Continuous and scalable fabrication and multifunctional properties of carbon nanotube aerogels from the floating catalyst method

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A B S T R A C T

In this work, we report on the effective implementation of the direct and scalable floating catalyst method to synthesize self-supporting carbon nanotube (CNT) aerogels at high deposition rates. Through the adaptable process conditions, the highly porous and ultralight CNT aerogels with densities ranging from 0.55 to 32 mg/cm³ are synthesized. The aerogels exhibit high porosity (>98%) and surface areas of up to 170 m²/g with tortuous pores easy accessible to molecules of interest. Their superior electrical conductivity (up to 10⁶ S/m), in comparison with CNT aerogels produced through other methods, indicates high potential for energy applications. The thermal conductivity has been observed to be within the range of 0.127–0.137 W/mK as a consequence of the ultralight structure. Polymer infiltration and subsequent curing do not disturb the three-dimensional percolating CNT network and constitute an accessible method for the production of various lightweight polymeric composites. The polydimethylsiloxane-based composites (4.5% wt) with electrical conductivity enhanced by ~16 orders of magnitude and thermal conductivity double that of pure matrix are particularly promising for use in bio-integrated devices and flexible composites.

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1. Introduction

The macro-assembling of individual carbon nanotubes (CNT) reveals an engineering approach that transforms their superior properties into versatile performance delivered by anisotropic CNT fibers [1,2], yarns [3], or two-dimensional mats and sheets [4]. The three-dimensional (3D) porous architectures of interconnected CNTs are of paramount interest with regard to a broad range of practical applications: from sustainable energy development [5] to environmentally friendly [6,7], bio-responsive [8,9], and other hi-tech materials.

3D CNT networks were first observed [10,11] in the form of viscous organogels, in which all interstitial spaces between CNTs were filled with organic liquids. Later, Chen J. et al. [12] showed that after noncovalent functionalization a robust CNT gel could not be redispersed in any organic solvents. Although their first attempt to dry this CNT gel in air at atmospheric pressure finished with its structural collapse, the idea of an appropriate drying implementation has boosted further exploration of CNT aerogels.

During the last decade, freeze- [13–15] and supercritical point drying [16–18] techniques were employed for a CNT gel-state to replace trapped solvents with air, thus giving rise to the ‘CNT aerogel’ terminology. Both these approaches are based on a stable organogel, while this technological stage demands the usage of specific chemicals like chlorobenzene, ethanol [17], and/or cross-link agents, like poly(p-phenylethynylene) [17]. In addition, the CNT aerogels derived from these methods are usually fragile [13,15,17] and require the introduction of additional binders such as poly(vinyl alcohol) [13,18] or sodium carboxymethylcellulose [15] to retain their constitution. Moreover, a thermal annealing or purification step could be necessary for enhancing the surface area and porosity [17] or removing the low-molecular-weight components of a binder after drying [18], respectively. The drying stage itself can take up to two days, or, with post-processing, may continue for one more week, as reported by Zhang et al. [18]; thus the overall process becomes enormously time-consuming.

Other methods subsequently developed on the basis of sol–gel chemistry or the so-called ‘chemical fusion’ reaction [16,19] also require a stable CNT suspension as a starting technological point. The difference, however, is the usage of an additional carbon
source, such as resorcinol and formaldehyde [16] or dextrose plus citric acid [19], and a pore foaming agent (usually ammonium or sodium carbonates), which are mandatory for the formation of a porous structure. The final porous material can be additionally annealed in an inert atmosphere at a temperature range of 900–1050 °C for pyrolytic re-organization of a disordered carbon phase into a more graphitic one [16], and the enhancement of its hydrophobicity [19].

Later, Gui et al. [20] revealed the possibility of the direct synthesis of macroscopic CNT-based porous structures using the floating catalyst chemical vapor deposition (FC-CVD) method. Dichlorobenzene was chosen as a carbon source to disturb the aligned CNT growth and obtain randomly interconnected CNTs of 30–50 nm in diameter. The reported growth rate was only 2–3 mm per hour, and, typically, a 1 cm-thick sample could be collected in 4 h. Next, Shan et al. [21] proposed nitrogen and sulphur to synergistically promote the ‘elbow’ and ‘welded’ junctions, while Hashim D.P. et al. [22] used a boron-doping CVD strategy to provide the entangled CNT network. In the latter case, even the synthesis rate was quite impressive, the results revealed predominant macroporosity (pore size >50 nm) and modest electrical conductivity of the CNT aerogels, possibly due to the large diameters of individual CNTs (up to 150 nm), and the synthesis-induced ‘elbow’ and Y-type atomic-scale defects.

In contrast to the time-consuming freeze- or critical point drying and chemical fusion methods developed so far, the single-step straightforward FC-CVD synthesis appears to be a manageable and cost-effective strategy for the production of CNT aerogels. However, until now, the process scalability to higher deposition rates in combination with precise structural control of the CNT aerogels had not been explored entirely. In this paper, we report on the efficient manufacturing of ultralight CNT aerogels with densities below 32 mg/cm³, and the possibility of synthesizing the weightless ones of densities less than 1 mg/cm³, comparable with the lightest aerogels ever reported [14]. We systematically investigate their porous structure and electrical and thermal properties with respect to the controllable morphology. Due to their porosity and superior electrical conductivity, the CNT aerogels are potentially useful for energy-storage devices, including batteries [5] and optimized binder-free supercapacitors [23]. In addition, we show that the 3D CNT network is maintained upon polymer infiltration and curing, resulting in a substantial increase in the electrical and thermal performance of their polydimethylsiloxane-based composites applicable for advanced flexible electronics [24,25] and bionic devices [26].

8.5 cm) were purchased from Rayshine Optics & Film Materials Pte Ltd. Conductive silver paste (RS 186-3600) was purchased from RS Components, UK. All the chemicals were used as received. 2. Results and discussion 3.1. Synthesis and structure characterization of the CNT aerogels 3.1.1. High-rate FC-CVD synthesis of the ultralight CNT aerogels In the floating catalyst CVD method, ferrocene is widely used as a catalyst source [129–34] and thiophene as a source of sulphur, acting as a ‘promoter’ in the field of carbon nanotube synthesis

2. Experimental 2.1. Materials Ferrocene, thiophene, ethanol, and acetone were purchased from Sigma–Aldrich Company Ltd. Methane (CH₄), hydrogen (H₂), nitrogen (N₂), and helium (He) were purchased from Chem-Gas Pte Ltd. Sapphire substrates of different dimensions (2.54 × 2.54; 5.0 × 8.5 cm) were purchased from Rayshine Optics & Film Materials Pte Ltd, and were subsequently cleaned in the ultrasonic bath for 5 min in acetone, ethanol, and DI water prior to the experiments. Polydimethylsiloxane (SYLGARD®184 silicone elastomer kit, Dow Corning) was obtained from Tat Lee Engineering Pte Ltd. Conductive silver paste (RS 186-3600) was purchased from RS Components, UK. All the chemicals were used as received.

The CNT aerogels were synthesized via the FC-CVD method by using methane (CH₄, 160 mL/min) as a carbon-source, hydrogen (H₂, 1.5–2.0 L/min) as a carrier gas, and ferrocene and thiophene as a catalyst and promoter, continuously injected at the feeding rate of 250 and 20 mL/min, respectively. Upon the chemical reaction at 1200 °C, fluffy so-called ‘elastic CNT smoke’ was self-deposited onto the clean and smooth sapphire substrate forming the 3D assembly referred to as an ‘aerogel’ (Supplementary video). Generally, the deposition time was fixed at 20 min to enable the comparable samples to be collected.

Supplementary video related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2016.02.057.

2.3. CNT aerogel composite preparation

The CNT aerogel/polydimethylsiloxane (PDMS) composites were made by direct polymer infiltration, in which a mixture of resin and hardener at a volume ratio of 10:1, as recommended by a supplier, was used as the matrix. The infiltrated specimen was then placed in the oven and cured for 2 h at 70 °C, followed by an additional 30 min at 100 °C.

2.4. Characterisation

The bulk density of the CNT aerogels was calculated as their mass-to-volume ratio. The structure and morphology of the aerogels and their composites were analyzed at 15 kV using a field emission scanning electron microscope with EDS-option (FE-SEM S4300, Hitachi); prior to this, the samples were coated with gold to minimize charging. The alignment analysis via the 2D Fast Fourier Transform (2D FFT) approach was done with ImageJ software (developed by the National Institutes of Health) and an oval-profile plug-in (authored by Bill O’Connell) available from the public domain http://rsb.info.nih.gov/ij. For analysis [27], the grayscale 8-bit images, taken at the same magnification, were cropped to 1024×1024 pixels.

Thermogravimetric analysis (TGA Shimadzu DTG60H) was done in synthetic air (oxygen 21.5%, water 5.00 ppm) from room temperature to 1000 °C at a heating rate of 10 °C/min. Nitrogen adsorption/desorption analysis was performed with a Nova 3200e (Quantrachrome) machine to characterize their structural and sorption properties; initially, the specimens were degassed at 120 °C in a vacuum for 6 h to remove water and other adsorbed molecules. Characterization of the porous structure of the CNT aerogels was done with the nitrogen adsorption/desorption analysis; the Brunauer–Emmett–Teller (BET) and Barret–Joyner–Halenda (BJH) methods were implemented to calculate the specific surface area and pore size distribution.

Electrical characterization was carried out with a two-probe method, by attaching the modified copper electrodes to the near-rectangular-shaped aerogels. Cyclic voltammograms (five cycles) were obtained over a potential range of 0.0–0.6 V at a scan rate of 30 mV/s using the Solartron 1470E analytical system. Thermal properties were characterized at room temperature using the C-Therm TCI thermal conductivity analyzer (C-Therm Technologies Ltd), based on the direct measurement of the thermal effusivity (thermal inertia) of the material [28].

3. Results and discussion 3.1. Synthesis and structure characterization of the CNT aerogels 3.1.1. High-rate FC-CVD synthesis of the ultralight CNT aerogels
[31,35]. Upon the thermal decomposition, ferrocene liberates iron nanoparticles in situ, which then efficiently catalyze the hydrocarbon decomposition and participate in the CNT nucleation and growth [29,31]. The proposed FC-CVD method does not require the catalyst pre-deposition on a substrate and the subsequent step of catalyst activation, in contrast to the common CVD process [36,37]. Moreover, because the reaction in this case is operated continuously, this principle is more suitable for a large-scale synthesis [38]. Although the carbon component available from the decomposition of both ferrocene and thiophene may enable nanotube nucleation, CNT growth via FC-CVD to a length at which they entangle and form so-called ‘elastic smoke’ mainly depends on the carbon available from the carbon precursor [31], which is methane in this work.

The high-temperature synthesis route prevents CNT growth on the reactor’s wall [29,31,39] and facilitates high reaction rates so that very long CNTs grow in the gas stream (hydrogen, used as a carrier gas and the reaction medium) within a few seconds [29,31,32]. They eventually coagulate into bundles and form an ‘elastic smoke’ by the synergy of van der Waals interactions and in situ entanglement [14,29,40] (Fig. 1 below). The ‘elastic smoke’ then travels with the carrier gas to the cold zone (with the temperature lower than ~300 °C) and the reactor’s outlet, where it can be continuously withdrawn as a fiber or mat [129–32,41] or collected on a substrate as an aerogel through the self-deposition.

Here we successfully adapt all the advantages of the established FC-CVD process for direct and fast CNT aerogel production. The aerogels can be synthesized within 10–20 min (Fig. 2 below), or collected for a longer time, depending on the specific requirements.

The sapphire substrates were chosen for their extremely high working temperature (up to 2000 °C) and exceptional hardness and scratch-resistance [42], which allows their operation at the applied synthesis temperature without degrading. Other substrates like silicone oxide [43] or quartz [6,20,22] can be potentially used in our system; the specific role of the substrate in the CNT aerogel deposition process will be the subject of future work.

By varying the size of the substrates with control of other parameters to ensure a proper comparison, a range of CNT aerogels with different sizes and densities can be produced. For example, big (several tens of cubic centimeters) yet impressively ultralight CNT aerogels with densities of 0.55–1.50 mg/cm3 were synthesized using the substrate of 5.0 × 8.5 cm (Fig. 3 below). These aerogels are noticeably lighter than the CNT aerogels synthesized so far via thefreeze-drying [13–15], critical point drying [16–18], FC-CVD [20], and boron-doping CVD [22] methods, and are even comparable with the lightest graphene aerogels ever reported [14].

In addition, the CNT aerogels are not brittle and are extremely stable during handling, which means that they can be easily transferred from the substrate and undergo further manipulations. As shown in Fig. 4 below, even the ultralight aerogels can withstand a weight of up to 150 times higher than their own (~15,000 times higher than their density) without collapsing.

However, it should be mentioned that our lightest aerogels, although undoubtedly stable in air, were not stable in a liquid medium. In contact with solvents (ethanol, acetone), their intrinsic 3D CNT network underwent further condensation into the dense structure, the process similar to the in situ condensation of the ‘elastic smoke’ into CNT fibers [1]. Despite this present difficulty, the aerogels have great potential for further structural modification (macromolecule cross-linking or carbon/graphene coating [40]) to stabilize their ultralight structure in a different chemical environment, and especially in contact with polymetric, metal, or ceramic matrixes. In any case, the unique combination of light density and mechanical stability potentially enables the CNT aerogels to compete in the future with conventional porous materials like Rohacell [46,47] for usage in low-density sandwich constructions and complex 3D geometry composites.

Subsequently, to unify the synthesis route and to control the structure and multifunctional performance of the CNT aerogels, the aerogels were collected equally on the substrates of the same size (2.54 × 2.54 cm) for 20 min, resulting in a similar near cubic-shape with dimensions of about 1.5–2.0 cm for width, length, and height.

3.1.2. Porous structure and morphology of the CNT aerogels

Fig. 5 below displays the typical nitrogen sorption isotherms, with the pore size and cumulative sorption volume data, for the CNT aerogels synthesized under different conditions (with variations in H2 flow rate and catalyst input).

According to the IUPAC classification, the type IV isotherms with a very small hysteresis provide evidence of the porous structure of the aerogels.
predominantly formed by mesopores. Indeed, the pore size distribution analysis of all aerogels reveals multiple narrow peaks with an average diameter of 3.6 nm, which is very close to the low limit for the mesopore range (2–5 nm). The observed hysteresis loops are the H3 type with noticeable characteristic desorption shoulders and lower closure points located in the region of ~0.45 P/P₀. Isotherms with the type H3 hysteresis do not exhibit any limiting adsorption at high P/P₀, which can be associated with a low degree of pore curvature [48] and non-rigidity of the aerogel structure [49] formed by the interconnected CNT bundles, and is also typical of disordered mesoporous systems and materials consisting of three-dimensional pore networks [50].

In practice, the CNT assemblies synthesized via FC-CVD consist of highly oriented CNT bundles, which are aligned in the synthesis direction in the case of CNT fibers and mats [1,31,32,34,51]. The 3D structure of CNT aerogels can be considered an example of the reticulated (net-like), extremely open foam, where only the lineal boundaries remain (presented by nanotube bundles), while all the classical “bubbles” or “cells” (attributes of the closed-cells or semi-closed foams) have disappeared [52]. The detected mesopores of several nanometers can be attributed to the distance between the CNT bundles in the points of their contact and entanglement. At the same time, the specifics of the pore network may affect the shape of the H3 loop, where the lower closure point depends on the pore size and geometry, as was shown for pore diameters smaller than about 11 nm [49]. In light of this, the number of co-synthesized impurities may change the hysteresis appearance and shape, from a very narrow split between the adsorption and desorption branches for the CNT aerogels synthesized at a 1.5 H₂ flow rate to a hysteresis with noticeable desorption shoulders for a higher H₂ flow rate.
As is known from existing literature, synthesis parameters such as the carrier gas flow rate and catalyst input may affect the synthesis of the CNT materials, causing formation of different amounts of carbonaceous impurities and residual catalyst particles, which can be trapped by the growing CNT network [29,31]. In our case, a higher H2 flow rate leads to a higher amount of Fe-catalyst residue fixed within the aerogel (Supplementary information, S1), with a negative impact on the specific surface area and adsorption volume as a result (Table 1 below, samples 3 and 4).

The aerogels collected at the same carrier gas flow rate, on the same substrate, for the same deposition time, and with similar shapes and dimensions exhibit densities nearly twice as low as the others’, as a possible consequence of the 2.5-times-lower catalyst input (Table 1, samples 1 and 2), indicating that a lower number of impurities are co-synthesized.

In fact, morphological analysis shows that for the standard synthesis regime (sample 1) the co-synthesized impurities are mostly located in the points of contact between the CNT bundles with an average diameter of 31.5 ± 4.0 nm (Fig. 6 a, b below). Instead, reducing the catalyst input (sample 2) results in fewer impurities obviously detectable within the CNT network (Figs. 6 c, d), while the bundle diameter increases to 37.4 ± 3.5 nm. The aerogel possesses a slightly lower surface area of 158 m2/g, possibly due to the formation of more clean CNT bundles with larger diameters. A similar relationship between the bundle size and surface area has been theoretically predicted [53] and observed for an aerogel made of single- and double-walled CNTs [17].

The highest surface area (170.1 m2/g) and pore volume (0.276 cm3/g) were detected at the conditions corresponding to the stable spinning process (Table 1, sample 1). According to our recent TEM observations [54], the synthesized multi-walled carbon nanotubes have an average outer diameter of ~15 nm, with a Raman intensity ratio, I_G/I_D, of about 2.4 [55], highlighting the relatively low number of structural imperfections (Supplementary information, S2). The aerogels possess high porosity (>98%), calculated on the basis of their bulk density and the CNT density being assumed to be 2.0 g/cm3, according to the proposed values for CNTs with outer diameters of 15–20 nm and 15–20 walls [56]. However, the macro pores, which are formed as the spare space of hundreds of nanometers between the bundles (Figs. 6 a, c), cannot be analyzed by the N2 adsorption/desorption method.

The observed specific surface area was at a level comparable to that of some aerogels formed through the critical point drying [16] or freeze-drying methods [13–15]. The porous structure and surface area can be further enhanced by minimizing the number of co-synthesized impurities [29,31], by the tailored synthesis of double- or single-walled CNTs with controllable diameter [29–32,57], or by chemical post-treatments [58], while the density can be varied by utilizing the densification techniques used for CNT arrays [59,60]. High sorption properties make the CNT aerogels exceptional materials for environment-targeted functions, such as sorption, filtration, and separation [6,7]. Apart from this, their porous structure remains easily accessible to host any other molecules of interest (metal/colloids nanoparticles, bio-molecules etc.), thus broadening their practical utilization.

### Table 1

<table>
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<tr>
<th>No</th>
<th>Synthesis parameters</th>
<th>Density, mg/cm³</th>
<th>Porosity, %</th>
<th>BET surface area, m²/g</th>
<th>Total pore volume, cm³/g</th>
<th>BJH mean pore size, nm</th>
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<td>H₂ flow, L/min</td>
<td>Fe input, mL/min</td>
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<td>1</td>
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<td>98.81</td>
<td>170.1</td>
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<td>100</td>
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<td>98.34</td>
<td>158.2</td>
<td>0.248</td>
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<tr>
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<td>250</td>
<td>31.8</td>
<td>98.41</td>
<td>153.2</td>
<td>0.198</td>
</tr>
<tr>
<td>4</td>
<td>2.0</td>
<td>100</td>
<td>22.3</td>
<td>98.89</td>
<td>120.0</td>
<td>0.206</td>
</tr>
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</table>

### 3.2. Electrical properties of the CNT aerogels

In order to investigate the electrical conductivity of the aerogels, the current–voltage (I–V) curves were taken with a two-probe technique using the Solatron analytical system. Usually, a sample should be connected to two electrodes with a conductive paste to minimize the contact resistance [61]. However, due to its highly porous structure, an aerogel can absorb a paste uncontrollably, leading to potential misrepresentation of the electrical performance and the impossibility of re-using the sample. To avoid these problems, we have modified the copper electrodes instead of the tested specimens, as shown in Fig. 7 (a) below. The main aim was to enhance contact between the smooth copper plate and the rough aerogel surface, in a manner that would not destroy or damage the samples; we achieved this by attaching a thin wavy CNT mat to the copper surface with several pattern lines of a conductive silver paste. In each case, the synthesis conditions and size of the CNT mat were the same as those of the tested aerogel, minimizing any potential effect.

The typical I–V curves (Fig. 7 a), according to Ohm’s Law, exhibited a linear relationship between the applied voltage and the resulting electric current, which were then used for conductivity evaluation.

Interestingly, while measuring the electrical conductivity of the 3D nanotube network through thickness (electrodes were attached to the top and bottom of the aerogel) and in-plane (electrodes were connected to the left and right sides of the aerogel), we observed anisotropic behavior, with the in-plane conductivity 3–5 times higher than in the through-thickness direction. Despite numerous strong and divergent connections throughout the whole 3D structure of the CNT aerogels (Fig. 7 c), some nanotube bundles may have intrinsic preferences for and/or more compact organization in one plane rather than another, as a consequence of the self-deposition process. As can be seen in Fig. 4 (a) and the Supplementary video, rapidly grown ‘elastic CNT smoke’ initially forms a planar network of randomly oriented CNT bundles, then undergoes layer-by-layer stacking, forming the 3D aerogel structure.

In terms of practical applications, further understanding of the CNT network formation and its anisotropy is necessary. However, the obtained results show that the CNT aerogels synthesized in this study possess superior electrical conductivity even at a certain degree of anisotropy. The through-thickness conductivity (20–27 S/m) is comparable to or noticeably higher than the values achieved for the CNT aerogel coated with graphene [40], pure graphene, or graphene/CNT aerogels [62]. The in-plane conductivity (90–106 S/m) is far beyond that of the CNT aerogels synthesized using the freeze-drying [14,15], critical point drying [17,18], or boron-doping CVD [22] methods.

### 3.3. Thermal properties of the CNT aerogels

The thermal conductivities of the aerogels measured through-thickness by the TCI thermal conductivity analyzer were found to be only 0.197 and 0.127 W/m·K (for the carrier gas flow rates of 1.5 L/min and 2.0 L/min, respectively). These values are generally
comparable with the thermal properties of other highly porous carbon materials [20,63] (Table 2 below; note that the specifics of different experimental techniques were not compared), including graphene-based aerogels (0.120–0.360 W/m K) [64] and commercial carbon fiber paper (0.210 W/m K) [65]. Although the theoretically predicted and experimentally proven thermal conductivity of individual multi-walled CNTs can approach 3000 W/m K [66,67], it is not surprising that such low values were obtained

Fig. 6. Typical CNT network of the aerogel samples synthesized at (a, b) normal and (c, d) low catalyst input regimes, with the histograms of CNT bundle diameter distribution (b, d). (A color version of this figure can be viewed online.)

Fig. 7. (a) Representative current–voltage (I–V) curves (5 cycles). The insert is a general view (not scaled to the real size) of the modified copper electrode: (1) a copper plate, (2) CNT mat used for better contact between the smooth copper plate and the rough aerogel surface, (3) silver paste. (b) Anisotropic electrical behavior of the CNT aerogels. (c) Side-view of the CNT aerogel showing its layer-sequence of randomly oriented CNT bundles with numerous connections between layers. (A color version of this figure can be viewed online.)
for the CNT aerogels. Aside from the possible structural defects and the coupling of CNTs into bundles [68], the low density and extremely high porosity (>98%) of the aerogels, in which all tortuous pores are occupied by air (thermal insulator, 0.026 W/m K), have been revealed to be the primary factors affecting the thermal transport.

Speaking of the different CNT assemblies (fibers, mats, or aerogels), it is to be expected that their thermal conductivity would be hugely affected by the complex morphology (alignment etc.), structural density, and contact resistance between nanotubes [69]. In view of this, the more compact structure potentially results in higher thermal conductivity.

Therefore, condensed CNT fibers exhibit thermal conductivity at the level of 400 W/m K [2,70], while vertical CNT arrays [71,72] or CNT mats on their basis [68] show significantly smaller values as a consequence of larger tube-to-tube spacing and structural imperfections like CNT loops, misalignment [68], and crossing [69]. Thermal transport is hindered even more within randomly oriented CNT mats [73], whose conductivity is at the level of CNT aerogels and thermally insulating polymers (0.13–0.19 W/m K). Due to their low thermal conductivity and high surface area, the CNT aerogels are potentially useful in thermal insulation [74], thermoacoustics [75,76], and other applications for which this synergy is profitable.

Our first experiment with conditions less catalyst input proved successful in reducing the overall number of co-synthesized impurities and amount of catalyst residue trapped by the CNT network, with more clean bundles formed, as illustrated in Fig. 5. As a result, the thermal conductivity of the aerogel was enhanced from 0.197 to 0.237 W/m K, possibly due to better contact between the CNT bundles. Other factors such as the presence of defects and impurities, as well as the preferential orientation of CNT bundles, would be of interest for further investigation.

### Table 2
Thermal properties of the CNT assemblies with highly porous and compacted structures.

<table>
<thead>
<tr>
<th>Material</th>
<th>Synthesis/assembly method</th>
<th>Thermal conductivity, W/m K</th>
<th>Experimental technique*</th>
<th>Reference</th>
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<tr>
<td>Highly porous CNT assemblies</td>
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<tr>
<td>CNT aerogel</td>
<td>FC-CVD</td>
<td>0.080–0.140</td>
<td>—</td>
<td>[20]</td>
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<td>Freeze-drying</td>
<td>0.160–0.710</td>
<td>Comparative method</td>
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<td>CNT aerogel</td>
<td>FC-CVD</td>
<td>0.127–0.237</td>
<td>MTPS</td>
<td>This work</td>
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<td>Compacted CNT assemblies</td>
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<tr>
<td>CNT fibers</td>
<td>Dry-spinning from vertical CNT arrays</td>
<td>448</td>
<td>T-type probe</td>
<td>[70]</td>
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<tr>
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<td>Wet-spinning</td>
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<tr>
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<td>2.1–3.5/up to 267</td>
<td>FDTD/PSTTR</td>
<td>[71][72]</td>
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<tr>
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<td>Drawing from vertical CNT arrays</td>
<td>50</td>
<td>3 Ω</td>
<td>[68]</td>
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<tr>
<td>Random CNT mats</td>
<td>Pressing a CNT powder</td>
<td>0.13–0.19</td>
<td>ASTM D5470</td>
<td>[73]</td>
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</tbody>
</table>

*MTPS — Modified transient plane source.
FDTD – Frequency domain thermo reflectance.
PSTTR – Phase-sensitive transient thermo reflectance.

Note that the specifics of different experimental techniques are not compared, and can be found in the appropriate literature source.

#### 3.4. Structure and multifunctional properties of the CNT aerogel/PDMS composites

Due to the highly porous structure formed by the interconnected CNT bundles, which is easily accessible for direct polymer infiltration, the CNT aerogels possess high potential for the development of composites. In this work, the CNT aerogel composites were manufactured using polydimethylsiloxane (PDMS) as a matrix. This silicon-based polymer was chosen as a reference point to compare the effects of our CNT aerogels with those of other CNT or graphene assemblies previously used for PDMS composites [77–79]. However, being generally inert, nontoxic, and non-flammable, PDMS is a preferable matrix for bio-integrated applications [24,26,80] and advanced flexible electronic composites [81].

The structure’s formation occurred through the self-driven infiltration with the liquid polymer precursor (the resin/hardener mixture) and its subsequent curing within the CNT network. Morphological analysis showed that the CNT aerogel was completely infiltrated with the polymer at 4.5% weight fraction of CNTs (Fig. 8 below). Even though no pressure or vacuum was applied for infiltration, we should note that the initial thickness of the aerogel was slightly reduced as an outcome of polymer wetting. In addition, distinctively different surface patterns were observed as a possible consequence of the CNT bundles’ re-arrangement. Fig. 8 (a) illustrates the CNT bundles fully covered with the matrix, and Fig. 8 (b) shows that some of them were preferentially aligned and stacked together. Liquid polymer infiltration may induce condensation of the CNT network into a more compact structure via re-arrangement and merging of some CNT bundles [41,82], while still preserving their 3D macro-organisation and overall flexibility.

![Fig. 8. Surface morphology of the CNT aerogel/PDMS composite with (a) randomly and (b) preferentially aligned CNT bundles as a consequence of CNT arrangement and polymer infiltration. The inserts are derived from the 2D FFT analysis of the corresponding images, showing (a) random and (b) anisotropic intensity distribution. (A color version of this figure can be viewed online.)](image-url)
The electrical conductivity of 33 S/m reached in this study (Table 3) is noticeably higher than values reported for the PDMS composites with graphene [79], CNT vertical arrays [78], and CNT powder at the same weight fraction [77]. The significant increase (~16 orders of magnitude) in the electrical conductivity in comparison with the pure PDMS matrix (Table 3) confirms the fact that the CNT percolated network was not disturbed by polymer macromolecules upon infiltration and curing. Furthermore, the thermal conductivity of the composite was found to be twice as high as that of the pure matrix and almost three times as high as that of the CNT aerogel itself.

We can explain these results with a synergy of two factors. The first is the formation of a more compact CNT network during the polymer infiltration, which increases the number of contacts and provides more opportunities for phonon transfer between neighboring CNTs. The increased packing density of the nanotubes can simultaneously enhance the thermal conductivity of the aerogels [84]. A similar increment in the thermal conductivity as a result of enhanced density of the vertical CNT arrays caused by epoxy infiltration has also been reported in the literature [82]. The second factor is the replacing of air within the spaces between the CNT bundles with the polymer, resulting in relatively lower thermal resistance, and thus more effective thermal transport within the composite.

4. Conclusions

We have demonstrated the efficiency of the scalable FC-CVD method for direct facile manufacturing of the self-supporting CNT aerogels. High process rates and conditions implemented for the synthesis of the high-performance CNT fibers have been shown to be effective for aerogel formation with controllable density and porosity. With the established process, the ultralight CNT aerogels were synthesized with densities below 32 mg/cm³, with the density of the lightest ones being only 0.55 mg/cm³. To the best of our knowledge, these are the first reported CNT aerogels lighter than 1 mg/cm³, and are comparable with the lightest graphene aerogels ever reported.

The obtained aerogels exhibit high porosity (>98%), surface areas up to 170 m²/g, and superior electrical conductivity (up to 106 S/m), which is beneficial to sustainable energy development and environmental applications. The thermal conductivity has been observed to be within the range for other porous carbon materials (0.127–0.137 W/mK), making the CNT aerogels potentially useful in thermal insulation, thermoacoustics, and other spheres in which the combination of low thermal conductivity and high surface area is important.

Polymer infiltration does not disturb the 3D CNT network, but can cause its compaction, enhancing electrical and thermal transport within the composite. The high electrical conductivity of a CNT aerogel/PDMS composite (33 S/m) indicates its potential for use in bio-integrated materials and devices. In addition, the intrinsic 3D organization of CNTs and their easily accessible fabrication method offer an effective approach for the production of various lightweight polymeric composites.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2016.02.057.

References


Table 3

<table>
<thead>
<tr>
<th>Material</th>
<th>CNT fraction, %wt</th>
<th>Electrical conductivity, S/m</th>
<th>Thermal conductivity, W/m K</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS pure</td>
<td>0</td>
<td>0.35 10^-14</td>
<td>0.270</td>
</tr>
<tr>
<td>CNT aerogel/PDMS</td>
<td>4.5</td>
<td>33</td>
<td>0.583</td>
</tr>
<tr>
<td>CNT powder/PDMS</td>
<td>4.5</td>
<td>10^-4 10</td>
<td>182</td>
</tr>
<tr>
<td>CNT vertical arrays/PDMS</td>
<td>1% vol</td>
<td>0.35 (in axial direction)</td>
<td>–</td>
</tr>
<tr>
<td>Graphene/PDMS</td>
<td>0.6</td>
<td>0.07–0.10</td>
<td>–</td>
</tr>
</tbody>
</table>

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