

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

4,800

Open access books available

122,000

International authors and editors

135M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Rapid Growth of Dense and Long Carbon Nanotube Arrays and Its Application in Spinning Thread

Yasuhiko Hayashi, Karthik Paneer Selvam and
Maik Scholz

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/intechopen.70702>

Abstract

Carbon nanotubes (CNTs), a dependable allotrope of carbon, are foreseen to lead technology further to its reach. Also, the most researched carbon allotrope in its form. Drawable CNTs have recently unraveled numerous possible applications utilizing vertically aligned CNTs also termed as “CNT forest.” In recent years, the rapid growth of dense and long carbon nanotube arrays has succeeded in surpassing its challenges by synthesizing dense and long CNT arrays. Length, density, and drawability tuning in the synthesis of CNT arrays have always been a complex issue lately. However, numerous research techniques emerged focusing on length and density control. Hence, this book chapter aids in unveiling the current achievements in the growth of dense and long CNT arrays and their application in spinning threads or CNT yarns with numerous other possible applications.

Keywords: CNTs, rapid growth, CNT yarns, dry spinning, vertically aligned CNTs

1. Introduction

Carbon nanotubes (CNTs) have not yet been into its full-fledged practical applications. However, it is prophesied to acquire the industrial and commercial market soon confidently. CNT arrays aka vertically aligned CNTs (VACNTs) itself are broad areas of research apart from its originator CNT. As one can expect the complexity to grow long continuous CNTs [1, 2], scientists and researchers have derived out a brilliantly new idea of CNT yarn. The idea of aligning carbon nanotubes into arrays was perceived in 1994 by Ajayan et al. [3] by cutting thin slices of the nanotube-polymer composite, which followed by the idea of aligned phases in applications like aligned liquid crystals [4], carbon fiber-reinforced polymer [5], and so on. Soon in 1995, Heer et al. produced CNT films from aligned CNT [6]. Later, in 1996 large-scale synthesis of aligned

carbon nanotubes was reported by Li et al. [7] with chemical vapor deposition (CVD) growth of CNTs using iron nanoparticles catalyzed mesoporous silica, which extended the research on aligned carbon nanotubes. The urge to produce long CNTs gave rise to CNT yarns, and therefore CNT yarns were introduced as a substitute to long CNTs. On the other hand, CNT films from aligned CNT have also gained attention and encouraged research in those directions.

The understanding of the VACNTs and their growth parameters is a cumbersome issue, as too many factors are interlinked to each other making it a slightly challenging and complicated discussion. Nevertheless, for the easy understanding, we have mentioned subheadings in this chapter discussing each issue detailing all factors as deeply as possible to attain the VACNT growth and application in the spinning thread.

CNT forest aka aligned carbon nanotubes (ACNTs) or vertically aligned CNT (VACNT) arrays have been disabling its limitations as aggressive research is going on worldwide. Many practical applications have been demonstrated using CNT forest. CNT array research has grown widely in all directions. Not long ago, the research on CNT arrays has peaked, and relatively high number of research reports has published lately. Pushing the limit and experimenting with all possible applications.

The pathway to CNT yarns can be realized by the chart shown in **Figure 1**.

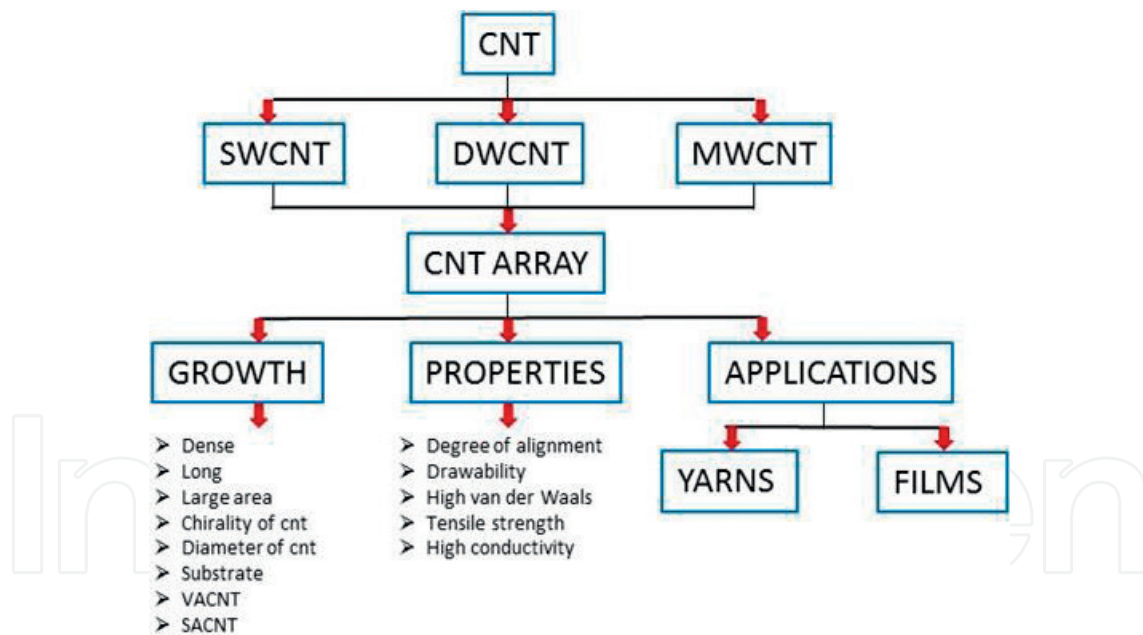


Figure 1. Showing all the parameters of CNT in application to CNT yarn and the factors for this growth.

2. Growth of CNT arrays/VACNTs

Before proceeding to the segment of dealing with the properties and modification of VACNTs, their various applications and research background and potential applications as CNT yarns

and sheets. The growth mechanism and types should be apparently introduced to give a bright idea about all the necessary factors employed in growing the VACNTs.

Many experiments performed by numerous research groups worldwide are taken into consideration in briefing all the possibilities of growth and application of CNT array and CNT yarns/films derived from them. After seeing the background of the research and how CNT array research has been disabling its limitations and improvising every year, the potential applications of CNT arrays can be estimated.

The methods that can grow CNTs or specifically VACNTs are discussed below.

2.1. Chemical vapor deposition (CVD)

Chemical vapor deposition is the most practiced and renowned method for growing CNT arrays. The initial steps include substrate preparation for the growth of CNT arrays, and the most common substrate used is silicon with several tens to few hundred nanometres thick layer of Al_2O_3 or SiO_2 . To this substrate, a metal catalyst is deposited such as ferrocene which deposits Fe nanoparticles of few tens of nanometers. In a quartz tube, the Fe-coated substrate is placed. Then, this setup is put into a furnace, with one end of the quartz tube fed with reactive mixture gases (carbon precursor gas and carrier gas) and the other end to a vacuum pump. The quartz tube is then pressurized to certain total pressure say 200 Torr, and gases flow rates of 380 sccm for carbon precursor (C_2H_4) and carrier gas flow rate at 190 sccm. The temperature in the furnace increased to 650 °C which allows the catalyst to decompose the carbon and grow into CNT array. The reaction time and the flow rate decide the lengths of the CNT arrays [60]. CVD technique has further progressed into water-assisted CVD, where the reaction gas mixture and water vapor are combined. This method yielded in producing long and aligned CNT arrays [8, 9].

2.2. Floating catalyst chemical vapor deposition (FCCVD)

Floating catalyst chemical vapor deposition (FCCVD) method is also carried out in a quartz tube reactor and all other parameters being alike with CVD. The difference is avoiding metal catalyst deposition onto the substrate used for CNT growth. Instead, it the metal catalyst is passed into the quartz tube along with the reaction mixture gas. Hence, the name is derived as floating catalyst CVD, considering an example for the growth of CNT arrays. Ferrocene is injected into the reactor along with ethanol and thiophene at a rate of 0.15 ml min^{-1} , and the Ar- H_2 gas mixture is fed as a carrier gas at 4000 sccm with the temperature being 1300 °C [10]. FCCV methods avoid the deposition of the catalyst layer onto the substrate reducing one step of processing of CNT arrays. In another experiment, a comparatively low temperature of 800 °C was used to grow a 500 μm height of CNT array. Ferrocene was dissolved in xylene and fed to a horizontal furnace containing quartz tube with the substrate [11].

Thus, it leaves us with the idea about all the parameters involved in growing a CNT array by CVD technique as listed below:

1. Substrate
2. Oxide layer
3. Metal catalyst
4. Reaction gas mixture
5. Carbon precursor
6. Carrier gas
7. Pressure
8. Flow rate
9. Temperature
10. Reaction time

Now, a careful observation to make is that the parameters mentioned above are variable. Hence, it opens a broad range of experimental possibilities to grow CNT arrays.

3. Drawing of yarns and sheets

There are two methods employed commonly to spin or to draw the CNTs or CNT arrays into CNT yarn and CNT sheets/films.

3.1. Wet process

In a broad sense, wet process method to draw CNT yarns/fibers/threads does not have a direct comparison with dry-drawing method. It is naturally due to the dissimilarities between wet and dry processes. Though technically both process yield CNT yarns as the final product, the initial process is vastly different. The wet chemical process uses CNTs, whereas dry process uses VACNT. However, considering the end product's perspective, both methods can be compared.

In the wet process, CNTs are dispersed in a dispersant (acid), and then the CNTs are pumped out through a nozzle via coagulant, which aligns the CNTs into yarns/fibers. Chlorosulfonic acid is one such superacid allowing the CNTs to dissolve [12].

3.2. Dry process

Spinning CNT yarns or drawing CNT sheets from CNT arrays is among the two-step dry methods the most widely used. The synthesis mentioned above CNT forests is the first step. In the second phase of fabricating yarns or sheets, a cluster or bundle of CNT is pulled out of the assembly. The following nanotubes get attached through interconnected bundles at the top and bottom of the previous CNTs, thus forming a network of axially aligned CNTs. Kuznetsov et al. [13] show that the interconnection density is a key parameter for the ability

of an MWNT forest to be drily drawable into sheets and yarns. After drawing out the CNT network from the forest in most of the cases to forming yarns, the network is twisted [14–16]. It leads to a rapid densification and increases the mechanical strength considerably. Some research groups apply additional liquid agents instead of twisting [17]. These agents help to densify the yarns leading to a functionalized surface of the yarns [18]. With this additional treatment, mechanical strength is further increased. Additional investigations were done in the direction of heating the yarns while spinning and using multiple arrays at once to form yarns [19] as shown in **Figure 2**.

The comparison of wet process and dry process is mentioned in **Table 1**.

The understanding of aligned carbon nanotubes and its possible applications as yarns and films can be divided into the following segments.

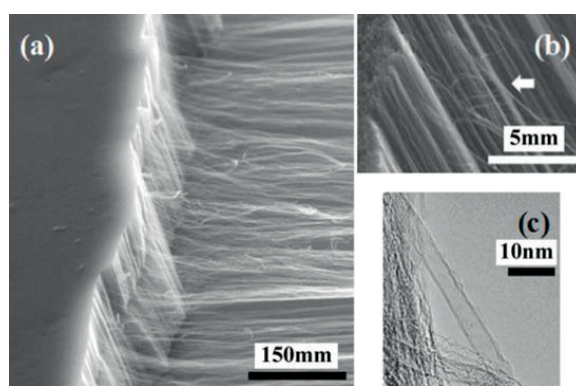


Figure 2. Showing a typical CNT forest observed under scanning electron microscopy produced by our group.

	Wet process	Dry process
Binder	Required	Not required
Residual catalyst particle	Can sometimes be found	No particle (bottom growth)
CNT dispersion	Required	Not required
NT length	Uses very short CNTs	Uses long and aligned CNTs
Simplicity in process	Complicated	Very simple

Table 1. The comparison between wet and dry processes of CNT yarn spinning.

4. Factors influencing drawing/spinning of CNT yarns and CNT films

- 4.1. Long and dense growth of Vertically Aligned/Super aligned CNTs (VACNT/SACNT)
- 4.2. Drawing of CNT Yarns/fibers using ACNTs
- 4.3. Drawing of CNT sheets/films using ACNTs

4.1. Long and dense growth of aligned/super-aligned CNTs

Some of the core challenges relating to CNT array's growth are:

4.1.1. Long heights of the CNT

4.1.2. Area of the substrate

4.1.3. Density of the CNTs per unit area

4.1.4. Degree of alignment of the CNTs

Other parameters concerning growth of VACNTs

4.1.5. Directing number of walls and diameter of the CNT array

4.1.6. Directing the chirality of the CNT in the array

4.1.7. Directing purity and catalyst

4.1.1. Long heights/lengths of CNT forest

Growing CNTs vertically in a long length is a critical challenge in the CNT array growth. Achieving long CNT forest can result in higher lengths of CNT yarns or films per unit area. In the application's point of view, obtaining drawable CNT forest is the real challenge. Many researchers have reported many possible lengths of drawable CNT forests. Hence, the following discussion is the current possible maximum drawable CNT forest heights which give an insight in the initial heights obtained for CNT forests. Few examples are briefed below for taming the inkling of the process for lengthy heights of CNT forest.

The record for the large height of VACNT array was reported in 2014 by Cho et al. [20], with a height of 21.7 mm, and not tested for drawability. Its water-assisted thermal CVD process produced such long VACNTs, and most of the CNTs were double walled. The growth rate was calculated to be $27.47 \mu\text{m min}^{-1}$.

Another report stated that 4.7-mm-long CNT arrays were grown with high efficiency and long-life catalyst film using Al_2O_3 and Fe as buffer layer and catalyst. The VACNTs were spinnable [21]. Similarly, in another event, 4-mm high-quality CNT array was grown without water assistance and showed that the catalyst lifetime lasted for 3 h [22] as illustrated in **Figure 3**.

In a recent report, aligned spinnable CNTs of heights $400 \mu\text{m}$ were synthesized by Alvarez et al. [23]; Fe and Co are used as the catalyst sources with 1.2 nm thin film. About 5 nm Al_2O_3 -layered Si wafer was used to accommodate the Fe and Co catalyst. The substrate was annealed at 400°C under Ar gas flow; then, the temperature was increased to 700°C , and ethylene was fed at 300 sccm with 1000 sccm of Ar for 20 min. In another report of drawable VAMWCNT, the height of was 2.0 mm ($2000 \mu\text{m}$) grown in 16 min that account for 0.1 mm min^{-1} by Inoue et al. [24]. It was synthesized by conventional CVD system with iron chloride (FeCl_2) as catalyst and acetylene as a carbon source. The same group has previously reported drawable VAMWCNT array measuring a height of 2.1 mm with same precursor material, but



Figure 3. Depicting the lengths of VACNTs grown with growth time of 3 h, 2 h, 1 h 30 min 10 min (reprint from Ref. [22] with permission).

the process time was 20 min [25]. The method does not include pre-deposition of the catalyst layer. Instead, it uses iron chloride powder and acetylene gas because iron chloride has a high dehydrogenation activity on acetylene. They termed the process as chlorine-mediated chemical vapor deposition (CM-CVD).

In 1999, Shoushan et al. [26] have achieved 30–240 μm heights of MWCNT-VACNT grown by CVD reaction times of 5–60 min. The condition for growth is electrochemical etching of porous silicon of 2 in diameter, patterning with 5-nm-thick layer of Fe by electron beam evaporation with a shadow mask. The substrate was placed in the quartz tube reactor housed in a tube furnace. The operating temperature was 700 $^{\circ}\text{C}$ with Ar flow; ethylene was then flown at 1000 sccm for 15–60 min. The diameters of the MWCNT-VACNT were found to be 16 ± 2 nm. Ren et al. [27] have grown 0.1–50 μm heights of VACNTs using plasma-enhanced chemical vapor deposition (PECVD).

Lee et al. measured the possibility in factor determining the upper limit to the height of spinable carbon nanotube forests [28]. By synthesizing CNT forests at different growth times such as 3, 6, 9, 12, 15, and 60 min. The heights were found to be 260 μm for 3 min growth time and 1.7 mm height for 60 mm growth time. An important observation was made, as the growth time increased the degree of alignment decreased. It was verified by Raman analysis as it showed G and D bands intensity ratios different at top and bottom.

Hence a clear observation can be made by all the reports is that the process time with a certain flow rate of the precursor yields in governing the lengths of VACNT. Also, these parameters have a grave effect on the degree of alignment of the VACNTs.

4.1.2. Large area growth of VACNT

It can be understood that the first challenge which lies in the geometry for VACNTs has a large area with long and densely aligned CNTs arrays. For large scale growth of CNT on a large area array, many researcher groups have been experimenting with it since a decade. CNT array growth area on large wafers has attained a growth area of 8-inch (18 cm) by Chen et al. [29]

in 2010, and the super-aligned CNT film (SACNT) was free-standing, ultra-thin, lightweight transparent and conductive. The height of the SACNT array was 250 μm , and transmittance was measured up to 83%. This high area SACNT can be employed in many advanced applications such as transparent conducting films by replacing conventional indium tin oxide (ITO).

Previously, Zhang et al. [30], have grown SACNT on a 4-inch diameter wafer, using low-pressure CVD (LP-CVD) system. To guarantee the uniformity LP-CVD system was suggested. Also, SWCNT arrays were grown using water-assisted CVD method on a 100 mm (3.9 inches) substrate [9].

4.1.3. Dense CNT forest (yarns/films)

Similar to the height of the CNTs in the CNT array, CNTs density is also a key factor classifying the application of the grown CNT array. The density depends on two factors mainly the thickness of the CNTs in the array and number of walls of the CNTs in the array and to some extent on the degree of the alignment of the CNTs in the array.

Many researcher groups have succeeded to obtain persistent densities in the past decade; one such report attained a density of 22 SWNTs in $1 \times 0.75 \mu\text{m}$ [31]. Nevertheless, the drawability was not determined this VACNT. Furthermore, SWCNT array is grown by a water-assisted report a high density of $6.4 \times 10^{11} \text{ cm}^{-2}$. High-density growth was possible due to the petite catalyst size of 0.5 nm [9].

In a recent report, density of CNT arrays in CNT films was improved by eliminating the pores and gaps in the thin film resulting in density improvement by 109% [32], which also, in turn, improved the mechanical strength of 765 ± 15 and 184 ± 58 MPa and electrical conductivity to $(1.65 \pm 0.15) \times 10^5$ and $(1.04 \pm 0.10) \times 10^5 \text{ S m}^{-1}$. The pores and gaps were eliminated by synthesizing continuous CNT aerogel by FCCVD method. With precursor containing ethanol as the carbon source with ferrocene, thiophene, and deionized water carrier gas was a mixture of H_2 and Ar which was fed to the furnace at 1200–1300 $^\circ\text{C}$. Sock-like aerogel was formed by millions of CNTs which was densified by spraying ethanol. After that the film was passed through smooth plates at 100 N pressure, which further densified the film, again the film was rolled by two oppositely rolling rollers to improve the packing density.

As noticed, two approaches can be established to obtain dense CNT arrays, that is, by growing dense CNT arrays in the initial process, or densifying the CNT yarns after drawing/spinning (post-treatment) of CNT arrays.

4.1.4. Alignment of carbon nanotubes

Ordinary CNT array and super-aligned CNT array are presently known classifications of CNT arrays concerning the degree of alignment of CNTs.

The degree of alignment is a deciding factor for the successful drawing of the CNT yarn or CNT films. The degree of alignment is a subject depending upon the van der Waals forces between two consecutive CNTs in the array. Hence van der Waals forces are responsible for holding the successive CNTs together. These, van der Waals forces are dependent on the

surface property of the CNTs. Therefore, the surface purity of the CNTs is crucial for the drawability of the CNT array.

High alignment: floating catalyst; chemical vapor deposition method, is a reliable method to synthesize highly aligned CNT sheets, as the fabrication process is easy and low cost [10].

Other growth governing parameters are:

Directing number of walls and diameter of the CNT array.

Directing the chirality of the CNT in the array.

Directing purity and catalyst.

As mentioned above the many factors govern the growth and alignment of VACNT in such regard it involves parameters like a catalyst, the thickness of the catalyst nanoparticles thin film, precursor, growth method, carrier gas, flow rate, time of the process, initialization and termination of VACNT growth process, and substrates of growth.

4.1.5. Directing number of walls and diameter of the CNT array

Principally, a number of walls and diameter control is a significant research alongside VACNTs, and numerous fruitful and reproducible synthesis parameters have been established.

Controlling the catalyst size by sulfur is a recent report which claimed that the controlling of particle size by influencing the catalyst size by sulfur. The injecting time and temperature of sulfur resulted in controlling the majority of the CNTs walls to SWCNT, DWCNT, and MWCNT [33]. In another event, water-assisted growth CNT arrays yielded in SWCNTs with a uniform diameter. The mechanism behind the uniformity was prophesied as water contributes to uniform catalyst distribution. Hence high-density uniform SWCNT arrays were obtained [9]. By using FCCVD method DWCNTs were achieved by coating a monolayer of the organic polymer during the process of CVD [34]. An example is shown in **Figure 4**.

Buffer layer influence on catalyst morphology and spinnability of VACNT.

The spinnability of VACNT depends on buffer layer thickness such as Al_2O_3 of a narrow window. Also, the buffer layer thickness regulates size and distribution of catalyst particles. In an ideal circumstance, uniformly distributed, dense and small-sized catalyst nanoparticles yield the excellent product. Al_2O_3 was thermally grown followed by Fe layer, and VACNT was grown, and spinnability was tested at different thicknesses keeping one constant at a time. It was found that at a low thickness of Fe like <0.8 nm VACNTs grown are short. However, for 1 nm Fe layer the VACNT averaged to $0.7 \mu\text{m}$ and the thickness of 1–1.2 nm resulted in highly spinnable VACNTs. Moreover, it was found that Al_2O_3 layer is beneficial for the spinnability of VACNTs [35].

4.1.6. Directing the chirality of the CNT in the array

As it is quite familiar that CNTs can be classified into three types of chirality, that is, arm-chair, chiral, and zigzag, depending on the specific discrete angle rolling of the graphene. Not

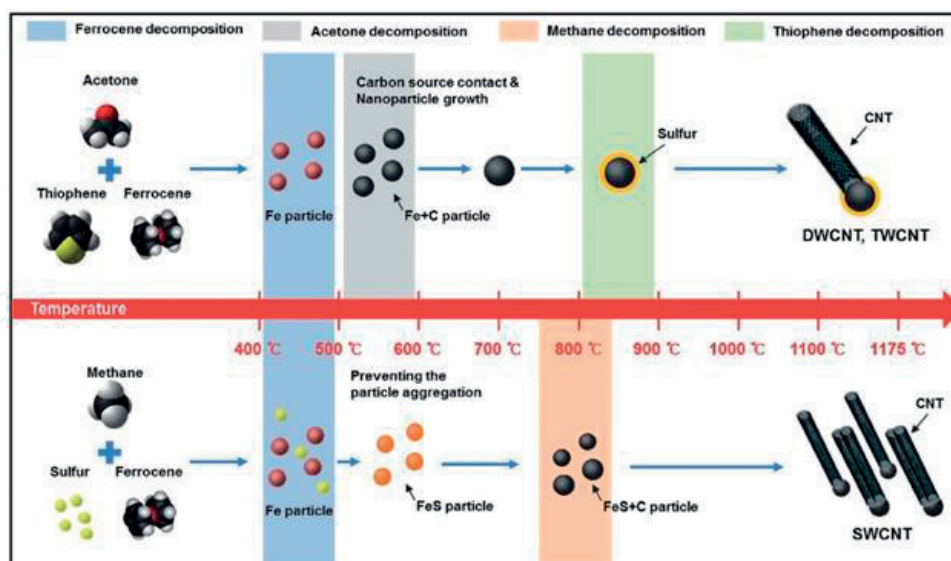


Figure 4. Showing the growth of CNTs at various temperatures (reprinted from Ref. [33] with permission).

considerable research has driven researchers in atomic level structural control for directing the chirality of the CNT in the array.

4.1.7. Directing the purity and catalyst

The most commonly used catalyst for synthesizing ACNTs is ferrocene; the catalyst plays a crucial role in guiding the number of walls, size, and layers of CNTs in the ACNTs. This catalyst can also be a cause for impurity as there is a possibility of the catalyst embeds into the CNTs while growing. Mostly the concentration of catalyst particle depends on the type of synthesis. If the synthesis is CVD method, the impurity is relatively less than that of FCCVD method.

4.2. Drawing of CNT yarns and fibers using VACNTs

It is challenging to grow long CNTs which lead to a spinning method to obtain long CNT spinning threads. A typical CNT yarn drawing is shown in **Figure 5**.

The model anticipated for drawing of VACNTs into yarns is realized by Zhang et al. [30]. It is recorded that pulling of yarns while observing under scanning electron microscope and optical microscope revealed that super-aligned CNTs (SACNTs) hold strong van der Waal forces which keep the CNTs aligned. Also, the SACNTs bundles are joined end to end resulting in a continuous yarn, which was not for the case of normally aligned CNTs. Hence SACNTs possess van der Waals forces which can be used to spinning CNT yarn. It was also stated that the difference between normally aligned CNTs and SACNTs was that the SACNTs had very clean surfaces.

An optimum condition for the growth and direct drawing of, number of walls controlled VACNTs was performed by design of experiment method. All factors responsible for the direct spinning process such as regulating the flow rates of carbon source, catalyst source, sulfur, water, hydrogen, and reaction temperature were evaluated [36].

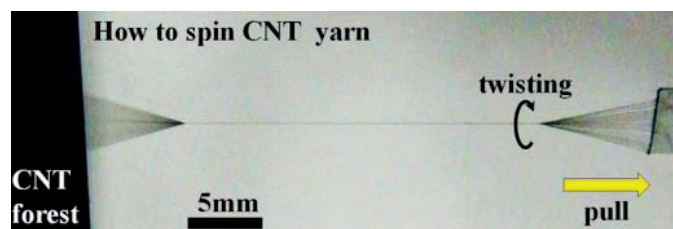


Figure 5. A simple dry drawing of CNT forest into yarns by twisting.

CNT yarn drawing speed and spinning rates.

Apart from the challenges mentioned above in growing VACNTs, regarding industrial application and mass production of CNTs, drawing speed and spinning rates play a prominent role.

Alvarez et al. developed a dry spinning process which has improved drawing rates at about 15.93 m s^{-1} [23]. Improved drawing rates were achieved by using spinnable CNT arrays which get entirely separated from the growth substrate and the growing nanoparticle. Due to the nature of separating from the growth substrate, the CNT threads have higher diameter uniformity. The substrates can be reused for CNT forest growth as the CNT is wholly detached from the substrate and the nanoparticle. It was also possible to produce long CNT fibers by joining CNT ribbons from different batches. A typical 8-inch diameter substrate can spin 316 m length of CNT yarn [37].

4.3. Drawing of CNT sheets/films using ACNTs

Like the drawing of CNT yarns, CNT sheets can be drawn using ACNTs produced by CVD process or rolled out from when produced by FCCVD process, or to deposit on to a surface while synthesizing CNTs. The CNT sheet drawing process is slightly different from CNT yarn. In a recent report CNTs synthesized by FCCVD method could deposit on an ethanol pre-wetted paper [38]. Xu et al. reported continuous production of CNT cylinder film. Moreover, the film had the strength of 9.6 GPa. FCCVD method was used to synthesize continuous production of CNT cylinder which was rolled onto a roller with densifying by ethanol [39].

5. Properties of CNT yarns and CNT films

5.1. Electrical properties

Electrical properties of CNT yarns can be stated as the most important property of CNT yarns, as the CNT yarns are highly suitable for electrical and electronic applications. Many researchers suggest numerous methods to improve the conductivity of the CNT yarns. Ideally, yarns drawn from metallic SWCNT would constitute for maximum electrical conductivity. However, the growth of metallic SWCNT is a great challenge. The electrical conductivity of CNT yarns is dependent on the intertube spacing, purity, and as mentioned before chirality of the CNT. Therefore, densification, eliminating impurities, and controlling chirality are a possible technique to improve the electrical conductivity.

For CNT yarns spun from DWCNT with diameters of 5–20 μm , the electrical conductivity and maximum current carrying, the capability was calculated to be $5.9 \times 10^5 \text{ S m}^{-1}$ and $1 \times 10^5 \text{ A cm}^{-1}$ [40] by high current-induced thermal burnout analysis in the air. Doping is also a possible approach to improve the electrical conductivity of CNT yarns, in such an event iodine doped CNT cables have resulted in specific conductivity greater than that of metals [41]. With an electrical resistivity of 10^{-7} ohm , for DWCNT drew cables.

Improving the electrical conductivity methods include mechanical condensation and acid treatment of CNT yarns, which increased the conductivity of the CNT yarns by nine times [42]. Which leads to a maximum current density of $66,000 \text{ A cm}^{-2}$. It was also observed that mechanical condensation reduced resistance only a few ohms but increased the electrical conductivity by four times. Further acid (HNO_3) treatment drastically reduced resistance by 50% and improving the conductivity. Acid treatment helps in eliminating amorphous carbon and catalyst particle on the surface of the CNTs hence improving the conductivity. Metal deposition on CNT yarn has also been produced by depositing Cu and Au, on CNT yarns by electrodeless deposition, the metal-doped CNT yarns had metal like conductivities but the strength reduced by 30–50% [43].

5.2. Mechanical properties

The mechanical strength of CNT yarn relies upon all the major components of CNT yarn synthesis. Mechanical strength also varies with the length of the CNT yarn. Hence comparing all the reports about mechanical strength with constant length is a difficult issue. Researchers mostly pick the most suitable lengths to determine the mechanical properties and many methods to improve the mechanical strength. Hence it takes the sharp eye in concluding the best-obtained result till date, however, it is very beneficial to know all the approaches taken in improving the mechanical strength.

Oxygen plasma-treated CNT yarn improved the tensile strength and Young's moduli to 2.2 GPa and 200 GPa, respectively [44]. Crosslinking technique is a new technology established in CNT yarns and found to improve the strength from 0.2 to 1.4 GPa [45]. Shrinking effect caused by passing freshly produced CNT yarn into volatile solvents (water, ethanol, and acetone) has found to increase the tensile strength to 1 GPa, in which acetone is resulting in the best tensile strength [46]. Small-molecule functionalized with electron beam irradiation improved the tensile strength by 25% upon functionalization, and a total increase of 88% tensile strength was observed when irradiated with the electron beam after functionalization [47]. In a report, recently it was found that mechanical strength of CNT yarns can improve by acid treatment followed by epoxy treatment [48]. Moreover, a maximum stiffness of 62.0 GPa was recorded. Also, CNT films have strengths up to 9.6 GPa produced by FCCVD method [39].

5.3. Other properties

Apart from the mechanical and electrical properties of VACNT, thermal properties of VACNTs has also been a locus point in determining the underlying properties of VACNTs. In a study, thermal transfer speed in highly aligned CNTs was investigated to determine

the thermal damping mechanism in SACNT Bucky papers. It is found that the heat transfer speed is different for different densities of SACNT Bucky papers. It was about 562.2 to 55.4 mm² s⁻¹ for parallel SACNT Bucky papers [49]. Concerning with the electrochemical property of SACNTs a surface oxidized by H₂O₂ and HNO₃ to CNT film was observed to have a high cycle performance rate of 364 and 391 mA h g⁻¹ [50]. FCCVD grown CNTA electrode in an organic electrolyte had a specific capacitance of 24.5 Fg⁻¹ higher than that of aqueous electrolyte [11].

6. Applications

6.1. CNT fiber/yarn/thread

Replacing electrical wires with CNT yarns is the primary application of CNT yarns, in such an attempt insulation of CNT yarns, was made to replace existing copper wiring [51].

CNT fibre microelectrodes as dopamine sensor [52], as special oxygen-containing functional groups, were observed on the surface of carbon.

Weavable non-volatile memory devices by carbon fibers [53] using MWCNT fibers for an electrode with graphene oxide as the active material. In which MWCNT array is wound over a glass rod and densifying with ethanol and coating with graphene oxide of 10–20 nm. MWCNT and graphene oxide are joined non-covalently. With further processing, it works as a fiber based memory cell which exhibits write once and read many times type memory effect.

Pure 3D CNT aerogels were produced by the spontaneous expansion of SACNT films, the expansion of SACNT films was formed by soaking in a mixture of H₂SO₄ and H₂O₂. This soaking resulted in producing aerogels with a tremendously low apparent density of 0.12 mg cm⁻³ and a porosity of 99.95% [54], which leads to applications such as energy storage, catalysis as they show high adsorption abilities.

Water transport phenomena through VADWCNT array was reported by Matsumoto et al. [55]. By Parylene-C coating one side of the VADWCNT array and then peeling off the other end of VADWCNT array from the Si substrate. Finally, the Parylene-C was finely milled to expose the CNT array which was a flexible and durable membrane. Then it was used to be tested for water transport by dead-end filtration apparatus.

Wire-shaped micro-supercapacitors with aligned titania wire were wound by CNT yarn [56]. Field emission applications [26, 57]. By functionalizing walls by H₂O₂ and HNO₃ treatment and increasing the cycle rate performance, CNT yarns can be used as electrodes for Li-ion batteries [50]. Neurotransmitter dynamic detection by CNT yarn electrodes [58].

6.2. Applications of CNT films/sheets

Platinum-coated CNT films were demonstrated to have used in fuel cells and solar cells [38]. CNT sheets are produced by SWCNTs as electrochemical actuators [59].

Acknowledgements

The authors thank SGU-MEXT for their kind support for providing funds for PhD degree students in Japan.

Author details

Yasuhiko Hayashi^{1*}, Karthik Paneer Selvam¹ and Maik Scholz²

*Address all correspondence to: hayashi.yasuhiko@okayama-u.ac.jp

1 Graduate School of Natural Science and Technology, Okayama University, Okayama, Japan

2 Leibniz Institute for Solid State and Material Research Dresden, Dresden, Germany

References

- [1] Pan ZW, Xie SS, Chang BH, Wang CY, Lu L, Liu W, Zhou WY, Li WZ, Qian LX. Very long carbon nanotubes. *Nature*. 1998;**13**:631-632
- [2] Zhu HW, CL X, DH W, Wei BQ, Vajtai R, Ajayan PM. Direct synthesis of long single-walled carbon nanotube strands. *Science*. 2002;**3**:884-886
- [3] Ajayan PM, Stephan O, Colliex C, Trauth D. Aligned carbon nanotube arrays formed by cutting a polymer resin-nanotube composite. *Science-AAAS-Weekly Paper Edition*. 1994;**265**(5176):1212-1214
- [4] Gray GW, Winsor PA. *Liquid Crystals and Plastic Crystals*. Vol. 2. London: Ellis Horwood; 1974
- [5] Dresselhaus MS, Dresselhaus G, Sugihara K, Spain IL, Goldberg HA. Synthesis of graphite fibres and filaments. In: *Graphite fibers and filaments*. Berlin, Heidelberg: Springer; 1988. pp. 12-34
- [6] de Heer WA, Bacsá WS, Chatelain A, Gerfin T, Humphrey-Baker R. Aligned carbon nanotube films: Production and optical and electronic properties. *Science*. 1995;**12**(5212):845
- [7] Li WZ, Xie SS, Qian L, Chang BH. Large-scale synthesis of aligned carbon nanotubes. *Science*. 1996, 1701;**274**(5293):6
- [8] Yun Y, Shanov V, Tu Y, Subramaniam S, Schulz M. Growth mechanism of long aligned multiwall carbon nanotube arrays by water-assisted chemical vapor deposition. *The Journal of Physical Chemistry. B*. 2006;**110**:23920-23925

- [9] Wyss R, Klare J, Park H, Noy A, Bakajin O, Lulevich V. Water-assisted growth of uniform 100 nm diameter SWCNT arrays. *ACS Applied Materials & Interfaces*. 2014;**6**: 21019-21025
- [10] Liu Q, Li M, Gu Y, Zhang Y, Wang S, Li Q, Zhang Z. Highly aligned dense carbon nanotube sheets induced by multiple stretching and pressing. *Nanoscale*. 2014;**6**:4338-4344
- [11] Zhang H, Cao G, Yang Y. Electrochemical properties of ultra-long, aligned, carbon nanotube array electrode in organic electrolyte. *Journal of Power Sources*. 2007;**172**:476-480
- [12] Davis V, Parra-Vasquez A, Green M, Rai P, Behabtu N, Prieto V, Booker R, Schmidt J, Kesselman E, Zhou W, Fan H, Adams W, Hauge R, Fischer J, Cohen Y, Talmon Y, Smalley R, Pasquali M. True solutions of single-walled carbon nanotubes for assembly into macroscopic materials. *Nature Nanotechnology*. 2009;**4**:830-834
- [13] Kuznetsov AA, Fonseca AF, Baughman RH, Zakhidov AA. Structural model for dry-drawing of sheets and yarns from carbon nanotube forests. *ACS Nano*. 2011;**5**:985-993
- [14] Miao M. Electrical conductivity of pure carbon nanotube yarns. *Carbon*. 2011;**49**:3755-3761
- [15] Miao M. The role of twist in dry spun carbon nanotube yarns. *Carbon*. 2016;**96**:819-826
- [16] Zhao J, Zhang X, Di J, Xu G, Yang X, Liu X, Yong Z, Chen M, Li Q. Double-peak mechanical properties of carbon-nanotube fibers. *Small*. 2010;**6**:2612-2617
- [17] Liu K, Sun Y, Lin X, Zhou R, Wang J, Fan S, Jiang K. Scratch-resistant, highly conductive, and high-strength carbon nanotube-based composite yarns. *ACS Nano*. 2010;**4**:5827-5834
- [18] Cai J, Min J, McDonnell J, Church J, Easton C, Humphries W, Lucas S, Woodhead A. An improved method for functionalisation of carbon nanotube spun yarns with aryldiazonium compounds. *Carbon*. 2012;**50**:4655-4662
- [19] Jayasinghe C, Amstutz T, Schulz M, Shanov V. Improved processing of carbon nanotube yarn. *Journal of Nanomaterials*. 2013:1-7
- [20] Cho W, Schulz M, Shanov V. Growth and characterization of vertically aligned centimeter long CNT arrays. *Carbon*. 2014;**72**:264-273
- [21] Li QW, Zhang XF, DePaula RF, Zheng LX, Zhao YH, Stan L, Holesinger TG, Arendt PN, Peterson DE, Zhu YT. Sustained growth of ultralong carbon nanotube arrays for fiber spinning. *Advanced Materials*. 2006;**18**:3160-3163
- [22] Luo Y, Wang X, He M, Li X, Chen H. Synthesis of high-quality carbon nanotube arrays without the assistance of water. *Journal of Nanomaterials*. 2012:1-5
- [23] Alvarez N, Miller P, Haase M, Kienzle N, Zhang L, Schulz M, Shanov V. Carbon nanotube assembly at near-industrial natural-fiber spinning rates. *Carbon*. 2015;**86**:350-357
- [24] Inoue Y, Suzuki Y, Minami Y, Muramatsu J, Shimamura Y, Suzuki K, Ghemes A, Okada M, Sakakibara S, Mimura H, Naito K. Anisotropic carbon nanotube papers fabricated from multiwalled carbon nanotube webs. *Carbon*. 2011;**49**:2437-2443

- [25] Inoue Y, Kakihata K, Hirono Y, Horie T, Ishida A, Mimura H. One-step grown aligned bulk carbon nanotubes by chloride mediated chemical vapor deposition. *Applied Physics Letters*. 2008;**92**:213113
- [26] Fan S, Chapline MG, Franklin NR, Tomblor TW, Cassell AM, Dai H. Self-oriented regular arrays of carbon nanotubes and their field emission properties. *Science*. 1999;**22**:512-514
- [27] Ren ZF, Huang ZP, Xu JW, Wang JH, Bush P, Siegal MP, Provencio PN. Synthesis of large arrays of well-aligned carbon nanotubes on glass. *Science*. 1998;**6**:1105-1107
- [28] J Lee EO, Kim H-J, Cho S, Kim T, Lee S, Park J, Kim H, Lee K-H. *Journal of Materials Science*. The reason for an upper limit to the height of spinnable carbon nanotube forests. 2013;**48**:6897-6904
- [29] Feng C, Liu K, Wu J, Liu L, Cheng J, Zhang Y, Sun Y, Li Q, Fan S, Jiang K. Flexible, stretchable, transparent conducting films made from superaligned carbon nanotubes. *Advanced Functional Materials*. 2010;**20**:885-891
- [30] Zhang X, Jiang K, Feng C, Liu P, Zhang L, Kong J, Zhang T, Li Q, Fan S. Spinning and processing continuous yarns from 4-inch wafer scale super-aligned carbon nanotube arrays. *Advanced Materials*. 2006;**19**:1505-1510
- [31] Ding DY, Liu J. Growth of high-density parallel arrays of long single-walled carbon nanotubes on quartz substrates. *Journal of the American Chemical Society*. 2008;**130**:5428-5542
- [32] Han B, Xue X, Xu Y, Zhao Z, Guo E, Liu C, Luo L, Hou H. Preparation of carbon nanotube film with high alignment and elevated density. *Carbon* 2017;**122**:496-503
- [33] Lee S-H, Park J, Kim H-R, Lee J, Lee K-H. Synthesis of high-quality carbon nanotube fibers by controlling the effects of sulfur on the catalyst agglomeration during the direct spinning process. *RSC Advances*. 2015;**5**:41894-41900
- [34] Naraghi M, Filleter T, Moravsky A, Locascio M, Loutfy R, Espinosa H. A multiscale study of high performance double-walled nanotube-polymer fibers. *ACS Nano*. 2010;**4**:6463-6476
- [35] Zhang Y, Sun G, Zhan Z, Zheng L. Influence of Al₂O₃ buffer layer on catalyst morphology and spinnability of carbon nanotube arrays. *Journal of Materials Science*. 2017;**52**:6196-6204
- [36] Lee S-H, Park J, Kim H-R, Lee T, Lee J, Im Y-O, Lee C-H, Cho H, Lee H, Jun C-H, Ahn Y-C, Lee I-B, Lee K-H. Synthesis of carbon nanotube fibers using the direct spinning process based on design of experiment DOE. *Carbon*. 2016;**100**:647-655
- [37] Liu K, Zhu F, Liu L, Sun Y, Fan S, Jiang K. Fabrication and processing of high-strength densely packed carbon nanotube yarns without solution processes. *Nanoscale*. 2012; **4**(11):3389-3393
- [38] Luo X, Huang X, Wang X, Zhong X, Meng X, Wang J. Continuous preparation of carbon nanotube film and its applications in fuel and solar cells. *ACS Applied Materials & Interfaces*. 2016;**8**:7818-7825

- [39] Xu W, Chen Y, Zhan H, Wang J. High-strength carbon nanotube film from improving alignment and densification. *Nano Letters*. 2016;**16**:946-952
- [40] Song L, Toth G, Wei J, Liu Z, Gao W, Ci L, Vajtai R, Endo M, Ajayan PM. Sharp burn-out failure observed in high current-carrying double-walled carbon nanotube fibers. *Nanotechnology*. 2011;**8**(1):015703
- [41] Zhao Y, Wei J, Vajtai R, Ajayan PM, Barrera EV. Iodine doped carbon nanotube cables exceeding specific electrical conductivity of metals. *Scientific Reports*. 2011;**1**:83
- [42] Liu P, Hu D, Tran T, Jewell D, Duong H. Electrical property enhancement of carbon nanotube fibers from post treatments. *Colloids Surfaces Physicochem Engineering Aspects*. 2016;**509**:384-389
- [43] Randeniya L, Bendavid A, Martin P, Tran C. Composite yarns of multiwalled carbon nanotubes with metallic electrical conductivity. *Small*. 2010;**6**:1806-1811
- [44] Wei H, Wei Y, Wu Y, Liu L, Fan S, Jiang K. High-strength composite yarns derived from oxygen plasma modified super-aligned carbon nanotube arrays. *Nano Research*. 2013;**6**:208-215
- [45] Kim H, Lee J, Park B, Sa J-H, Jung A, Kim T, Park J, Hwang W, Lee K-H. Improving the tensile strength of carbon nanotube yarn via one-step double [2+1] cycloadditions. *Korean Journal of Chemical Engineering*. 2016;**33**:299-304
- [46] Liu K, Sun Y, Zhou R, Zhu H, Wang J, Liu L, Fan S, Jiang K. Carbon nanotube yarns with high tensile strength made by a twisting and shrinking method. *Proceedings of SPIE*. 2010;**21**:045708
- [47] Miller S, Williams T, Baker J, Solá F, Lebron-Colon M, McCorkle L, Wilmoth N, Gaier J, Chen M, Meador M. Increased tensile strength of carbon nanotube yarns and sheets through chemical modification and electron beam irradiation. *ACS Applied Materials & Interfaces*. 2014;**6**:6120-6126
- [48] Tran T, Fan Z, Mikhalchan A, Liu P, Duong H. Post-treatments for multifunctional property enhancement of carbon nanotube fibers from the floating catalyst method. *ACS Applied Materials & Interfaces*. 2016;**8**:7948-7956
- [49] Zhang G, Liu C, Fan S. Directly measuring of thermal pulse transfer in one-dimensional highly aligned carbon nanotubes. *Scientific Reports*. 2013;**3**:2549
- [50] Li M, Wu Y, Zhao F, Wei Y, Wang J, Jiang K, Fan S. Cycle and rate performance of chemically modified super-aligned carbon nanotube electrodes for lithium ion batteries. *Carbon*. 2014;**69**:444-451
- [51] Kurzepa L, Lekawa-Raus A, Patmore J, Koziol K. Replacing copper wires with carbon nanotube wires in electrical transformers. *Advanced Functional Materials*. 2014;**24**:619-624
- [52] Roberts J, Moody B, McCarty G, Sombers L. Specific oxygen-containing functional groups on the carbon surface underlie an enhanced sensitivity to dopamine at electrochemically pretreated carbon fiber microelectrodes. *Langmuir*. 2010;**26**:9116-9122

- [53] Sun G, Liu J, Zheng L, Huang W, Zhang H. Preparation of Weavable, All-Carbon Fibers for Non-Volatile Memory Devices. *Angew Chem-ger Edit.* 2013;**125**:13593-13597
- [54] Luo Y, Luo S, Wu H, Li M, Wang K, Yan L, Jiang K, Li Q, Fan S, Wang J. Self-expansion construction of ultralight carbon nanotube aerogels with a 3D and hierarchical cellular structure. *Small.* 2017:1700966
- [55] Matsumoto H, Tsuruoka S, Hayashi Y, Abe K, Hata K, Zhang S, Saito Y, Aiba M, Tokunaga T, Iijima T, Hayashi T, Inoue H, Amaratunga G. Water transport phenomena through membranes consisting of vertically-aligned double-walled carbon nanotube array. *Carbon.* 2017;**120**:358-365
- [56] Chen T, Dai L. Flexible and wearable wire-shaped micro supercapacitors based on highly aligned titania and carbon nanotubes. *Energy Storage Materials.* 2016;**2**:21-26
- [57] Wei Y, Jiang J, Liu L, Chen Z, Fan F. Vacuum-breakdown-induced needle-shaped ends of multiwalled carbon nanotube yarns and their field emission applications. *Nano Letters.* 2007;**7**:3792-3797
- [58] Schmidt A, Wang X, Zhu Y, Sombers L. Carbon nanotube yarn electrodes for enhanced detection of neurotransmitter dynamics in live brain tissue. *ACS Nano.* 2013;**7**:7864-7873
- [59] Mukai K, Asaka K, Sugino T, Kiyohara K, Takeuchi I, Terasawa N, Futaba D, Hata K, Fukushima T, Aida T. Highly conductive sheets from millimeter-long single-walled carbon nanotubes and ionic liquids: Application to fast-moving, low-voltage electromechanical actuators operable in air. *Advanced Materials.* 2009;**21**:1582-1585
- [60] Bronikowski M. CVD growth of carbon nanotube bundle arrays. *Carbon.* 2006;**44**:2822-2832