Carbon nanotube yarns for electronic textiles

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3.1 Introduction

Carbon nanotubes (CNTs) possess extraordinarily high mechanical properties combined with electrical and thermal conductances. The challenge is to organize these building blocks into macroscale structures that express similar properties. Without considering their detailed atomic structures, CNTs are nanoscale fibres that resemble the diameter of microfibrils in plant and animal fibres. The CNTs used to spin yarns are very long relative to their diameters, with aspect ratios at least one order of magnitude greater than common textile fibres (Miao, 2013).

CNTs can be processed into fibres and yarns in several ways: (1) extruding a fibre from a CNT/polymer solution, (2) spinning a yarn from a vertically aligned array (known as a forest) of multi-walled CNTs (MWCNTs) grown on a substrate, (3) spinning a yarn directly from an aerogel of CNTs as they are formed in a chemical vapour deposition (CVD) reactor and (4) twisting or rolling a macroscale CNT sheet into a yarn. Yarns fabricated by dry-state drawing and spinning of CNT forests have demonstrated the best mechanical properties to date.

3.2 CNT forests and drawability

3.2.1 CNT synthesis

All known spinnable CNT forests are produced using CVD methods. The carbon source is deposited on a catalyst that causes it to decompose into carbon atoms, and tubular CNTs are formed at the catalyst site. In comparison to arc discharge and laser ablation methods, CVD has the advantages of mild operating conditions, low costs and controllable synthesis, and it is the most promising method for CNT mass production (Zhang et al., 2011).

Typically, aligned CNTs are grown in a reaction furnace with flowing gaseous carbon feedstock in the presence of a catalyst on a silicon wafer substrate. A layer of catalyst particles (e.g., Fe) is deposited on the silicon wafer. A carrier gas (e.g., helium) and a carbon source (e.g., acetylene, ethylene) are used. Figure 3.1 shows transmission electron microscope images of CNTs in a web drawn from such a CNT forest. The diameter distribution and number of walls of the CNTs in a forest can be controlled to some extent by varying the thicknesses of the catalyst layer, and the length

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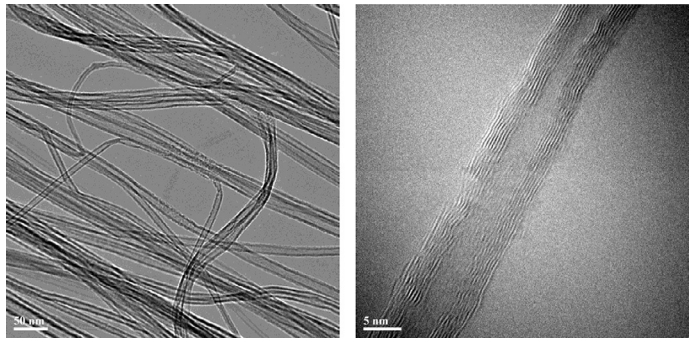

Figure 3.1 TEM images of the multi-walled spinnable CNTs (Miao et al., 2010).

of nanotubes can be tuned by growth time to a certain extent. Water vapour can be used to prolong CNT growth, resulting in longer CNT forests.

Spinnable CNT forests can also be grown on highly flexible stainless steel sheets. The flexible CNT forest could be transported like a long belt, where at one end of the belt, the CNTs are grown in the furnace, and at the opposite end, the CNTs are converted into a yarn, providing a continuous process for the solid-state fabrication of CNT yarn (Lepró et al., 2010).

3.2.2 Drawability of CNT forests

The conversion of a vertically aligned CNT forest into a continuous length of interconnected CNT web was discovered accidentally (Jiang et al., 2002). While attempting to pull out a bundle of CNTs from an array several hundred micrometres high, grown on a silicon substrate, the researchers obtained instead a continuous ribbon-like web of pure CNTs, in a similar way to the drawing of a thread from a silk cocoon. The drawing of a web from a CNT forest is shown in Figure 3.2.

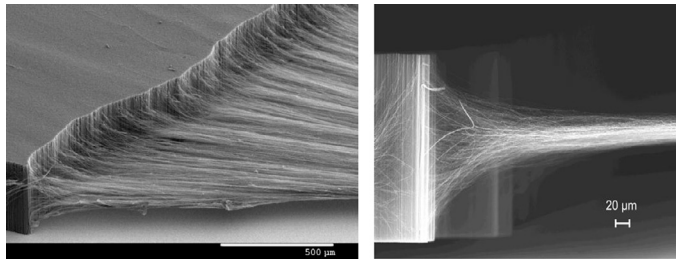

Figure 3.2 SEM micrograph showing that the MWCNTs in a forest are rotated 90° to form a continuous length web.
Reprinted with permission from Miao et al. (2010).

The drawability of CNT forests is closely related to the morphology of the CNT arrays and can be altered, for example, by adjusting catalyst pretreatment time or by introducing a small amount of hydrogen or oxygen during CVD growth (Huynh and Hawkins, 2010). Prolonged pretreatment resulted in coarsening of catalyst particles and non-drawable CNT forests. Well-aligned CNT arrays were obtained from the hydrogen-assisted growth, and wave-like arrays were the result of oxygen-assisted growth.

3.3 CNT yarns

The CNT web drawn from a forest has a rather low mechanical strength. Its strength can be increased dramatically by twist insertion, which condenses the CNT web into a yarn of much higher density; see Figure 3.3 (Zhang et al., 2004).

The CNT web can also be 'shrunk' into a compact yarn of irregular cross section by passing through a droplet of volatile solvent (Zhang et al., 2006). CNTs are hydrophobic but can be wetted by volatile solvents. The surface tension pulls the CNT bundles together, as the yarn leaves the meniscus. With the evaporation of the volatile solvent, a dry-densified CNT yarn is formed.

3.3.1 Flyer spinning

Research efforts at the Commonwealth Scientific and Industrial Research Organisation (CSIRO) resulted in several high-speed CNT yarn-spinning methods. The first automated continuous CNT yarn-spinning machine was built based on the conventional flyer-spinning principle (Figure 3.4). The twisting and winding operations are realized by two coaxial shafts that rotate at differential speeds, causing the yarn to be wound onto the yarn collection bobbin carried on the spindle. The spindle also performs a linear motion to spread the yarn on the bobbin in an orderly fashion. A computer is used to coordinate these motions. A series of friction pins can be introduced between the CNT forest and the spindle on the flyer-spinning machine (Tran et al., 2009). These pins affect the spinning process in two ways: increasing the yarn

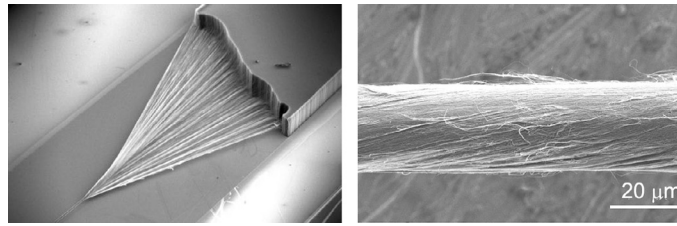

Figure 3.3 Formation of a CNT yarn by twist insertion (left) and SEM image of a CNT yarn (right) (Miao, 2013).

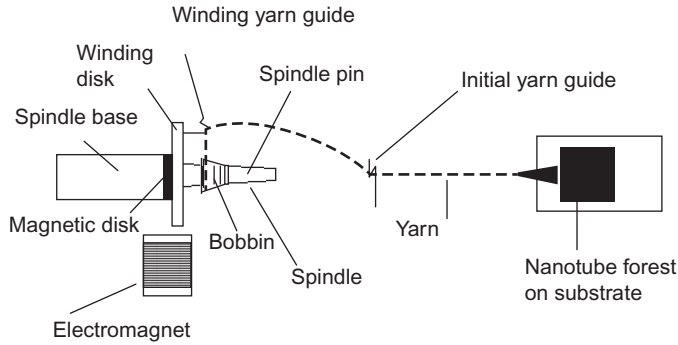

Figure 3.4 Schematic of CNT yarn flyer-spinner (Miao, 2013).

tension and causing the twist to be inserted into the yarn in steps along the zones separated by the pins. The increased tension further increases yarn density, leading to a more compact yarn structure and higher stress-based strength and elastic modulus but lower breaking strain.

3.3.2 Up-spinning

Figure 3.5 shows what is dubbed as the CSIRO 'up-spinner' (Miao et al., 2010). The CNT forest is attached to a spindle that can be rotated at high speed. The continuous CNT web drawn from the forest is pulled up (hence the name up-spinner) to the yarn bobbin, while twist is being inserted by the spindle. On the up-spinner, the two essential functions of continuous yarn spinning are carried out independently: twist is inserted by the fast rotating vertical spindle, and yarn taking-up is carried out by the slow rotating horizontal yarn bobbin. Additionally, a yarn guide or the bobbin

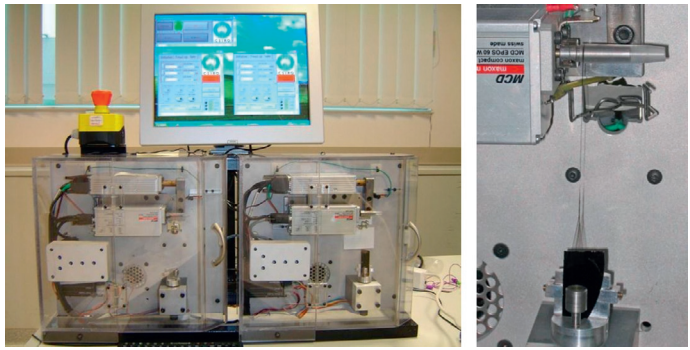

Figure 3.5 Overview of a two-position up-spinning machine controlled by a touchscreen computer (left) and main operating elements of the up-spinner (right) (Miao, 2013).

itself traverses longitudinally to spread the yarn along the bobbin. The up-spinner is a much simpler machine design than the flyer-spinner. The mass carried on the high-speed spindle is immensely smaller than that of the spindle assembly in the flyer-spinning method. The yarn path on the up-spinner is essentially a straight line, resulting in much lower yarn tension during spinning, so that very delicate CNT webs can be spun into yarns at high speeds.

Because of its engineering simplicity, the up-spinner has been run at spindle speeds up to 18,000 rpm, comparable to that of modern spinning machines used to produce fine-count conventional textile yarns. Another advantage of the up-spinner is that the operations required to start a new yarn or to piece up a broken yarn end are greatly simplified.

3.3.3 Rub densification

Because of the small yarn diameter, many thousands of twist turns must be inserted to produce 1 m of yarn. The large number of twists per metre limits the rate of yarn production and demands highly engineered spinning machinery.

Mechanical rubbing action can be used to produce a highly densified CNT yarn (Figure 3.6), in which the CNTs are substantially straight and parallel with each other and are aligned in the direction of the yarn axis (Miao, 2012). The main working parts of the machine are a pair of padded rollers that participate in both rotation and longitudinal oscillation. The rotational motion of the two rollers transports the CNT web drawn from the CNT forest to the yarn take-up bobbin. The axial oscillations of the two rollers work in opposite directions to apply a rubbing action that densifies the CNT web into a yarn.

The main mechanism of interaction between CNTs in the rub-densified yarn is van der Waals force. When the pressure between the rubbing rollers is low, the resulting rub-densified CNT yarn has a unique structure consisting of a high packing density sheath and a low-density core. The low-density core can be eliminated by increasing the pressure between the rubbing rollers and lowering the tension in the yarn (Miao, 2012). The rub-densified CNT yarn has shown similar tensile strength but significantly improved elastic modulus in comparison with the twist-densified CNT yarn.

3.3.4 Core-spun CNT yarn

A core-spun yarn consisting of a metal filament core and a CNT sheath was constructed for application in two-ply yarn supercapacitors (Zhang et al., 2014a). The core/sheath-structured CNT yarn can be manufactured on a flyer-spinner, as shown schematically in Figure 3.7. The CNTs forming the sheath are drawn from the MWCNT forest as a continuous web. The core material is pulled out from a supply bobbin to merge with the CNT web. The twisting action of the spindle at the right-hand side causes the metal filament and the CNT web to rotate together, resulting in the wrapping of the CNT web around the metal filament to form a core/sheath structured yarn (Figure 3.7). Because of the very large width of the CNT web in relation to the diameter of the metal filament, the core is completely covered by the CNT sheath in the resultant core-spun yarn.

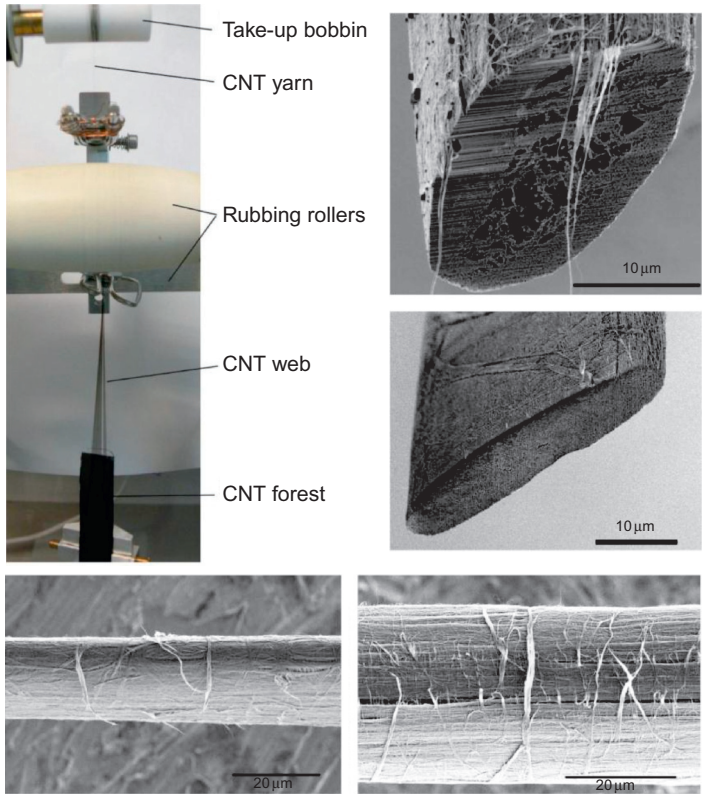

Figure 3.6 CNT yarn production by rub densification (Miao, 2012).

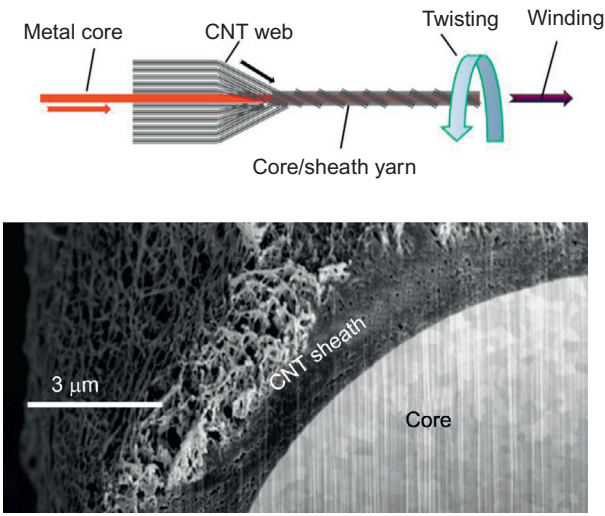

Figure 3.7 Core-spun yarns. Top: schematic of core-spun yarn process. Bottom: cross sectional view of core-spun CNT yarn. Reprinted with permission from Zhang et al. (2014a), copyright (2014) American Chemical Society.

3.4 CNT yarn structure and properties

3.4.1 Yarn structures and formation

It is well understood in the textile industry that yarn production efficiency goes down, and production cost goes up dramatically, as yarns get finer. This is because, first, a fine yarn requires a large number of twist turns per metre to acquire the necessary strength, and second, a fine yarn has many weak spots as a result of the small number of fibres in the yarn cross section, leading to yarn breakage during spinning. A major difference between the CNT yarns and conventional textile yarns is the number of 'fibres' in the yarn cross section. The number of CNTs in the yarn cross section is in the order of 10^5–10^6, which is 10^3–10^4 times more than the number of fibres in a conventional textile yarn, which is typically about 40 fibres in worsted yarns and about 100 fibres for cotton yarns.

Most CNTs appear as bundles in the forest, and these bundles persist into the final yarn structure. Slackness, misalignment and entanglement of nanotubes exist in the web drawn from the forest. The CNT web without being twisted is like an aerogel with an estimated porosity of 99.97% (Miao, 2011). Twist densification can greatly reduce the yarn porosity, approaching the theoretical minimum porosity (pores exist both inside and outside individual CNTs) of 23.8% (Miao et al., 2010). Figure 3.8 shows

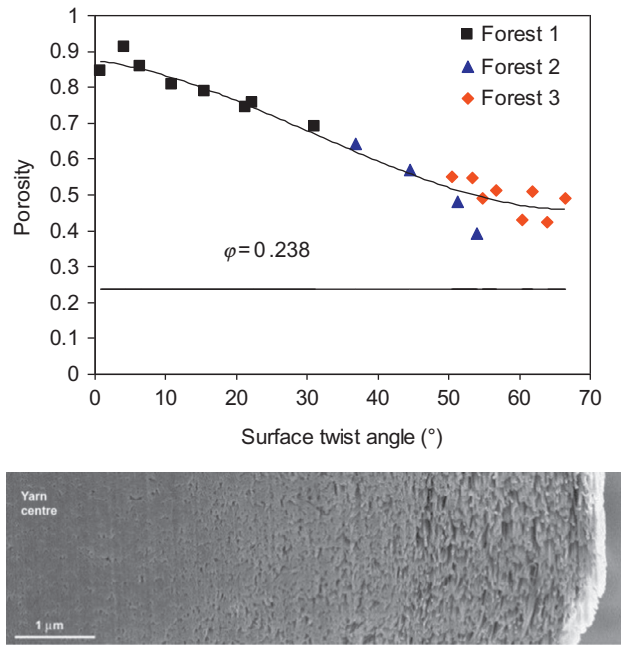

Figure 3.8 CNT yarn porosity. (a) Influence of twist on CNT yarn porosity (Miao et al., 2010). (b) SEM image showing a slice milled through a highly twisted CNT yarn, revealing a densely packed core and a porous sheath (Sears et al., 2010).

the relationship between CNT yarn twist and porosity and a scanning electron microscope image of CNT yarn section prepared by focused ion beam.

The load transfer between CNTs in a yarn mainly relies on the van der Waals force between the constituent nanotubes. CNTs at different radial positions of a twisted yarn follow different helix angle paths and thus form point contacts where they cross over each other. To maximize CNT interconnections, all the constituent CNTs in the yarn need to lie parallel and close with each other so that line contacts between them can be formed. Traditionally, fibre straightening and parallelization is achieved by high-ratio roller drafting. As-prepared CNT web cannot be drafted. Upon application of a tensile force, a dry CNT web breaks at about 3% strain, indicating that individual CNTs do not slide relative to each other. This can be changed by adding a lubricant (e.g., paraffin oil) to the web. The CNTs in the lubricated web can slide relative to each other (Wang et al., 2013b). Using a highly drawable gel containing ultra-high molecular weight polyethylene dispersed in paraffin oil as a carrier, the CNT web can be drafted 14 times its original length. This method has so far been used only to produce a high-strength composite fibre consisting of highly aligned CNTs (Wang et al., 2013b).

3.4.2 Tensile properties

The majority of spinnable nanotubes have diameters between 6 and 15 nm with multiple walls. Published results do not suggest any consistent relationship between the diameter or number of walls of the CNTs and the strength of the resultant yarns (Miao, 2013).

As shown in Figure 3.9, the tenacity and modulus of twisted CNT yarns initially increase with twist angle, reach a plateau and then start to decrease as twist becomes excessive. The yarn tenacity achieves its maximum at a surface twist angle of about 20°, while the modulus reaches its peak value at about 10°. This general trend is similar to the twist–tenacity relationship of conventional textile yarns.

The flyer-spinner and the up-spinner were run in parallel for a number of years. There had been several trials to compare the properties of yarns produced on the two systems. In general, the up-spun yarns are more porous than the flyer-spun yarns, which can be attributed to the different spinning tensions in the two spinning systems. The elastic modulus of the flyer-spun yarns tends to be higher, but strain at break tends to be lower. However, the tenacity and work-to-rupture (toughness) of the yarns' spun on the two systems are similar.

Gamma irradiation of CNT yarns in air was found to improve their tensile strength and modulus (Miao et al., 2011). The improvement was greater for tightly structured yarns than for loosely structured yarns. X-ray photoelectron spectroscopic analyses on parent CNT forests showed that gamma irradiation treatment in air had dramatically increased the concentration of oxygen in the CNT assemblies in proportion to radiation dose. This indicates that CNTs are oxidized under the ionizing effect of the gamma irradiation. Such oxygen species contribute to the interaction between CNTs and thus the improvement of CNT yarn mechanical properties.

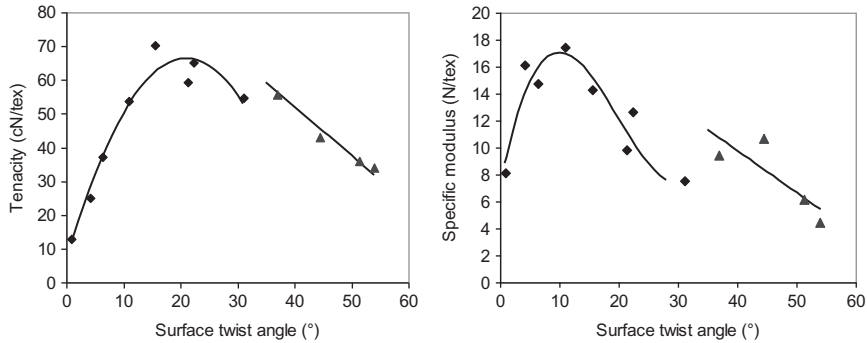

Figure 3.9 Relationships between CNT yarn surface twist angle and specific tensile properties. Note that two CNT forests were used, as indicated by two separate curves in each plot (Miao et al., 2010).

3.4.3 Electrical conductivity

Single-walled CNTs may be either metallic conducting or semiconducting, depending on how the graphene layer is wrapped into a cylinder. The electrical resistivity of MWCNTs produced by carbon-arc method has been reported to be in the range of 6×10^{-2}–5×10^{-8} Ωm, spanning from metallic to semiconducting. The resistivity of MWCNTs produced by catalytic process was found to be in the semiconducting range of 1×10^{-5}–2×10^{-5} Ωm. Contact resistance between nanotubes depends strongly on the atomic structure in the contact area and can vary by more than one order of magnitude. The electrical conductivity of MWCNT-based macrostructures, such as CNT yarns and CNT films (buckypaper), is generally much lower than that of defect-free individual CNTs due to the presence of amorphous carbon and other impurities, which cause scattering and contact resistance.

The reported values of electrical conductivity of pure CNT yarns' spun from forests are between 1.5×10^4 and 4.1×10^4 S/m. A major reason for this spread of value is yarn porosity, which is typically determined by twist and after treatments (Miao, 2011). The electrical conductivity is highly dependent on the CNT yarn porosity. However, when the electrical conductivity is normalized to specific conductivity, there is no significant change that can be attributed to CNT yarn porosity, as shown in Figure 3.10. The gamma irradiation treatment mentioned earlier can improve the electrical conductivity of pure CNT yarns by about 30% (Su et al., 2014).

One approach to dramatically increase the electrical conductivity of CNT yarns is to apply a metal coating on the pure CNT yarns. Randeniya et al. (2010) reported a composite yarn with high electrical conductivity by self-fuelled electro-deposition of metal nanoparticles onto a dry-spun CNT yarn. Cu–CNT and Au–CNT composite yarns prepared by this method had metal-like electrical conductivities ($2–3 \times 10^7$ S/m). However, the tensile strength of the composite yarns was 30–50% lower than that of the original CNT yarn.

Dramatic improvement of electrical conductivity can also be achieved by a simple silver paste dip-coating treatment on the CNT yarn (Zhang et al., 2014b). It has been

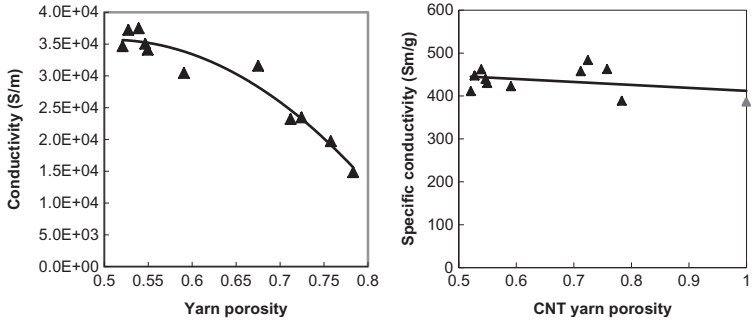

Figure 3.10 Effect of yarn porosity on electrical conductivity (left) and specific conductivity (right) of CNT yarns (Miao, 2011).

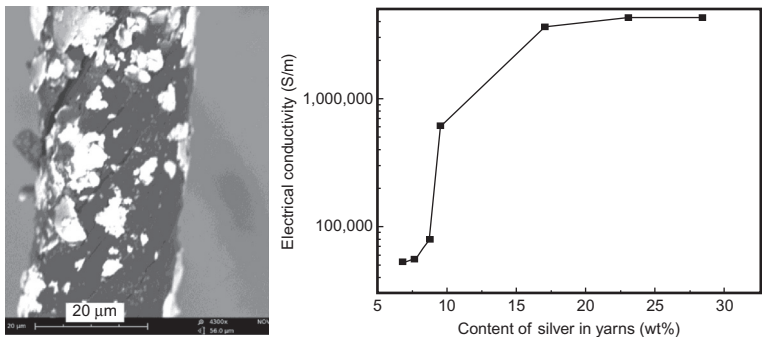

Figure 3.11 Electrical conductivity of silver-paste-treated CNT yarn. Left: SEM of silver-paste-coated CNT yarn. Right: effect of silver content.
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found that a step transition to metallic conductivity took place at about 7 wt% silver content (Figure 3.11). This step change in electrical conductivity is known as electrical percolation, which happens when the high-conductivity particles form electrical contact paths. Because of the small quantity and nature of the silver paste, the coated CNT yarn maintains its original strength.

3.5 Applications

3.5.1 CNT yarn textiles

CNT yarns can consistently achieve higher tenacity (70–80 cN/tex) than many traditional textile yarns such as wool yarns (∼10 cN/tex) and cotton yarns (∼20 cN/tex). They are also less twist-lively than conventional textile yarns when a cut end is

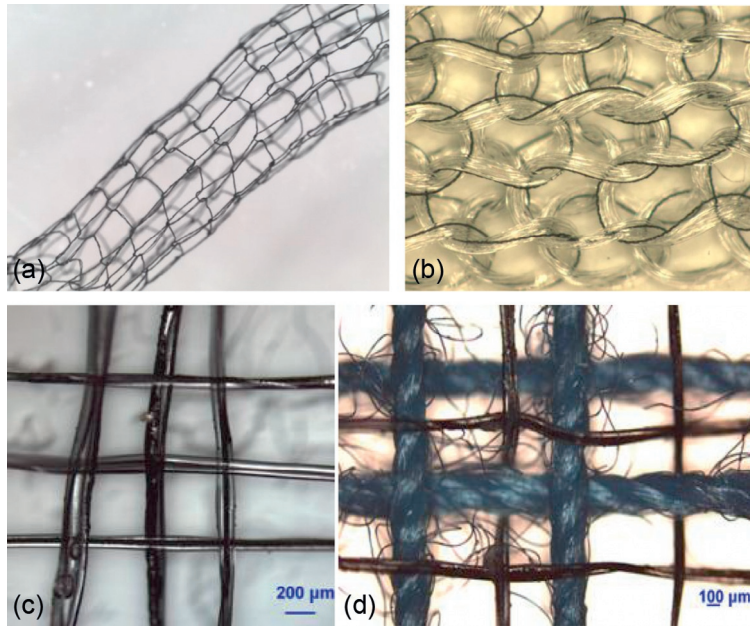

Figure 3.12 MWNT yarn structures. (a) Optical image of a CNT yarn-knitted tube. (b) SEM image of a CNT yarn/cotton yarn co-knitted fabric. (c and d) Optical images of woven and co-woven fabrics from a two-ply CNT yarn supercapacitor.
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released, and they possess high resistance to abrasion and knotting. These properties make downstream processing, such as knitting, braiding and weaving of CNT yarns, more convenient. The electrical conductivity of CNT yarns makes these fabrics suitable material for applications in electronic textiles. Figure 3.12 shows some textile structures made from CNT yarns.

3.5.2 CNT yarn sensors

The electrical resistance of a twisted CNT yarn changes when a strain is applied to the yarn. CNT yarns can be used as a sensor for simultaneous sensing of strain and temperature using a Wheatstone bridge configuration (Kahng et al., 2008). The strain sensitivities of the CNT yarn sensors ranged from 1.4 to 1.8 mV/V/1000 μ strain at room temperature, and the temperature sensitivity of the CNT yarn bridge was 91 μA/°C.

Short segments of heat-treated CNT yarns could be made into field electron emitters (Wei et al., 2006). The emission current could reach several milli-amperes, with a large enhancement factor over 10^5 in proportion to yarn segment length. The field emission could also be realized from the lateral side of a twisted CNT yarn (Zakhidov et al., 2007). Prototypes of cathodoluminescent lamps and alphanumerical indicators based on the twisted CNT yarn cold cathodes have been demonstrated.

3.5.3 Flexible supercapacitors

The use of capacitors (Leyden jar) for electrical energy storage predates the invention of the battery (Volta's pile). The new generation of capacitors, known as supercapacitors, stores electrical energy with two different storage principles: static double-layer capacitance and electrochemical pseudocapacitance. The supercapacitors have energy densities that are approximately 10% of conventional batteries, but their power density is generally 10–100 times greater (Figure 3.13). This results in much shorter charge/discharge cycles than those of batteries. The supercapacitor family may be divided into three types: double-layer capacitors, pseudocapacitors and hybrid capacitors with asymmetric electrodes.

Flexible batteries and supercapacitors are desirable power sources for portable electronics that have become symbolic of modern life and for wearable electronics that are on the horizon. These flexible energy storage devices may be of one-dimensional (or linear) or two-dimensional (planar) architectures. Planar supercapacitors are mostly built on metal sheets, plastic films, papers and textile fabric substrates. After depositing impermeable layers of active materials, separation membranes and current collectors, the 2D supercapacitors often become quite bulky, and their flexibility deteriorates considerably. These problems will become major concerns, if the devices cover a large area of the clothing system. In comparison, linear energy storage devices may be woven or knitted, alone or in combination with textile yarns, into fabrics that are both robust and more comfortable to wear. The freedom for body movement and breathability of the fabrics originates from the fabric structures.

Linear supercapacitor devices can be built on linear substrates such as metal wires, plastic/rubber wires, carbon fibres, carbon nanofibres, CNT yarns, CNT composite fibres, graphene fibres and graphene composite fibres. These substrates serve as the reinforcement as well as the charge collector for the active materials. Active materials used in linear supercapacitors may be carbon nanoparticles, transition metal oxides and conducting polymers. Transition metal oxides and conducting polymers are high-performance materials because of their high pseudocapacitance and the capability to charge and discharge at high rates.

3.5.3.1 CNT yarn as active material

As in conventional carbon materials, the electrical charge storage on CNTs is primarily capacitive in the electrochemical double layer. The capacitance values achieved with pure CNT powders and yarns are much lower than those of pseudocapacitance materials. Enhancement of capacitance of CNT yarns can be reached by utilizing different types of faradaic reactions originating from oxygen and nitrogen heteroatoms in the carbon network. Gamma irradiation of CNT yarn in the presence of air can introduce pseudocapacitance to CNT yarns (Su et al., 2014).

Figure 3.14a shows the cyclic voltammographs (CV curves) of supercapacitors made from an as-spun CNT yarn and a gamma-irradiated CNT (IR-CNT) yarn. The CV curve for the as-spun CNT yarn supercapacitor shows a rounded rectangular shape, which is typical for electrical double-layer capacitors. The IR-CNT yarn

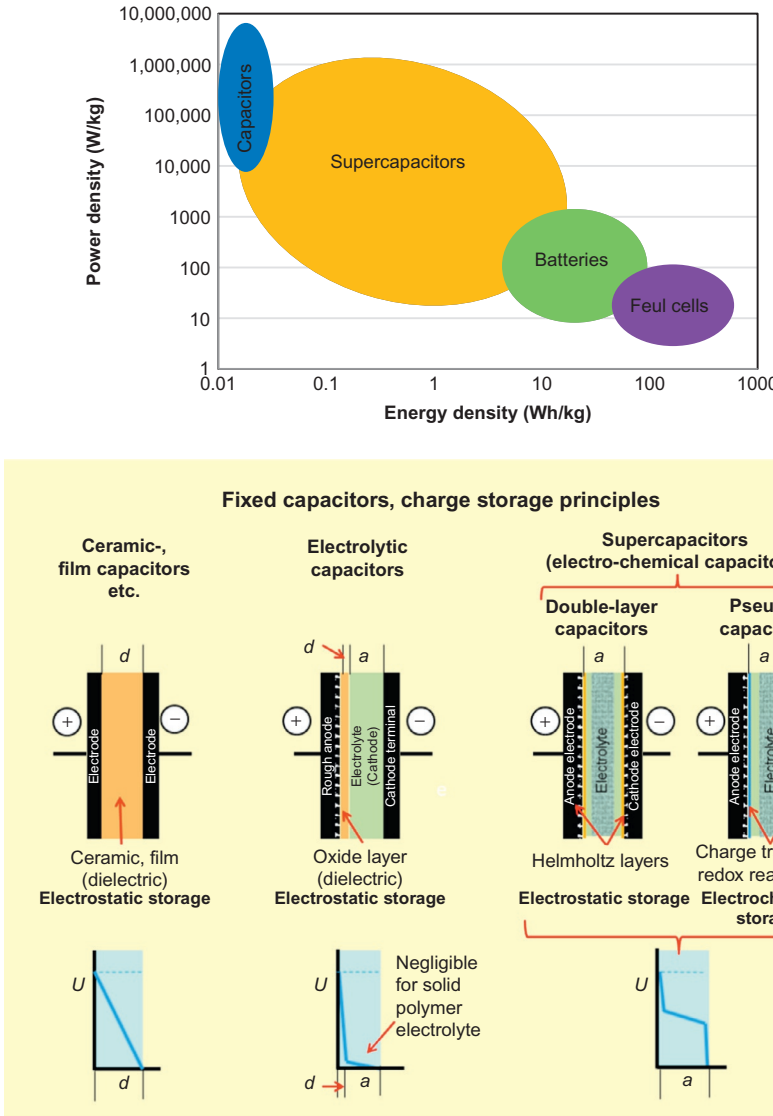

Figure 3.13 Power storage devices. Top: Ragone chart of batteries and supercapacitors. Bottom: different types of capacitors.
Courtesy of http//en.wikipedia.org.

supercapacitor, on the other hand, shows a significantly higher current density than the as-spun CNT yarn supercapacitor, with peaks that are usually associated with redox reactions displayed by pseudocapacitance materials. These peaks could be attributed to the oxygen groups introduced by gamma irradiation treatment (Miao et al., 2011). The Nyquist plots for the two supercapacitors in Figure 3.14b show the impedances of

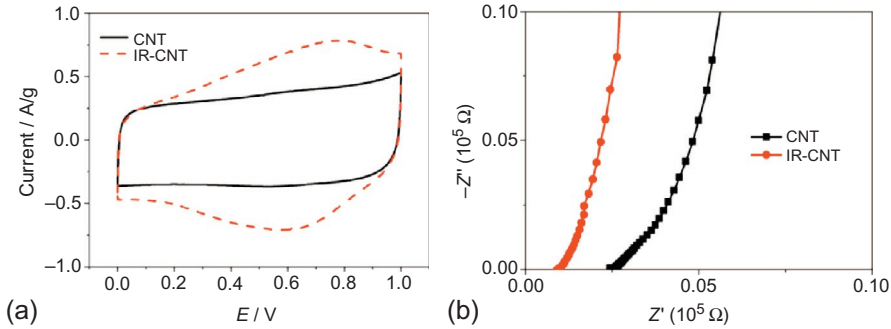

Figure 3.14 Electrochemical properties of CNT and IR-CNT two-ply yarn supercapacitors. (a) Cyclic voltammographs at 0.1 V/s. (b) Enlarged electrochemical impedance spectra at high frequency range.
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the two supercapacitors at high frequencies. The *x*-intercept of the Nyquist plot represents the equivalent series resistance (ESR) that corresponds to charge transport resistance for the two-electrode supercapacitors. The IR-CNT yarn supercapacitor has less than half the ESR of the as-spun CNT yarn supercapacitor (Su et al., 2014).

3.5.3.2 CNT yarn as substrate

Conducting polymers suffer from poor cyclic stability as electrode materials for supercapacitors because of the mechanical stress caused by material swelling and shrinking during the charge–discharge process. Transition metal oxides such as RuO_2, NiO_2, CoO_2 and MnO_2 are brittle materials and have not been made into fibre- or thread-like supercapacitors for use in wearable electronics. These problems can be largely mitigated or eliminated by using a CNT yarn as substrate. In addition to their high strength, flexibility and dimensional stability for seamless weaving and knitting, CNT yarns have a porous structure and are electrically conductive. As-spun CNT yarns are up to three orders of magnitude more conductive than conducting polymer films and fibres. The porous CNT yarn structure provides high electrolyte accessibility.

Pseudocapacitive materials can be applied to CNT yarn substrates by coating or *in situ* polymerization. The composite yarns are then coated with polymer electrolytes (e.g., polyvinyl alcohol–phosphoric acid gel electrolyte (PVA–H_3PO_4)). The yarn coated with electrolytes was then two-folded and twisted to form a two-ply yarn supercapacitor. The above preparation procedures are illustrated in Figure 3.15. Conducting polymers (e.g., polyaniline nanowires, Zhang et al., 2014a; Su et al., 2014, and poly (3,4-ethylenedioxythiophene)-poly(styrenesulphonate), known as PEDOT/PSS, Su and Miao, 2014b) and transition metal oxide (e.g., PVA/MnO_2 composite, Su and Miao, 2014a) have been used as coating materials for CNT yarn electrodes. The *in situ* polymerization method can produce highly aligned arrays of polyaniline nanowires on the CNT yarn surface, which demonstrates very high supercapacitance, as shown in Figure 3.16 (Wang et al., 2013a).

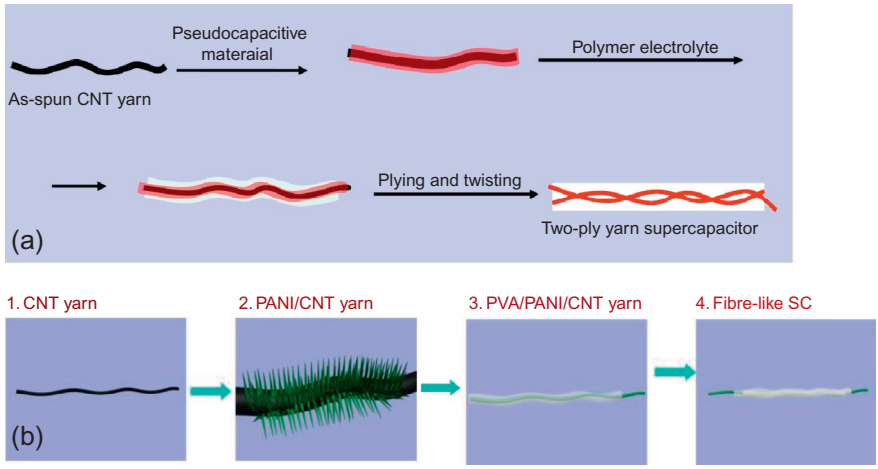

Figure 3.15 Preparation of two-ply CNT yarn-based pseudocapacitors. (a) Coating method. (b) *In situ* polymerization method.
Reprinted with permission from Wang et al. (2013a), copyright (2013) John Wiley and Sons. Panel (a): Adapted from Su et al. (2014) and Su and Miao (2014b).

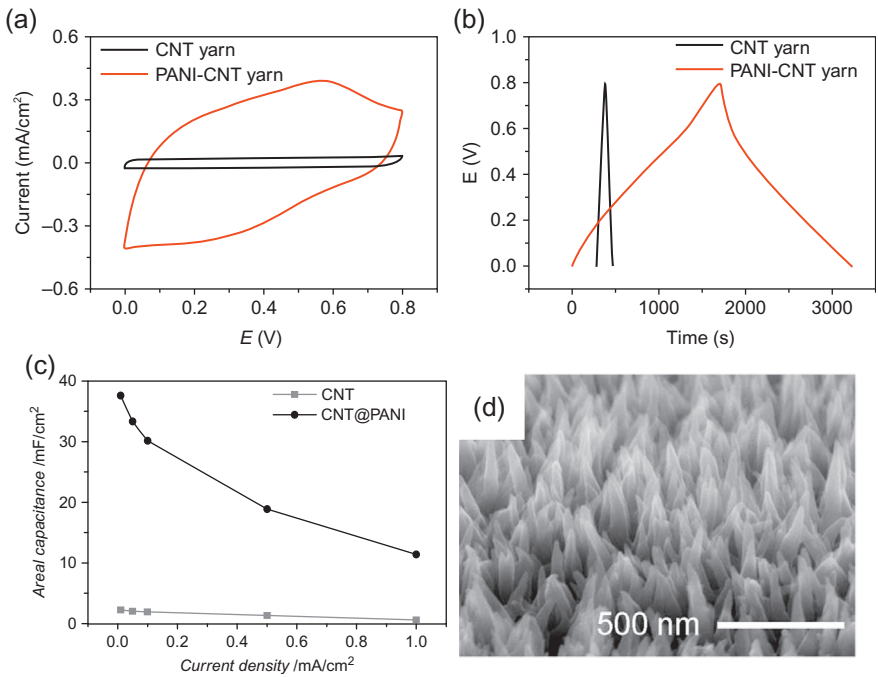

Figure 3.16 Electrochemical performance of two-ply yarn supercapacitor based on the CNT yarn and *in situ* polymerized aligned polyaniline nanowires. (a) Cyclic voltammograph curves. (b) Galvanostatic charge/discharge curves. (c) Gram capacitances at different current densities. (d) SEM image of ordered polyaniline nanowire arrays on the surface of CNT yarn.
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3.5.3.3 Core-spun CNT yarn

Although CNT yarns have much higher electrical conductivity than pseudocapacitance materials as current collectors, their conductivity is still 100 times lower than that of metal wires. The electrochemical performance of two-ply yarn supercapacitors based on the pure CNT yarn substrate decreases rapidly as the yarn length increases. A key challenge is therefore to scale them up to a length that is suitable for textile manufacturing, while their electrochemical performance is maintained or preferably further improved. This can be achieved by embedding a very thin metal wire (filament) in the centre of a CNT yarn, as shown in Figure 3.7. In the core/sheath structured yarn (Zhang et al., 2014a), the CNTs form a thin surface layer with high electrolyte accessibility and much shorter routes for transporting charges produced on the main active materials to the highly conductive metal core. In this way, charges stored along the length of the linear supercapacitors can be transported at very high efficiency.

3.5.3.4 Asymmetric supercapacitor

The energy density (E) of a supercapacitor is proportional to the specific capacitance (C) and the square of the operating voltage (U) of the supercapacitor, $E = CU^2/2$. The cell voltage in metal oxide-based symmetrical devices (<1 V) seriously limits the energy density of supercapacitors. This cell voltage can be increased to 2 V by using an asymmetric two-ply yarn supercapacitor architecture, in which the negative electrode is an as-spun CNT yarn, and the positive electrode is a CNT yarn coated with MnO_2/polymer composite (Su and Miao, 2014a). The asymmetric two-ply yarn supercapacitor demonstrates significantly higher energy density than its symmetric supercapacitor counterpart (Figure 3.17).

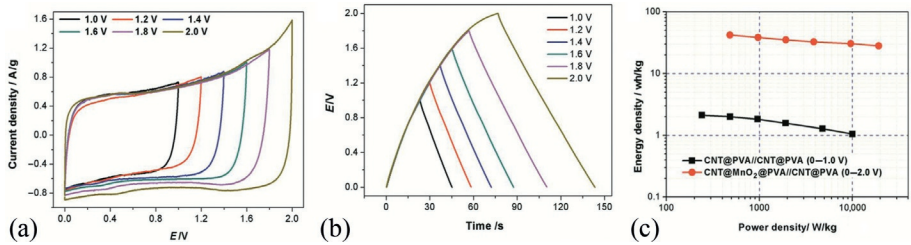

Figure 3.17 Electrochemical properties of the asymmetric two-ply yarn supercapacitor CNT@MnO_2/CNT. (a) CV curves in different potential windows. (b) Galvanostatic charge–discharge curves in the different potential windows. (c) Ragone plot showing the relationship between energy density and power density for a symmetric two-ply yarn supercapacitor CNT/CNT and an asymmetric two-ply yarn supercapacitor CNT@MnO_2/CNT.
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3.6 Summary and outlook

This chapter has described the various aspects of drawable CNT forests and their resulting yarns, including synthesis and drawability of the CNT forests, and the formation, structure, production, properties and applications of the resulting yarns.

Research on the synthesis of CNT forests has been focused on achieving consistent drawability and increased CNT length. Consistently drawable forests are essential for the production of yarns with controlled structure and properties. The drawn CNT webs can be converted into continuous yarns by a number of methods, including twisting, mechanical rubbing, solvent shrinking and core-yarn spinning. CNT yarn production can be scaled up to speeds that are comparable to state-of-the-art extra-fine-count conventional textile yarn production using specially engineered spinning machinery or modified conventional textile machinery.

CNT yarns have utilized only a very small fraction (<5%) of the strength of the constituent CNTs, one order of magnitude lower than what is achievable for conventional textile yarns. The structural mechanics of conventional textile yarns is well understood and is the starting point for understanding the relationship between structure and properties of CNT yarns. The strong van der Waals force, the geometrical disorder of CNTs in the drawn web and the unique CNT fracture mechanisms present new dimensions for yarn structural mechanics research.

CNT yarns are multifunctional materials. They have been demonstrated as feasible materials for constructing flexible sensors and linear energy storage devices that are suitable for use in electronic textiles. There is little doubt that the development of novel CNT yarn-based applications will continue to be a very active area of research.

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