Synthesis and mechanism perspectives of a carbon nanotube aerogel *via* a floating catalyst chemical vapour deposition method

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Abstract. An effective and cost-effective approach to synthesize new materials can be determined *via* research on a carbon nanotube (CNT) aerogel. This review paper gives an overview of the current synthetic methodologies and routes to enhance understanding. It also investigates the appropriate issues on the development of CNT-based three-dimensional (3-D) porous materials in an attempt to fill the knowledge gap regarding viability. First, an elaborate description on CNTs is provided, followed by a focus on CNT macrostructure fabrication, showcasing their key features, disadvantages, advantages and other aspects that were considered as related. Then, the methods for synthesis pertaining to the CNT aerogel are discussed with a focus on a floating catalyst chemical vapour deposition method as well as the growth mechanism pertaining to CNTs employing the method. Key parameters, including catalyst, reaction time, carbon source, carrier gas and reaction temperature, which could cast an impact on the efficiency of the process are discussed subsequently.

Keywords. Carbon nanotubes; carbon nanotube aerogel; floating catalyst chemical vapour deposition; mechanism.

1. Introduction

Developing technologies, such as sensors, energy storage and water treatment, have contributed to the rise in demand for synthesizing elastic, lightweight and robust materials. Apart from these, controlled porosity is capable of offering a range of functionalities like low density, high-surface area, great transport characteristics and mechanical integrity [1]. Engineering and scientific challenges are faced when producing and designing these structures with regard to the applied dimensions and simultaneously managing precise control over their physical and chemical characteristics at the nanoscale level. Low density and broad usage of carbon nanotubes (CNTs) in numerous applications make them more attractive. Encouraged by natural structures [2], three-dimensional (3D) porous CNTs can be created with macroscopic design, possessing all characteristics of CNTs, which could be leveraged to enjoy the superior performance for a range of applications. The major forms of 3D macroscopic design pertaining to CNTs include CNT yarn [3], CNT array [4], CNT sponge [5], CNT ribbon [6] and CNT aerogel [7].

CNT aerogel is deemed as a potential candidate material that can be used in different types of critical applications like sensors for photocatalysis, water treatment, detecting gas, pressure and chemical vapour, catalysts for chemical

adsorption, electrodes in supercapacitors, Li-ion batteries, microbial fuel cells, environmental materials to remove chemicals, dye-sensitized solar cells, biomaterials for tissue engineering and for the capacitive desalination process. Thus, the development of reliable routes pertaining to CNT aerogel fabrication can be attributed to such high-value applications [8].

CNTs can be generally synthesized by practicing three methods: arc discharge, laser ablation and chemical vapour deposition (CVD). Single-walled carbon nanotubes (SWCNTs) are practically synthesized through arc discharge and laser ablation methods, these techniques imply using graphite or coal as a carbon source, consequently vapourized to deposit CNTs. These techniques produce high-quality CNTs, nonetheless, arc discharge generation and laser ablation consume high energy, leading to high costs for energy source and equipment. In contrast, multi-walled (MW) and SW CNTs are able to grow conveniently by using the CVD technique. Furthermore, for the large scale production of CNTs, CVD is conceded the adequate choice in comparatively low cost under moderate growth conditions [9].

Moreover, the floating catalyst chemical vapour deposition (FCCVD) method can be employed to prepare a CNT aerogel by the direct self-sustaining assembly of CNTs when in the vapour phase [10–12]. With this approach, dens of the CNT aerogel can be produced in just one step, which is beneficial for large-scale productions.

Figure 1. Conceptual diagram of (a) SWCNTs and (b) MWCNTs depicting typical dimensions of length, width and inter-tube separation in MWCNTs [14].

2. CNTs

CNTs include rolled graphene sheets that have a tendency to form cylinders along with a hexagonal sp^2 carbon layer. The diameter of tubes is measured in terms of a nanometre, while their lengths can reach several micrometres. The curved sp^2 graphene layers confer the unique properties of CNTs by employing additional quantum restraining as well as topological limitations of graphene cylinders' circumferential direction [13]. CNTs can be segmented into two major groups: MWCNTs and SWCNTs. A single graphene layer can be found in SWCNTs rolled up into a cylinder, while MWCNTs consist of two or more graphene sheets' coaxial cylindrical layers held by van der Waals forces due to the proximity of layers cluttered around a central hollow core [14] (figure 1). MWCNTs are provided high-electrical conductivity, outstanding tensile strength, thermal stability and appropriate chemical stability, so as to improve the composite characteristic of the materials, which revealed the most promising prospects for practical applications [15].

As presented in figure 2, the fold direction of graphene sheets directly impacts the characteristics of SWCNTs. Integer indices (n, m) define the fold direction of the graphene sheets. The number of unit paths is signified by integers n and m , which are along two directions in graphene's honeycomb-like crystal lattice. The CNTs are referred as zigzag nanotubes when $m = 0$, while they are referred as armchair nanotubes when $n = m$; else, they are referred as chiral [16,17]. SWCNTs show more electrical conductivity than MWCNTs. Depending on chirality which determines the electrical conductivity, the band gap of SWCNTs is varied from 0 to 2 eV which exhibit semiconducting or metallic behaviour. While MWCNTs' electrical conductivity relatively complex due to the multi-wall interactions distributes the current irregularly through individual tubes. SWCNTs reveal an extraordinary fluorescence response and optical absorption as the chirality indicates their individual characteristics [18,19]. Meanwhile, the distinctive multi-wall structure of MWCNTs, which

Figure 2. (a) Roll-up of a graphene sheet leading to three different kinds of SWCNTs and (b) the structure of MWCNTs made up of three shells of differing chirality [17].

permits the outer wall to be functionalized selectively, while preserving intact inner tubes, MWCNTs can obtain more chemical stability than SWCNTs [20]. This property is crucial for the functionalization of CNTs, especially when CNTs' surface structure is modified *via* chemical methods to match the requirements pertaining to a specific application [17].

3. CNT macrostructure fabrication

The CNTs' macrostructure includes 3-D macroscopic CNT-based hierarchical porous structures, like sponge, foam and cotton or aerogel under different conditions. Considerable interest has been attracted by the CNT macrostructure, thereby expanding the importance of CNTs, both in practical applications and fundamental sciences. High-surface area, high-mechanical strength, high elasticity, high porosity, excellent conductivity and significant absorption properties even at extremely low density are associated with different CNT macrostructures. Generally, the fabrication pertaining to the CNT macrostructure can be categorized into randomly interconnected and vertically aligned arrays. The recent progress pertaining to the rational design as well as the preparation of the CNT macrostructure is reviewed in the following subsection.

3.1 Vertically aligned and randomly interconnected array CNTs

Three major techniques can be employed to directly create CNTs: laser ablation, arc-discharge and CVD [21]. Amongst all synthesis approaches, the most frequently employed method to prepare CNT is CVD, due to its ability to grow all types of CNTs with long individual tube lengths, which achieves better electrical properties. Furthermore, CVD is

Figure 3. Growing of SWCNT forest along with water-assisted CVD. (a) Image of a 2.5 mm tall SWCNT forest on a 7×7 mm silicon wafer. A matchstick placed on the left and on the right, ruler showing millimetre markings to refer the size. (b) The SWCNT forest SEM image; scale bar = 1 mm. (c) The SWCNT forest ledge's SEM image; scale bar = 1 mm. (d) Nanotubes' low-resolution TEM image; scale bar = 100 nm. (e) SWCNTs' high-resolution TEM image; scale bar = 5 nm [28].

unique for large-scale production of CNTs at a relatively low cost and under appropriate growth conditions [22]. The common procedure employed here is decomposition of carbon sources near the catalyst particle surface at the pre-specified temperature and pressure, when CNTs start to grow from the catalyst particles *via* the vapour–liquid–solid (VLS) mechanism [23]. Moreover, CVD is considered the most efficient technique to perform scalable manufacturing for many oriented and aligned CNTs possessing macro- and micro-lengths [24–27]. Thus, CVD is employed to produce high-quality CNT macrostructures as well as long individual CNTs. Hata *et al* [28] employed the CVD method (figure 3) to prepare vertically aligned SWCNT arrays. Nonetheless, the large-scale synthesis of SWCNTs involves the production of impurities that can be removed *via* purification steps, which could be detrimental for SWCNTs. To resolve this issue, the amorphous carbon from the catalyst surface was eliminated *via* the water-assisted CVD approach, which allowed millimetre scale formation of vertically aligned SWCNT arrays.

Also, a measured quantity of water is supplemented to enhance the activity and lifetime of the catalysts. It was found that maximizing the catalytic lifetime was crucial and was achieved by maintaining a balance between the qualified

amount of water and precursors. With this regard, 2.5 mm-high SWCNT forest grown over 10 min was considered as the best result.

Later, carbon macrostructure fabrication generally involved in modifying and employing the CVD technique. In addition, Zhang *et al* [29] put forward a molecular oxygen-assisted plasma enhanced-CVD (PE-CVD) method to synthesize high yields of vertically aligned SWCNT arrays. Ci *et al* [30] made use of the water-assisted CVD route for growing free-standing and MWCNT arrays, which allowed extending the CVD techniques to construct 3-D CNT arrays. At large, the potential applications were always found to be limited due to the substrate choice and tube length.

Thus, it is important to grow longer tubes with regard to new substrates for different types of situations. Cao *et al* [31] employed an advanced FCCVD approach for growing free-standing CNT arrays, ca. 1 mm high that possessed super-compressibility characteristics. Also, the same technique was used in the synthesis of CNT arrays on metallic substrates, which showed improved electron field emission characteristics [32]. In this approach, first, a solution was prepared in 100 ml of xylene by dissolving 1 g of ferrocene, after which a syringe pump was employed to inject into a quartz tube. In their study, each nanotube was electrically end-contacted, after which they were metallized for realistic devices. The same authors also developed a 3-D substrate (Inconel 600 substrate) that was structurally tuneable by making use of vertically aligned CNT arrays, which demonstrated an exceptional surface-enhanced Raman scattering performance [33]. Based on this investigation, the floating catalyst method was seen to produce high-density CNT forests, while low-density CNT forests were produced by the fixed catalyst method [34]. Recently, Cho *et al* [35] presented a growing of record-long (21.7 mm) MWCNT arrays that were vertically aligned. They perfectly optimized the ethylene and H_2 ratios as well as water concentration to extend the lifetime of the catalyst. They found profound differences in mechanical characteristics when CNT diameter and density were tuned for the vertically aligned CNTs grown *via* floating-catalyst or fixed-catalyst CVD approaches.

Alternatively, the CVD technique can also be employed to produce randomly interconnected CNT arrays. For example, other forms of the CNT material (CNT cotton) were reported by Zheng *et al* [36] (figure 4). This CNT cotton was similar to traditional cotton in terms of several characteristics like fluffiness, colour and lightweight and could also be spun. CNT cotton showed properties such as low density, hydrophobic in nature and ultra-long distinct three-dimensional CNTs. A catalytic chemical vapour deposition (CCVD) technique was employed to produce CNT cotton. $CoCl_3$ and $FeCl_3$ were dissolved in ethanol to prepare a catalyst solution. Then, the coating of the catalyst solution was applied to a silicon substrate. The substrate was positioned at a quartz plate focal point, after which it was placed on the quartz plate into the quartz tube furnace. Then, a mixture of gases containing hydrogen (H_2) and argon (Ar) was introduced, after which the

Figure 4. (a) CNT cotton on a 35 mm long. (b) SEM images depicting CNT cotton spun into fibres. (c) A segment of a CNT fibre spun from the CNT cotton [36].

furnace was heated at 900°C. Towards the end of the quartz tube, the produced CNT cotton could be identified. An in-house spinning setup was employed to spin the CNT cotton into fibres. An adjustable speed drill that had a metal tip size of 25 μm was employed to spin the fibres continuously out of the CNT cotton. For the initial attachment to occur, a layer of glue was used for coating to a CNT sliver, and then, the drill was dragged from CNT cotton at a speed rate of 10 mm min^{-1} and 1000–2000 rpm. Figure 4b and c shows individual CNT collection in the form of cotton *via* fibre spinning. The collected fibre is aligned towards the pulling direction [36].

Gui *et al* [37] randomly self-assembled CNTs into a 3-D framework that had great robustness as well as high flexibility to prepare macroscopic CNT sponge (figure 5). To achieve this, they used a modified-FCCVD technique. Dichlorobenzene was added as a carbon source to interfere with the growth pertaining to CNTs' alignment. Thus, random stacking of CNTs into an interconnected structure was carried out. Great robustness and high-mechanical flexibility were found with the obtained CNT sponge that had self-assembled CNT frameworks.

In a different case, a viscoelastic CNT macrostructure was developed by Xu *et al* [38] by employing a random network of long CNTs. Here, reactive ion etching (RIE) was combined with a film of the catalyst by making use of the water-assisted CVD method to decrease the CNT area density. Long CNT assemblies were found to have crossed with high-density irregular physical interconnections, analogous to aggregating hair. Addition of RIE disclosure was found to decrease the density of the catalyst to construct randomly oriented 3D CNTs. At the same time, long and pure CNTs can be prepared by employing the water-assisted CVD technique. The material density could increase due to the final compression process. Temperature-stable viscoelasticity was demonstrated by the as-prepared CNT material, in the range of -196 to 1000°C .

Figure 5. Optical and SEM images of CNT sponges: (a) optical image of CNT sponges, (b) cross-sectional SEM image of the sponge, (c) TEM image of large-cavity, thin-walled CNTs and (d) elucidation of the sponge comprising CNT piles [37].

Zhong *et al* [39] employed water vapour to spin CNT yarn from CNT sock. Thiophene was used as a promoter, ferrocene as a catalyst and ethanol as a carbon source. The temperature was increased and the flow of argon was employed to evacuate the furnace tube. At 1150°C, the furnace temperature was stabilized, after which hydrogen was allowed to flow into the furnace tube at a rate of 1000 sccm. A stable CNT assembly and continuous densification and spinning could be achieved by employing the gas-phase CVD technique.

Recently, the FCCVD method has gained popularity in preparing CNT aerogels (figure 6) with hydrogen as a carrier gas and methane as a carbon source. The process is initiated by first preparing a solution with the help of thiophene as a promoter and ferrocene as a catalyst, and then an injection pump was employed to inject the solution into the furnace tube at 250 and 100 ml min^{-1} flow rates for a period of 20 min. At 1200°C, the reaction temperature was set. On a sapphire substrate, the production of fluffy CNTs was performed, which appear as 'elastic CNT smoke'. The production involved a 3D assembly referred to as 'aerogel'. The acquired aerogel demonstrated high porosity that reached 98% with an electrical conductivity at 106 S m^{-1} and a BET surface area at 170 $\text{m}^2 \text{g}^{-1}$. The results proved to be useful for applications like environmental application and sustainable energy development. Moreover, the thermal conductivity was found to be 0.127–0.137 W $\text{m}^{-1} \text{K}^{-1}$, which fell within the range of other porous carbon materials. Thus, the prepared CNT aerogel also has application in thermal insulation, thermoacoustics as well as other domains that involve the combination of low-thermal conductivity and high-surface area [12].

The FCCVD method was employed to synthesize a raw CNT aerogel, utilizing a solution of ferrocene and thiophene

Figure 6. CNT aerogels: (a) snapshot of the CNT aerogel deposition process taken by a camera located outside the reactor, (b) the CNT aerogel withstanding a weight of 8.5 g, (c) 1.50 mg cm^{-3} -density CNT aerogel and (d) 20 mg cm^{-3} -density aerogel synthesized in 15–20 min [12].

in ethanol, 20 ml of this solution was injected and carried by Ar/H₂ into a furnace tube at 1300°C. The resulting raw CNT aerogel was treated with a secondary CVD synthesizing a stable and robust CNT aerogel by applying 400 sccm argon and 400 sccm hydrogen at 720°C. Scanning electron microscopy (SEM) of the raw aerogel film illustrates that CNTs are randomly aligned, assembling a 3D interconnected structure. The BET surface area of the prepared CNT aerogel film is at $53 \text{ m}^2 \text{ g}^{-1}$. This was followed by preparing a Co₃O₄/N-CNT conductive aerogel film.

We prepared a free-standing cobalt oxide with a nitrogen-doped CNT composite aerogel, and this composite was prepared by applying catalysts within the prepared conductive CNT aerogel film for flexible Zn–air batteries like an air electrode. The composite aerogel film displays high-bifunctional catalytic activities. The produced batteries display high-charging–discharging stabilities and low-electrical resistance with appropriate flexibility, supposing them as promising candidates for adaptable energy storage devices [40].

4. Aerogel

Aerogels are in the form of solid materials derived from a gel, in which air substitutes liquid in the wet gels *via* unique drying processes like supercritical and freeze drying without harming the network structure of the gel. The aerogel properties promote as well as restrict the aerogel application design, which depends on the microstructure. Thus, during the preparation, it is vital to identify the microstructure control. The preparation process of the aerogel, generally, consists of the succeeding four crucial steps: firstly, sol–sol conversion, the colloidal particles in the nanoscale are formed spontaneously in the solution. Secondly, the produced solution is deposited on substrates by spinning, dipping or spraying. Thirdly, sol–gel conversion, the sol particles are polymerized (cross-linked) and orderly assembled producing a wet

gel in the case of a compact network. Fourthly, gel–aerogel transition, this step commonly named ‘drying’, the wet gel containing the solvent is retreated by air without damaging the microstructure critically to form an aerogel [41].

There are established and numerous drying methods, comprising surface-modified ambient drying, solvent-replaced ambient drying, natural drying, low- and high-temperature supercritical fluid drying and freezing drying.

All four steps could control the aerogel microstructure and affect its properties and applications [42].

The produced materials are mesoporous in nature containing a network of stable solid gels exhibiting high porosity in the range of 80–99% [43,44]. Mesoporous materials are those that can cover pores of diameter 2–50 nm. The term aerogels do not specifically denote to a definite substance, but represent a network structure that can be acquired by materials. The preparation of aerogels can be carried out from various materials, like metals, silica, oxides of a transition metal, certain main group metal oxide, organic polymers, oxides of lanthanide and actinide metal and carbon-based nanomaterials (CNTs, carbon powder and graphene) [45].

Aerogels are generally characterized through their particularly low density, in the range of $0.00016\text{--}0.5 \text{ g cm}^{-3}$, and air represents 95–99% of the total volume [42]. With regard to solid materials, they have been measured as possessing the lowest density ever existed [46]. The aerogels can show several advanced characteristics surpassing the same substances, including high porosity and surface area, because of their exceptional 3D and low-density impacts from the nanostructure characteristics. However, aerogel structures could possess reduced mechanical strength [42].

4.1 Fabrication of CNT aerogels

In 2007, the synthesis of the CNT aerogel was reported for the first time. It involved the dispersion of CNTs with the help of a surfactant solution exposed to sonication, after which gelling and drying were performed. The aerogel’s physical

Figure 7. SWCNT aerogel (left, 17.4 mg, density: 9.8 mg cm^{-3}); the same sample supporting a 20 g weight (middle, ~ 1150 times its weight); the same sample after removal of the weight (right) [48].

properties could be improved by the addition of polyvinyl alcohol with CNTs [7]. In 2009, Aliev *et al* [47] synthesized CNT aerogel muscle sheets derived from the forests of MWCNTs. These sheets were normally characterized with a density of 1.5 mg cm^{-3} , a thickness of 20 mm and an areal density of $1\text{--}3 \text{ mg cm}^{-2}$ in the sheet plane. The functionalization of MWCNTs and SWCNTs with an organic organo gelator was found to result in the production of free-standing CNT organogels. For instance, common organic solvents, such as chlorobenzene, can be employed to yield an aerogel by gelation of ferrocene functionalization of grafted poly(*p*-phenylene ethynylene) and SWCNTs. Then, water was substituted with ethanol, followed by drying *via* a supercritical technique that employed liquid CO_2 . Annealing of the prepared CNT aerogels with air was performed to develop their electrical and mechanical properties, porosities and surface areas along with the creation of meso- and micro-porous structures in their monoliths. The produced annealed CNT aerogels were found to be highly porous (99%), mechanically stable and rigid (figure 7), display excellent electrical conductivity (ca. $1\text{--}2 \text{ S cm}^{-1}$) and with a large surface area ($590\text{--}680 \text{ m}^2 \text{ g}^{-1}$) [48].

CNTs can be combined with other 3-D aerogel materials to produce CNT aerogels. Worsley *et al* [49,50] combined CNTs with carbon aerogels to yield DWCNT and SWCNT aerogels. At 1050°C , the acquired gels were subjected to drying and annealing, which facilitated the carbonization of organic components to produce CNT aerogels. Surfactants can also be employed for CNT dispersion to form aerogels. For instance, in 1% w/v aqueous solution of sodium dodecyl sulphate (SDS), solubilization of SWCNTs was performed. Afterwards, SDS was substituted by employing streptavidin phosphate and DNA complexes, which led to gelation of SWCNTs. SWCNT aerogels were produced after replacing water with ethanol solvent followed by super critical drying [51].

4.2 Graphene and CNT aerogel

In recent years, two of the most widely studied carbon species include CNTs and graphene. Both these allotropes have unique versatile characteristics, like high-electrical conductivity reaching 104 S cm^{-1} [52,53], impressive Young's

modulus of $\sim 1 \text{ TPa}$ [54] and superior thermal conductivity in the range of $2000\text{--}5300 \text{ W m}^{-1} \text{ K}^{-1}$ [55]. Developing such unique carbon nanomaterial structures in the form of aerogel macrostructure, not only enriches material groups pertaining to the carbon-based aerogel macrostructure, but also allows creating interconnected networks with highly porous and multifunctional characteristics. Both allotrope graphene and CNTs can be combined for certain applications to reap the benefits of correlation properties and synergies allowing the concurrent assembly of 2-D graphene sheets and 1-D CNTs. Moreover, CNTs allow increase in the spacing level within graphene sheets and link the defective region for electron transfer. In the concurrent assembly of SWCNTs, conjugated poly(3,4-ethylenedioxythiophene) and graphene oxide: poly(styrene sulphonate) (PEDOT:PSS polymer) were seen to form conductive glue with adhesive properties in an aqueous solution, which is appropriate to be used as an electrode in supercapacitors [56]. For graphene CNT hybrid aerogels, physical enfolding of CNTs was carried out in the graphene networks without changing the graphene structures. Moreover, CNTs could cast an inhibition effect on graphene sheets' accumulation and specifically improve the aerogels' surface area [57,58].

When compared to all other popular aerogels, the production of CNT aerogels was recent, carried out as intermediate phases when nanotube fibres are drawn through CCVD. The dry synthetic method was employed for the production of the CNT aerogel as well as the carbon-based aerogel in just one step [59]. The single-step direct FCCVD synthesis has established itself as a feasible, practicable and cost-effective method to produce CNT aerogels *vs.* the current time-consuming, critical point drying [7] or freeze drying [12,60]. In this technique, the FCCVD method can be used directly to spin CNTs from the gas phase. This process involves different approaches for synthesis conditions when compared to conventional CVD by adding hydrogen and sulphur in the reactor at high temperature ($>1000^\circ\text{C}$). This technique yields remarkably fast growth of long nanotubes (length in millimetres) in the gas phase, which *via* entanglements [61,62] turn into larger objects. Thus, the CNT aerogel can also be drawn as a CNT fibre with up to 18 draw ratio and achieve faster rates of spinning (up to 50 m min^{-1}) [63]. During the assembly process of nanotubes, drawing of the entangled CNTs' mass is performed first, which yields 'aerogel' [64]. Table 1 lists out the recent publication regarding CNT aerogels and graphene as well as their characteristics.

5. FCCVD method for CNT aerogel synthesis

The FCCVD method has been developed from the thermal CVD method. In an FCCVD process, direct simultaneous introduction of the carbon source and catalyst into the system reactor is performed (figure 8), which is not the case in traditional thermal CVD [9]. This method generally employs

Table 1. Properties and applications of CNT and graphene aerogel.

Type of aerogel	Aerogel method	Properties	Application	References
CNT	Polymer dispersed, then sol-gel	Density = 4 mg cm^{-3} , SSA = $580 \text{ m}^2 \text{ g}^{-1}$	Synthesis and properties	[65]
CNT	Chemical cross-linker, supercritical CO_2 drying	E.C. = $1-2 \text{ S cm}^{-1}$ (four probe method), SSA = $590-680 \text{ m}^2 \text{ g}^{-1}$, porosity = 99%	Synthesis and properties	[48]
Polymer/CNT composite aerogels	Chemical treatment, supercritical CO_2 drying	E.C. = $1.2-6.9 \times 10^{-2} \text{ S cm}^{-1}$ (two-probe method), SSA = $280-400 \text{ m}^2 \text{ g}^{-1}$, density = $4.4-5.1 \times 10^{-2} \text{ g cm}^{-3}$	Synthesis and properties	[66]
CNT	SWCNT/SDS solution, supercritical CO_2 drying	E.C. = $5 \times 10^{-7} \text{ S cm}^{-1}$, density = 0.75 mg cm^{-3}	Synthesis and properties	[51]
Graphene-CNT	Chemical treatment, supercritical CO_2 drying	E.C. = $7.5 \times 10^{-2} \text{ S cm}^{-1}$, SSA = $435 \text{ m}^2 \text{ g}^{-1}$	Water purification to remove heavy metal ions, and organic dyes	[58]
Graphene-CNT	Chemical treatment, freeze-drying	SSA = $442-656 \text{ m}^2 \text{ g}^{-1}$, pore diameter = 3.8 nm	Uric acid detection	[67]
Graphene-CNT	Chemical treatment-supercritical CO_2 drying	E.C. = $0.2-9 \text{ S cm}^{-1}$, SSA = $281-844 \text{ m}^2 \text{ g}^{-1}$, density = $16 \times 10^{-3}-41 \times 10^{-3}$	Synthesis and study the effect of the reducing agent	[68]
CNT-cellulose	Chemical treatment, freeze-drying	—	Vapour sensors	[69]
CNT	Freeze-drying	E.C. = $0.034-0.162 \text{ S cm}^{-1}$, density = $32.7-77.7 \text{ mg cm}^{-3}$, SSA = $44.9-130 \text{ m}^2 \text{ g}^{-1}$, pore diameter = $18-23.5 \text{ nm}$	Synthesis and properties	[70]
Graphene-CNT	Hydrothermal redox reaction, freeze-drying	Density = $6.2-12.8 \text{ mg cm}^{-3}$, SSA = $84.6-287 \text{ m}^2 \text{ g}^{-1}$	Oil and dye sorption study	[71]
CNT	Chemical treatment, supercritical CO_2 drying	E.C. = $0.56-4.55 \text{ S cm}^{-1}$, density = $0.06-0.35 \text{ g cm}^{-3}$, SSA = $100 \text{ m}^2 \text{ g}^{-1}$, pore diameter = $10-20 \text{ nm}$	Synthesis and properties	[72]
CNT	Floating catalyst	E.C. = 106 S cm^{-1} , density = $0.55-32 \text{ mg cm}^{-3}$, SSA = $170 \text{ m}^2 \text{ g}^{-1}$, thermal conductivity = $0.127-0.137 \text{ W m}^{-1} \text{ K}^{-1}$	Synthesis and properties	[12]

Figure 8. Schematic drawing of the FCCVD method for CNT aerogel production.

Figure 9. Scheme and optical images of different CNT macro-structure preparation *via* the FCCVD process [75].

solid organometallic species as the catalyst source (the catalyst needs to be dissolved by the liquid homogeneously) and liquid or gaseous precursors as the carbon source [73].

The decomposition of organometallic species occurs at lower temperature when comparing the temperature used for CNT growth. These can be positioned on a separate or the same furnace. Ferrocene is the most commonly employed catalyst precursor, but studies have been performed on other types of metallocenes as well. Vapourization of organometallic precursors results in the formation of the catalyst, which is transferred to the substrate with the help of carrier gas. On the substrate, catalyst particles get deposited in high densities, allowing to obtain vertically aligned arrays of CNTs [74] or randomly aligned arrays leading to the formation of the CNT aerogel when there is no substrate [11,75] (figure 9).

The benefit with the FCCVD method is that extra steps to prepare a catalyst are not needed. It offers a controlled approach to directly spray a range of carbonaceous liquids into the deposition chamber, eliminating the need for an intermediate stage to prepare the catalyst, and simultaneously ensuring that there is a continuous growth for CNTs. These benefits show great promise for scale-up production regarding CNTs at prices that are commercially viable [12,76,77].

The synthesis process is generally performed at 1000–1250°C based on the kind of catalyst precursor and carbon feed employed and there is a need to break down promoter *via* pyrolysis. The components are decomposed at a sufficiently high temperature in a short-residence time. However, if the temperature is too high, it can lead to the formation of amorphous carbon because of the occurrence of non-catalytic fragmentation of carbon feed in the absence of iron [78].

The CNTs' growth within the FCCVD reactor needs to be understood in depth for preparing the desired CNT aerogel as well as to productively scale up the overall process. Figure 10 shows SEM images, where CNTs' growth includes four distinct regions. The various structural characteristics can be directly associated with the behaviour of the nanoparticle. At the start of the reaction region, the micrograph was seen to be consistent with that of nanoparticle's nucleation in the carbon environment, which stimulates the CNTs' growth, accompanied by a little impurity. The second zone has a higher impurity level, characterized by inconsistent nucleations of catalyst particles as well as nanoparticle agglomeration. Some of these particles are subjected to catalyst encapsulation. The hottest region (the third zone) of the reactor has the lowest impurity since unreacted nanoparticles get evaporated, thereby offering a conducive environment favouring the growth of a pure CNT aerogel along with self-assembly CNT formation. Finally, near the reactor's exit region, a decrease in temperature leads to re-nucleation of iron nanoparticles through the saturated vapour in a carbon-rich environment, which also speed up the growth of carbon nanostructures accompanied by the presence of carbon impurities [76].

5.1 Carrier gas and gas flow rate

The reactants are delivered into the reactor *via* a carrier gas, which also helps in maintaining an inert environment to block nanotubes' oxidation *in situ* by air and keep a check on the reactant concentrations. The most commonly employed carrier gases are nitrogen and argon [75,79].

Hydrogen is typically employed in the floating catalyst and plays an essential role in controlling the final CNT structure *via* its effect on the catalyst nanostructure and morphology. The yield of CNTs was found to be responsive to the hydrogen concentration. Increasing the hydrogen concentrations results in a decrease in the metal particle size, and consequently increases the CNT yield [80,81]. Neumayer and Haubner [82] confirmed this finding where they observed that there was an increase in carbon yield by 3–8% with a rise in the concentration of hydrogen. More importantly, they reported that the carbon concentration in the reactor decreased due to the presence of hydrogen that induces hydrogenation to form hydrocarbons, thereby averting supersaturation. This, in turn, discourages additional soot deposition and enhances nanotube graphitization. Van der Wal and Ticich [83] reported another role for hydrogen, in which dangling bonds on the carbon atom edge-plane are removed by hydrogen to prevent the formation of herringbone-type nanotubes. Motta *et al* [10] investigated the impact of various parameters on the CNTs. They found that thinner CNTs with less amorphous carbon could be achieved in environments with higher hydrogen flow rates. Raising the flow rate of carrier gas led to a steady increase in hydrogen atoms in the reaction chamber, while sulphur, carbon, oxygen and iron contents remained constant. Moreover, the rise in the flow rate of carrier gas led

Figure 10. SEM images of CNTs formed in the reactor at different axial locations. The nature of the impurities and their concentration in the CNT material change depending on the location and the corresponding temperature with (a) being closest to the outlet, (b) near the middle, (c) next to the inlet and (d) nearest to the inlet [76].

to the corresponding reduction in nanotube diameter. This finding was observed in terms of dilution of iron nanoparticles. In general, a decrease in the concentration of iron nanoparticles led to a reduction in the average size of iron nanoparticles caused by a lower probability of the iron cluster assembly in the reaction zone [11]. Thus, iron nanoparticles with a smaller diameter resulted in the production of smaller size CNTs. At the two-highest flow rates (0.15 and 04.6 l min⁻¹), the production of DWCNTs, SWCNTs and MWCNTs was carried out. With a further rise in the flow rate of H₂, thinning of the CNT aerogel occurred at a flow rate of 2 l min⁻¹. The CNT aerogel is characterized as being highly fragile as well as delicate to handle [10].

Meanwhile, the study was carried by increasing the flow rate of reactants, while maintaining a constant flow for the carrier gas. As per the result, it was concluded that the rise in the reactant flow rate did not result in the construction of thicker MWCNTs, which otherwise was expected due to the high concentration of iron nanoparticles. This could be attributed to the maintenance of a constant ratio of iron to carbon.

However, the growth of iron nanoparticles was hindered due to the presence of excess carbon atoms, resulting in a greater yield of CNTs that possessed similar diameter [10].

The carrier gas flow rates in the range of 700 [84] to 1300 sccm [10] were commonly used. As per the previous reports, the carrier gas flow rate is a crucial factor to determine the diameters of CNT with higher flow rates, which led to decreased diameters [85]. However, there is a limit to increase the flow rate further, since a high flow rate results in decreased efficiency as few of the unreacted carbon source were allowed to pass *via* the reactor, and the CNT aerogel handling becomes too fragile [10,11].

5.2 Effect of carbon source

The FCCVD method was employed to prepare the CNT aerogel, which reckons with CNTs' self-assembly in the gas phase due to van der Waals interactions. CNTs seemed to assemble in the gas phase when an appropriately high yield of CNTs was produced along with high purity. Hence, the type of carbon sources determines their assembly significantly. When the gas flows, constant production of 'sock-like' CNT incorporation results due to the CNT assembly, which could be mechanically spun into a CNT yarn even outside the furnace [59]. In this process, ethanol was used as a carbon source, which could be spun by winding inside a furnace. As per Li *et al* [59], ethanol was dissociated to produce a spinning yarn from the aerogel. By modifying the conditions for the process, researchers replaced the ethanol source with polyethylene glycol, diethyl ether, ethyl formate, 1-propanol and acetone, which fall under oxygen-including substances, but with different oxygen groups comparatively. Moreover, aromatic hydrocarbons like mesitylene and benzene were also investigated. Both hinted towards the production of thick fibres or CNTs, but the aerogel was not synthesized in the continuous spinning process unless mixing with methanol was performed.

The spun material composition for SWCNTs or MWCNTs was controlled by tweaking the reaction conditions. By using ethanol as a carbon source, the production of MWCNTs was carried out at a synthesis temperature of 1100–1180°C, a thiophene concentration of 1.5–4 wt% and a hydrogen flow rate of 400–800 ml min⁻¹. On raising the hydrogen flow rate to 1200 ml min⁻¹ and decreasing the thiophene concentration to 0.5 wt%, at a synthesis temperature of 1200°C, the formation of SWCNTs occurred [62].

During the direct gas-phase spinning process, in a horizontal FCCVD reactor that employed water vapour flow, assembling of a continuous CNT fibre yarn *via* ethanol was performed, which mimicked the traditional cotton yarn's morphology, and included multiple fibres possessing high-purity DWCNTs. In the gas phase, water vapour interaction resulted in achieving homogeneous condensing for the assembly of the CNT aerogel. This facilitated continuous twisting for the condensed bundle within the reaction tube, which

was well-regulated [86]. Gspann *et al* [11] investigated the continuous process that involved CNT spinning. The experiments showed that toluene and methane were relied as sources for carbon at a temperature of 1290°C. Also, a substantially pure and dense assembly was demonstrated with SEM, which was not disturbed by any large impurity. The well-formed CNTs were seen to be in a MWCNT form. Double- and few-walled patterns were seen using transmission electron microscopy (TEM) and a diameter of 10 nm for the nanotube. For the continuous process, the main task was to achieve spinning by CNT fibres directly from the assembly region of CNTs. Thus, the requirements of the production as a fibre were met when the length is sufficient to entangle as well as form an aerogel. Through the gas-phase FCCVD process, the formation of the CNT aerogel was reported by employing methane as a carbon source. At 1200°C, during the synthesis process, constant addition of fluffy elastic CNT smoke onto the flat sapphire substrate was performed and 3-D substance assembly followed, referred as an 'aerogel' [12]. Hoecker *et al* [77] evaluated the effect of the catalyst nanoparticles and the carbon source on CNT aerogel production *via* the FCCVD method. The results demonstrated that the pyrolytic compounds formed through the decomposition of the carbon precursor were important for the production of the bulk CNT aerogel in the FCCVD reactor. Isotopically labelled methane ($^{13}\text{CH}_4$) was employed to track the source of carbon within CNTs, and Raman spectroscopy was used for analysis. The results revealed that in the CNT aerogel, the carbon origin was equivalent to the supplied ratio, where ~95% came from the carbon source (methane) for the entire reactor along with carbon from sulphur and iron precursors (thiophene and ferrocene), which was not found to dominate in early parts of the reactor. By the catalytic cracking of CH_4 , only a small yield quantity of the CNT aerogel was achieved with the initial catalyst nanoparticle nucleation zone *vs.* the catalytic nanoparticle re-nucleation zone in which the formation of bulk aerogel occurs.

However, due to environmental concerns, the use of natural precursors has gained much popularity as these were more sustainable and less harmful. Until now, there have been no reports on employing natural or waste materials as carbon sources for synthesizing the CNT aerogel.

5.3 Effect of catalyst precursor

Organometallic compounds are appropriate precursors to be employed in the floating catalyst method as these can decompose at relatively low temperatures, which are needed to yield the desired metal. Ferrocene is the most commonly employed catalyst [11,12,39]. As per the literature, thermal decomposition of ferrocene occurs at ~500°C to release iron. As the free iron becomes available, it instantly catalyses the further decomposition of ferrocene *via* autocatalysis. The iron deposit can be found in the reaction tube near the reactor with a temperature of 400°C. It is thus thought that freeing up of iron occurred directly after injection either through the

action of surface deposition or due to back-diffusion of iron nuclei from hotter areas opposite to the flow [11]. Should the catalyst particles' ratio be sufficiently high, the growth of poorly graphitized tubules possessing large diameter was likely to get catalysed and amalgamated. If the iron to carbon atom ratio is sufficiently low, a fraction of these carbon species is unable to reach catalyst sites, which results in the formation of carbon particles in place of nanotubes; sufficient nanotubes could still continue to grow to produce an aerogel [11]. The impact of the concentration of ferrocene on the CNT cotton was studied by Adnan *et al* [87] by employing the floating catalyst technique by altering the ferrocene concentration, which gave CNTs of different diameter sizes and was seen to cast an effect on the properties pertaining to electron transport in CNT cotton. Based on their work, it was found that the rise in ferrocene concentration led to the formation of the larger iron cluster for CNT nucleation.

5.4 Effect of sulphur

Sulphur is recognized for being a catalyst poison, where even a trace quantity in a hydrocarbon source could significantly reduce the catalyst activity [88,89]. However, based on the previous reports, the partial and controlled metal poisoning driven by sulphur could offer a distinct beneficial impact [90]. This, during the floating catalyst process, allows gaining an upper hand in controlling the presence of sulphur to offer just the partial support for the iron catalyst nanoparticles sufficient to give distinct benefits in terms of CNTs' growth.

The addition of sulphur determines the gas-phase high-temperature floating catalyst process for producing CNTs, wherein its role involves [11]: (a) 'acting as a promoter to improve carbon atom addition to the graphene tubes' growing ends'; (b) 'acting as a surfactant to promote tube nucleation, thereby avoiding catalyst particle's carbon encapsulation. Sulphur as a surfactant caused an impact on the growth of graphitic phase when solidification carried out for cast irons'; and (c) 'limiting the rate at collision cast a coarsen effect on iron particles'.

The formation of Y-junctions is enhanced by the addition of sulphur as thiophene [91]. Reports also advocated that sulphur helps in the formation of cleaner SWCNTs, containing lesser soot [92]. Sulphur probably cast an impact on the synthetic process *via* the formation of a eutectic mixture along with iron, which allows establishing a pseudo-liquid state appropriate for a VLS mechanism [93].

A range of sulphur sources have been identified, like carbon disulphide [94], thiophene [11,95,96] and elemental sulphur [94], wherein a different pyrolysis temperature is applicable to each. Temperature determination of the atomic sulphur released is crucial to predetermine how large can the iron particles grow, which will help to predict the type of produced CNT. As demonstrated in the work by Lee *et al* [97], changing to elemental sulphur (decomposition temperature: 400°C) from thiophene (high-pyrolysis temperature: 800°C) allows producing SWCNTs with a small diameter in

most cases due to early encapsulated or iron. The sulphur injector length can be varied to yield different sizes of produced particles (FeS) and CNTs. The length of the injector tube is increased to limit the contact between iron and sulphur until catalyst particles with an adequately large size have been grown, which results in larger MWCNTs in most cases [97]. As per Reguero *et al* [98], continuous CNT fibres can be created by controlling the sulphur precursor ratio when preparing the catalyst. At a low-sulphur ratio, CNTs were predominantly SWCNTs that had a diameter of ~ 1 nm. An increase in the concentration of sulphur could lead to growth in the catalyst particles' size as well as a rise in the number of layers along with the CNTs' inner diameter. A medium concentration of sulphur resulted in the formation of collapsed CNTs, while MWCNTs were produced at high-sulphur concentration.

6. Growth mechanism

6.1 Role of catalyst

Iron (Fe), nickel (Ni), cobalt (Co) as well as their alloys [99] are the commonly employed catalyst precursors because these metals present high adsorption and dissociation of carbon on their surface and consequently the carbon easily dissolve in the mass of the nanoparticles. Moreover, the low-vapour pressure equilibrium and the high-melting point of these metals present an extensive temperature range of the CVD method [100]. These species are employed as a catalyst in the decomposition of carbon sources as well as for CNT production on the material substance's surface [101]. A commonly accepted growth model pertaining to the catalyst precursor employs the vapour–liquid–solid (VLS) mechanism, which is comparable to the relative growth observed with a semiconductor nanowire from gold eutectic alloys [102]. As presented in figure 11, catalytic decomposition of the liquid phase of carbon source molecules occurs on the catalyst surface, which results in adsorption as well as dissociation of carbon atoms into catalyst particles. Due to this, carbon starts to diffuse within the particles resulting in supersaturation, where precipitation of solid carbons from the catalyst occurs. This leads in tubular graphene sheet formation around or on the catalyst to produce CNTs. When formations of the carbide segment and carbon solubility are considered, Fe, Ni and Co are apt for catalysing the growth of CNTs [103].

However, the liquid phase is not required for the VLS mechanism. Recently, as per *in situ* TEM elucidations, MWCNTs were found to grow continuously from crystalline Fe_3C particles at a temperature of 600°C [104]. Although the Fe_3C particle demonstrated fringes in the clear lattice, inconsistent fluctuation of the crystal structure during catalysis was seen, indicating that the particles were near to their melting points. In addition, below the melting point to be specific, the solid particle is likely to achieve a high density of vacancies that facilitate effective diffusion of carbon atoms into the metal

Figure 11. SWCNT formation process. (a) Decomposition of the carbon-bearing gas molecule on the catalyst surface. (b) Dissolution of carbon atoms into the catalyst. (c) Nucleation of the cap. (d) Extension of SWCNTs [103].

Figure 12. Effect of nanoparticle on cap nucleation [103].

particles and then precipitation of carbon from the metastable alloy of carbon–metal. A continuous supply of carbon from nanoparticles was crucial to the SWCNT's growth.

If nanoparticles are absent, SWCNT growth does not occur. This observation signifies that there is a need for large curvature at the nanoparticles' surface to produce SWCNTs. A cap on the SWCNT structure is identified that is present towards the opposite end to a catalyst nanoparticle, and the nanoparticles' surface needs to act as a mould for the shape of the cap. A logical description for the formation of this cap structure could be the self-formation of the individual graphene structure without the need for catalysis. Typically, the formed graphene's size does not need to be large, and the construction of such a small graphene structure is simple. For example, in the initial growth step of CNTs for a small graphene structure on the surface of Ni nanoparticles, a five-membered ring graphene structure was seen to be more favourable in terms of energy when compared with all the six-membered ring graphene structure [105]. A similar sp^2 was found to bond a cap structure that was made from five-membered rings, which subsequently moulded the association of carbon atoms as well as diffusion on a 1 nm iron nanoparticle surface by employing initio-molecular dynamic simulations [106]. Furthermore, partial designing of a five-membered ring graphene structure on nanoparticles showed that it moved up the nanoparticles' surface not including the graphene structure edge. Thus, as shown in figure 12, it became a cap for SWCNTs.

For continuous growth of SWCNTs, carbon atoms need to be delivered to the nanotube's edge. After dissociation and adsorption of carbon atoms, the edge of SWCNTs becomes chemically active and acts as an incorporation site for carbon atoms. The interaction of carbon atoms with the catalyst

Figure 13. Mechanics of CNT synthesis by the FCCVD method at high temperature [97].

surface's cap edge should not be too strong, such that the combination of carbon atoms that form graphene tube lattice is hindered, or too weak, such that the SWCNT open end is preserved for continuous growth [100]. Thus, a highly efficient approach to demonstrate SWCNTs' growth is *via* the VLS mechanism. When catalyst efficiency pertaining to the growth rate of SWCNTs was compared, the iron catalyst was found to be the highest. A high-growth rate is needed for the vertically aligned growth of SWCNTs, which can be attained with the help of cobalt and iron catalysts. The growth rate of SWCNTs with non-metal catalysts can be considered to be almost low.

6.2 Role of sulphur

The catalyst nanoparticle's diameter limits the CNT's diameter, especially in the range of smaller diameter. In the case of standard conditions employing methane as a carbon source, sulphur is available before carbon atoms and even eight sulphur atoms per iron atom. In a practical sense, the availability of 1 nm iron particles meant that approximately two-thirds of the iron atoms are present for the surfaced atoms. Thus, these conditions disposed off when it came to the total sulphur poisoning for the catalyst [11].

As a carbon source, into the furnace, injection of the catalyst and promoter mixture was performed and exposed to non-uniform temperature distribution that caused gradual pyrolysis of the compounds that were least stable. Above 400°C, breaking down of ferrocene iron atoms occurred along with a gradual release to act as catalytic sites for synthesizing CNTs. With the rise in temperature, since these particles

Figure 14. Schematic of the growth mechanism of different diameter SWCNTs controlled by thiophene [107].

shuttle within the furnace, agglomeration started that resulted in the growth of bigger clusters of iron. The bigger size of these aggregates led to the production of CNTs with a larger diameter, which most of the time were multi-walled structures [11,97]. Sulphur can block this conglomeration, surrounding the iron particles' surface segregating one from the other. Many different sulphur sources have been explored, like carbon disulphide, thiophene and elemental sulphur, each with varied temperatures for pyrolysis. The setting of the temperature of atomic sulphur released was crucial for pre-determining the growth in the size of iron particles and also the type of produced CNTs [95,97].

In the gas-phase FCCVD method, when employing acetone as a carbon source, decomposition of ferrocene occurred at 400°C, while decomposition of thiophene started at 800°C.

Then, the produced iron catalyst nanoparticles would grow along with iron atoms' addition or iron nanoparticles' aggregation, until the reaction reached 800°C. Then, there is a chance that sulphur atoms get accumulated on the iron catalyst nanoparticle surfaces, which subsequently hinder the growth of the catalyst. The huge difference between the decomposition temperatures of thiophene and ferrocene led to the formation of large catalyst nanoparticles, which in turn resulted in DWCNTs with large diameters. Meanwhile, when methane is used as a carbon source for the gas-phase FCCVD method, sulphur atoms are formed before ferrocene decomposition (figure 13). Thus, deep inside the iron catalyst nanoparticles, sulphur atoms started depositing, from the iron catalysts' nucleation phase, which blocks additional progress of iron catalyst nanoparticles. Consequently, the sulphur atoms are distributed among the iron catalyst nanoparticles in a consistent way, which facilitates the production of SWCNTs, the key products in this case [97].

The evaluation of the growth mechanism pertaining to SWCNTs was performed with the help of FCCVD employing ethanol by adding thiophene and ferrocene. The root growth mechanism led to the nucleation of SWCNTs that initiates with the creation of the Fe–S region, which offered different nucleation regions for SWCNTs. Addition of different ratios of thiophene led to the formation of different areas of the Fe–S region, which resulted in various SWCNT nucleation regions (figure 13). If thiophene is added in higher quantities, a larger catalytic Fe–S region can be created, which in turn allows forming larger tube diameter. Nonetheless, when an excess amount of thiophene was added, sulphur starts to surround Fe nanoparticles, and catalyst deactivation inhibits SWCNTs' growth as presented in figure 14d [107].

7. Conclusion

Research regarding the manufacturing of CNT macroscopic materials, especially CNT aerogel, continues to gain interest amongst the research community because of the plethora of applications employing multifunctional materials. Moreover, the practical application pertaining to the FCCVD method, which allows the large-scale production of the CNT aerogel, has opened up a huge opportunity for the mass production of materials. However, there need to be strategic methods designed for the catalytic reaction process, so that the aerogel structure can be controlled. In the vapour phase, the pure CNT aerogel starts to self-assemble. Factors such as the injection rate and type of catalyst, carbon source and promoter, as well as the reaction temperature and hydrogen flow rate need to be well controlled *via* process design. It can be said that the choice of carbon feedstock could cast a significant impact on the availability of carbon atom during synthesis, as decomposition of each of these compounds occurs at various temperatures. When the hydrogen flow rates were high, CNTs with smaller diameter were produced. Thus, by raising the hydrogen flow rate or decreasing the carbon feed

rate, the aerogel can be drawn even faster. As a result, the material's alignment can be considerably enhanced along with its mechanical properties by decreasing the needless entanglement of CNT bundles.

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