C.

Figure 57. SEM micrographs of 3D-C prior to compression at (a) 100 times magnification and, (b) 500 times magnification and (c) after compression at 100 times magnification and (d) 500 times magnification, respectively.

Following, Raman spectroscopy was conducted on Sample N to verify if the crystallinity of 3D-C had deteriorated after compression. The Raman spectrum of Sample N (Figure 58) showed the absence of D peak at wavenumber 1350 cm^{-1} and the presence of G and 2D peaks at wavenumbers 1580 cm^{-1} and 2705 cm^{-1} respectively. The Raman shift of Sample N are the same as Sample A, hence signifying that Sample N was of pristine crystallinity [26, 31, 34, 105, 145-147]. Examining the intensities of the 2D and G peaks of Sample N, the 2D peak has an intensity approximately 0.51 of its G peak ($\frac{I_{2D}}{I_G} \approx 0.51$), signifying the presence of few layers of graphene in 3D-C [148, 149]. This ratio is also lower than that of Sample A ($\frac{I_{2D}}{I_G} \approx 0.80$), which indicates a higher layer number of graphene layers. This increase in intensity ratio

of the 2D to G peak could also be attributed by an increase in material density. The increase in material density in Sample N resulted in the presence of more material per unit area, and hence a higher probability of Raman scattering to occur at the region where the Raman laser source is directed at the material. An increased probability of Raman scattering would increase the number of Raman signals reflected back into the signal detector, and hence decrease the 2D to G peak ratio.

Figure 58. Raman spectra of Sample A (black) and Sample N (red).

Thereafter, Sample N was mounted on a microscope glass slide using Ag conductive paint. Its sound generation *via* electro-thermoacoustics measured using the acoustic measurement set-up and the results tabulated (Figure 59). Figure 59a shows the graph of normalized SPL plotted against an acoustic frequency range of 0.5 to 50 kHz. At the acoustic frequency between 0.5 and 10 kHz, the Samples F and N have similar electro-thermoacoustic sound generation

performance with a negligible SPL difference of ~ 3 dB, which is in good agreement with simulations. This shows that mechanical compression had minimal impact on electro-thermoacoustic sound generation. At the acoustic frequency between 10 and 50 kHz, Sample N generated SPLs of ~ 6 dB higher than Sample F. This is attributed by the effect of mechanical compression on contact surface area with its surrounding medium. Mechanical compression of 3D-C to half its original height while maintaining its length and width resulted in the doubling of ppi of 3D-C. This increase in ppi leads to an increase in material contact surface area with its surrounding medium. Additional contact with the surrounding medium results in an improvement in the thermal dissipation of 3D-C when thermal energy is induced into it, hence improving its electro-thermoacoustic sound generation. This mechanical increase in ppi was reflected in the simulations with the same number of distinct layers, N , while material thickness remained unchanged. As acoustic frequency increases from 0.2 to 50 kHz, Sample N was simulated to have a linear increase in SPLs, which has good matching with the experimental results (Figure 59a).

Figure 59. Experimental and theoretical simulated acoustic performance of Sample F compared with Sample N. (a) Normalized SPL acoustic frequency and, (b) Temperature against input power at a constant acoustic frequency of 10 kHz.

Next, the operating temperatures of Sample N was taken from an input power of 0.2 to 9 W at a constant acoustic frequency of 10 kHz and the results tabulated in (Figure 59b). Both

Sample F and Sample N exhibited a linear relationship between operating temperatures and input power, verifying that they have the same basis of utilizing electro-thermoacoustics for sound generation. Comparing the operating temperatures of Sample F and Sample N, the operating temperature of Sample N increases at a faster rate than Sample F. At an input power of 4 W, the temperatures of Samples F and N were 102 °C and 147 °C respectively. This is attributed by the mechanical compression on Sample N. While the contact area of Sample N with its surrounding medium has increased, mechanical compression also resulted in an increase in the amount of material present per unit volume. With more material present in a fixed volume, there is increased difficulty in air flowing from within the material into its surroundings. The flow at which atmospheric air is able to enter the pores of 3D-C to cool it hence decreases. At low input powers below 0.8 W, the operating temperatures are similar with a negligible difference is 5 °C. At low input powers, less Joule heating occurs and less thermal energy is induced into 3D-C. This results in the low and similar operating temperatures, where the need for the surrounding atmospheric air to cool 3D-C is not as critical. As input power increases and more Joule heating occurs, more thermal energy is induced into 3D-C. A larger flow of the cooler surrounding air would hence be more critical in the reduction of operating temperature. Sample N, which has more material per unit volume and less air able to flow through its pores, will hence be unable to cool as rapidly as Sample F. This hence results in Sample N having a higher operating temperature than Sample F, and the difference in operating temperature increasing with increasing input power.

5.4 Comparison with literature

In this chapter, multiple methods to improve 3D-C has been studied, with Sample F generating the highest normalized SPL of 22.3 dB at an acoustic frequency of 3 kHz. To understand the standing of 3D-C among other carbon nanostructured materials and piezoelectric speakers, the efficiency of 3D-C was determined. Assuming 3D-C to be a speaker emitting spherical radiation, efficiency can be calculated using [179]

$$\eta = \frac{\text{Acoustic power}}{\text{Electrical input power}} = \frac{4\pi r^2 p_{rms}^2}{\rho C_0} \div \text{Electrical input power}, \quad (45)$$

where η represents efficiency (%), r represents distance between sound transmission and receiver (m), p_{rms} represents SPL (Pa) and ρ and C_0 represent density and speed of sound of surrounding medium respectively.

Based on the parameters of Sample F, the SPL at 3 kHz acoustic frequency was normalized to an input power of 1 W and measuring distance of 1 m, and the efficiency of 3D-C is calculated to be 2.0×10^{-7} %. This is higher than previously reported natural-dried 3D-C, which is attributed by the absence of defects in 3D-C, while being an order of magnitude less efficient than freeze-dried 3D-C. 3D-C is more efficient than poly(3,4-ethylenedioxythiophene): poly(styrenesulfonic) (PEDOT:PSS), indium tin oxide (ITO) and aluminum (Al) films. Due to different ways of adhesion and different electrical resistance values (2 – 2200 Ω) [71, 72, 77, 84, 86-88, 97, 98], CNT sheets remain the most efficient electro-thermoacoustic sound transmitter. At the same acoustic frequency, a commercial piezoelectric speaker (Murata, BX-070009) has an efficiency of 0.33 % [158, 159] (Table X). Increased material electrical resistance and better adhesion methods hence needs to be conducted to improve the electro-thermoacoustic sound generation efficiency of 3D-C as a potential alternative to piezoelectric speakers.

Table X. Comparison of efficiencies of reported electro-thermoacoustic materials and piezoelectric speaker at 3 kHz acoustic frequency. All values have been normalized to an input power of 1 W and measuring distance of 1 m.

Material	Normalized SPL (dB)	Normalized SPL (Pa)	η (%)	Reference
Sample F	22.3	2.60×10^{-4}	2.03×10^{-7}	This work
Natural-dried 3D-C	21.5	2.39×10^{-4}	1.70×10^{-7}	[34]
Freeze-dried 3D-C	32.5	8.48×10^{-4}	2.15×10^{-6}	[34]
PEDOT:PSS film	1.54	2.39×10^{-5}	1.70×10^{-9}	[88]
ITO film	3.54	3.01×10^{-5}	2.70×10^{-9}	[88]
Al film on porous silicon	10.5	6.73×10^{-5}	1.35×10^{-8}	[88]
CNT sheets	44.5	3.37×10^{-3}	3.40×10^{-5}	[88]
BX-070009	84.4	0.33	0.33	[158, 159]

5.5 Conclusion

The impact of varying material properties on the electro-thermoacoustic sound performance of 3D-C was investigated. Due to a proportionate increase of both DC resistance and material volume with material length, increasing the macro-dimensions of 3D-C did not have an influence on electro-thermoacoustic sound generation. On the other hand, successful improvement of electro-thermoacoustic sound generation of 3D-C was achieved through minimizing *HCPUA* and maximizing contact surface area. The former was accomplished through low strut thickness and sample macro-thickness, while the latter was achieved by increasing material porosity. Tripling strut thickness results in a decrease in normalized SPLs by ~25 dB, whilst an increase in material porosity achieved through the mechanical compression resulted in an increase in normalized SPLs of ~6 dB at the acoustic frequency between 10 and 50 kHz. The two-temperature simulation model conducted on the influence of material properties also showed good agreement with experimental results, and can hence be

used to determine optimal parameters for electro-thermoacoustic sound generation for 3D-C. Methods to improve the electro-thermoacoustic sound generation of 3D-C can hence be elicited from these experimental and theoretical studies.

6 Hybrid materials

6.1 Carbon nanostructured hybrid material

As shown in simulations and experimental results (chapter 5), an increase in material contact surface area with its surrounding medium improves heat dissipation and hence electro-thermoacoustic sound generation. While the addition of CNTs on rGO sheets with PET substrate have shown to improve its generated SPL [76], there had been little study on the effect of the addition of other carbon nanostructured materials on 3D-C.

6.1.1 rGO coated 3D-C

A possible method of increasing the contact surface area of 3D-C with its surrounding medium is the perpendicular deposition of another carbon nanostructured material on 3D-C (Figure 60).

Figure 60. Preferred orientation of rGO sheet deposition on 3D-C.

Graphene (section 2.6.2.1) and reduced graphene oxide (rGO) (section 2.6.2.2) were considered to be deposited on 3D-C due to literature studies having shown their ability to generate sound electro-thermoacoustically. Comparing their fabrication methods, graphene requires a catalytic metal template or silicon wafer, or the thermal decomposition of silicon carbide for synthesis [160]. These substrates and precursors cannot be deposited on 3D-C or its sacrificial catalytic Ni template for graphene fabrication. GO flakes, on the other hand can be deposited on the sacrificial catalytic Ni template prior to 3D-C growth and reduced to rGO to improve its thermal properties. A previous study by Yang *et al.* showed that the addition of

rGO sheets to 3D-C and infused within phase change material (PCM) improved its thermal conductivity compared to 3D-C infused PCM [161]. This shows that rGO deposition on 3D-C could improve its thermal conductivity, resulting in a steeper temperature gradient when an AC is injected into the material and hence improve electro-thermoacoustic sound generation performance.

rGO was coated on 3D-C *via* freeze-drying described in [161]. Firstly, the Ni foam (110ppi, 2mm thickness, Latech Scientific Supply Pte. Ltd.) was immersed in a graphene oxide (GO) solution (7.5 mg/mL) and the mixture ultrasonicated for 30 minutes to allow for the GO solution to infiltrate the pores of the sacrificial catalytic Ni template foam to ensure homogeneous GO coating on the sacrificial catalytic Ni template foam. The GO coated sacrificial catalytic Ni template foam was then frozen overnight in a freezer at temperatures less than 0°C before it is freeze-dried for 12 hours. Post freeze-drying, the freeze-dried GO coated sacrificial catalytic Ni template foam was placed in the middle of the split tube furnace and 3D-C was grown on the GO coated sacrificial catalytic Ni template foam with the same procedure in section 3.1. During 3D-C growth, the presence of H₂ at high temperatures reduced the GO flakes to rGO, resulting in rGO on 3D-C coated Ni. Next, the sacrificial catalytic Ni template foam was coated with a protective PMMA layer, chemically etched using HCl, and the PMMA layer removed as described in section 3.1 to obtain the final free-standing rGO coated 3D-C (rGO/3D-C).

Macro-density of the obtained free-standing rGO/3D-C was first calculated to determine the weight ratio of rGO and 3D-C present. The hybrid material has a macro-density of 11 mg·cm⁻³. The macro-density of the hybrid material is 366.67 % of pure 3D-C (3 mg·cm⁻³), suggesting that the hybrid material had a weight composition of 72.72 % rGO and 27.28 % 3D-C. The higher material density of rGO material density would have a proportionate increase in *HCPUA*, which indicates an increased amount of thermal energy stored along the material

surface when the material is induced with thermal energy. The deposition of rGO sheets could result in 3D-C storing more heat rather than dissipating it into its surroundings, reducing electro-thermoacoustic sound generation.

Next, SEM was conducted on rGO/3D-C for two purposes. Firstly, to evaluate the deposition of the rGO flakes and secondly, to observe if the interconnected structure of 3D-C had been damaged due to rGO deposition (Figure 61). Figure 61a and Figure 61b shows the SEM micrographs of the 3D-C and rGO/3D-C respectively at a magnification of 100 times. Comparing the general microstructures of the materials, they appear very similar except for the addition of rGO sheets on the hybrid material, verifying that rGO deposition did not alter the general microstructure of 3D-C. Additional magnification at 500 times was subsequently conducted to verify if rGO deposition resulted in damage to the morphology of 3D-C (circled in green in Figure 61a and Figure 61b), as well as understand how rGO had been deposited on to 3D-C (circled in red in Figure 61b). Comparing the SEM micrographs at a magnification of 500 times, the shape of 3D-C's struts (Figure 61c) were retained post rGO deposition (Figure 61d). However, several micro-holes can be observed, as seen in the blue circles in Figure 61d. These holes indicate physical damages, suggesting that there could be defects introduced to the material during rGO deposition. The SEM micrograph of the rGO/3D-C (Figure 61e) revealed a wrinkled uneven rGO sheet had covered a 3D-C pore during deposition instead of the desired deposition direction (Figure 60). This shows that the deposition of rGO onto 3D-C had reduced the porosity of the material. A decrease in porosity would result rGO/3D-C to have a reduction in contact surface area with its surrounding medium as compared to 3D-C, resulting in poorer thermal dissipation and a potential decrease in electro-thermoacoustic sound generation.

Figure 61. SEM micrographs of (a) 3D-C prior to rGO deposition, (b) 3D-C after rGO deposition at 100 times magnification respectively and, (c) 500 times magnification micrograph of 3D-C prior to and (circled in green in a) (d) after rGO deposition (circled in green in b) and (e) zoomed-in micrograph of rGO sheet (circled in red in b). The micro-holes present on 3D-C after rGO deposition are circled in blue in (d).

Raman spectroscopy was conducted on rGO/3D-C to verify the presence of defects and the presence of the synthesized materials (Figure 62). Raman spectrum of 3D-C in the hybrid material reveals the presence of the G and 2D peak at peaks 1580 cm^{-1} and 2705 cm^{-1} and the absence of the defect D peak at 1350 cm^{-1} , which is the same as 3D-C, signifies that the deposition of rGO sheets on the sacrificial catalytic Ni template foam did not affect quality of synthesized 3D-C [26, 31, 34, 105, 145-147]. The intensity of the 2D peak was approximately 0.48 of the G peak ($\frac{I_{2D}}{I_G} \approx 0.48$), indicating the presence of multiple layers of graphene in 3D-C [148, 149]. Comparing the 2D to G peak ratio with pure 3D-C (Sample A, $\frac{I_{2D}}{I_G} \approx 0.79$), the ratio in rGO coated 3D-C had decreased. This implies that there had been an increase in the number of graphene layers detected by the Raman spectrometer. This could be attributed by the presence of the deposited rGO sheets, which contribute to Raman scattering occurring at a higher probability where the Raman laser source is directed at the material. An increased probability of Raman scattering would increase the quantity of reflected Raman signals,

reducing the 2D to G peak ratio. The Raman spectrum of rGO sheets in the hybrid material revealed the presence of D peak and G peak at 1350 cm^{-1} and 1580 cm^{-1} respectively with the absence of the 2D peak at 2705 cm^{-1} , indicating the presence of rGO sheets [162-167]. Comparing the intensities of the D peak and G peak, the intensity of the D peak is 1.47 times that of the G peak ($\frac{I_D}{I_G} \approx 1.47$). The D to G peak intensity ratio being more than 1 implies that GO had been successfully reduced to rGO [164] as intended.

Figure 62. Raman spectra of 3D-C and rGO in rGO/3D-C compared with 3D-C.

Next, the rGO/3D-C was adhered to a microscope glass slide (Sample O) with Ag conductive paint and mounted onto the acoustic measurement system and its acoustic performances measured (Figure 63). Figure 63a shows the normalized plot of SPL against an acoustic frequency range of 1.2 to 14 kHz. Comparing the normalized SPL of Sample A and Sample O,

they both exhibit linear relationships with acoustic frequency, and is supported by past experimental results and simulations (chapter 5). Examining the amplitudes of normalized SPLs, Sample O consistently generated normalized SPLs of ~ 10 dB less than Sample A throughout the acoustic frequency spectrum. This is attributed by the increased material density of the hybrid carbon nanostructured material present in Sample O. The increase in material density of Sample O caused an increase in $HCPUA$ (Eq. (44), section 5.3), which is a critical factor indicating the ability of the material to store heat along its contact surface when heat is introduced to it. This increase in $HCPUA$ results in rGO/3D-C storing more heat along its contact surface than 3D-C rather than dissipating heat into its surroundings. With a decreased ability to dissipate heat, the ability of Sample O to generate sound via electro-thermoacoustic hence reduces, resulting in decreased normalized SPLs.

Figure 63. Acoustic performance of Sample A compared with Sample R. (a) Normalized SPL against acoustic frequency, and (b) normalized SPL against input power at a constant acoustic frequency of 10 kHz.

Next, the acoustic performances of the samples from input powers of 0.1 to 12 W were measured at a constant acoustic frequency of 10 kHz. Figure 63b shows the plot of normalized SPL values against input power. Both the normalized SPLs of Samples A and O increased linearly with input power and normalized SPL, which is supported by previous results and simulations (section 4.2). This indicates that the deposition of rGO did not affect the behavior

of electro-thermoacoustic sound generation. Examining the normalized SPL values of Samples A and O, a consistent ~10 dB difference is observed, which is the same magnitude as the acoustic frequency spectra (Figure 63a). An equal difference in normalized SPL reinforces the hypothesis on the impact of sample porosity and material density on electro-thermoacoustic sound generation.

6.2 Hexagonal boron nitride-graphene hybrid materials

6.2.1 h-BN coated 3D-C

Another potential method to improve electro-thermoacoustic sound generation performance would be to deposit 3D-C with layers of hexagonal-boron nitride (h-BN). h-BN is a nanostructured electrically insulating [168-172] material first discovered in 1842 [173]. Its high thermal conductivity [168-170, 174-177] allows for efficient thermal dissipation, potentially increasing the high temperature gradient required for efficient electro-thermoacoustics. Its high thermal stability [170, 171, 175] also allows it to endure high temperatures, which is critical during higher power operations. h-BN is hence an electrically insulating material with thermal properties suitable for electro-thermoacoustics. An exterior h-BN coating would therefore function as a thermal interface material to dissipate heat rapidly into its surroundings, hence inducing a steeper temperature gradient and improving electro-thermoacoustic sound generation efficiency.

h-BN with thickness of 1 μm was coated on 3D-C using a High Power Impulse Magnetron Sputtering (HiPIMS) system (Mantis Deposition Ltd) utilizing recipes from [105] and [178]. Free-standing 3D-C was first adhered on a grounded sample holder before being mounted into the HiPIMS chamber and evacuated to low pressures (less than 10^{-5} mbar). Ar and N_2 were then flowed into the system as an inert carrier gas and precursor respectively. Next, the

lanthanum hexaboride (LaB_6) target was reactively sputtered by pulsing it with a power supply (Hipster 1, Ionautics) to release lanthanum and boron (B) ions. The B cations (B^{3+}) reacted with nitrogen ions (N^{3-}) to produce h-BN layers, which coat onto 3D-C. Post synthesis, sputtering was halted and the system allowed to vent in order to return to room pressure before extraction of h-BN coated 3D-C (h-BN/3D-C). Visual images of 3D-C before (Figure 64a) and after (Figure 64b) h-BN deposition *via* HiPIMS show that the macro structure of 3D-C had not been altered by h-BN deposition.

Figure 64. Visual images of 3D-C (a) before and (b) after h-BN deposition *via* HiPIMS.

Next, SEM was conducted on the samples to investigate the effect of h-BN deposition on material microstructure (Figure 65). Comparing the SEM micrographs of 3D-C before (Figure 65a) and after h-BN deposition (Figure 65b), the microstructures of 3D-C appear unchanged after h-BN deposition. This verifies that h-BN deposition did not alter the porosity of the material. The contact surface area with its surrounding medium remains high and should hence be able to retain its high electro-thermoacoustic sound generation levels.

Figure 65. SEM micrographs of (a) 3D-C and (b) h-BN coated 3D-C. SEM-EDX elemental mapping of (c) boron and (d) nitrogen.

Next, SEM-EDX elemental mapping was conducted on the strut circled in red in Figure 65b to verify the homogenous coating of h-BN. Figure 65c and Figure 65d shows that boron and nitrogen were present in the hybrid material with a 1:1 ratio, with an even coating around the 3D-C strut, suggesting that the electrical current injected into the material would uniformly conduct through the entire material.

Next, Raman spectroscopy was conducted to determine crystallinity of the BN and graphene layers and detect the presence of defects. The Raman spectrum was then compared with 3D-C (Sample A) and plotted in Figure 66. Comparing the Raman spectra of 3D-C before and after h-BN deposition, the presence of the G and 2D peaks at wavenumbers 1580 cm^{-1} and 2705 cm^{-1} respectively were retained, hence implying that graphene is present [26, 31, 34, 105, 145-147]. The intensity of the 2D peak was approximately 0.74 of the G peak ($\frac{I_{2D}}{I_G} \approx 0.74$),

indicating the presence of a few layers of graphene in 3D-C [148, 149]. This ratio is similar to 3D-C's ($\frac{I_{2D}}{I_G} \approx 0.74$), suggesting that minimal graphene had been etched away by h-BN deposition. In h-BN/3D-C, an additional peak at wavenumber $\sim 1358 \text{ cm}^{-1}$, which was absent prior to h-BN deposition, was detected. This additional peak is attributed by the presence of the D peak in graphene at $\sim 1350 \text{ cm}^{-1}$, caused by the presence of defects or doping present in 3D-C due to the bombardment of h-BN layers during deposition, as well as the presence of E_{2g} vibration mode of h-BN at $\sim 1360 \text{ cm}^{-1}$, which is contributed by the presence of h-BN in the material [26, 179].

Figure 66. Raman spectra of 3D-C before (black) and after h-BN deposition (red).

Next, XPS was conducted to evaluate if the h-BN layers had bonded to the graphene layers in 3D-C during deposition. Deconvolution of the XPS spectra of B 1s, nitrogen (N) 1s and carbon (C) 1s can be seen in Figure 67a, Figure 67b and Figure 67c respectively. In Figure

67a, deconvoluted peaks were detected at 191.9 eV and 189.8 eV, which correspond to B-O and B-C-N bonds respectively [180-183]. In Figure 67b, deconvoluted peaks were detected at 399.3 eV and 397.5eV, which correspond to the N-C and N-B bonds respectively [179, 183]. In Figure 67c, deconvoluted peaks were detected at 287.7 eV, 286.2 eV and 284.3 eV, which correspond to C=O, C-N/C-O and C-C bonds respectively [179, 180, 182-184]. Doping of h-BN onto 3D-C, which was attributed by the bombardment of h-BN layers on 3D-C, have hence been confirmed by the presence of B-C-N, N-C and C-N bonds.

Figure 67. XPS spectra of h-BN/ 3D-C. (a) Deconvoluted peaks of B 1 s, (b) N 1 s and (c) C 1 s.

Next, TGA was conducted to determine if material decomposition temperature had been altered by h-BN deposition. Figure 68 shows the plots of weight percentage against chamber temperature for both 3D-C and h-BN/3D-C. Comparing the two graphs, it can be seen that bonding between the h-BN layers with 3D-C resulted in an increase in decomposition

temperature, resulting in an improvement in thermal stability of the material. Initially, both materials showed consistent weight percentages. Oxidation of 3D-C began at 515 °C and began experiencing significant reduction in weight percentage at 605 °C, indicating the pristine crystalline quality of graphene in 3D-C [151]. Above 915 °C, almost all material had oxidized, resulting in a relatively constant weight percentage of ~0 %. h-BN/3D-C, on the other hand, only began oxidizing at 800 °C and began experiencing significant reduction in weight percentage at 850 °C. Above 1050 °C, the hybrid material has a constant weight percentage of 49 %. This is due to the presence of thermally stable h-BN, which unlike 3D-C, did not decompose [105].

Figure 68. TGA results of 3D-C before (black) and after h-BN deposition (red).

h-BN/3D-C was then adhered onto a microscope glass slide using conductive Ag paint

(Sample P) and mounted onto the acoustic measurement set-up. Figure 69a shows the graph of normalized SPL plotted against an acoustic frequency range of 1 to 14 kHz. Examining Sample A and Sample P, both samples exhibited a linear relationship between SPL and acoustic frequency. This is consistent with previous experimental results and simulations (chapter 5). Comparing Sample A and Sample P, Sample P consistently generated SPLs ~8 dB lower than Sample A. This decreased sound generation of Sample P is attributed to the defects introduced in 3D-C during h-BN deposition. The presence of defects functioned as roadblocks to phonons. Phonons are packets of vibrational kinetic energy, whereby high levels of vibrational kinetic energy can be converted into heat. A decrease in phonon movement efficiency would result in reduced efficiency of heat dissipation in the material, hence reducing electro-thermoacoustic sound generation.

Figure 69. Acoustic performance of Sample A compared with Sample P. (a) Normalized SPL against acoustic frequency, and (b) Normalized SPL against input power at a constant acoustic frequency of 10 kHz.

Next, the acoustic performances of the samples from input powers of 0.1 to 6 W were measured at a constant acoustic frequency of 10 kHz. The normalized SPL values were tabulated as seen in Figure 69b. Comparing the Sample A and Sample P, the normalized SPLs of both samples increased linearly with input power. This is in agreement with previous simulations and experimental results (chapter 5). Sample P consistently generates SPLs ~8dB lower than Sample A. This magnitude of SPL difference is the same as the acoustic frequency

spectrum, reinforcing the reduced effect of h-BN deposition on 3D-C electro-thermoacoustic sound generation.

6.2.2 3D-BNC

Other than coating a layer of h-BN onto 3D-C, h-BN can also be hybridized with 3D-C to improve electro-thermoacoustic sound generation performance. Previous studies of electro-thermoacoustic sound generation utilized only carbon nanostructured materials. While these materials have high thermal conductivity ($200 - 5000 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) [22, 23] and low specific heat capacity ($0.71\text{-}0.74 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$) [24, 25], they have low electrical resistance ($2 - 2200 \Omega$) [33-35, 81, 86, 92, 94, 102, 103]. In electro-thermoacoustics, a pronounced temperature gradient is required for sound generation. This temperature gradient is produced by the Joule heating mechanism, which is triggered by an AC needing to overcome material electrical resistance to conduct across the material. The low electrical resistances ($2 - 2200 \Omega$) of carbon nanostructured materials result in non-optimal utilization of Joule heating. A material with higher electrical resistance is hence desired for more Joule heating to achieve higher SPL generation *via* electro-thermoacoustics.

One proposition to achieve higher material electrical resistance would be the addition of electrically insulating materials to electrically conducting 3D-C. The crystal structure of h-BN is very similar to that of graphene [168-170, 172, 175, 176], allowing it to be compatible to be hybridized with graphene. Its high thermal conductivity [168-170, 174-177] allows for efficient thermal dissipation, maintaining the high temperature gradient required for efficient electro-thermoacoustics. Its high thermal stability [170, 171, 175] also allows it to endure high temperatures, which is critical during higher power operations. Studies conducted on hybrid 3D boron nitride-graphene (3D-BNC) material show tunability of its electrical and Joule heating properties with material composition while retaining its high thermal conductivity

(Figure 70) [26, 106, 185]. These results indicate the potential of 3D-BNC to utilize electro-thermoacoustics more efficiently than previously studied carbon nanostructured materials.

Figure 70. (a) Electrical, and (b) and thermal properties of 3D-BNC [26].

One method of incorporating electrically insulating h-BN into 3D-C is TCVD. h-BN can be grown into its 3D form, 3D-BN, using TCVD with a sacrificial catalytic Ni template foam, similar to how graphene is grown on 3D-C, except that growth conditions and PMMA annealing differ due to their differing elements [143, 186, 187]. 3D-BNC of various concentrations were using recipes from [26] and [106]. Ni foam (110 ppi, 2 mm thickness, Latech Scientific Supply Pte. Ltd.), was placed in the middle of the split tube furnace and the system pumped down to achieve pressures below 10^{-2} mbar. Next, H_2 , which functions as a reducing agent, was introduced while the system was thermally ramped up to 1000 °C. Ammonia borane (BH_3N) powder, which is the precursor of h-BN, was then sublimed at 120 °C. Under high heat, BH_3N vapors are converted into polyborazylene and coats on the sacrificial catalytic Ni template foam [186]. Under catalytic influence, high temperatures and the presence of H_2 , polyborazylene further decomposes into borazine ($B_3H_6N_3$) and aminoborane (BH_2NH_2) [169], before the B-H and N-H bonds present in the compounds were broken down to form h-BN on Ni [186]. Post 3D-BN synthesis, the system was allowed to return back to room pressure and stabilized with Ar and H_2 flow prior to 3D-C growth. The gases were bubbled through an ethanol bubbler, where ethanol is dehydrogenated to produce

graphene, which was coated onto the h-BN patches and sacrificial catalytical Ni template foam as graphene layers. After fabrication has been completed, the split-tube furnace was opened to allow for rapid air cooling. Next, the samples were dip-coated with PMMA and chemically etched as described in section 3.1. PMMA was then removed by annealing the material at 300 °C for an hour to obtain free-standing 3D-BNC. A schematic of the TCVD set-up and time required for the growth of various 3D-BNC compositions are as seen in Figure 71 and Table XI respectively.

Figure 71. Schematic of 3D-BNC TCVD growth.

Table XI. Growth timings for various compositions of 3D-BNC

Composition of 3D-BNC	3D-BN Growth Time (min)	3D-C Growth Time (min)
75 % 3D-C 25 % 3D-BN	10	8
50 % 3D-C 50 % 3D-BN	23	6

Post-synthesis, Raman spectroscopy was conducted on the samples to verify material crystallinity (Figure 73). Comparing the wavenumbers of the peaks present in the Raman spectra, 3D-BNC retained the G and 2D peaks present at Raman shift wavenumbers 1580 cm^{-1} and 2705 cm^{-1} respectively present in the Raman spectrum of 3D-C. The intensity of the 2D peak was approximately 0.48 of the G peak ($\frac{I_{2D}}{I_G} \approx 0.48$), suggesting the presence of multiple layers of graphene in 3D-BNC [148, 149]. In addition, an additional peak at Raman shift

wavenumber 1355 cm^{-1} was detected in 3D-BNC. This is attributed by the vibration mode of h-BN at 1360 cm^{-1} [26, 179] as well as defects introduced during the bombardment of graphene to form the overlapping layers as depicted in Figure 72 [26].

Figure 73. Raman spectra of 3D-BNC and 3D-C in red and black respectively.

Figure 72. Schematics of 3D-BN and 3D-C growth during 3D-BNC synthesis. The white and black layers represent the h-BN and graphene layers respectively [26].

Next, SEM-EDX was conducted on 3D-BNC to determine the elemental distribution of boron nitride and graphene of 3D-BNC. The obtained micrographs are as seen in Figure 74 [26]. A widespread distribution of the elements can be observed in the micrographs, verifying that h-BN and graphene were present throughout the material. However, a non-uniform distribution of carbon was also observed at various spots of the micrographs (circled in black in Figure 74). This indicates that the material has uneven distribution of h-BN and graphene. This uneven distribution could result in the injected electrical current to go along the preferred path of least electrical resistance, hence not conducting through the electrical paths with h-BN. By avoiding the electrical path with h-BN, additional Joule heating would not be achieved, resulting in no improvement in electro-thermoacoustic sound generation.

Figure 74. SEM-EDX mapping of (a) 25 % 3D-C 75 % 3D-BN and (b) 50 % 3D-C 50 % 3D-BN respectively. Red, blue and green dots represent the carbon, nitrogen and boron elements respectively [26].

Following, measurements were conducted to understand the properties of 3D-BNC to hypothesize which composition would yield the highest electro-thermoacoustic efficiency.

Macro-densities of both 3D-C and 3D-BNC were calculated to be $2 - 4 \text{ mg} \cdot \text{cm}^{-3}$, implying that that both materials have similar amounts per unit volume.

Thereafter, the materials were crushed and placed in the MDSC to obtain heat flow measurements and deduce material C_p . The results are as tabulated in Table XII. Comparing the C_p values, 3D-C has the lowest C_p , followed by 3D-BNC with 75 % 3D-C and 25 % 3D-

BN and 3D-BNC with 50 % 3D-C and 50 % 3D-BN. $HCPUA$, which indicates ability of the material to store heat along its contact surface when heat is injected into the material, is a product of material thickness, macro-density and C_p (Eq. (44), section 5.3). An increase in C_p would increase material $HCPUA$, resulting in less heat being dissipated into its surroundings when heat is induced into it. Less heat dissipation results in a less pronounced temperature gradient, and hence electro-thermoacoustic sound generation. It can hence be hypothesized that the electro-thermoacoustic sound generation performance would be in the descending order of 3D-C, 3D-BNC with 75 % 3D-C and 25 % 3D-BN and 3D-BNC with 50 % 3D-C and 50 % 3D-BN.

Table XII. C_p of pure 3D-C, 3D-BNC comprising of 75 % 3D-C and 25 % 3D-BN and 3D-BNC comprising of 50 % 3D-C and 50 % 3D-BN.

Material	C_p at 25°C (J·g ⁻¹ ·°C ⁻¹)
3D-C	0.681
75 % 3D-C 25 % 3D-BN	1.00
50 % 3D-C 50 % 3D-BN	1.20

Electrical sheet resistances of the free-standing hybrid materials were measured using the VDP method *via* a 4-point prober. The samples were then mounted onto the glass slides and their DC resistances obtained by probing the two ends of the conductive Ag paint using a multimeter as detailed in section 3.2. As investigated in Loeblein *et al.*'s study, concentration of 3D-BN is proportional to material electrical sheet resistance (Table XIII) [26] and hence sample DC resistance (Table VIII), indicating that 3D-BNC consisting of 50 % 3D-BN 50 % 3D-C could have better electro-thermoacoustic performance than 3D-C despite its higher C_p due to higher electrical resistances resulting in more efficient Joule heating [106].

Table XIII. Material electrical sheet resistance of 3D-C, 3D-BNC with compositions of 75 % 3D-C 25 % 3D-BN and 50 % 3D-C and 50 % 3D-BN.

Material	Material electrical sheet resistance ($\Omega \cdot \square^{-1}$)
3D-C	0.58
75 % 3D-C 25 % 3D-BN	15
50 % 3D-C 50 % 3D-BN	40

Subsequently, the 3D-BNCs were each adhered to a microscope glass slide with the use of Ag conductive paint prior to being mounted onto the acoustic measurement system. Their acoustic performances were measured and their normalized SPLs plotted against the acoustic frequency range of 2 to 14 kHz in Figure 75a. Examining the normalized SPLs, all three samples exhibited a linear relationship between normalized SPL and acoustic frequency, which is consistent with previous simulations and experimental results (section 5). This signifies that the addition of h-BN layers did not affect the mechanism of electro-thermoacoustic sound generation. Comparing the normalized SPLs of the samples, 3D-C (Sample A) has the best performance, followed by 3D-BNC comprising of 50 % 3D-C 50 % 3D-BN (Sample R) and 3D-BNC comprising of 75 % 3D-C 25 % 3D-BN (Sample Q). This is attributed by the difference in material C_p . Sample A has the lowest C_p , and would hence have the lowest $HCPUA$ as well. This suggests that when heat is induced into the material, instead of storing it along its contact surface, 3D-C would transmit the most heat into its surrounding medium. With more heat transmitted into its surrounding medium, 3D-C has a steeper temperature gradient and would generate more sound electro-thermoacoustically. This results in Sample A generating normalized SPLs ~8 dB and ~12 dB higher than Sample R and Sample Q respectively. However, despite having a lower $HCPUA$, Sample Q generated SPLs of ~4 dB lower than Sample R. This was attributed not only by the Sample P having a lower material

electrical sheet resistance and sample electrical resistance, but also elemental distribution in the material. The SEM-EDX micrographs of 3D-BNC (Figure 74) show non-uniform elemental distribution of h-BN and graphene present in the hybrid material. Areas with more graphene have lower electrical resistance while areas with more h-BN have higher electrical resistance. When an electrical current is passed through the hybrid material, the electrical current travelled along the path of least electrical resistance, resulting in the avoidance of h-BN. This results in Sample Q not achieving the desired improved Joule heating optimization and hence a reduction in electro-thermoacoustic sound generation.

Figure 75. Acoustic performance of Sample A, Sample Q and Sample R. (a) Normalized SPL against acoustic frequency, and (b) normalized SPL against input power at a constant acoustic frequency of 10 kHz.

While majority of acoustic applications are focused on having a low input power, there are situations where a signal generator is only able to input a low electrical current to generate desired SPLs. The non-normalized SPLs of Samples A, Q and R at a constant acoustic frequency should hence be compared as a complete investigation on the effect of the incorporation of h-BN layers into 3D-C. Figure 75b shows the measured SPLs against an electrical input current range of 0.04 to 2 A at constant acoustic frequency of 10 kHz. Examining the measured SPLs, all three samples exhibited a linear relationship between normalized SPL and electrical input current, which is consistent with previous simulations and

experimental results (section 5). This signifies that the addition of h-BN layers did not affect the mechanism of electro-thermoacoustic sound generation. To generate a SPL of 42.5 dB, Samples A, Q and R require 0.18 A, 0.08 A and 0.06 A of electrical input current respectively, which is in the same order as the amount of h-BN present in the material. When an electrical current is conducted through the hybrid material, the electrical current travelled along the path of least electrical resistance, resulting in the avoidance of electrically resistive h-BN. An increasing presence of h-BN in a material results in an increase in the electron conduction path between the electrically conductive layers. This increases the DC resistance of the material leading to lower current required to reach similar levels of Joule heating needed to generate a SPL of 42.5 dB.

6.3 Conclusion

In this chapter, the effect of hybridizing 3D-C with rGO and h-BN have been investigated. The deposition of rGO sheets onto 3D-C was random and covered the pores of 3D-C, resulting in a decrease in contact surface area and reduced electro-thermoacoustic sound generation by ~10 dB. On the other hand, the utilization of HiPIMS to deposit h-BN onto 3D-C provided a homogeneous coating of thermally conducting h-BN. The deposition of h-BN introduced defects to 3D-C, resulting in a decrease in generated SPLs by ~8 dB. Additionally, 3D-BNC, which increased DC resistance, only required a third of the electrical current conducted through 3D-C to generate SPLs of similar levels. 3D-BNC is hence a potential material which can be implemented in acoustic applications which require low electrical input currents. These studies provide approaches on configuring the composition and structure on 3D-C to improve its electro-thermoacoustic sound generation capabilities.

7 Conclusion and recommendations

7.1 Conclusion

In this thesis, 3D-C with variable parameters (e.g., macroscale size, porosity, density and thickness) have been successfully fabricated and adopted as promising candidates for electro-thermoacoustic sound generation with improved efficiencies, all of which agreed well with the values obtained from the theoretical study. Three kinds of hybrid materials including rGO/3D-C, h-BN/3D-C and 3D-BNC have been synthesized and their electro-thermoacoustic sound generation performance have been investigated through various material characterizations, acoustic and thermal measurements to gain an in-depth understanding of the underlying mechanism and key parameters involved in electro-thermoacoustic sound generation.

Firstly, 3D-C has been synthesized and characterized systematically. When the 3D-C was utilized for electro-thermoacoustic sound generation, an improved normalized SPL of 30 dB can be generated at 10 kHz at 45 °C. This is because the as-fabricated 3D-C with a low C_p of $0.68 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ possesses a lower $HCPUA$ and thermal inertia, which in turn results in more efficient heat transfer between it and its surrounding medium. In addition, an increase in strut thickness of the 3D-C by 200 % resulted in a decrease in normalized SPLs by ~25 dB, while 3D-C with increased porosity, achieved by mechanical compression, improved the generated SPLs by ~6 dB at acoustic frequencies between 10 and 50 kHz. Therefore, 3D-C with low strut thickness and increased porosity would be preferred to maximize electro-thermoacoustic sound generation performance. These acoustic experimental results show good agreement with the theoretical simulations work on the impact of 3D-C with varying material properties on the performance of the electro-thermoacoustic sound generation. This work provides new strategies from both experimental and theoretical aspects to improve the overall efficiency of the electro-thermoacoustic sound generation by the 3D-C, enabling new opportunities for the

3D-C to be used in the next-generation electro-thermoacoustic sound generation.

Secondly, electro-thermoacoustic sound generation of the 3D-C has also been improved by utilizing a “line” connection and an acoustical backing. A “line” connection increases the electrical contact area by 90 %, resulting in a decrease of 40 °C in operating temperature at an input power of 5 W and acoustic frequency of 10 kHz while generating similar SPLs. On the other hand, an acoustical backing reflects the acoustic waves generated by 3D-C, thereby increasing SPLs by ~6 dB at the acoustic frequencies between 1 and 6 kHz. A “line” connection and acoustical backing should hence be employed to enhance electro-thermoacoustic sound generation performances. This work provides effective approaches to achieve the electro-thermoacoustic sound generation with high performance which is highly desired for the development of high-performance electro-thermoacoustic sound generator to be employed in diverse applications.

Lastly, three kinds of hybridized materials including rGO/3D-C, h-BN/3D-C and 3D-BNC have been synthesized and their potential to generate sound electro-thermoacoustically have been studied. It is noted that the rGO/3D-C synthesized by random deposition of rGO on 3D-C generated a normalized SPL of ~20 dB at an acoustic frequency of 10 kHz, which is ~10 dB lower than that of the 3D-C, attributing to a significant increase in material density and a reduction in contact surface area with its surrounding medium. In addition, the h-BN/3D-C fabricated by deposition of thermally conductive h-BN *via* HiPIMS showed a slight decrease of ~8 dB in SPLs due to the defects introduced into the 3D-C during the h-BN deposition process. While h-BN/3D-C generates lower SPLs, its higher decomposition temperature (above 800 °C) suggests its potential to be utilized at high operating temperatures and in environments with high surrounding temperatures. On the other hand, 3D-BNC with a higher electrical resistance and more efficient Joule heating than those of the 3D-C generated a SPL of 42.5 dB at an acoustic frequency of 10 kHz with an AC electrical input of 0.06 A, which is 0.12 A less

than 3D-C. Therefore, 3D-BNC shows great promise for a large variety of acoustic applications, where sound generation at low electrical currents inputs is necessary. This work provides useful guidance on how to improve the composition and structure of the 3D-C to improve its electro-thermoacoustic sound generation efficiency towards next-generation sound generation applications.

7.2 Recommendations for future research

Although several interesting studies have been conducted in this thesis, there are still some opportunities and challenges remaining in the field of electro-thermoacoustic sound generation. Based on the current status and research of electro-thermoacoustic sound generation as mentioned in this thesis, a general discussion is provided below on several topics that could be further investigated to achieve sound generators with higher efficiency and broader frequency range to be utilized in next-generation electro-thermoacoustic applications.

7.2.1 Optimization of acoustic measurement set-up

Section 3.7 in this thesis has shown an acoustic measurement set-up established for the measurement of SPLs in atmospheric air. As the electro-thermoacoustic measurements were not conducted in an anechoic chamber, which resulted in a relatively high background noise (~25 dB, Figure 76) and caused lower SPLs to be masked by the noise floor. To better qualify the thermoacoustic sound generation ability and efficiency of the 3D-C, additional measurements at lower input powers and acoustic frequencies are recommended to be conducted in an anechoic chamber with low background noise to have sufficient signal to noise ratio to distinguish acoustic waves emitted from the 3D-C from its surroundings. Acoustic

measurements are also suggested to be performed at high acoustic frequencies above 50 kHz with suitable equipment to investigate the ability of the 3D-C to generate sound at higher acoustic frequencies.

Figure 76. Acoustic spectrum of background noise measured in atmospheric air.

7.2.2 Influence of bending angle of 3D-C

Previous studies have shown that material bending angle has an effect on the efficiency of the electro-thermoacoustic sound generation. As displayed in Figure 77 and Figure 78 , a bent graphene/PET showed improved electro-thermoacoustic sound generation performance at acoustical frequencies between 1 and 10 kHz [33]. In this thesis, an initial proof of concept of the ability of the bent 3D-C to generate sound has been demonstrated as shown in a supplementary video. as shown in Video S3 (<https://tinyurl.com/SupportingVideos>). To better understand the effect of bending angle of the 3D-C on its electro-thermoacoustic sound generation performance, further studies are recommended to be conducted to evaluate the potential of the 3D-C as a flexible electro-thermoacoustic sound generator.

Figure 77. Demonstration by Suk *et al.* on flexibility of graphene with PET substrate [33].

Figure 78. SPLs of graphene on curved PET in (a) convex and (b) concave positions with respect to the microphone from acoustic frequency of 1 to 10 kHz [33].

7.2.3 Optimization of simulation model

Chapter 6 in this thesis validated the two-temperature theoretical model against experimental results. This model is able to simulate the effects of changes to electrical input power, frequency of electrical signal, material size, macro-density as well as porosity on the electro-thermoacoustic sound generation performance. However, changes done to the connection between the 3D-C and the acoustic set-up, and the chemical composition of the 3D-C, which are also critical to the electro-thermoacoustic sound generation, have not been reflected in the simulation model. Therefore, future work on the improvement of the two-temperature theoretical model to reflect the impact of the connection between the 3D-C and the acoustic

set-up, and the chemical composition of the 3D-C on the electro-thermoacoustic sound generation performance is highly desired.

7.2.4 Further underwater sound generation studies

Chapters 4 and 5 demonstrated the ability of 3D-C to generate sound over a wide range of operating frequencies in air. A prototype has been constructed as a proof of concept of the 3D-C as a potential SONAR acoustic source underwater and initial SPL measurements have been taken in a water tank. Due to limitations on the operating frequency of the acoustic set-up and water tank size, measurements have only been conducted at an acoustic frequency of 50 kHz. More measurements are to be conducted at lower acoustic frequencies in larger water bodies such as a swimming pool to evaluate the ability of the 3D-C to act as a broadband SONAR acoustic source.

7.2.5 h-BN/3D-C in electrical-grid off-loading

Section 6.2.1 discusses the synthesis and properties of a novel hybrid material – h-BN/3D-C. While h-BN/3D-C generates lower SPLs, its high decomposition temperature (above 800 °C) and thermal conductivity potentially allows the material to be used in novel high-temperature applications. A potential high-temperature application of h-BN/3D-C is electrical grid off-loading. During operation, the components of an electrical grid generate heat and could result in the device overheating and failing when the device temperature exceeds the tolerable range. The electrical resistance of h-BN/3D-C could be tuned for electrical current to preferentially conduct through it and allow for Joule heating to occur, assisting the electrical grid by off-loading the input power, while the high thermal conductivity of the material allows for rapid dissipation of heat, effectively cooling the electrical grid at a faster rate and preventing

overheating.

Author's Publications and Awards

Journal

1. Z. L. Ngoh[‡], P. Guiraud[‡], D. Tan, S. Giordano^{*}, O. Bou-Matar, E. H. T. Teo^{*}, P. Pernod, P. Coquet, R. Lardat, Experimental Characterization of Three-Dimensional Graphene's Thermoacoustic Response and its Theoretical Modelling, *Carbon*, vol. 169, pp. 382-394, 2020/11/01/2020
2. Z. L. Ngoh, R. Y. Tay, F. N. Leong, M. D. Whiteside, S.S. Chng, J. J. Yu, S. H. Tsang, D. Tan, G. I. Ng, E. H. T. Teo^{*}, "Electrically insulating boron nitride coating on thin-layer graphene foam as a thermally stable electromagnetic interference shield", (Manuscript in preparation)
3. H. Li[‡], L. Jing[‡], Z. L. Ngoh, R. Y. Tay, J. Lin, H. Wang, S. H. Tsang, E. H. T. Teo^{*}, "Engineering of High-Density Thin-Layer Graphite Foam-Based Composite Architectures with Superior Compressibility and Excellent Electromagnetic Interference Shielding Performance", *ACS Applied Materials & Interfaces*, vol. 10, pp. 41707-41716, 2018/12/05 2018.
4. M. Loeblein, A. Bolker, Z. L. Ngoh, L. Li, E. Wallach, S. H. Tsang, M. Pawlik, R. Verker, N. Atar, I. Gouzman, E. H. T. Teo, "Novel timed and self-resistive heating shape memory polymer hybrid for large area and energy efficient application," *Carbon*, vol. 139, pp. 626-634, 2018/11/01/ 2018.

Conference paper and Presentation

1. Z. L. Ngoh, F. N. Leong, R. Y. Tay, M. D. Whiteside, S. S. Chng, J. J. Yu, S. H. Tsang, D. Tan, G. I. Ng, E. H. T. Teo ^{*}, "Boron Nitride Coated Three-Dimensional Graphene as an Electrically Insulating Electromagnetic Interference Shield," in 2019 IEEE MTT-S International Microwave Workshop Series on Advanced Materials and Processes for RF and THz Applications (IMWS-AMP), 2019, pp. 127-129. Oral presentation and best student paper award.

Poster and Demonstration

1. Z. L. Ngoh, D. Tan, S. H. Tsang, E. H. T. Teo ^{*}, Application of 3D-Boron Nitride C in Underwater Thermoacoustics, 2017 Journée de Palaiseau, France

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