CHAPTER EIGHT

Synthesis, Characterization, and Applications Carbon Nanofibers

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8.1 INTRODUCTION

Carbon nanofibers (CNFs) have great potential application in the chemical industry, material science, reinforcement of composites, and energy storage fields due to their high surface area to volume ratio, nanoscale diameter, and mechanical properties [1–5]. Synthesis routes of CNFs are mainly chemical vapor deposition (CVD) [6], electrospinning [7], templating [8], drawing [9], and phase separation [10]. CNFs produced from different synthesis techniques have different carbon structures and morphologies. In CVD, several types of a substrate like magnesia, zeolite, kaolin, and anodic alumina have been utilized as templates to synthesize CNFs and other carbon nanomaterials [11,12]. The hydrocarbon gases, such as methane, ethane, and carbon monoxide are widely employed as carbon precursors for the production of CNFs [13–15]. There are generally three types of CNF: the herringbone, in which the graphene layers are

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stacked obliquely with respect to the fiber axis; the platelet, in which the graphene layers are perpendicular to the fiber axis; and the ribbon, in which the graphene layers are parallel to the growth axis [16]. CNFs are discontinuous, highly graphitic, highly compatible with most polymer processing techniques, and can be dispersed in an isotropic or anisotropic mode [17]. CNFs have excellent mechanical properties, high electrical conductivity, and high thermal conductivity, thus they can be used in a wide range of matrices including ceramics, metals, thermoplastics, and thermosets [18–20]. Additionally, CNFs have an interesting surface state, which encourages functionalization and other surface modification techniques to build the nanofibers to the host polymer or application. Comprehensive literature reviews highlight the properties of CNF-reinforced polymer composites [21–23]. In this chapter, we outline the synthesis technique and present the properties and applications of carbon nanofibers.

8.2 SYNTHESIS OF CARBON NANOFIBERS

This section discusses the synthesis of carbon nanofibers such as chemical vapor deposition, electrospinning, templating, drawing, and phase separation routes.

8.2.1 Catalytic Chemical Vapor Deposition

CVD is among the most general procedures utilized for producing vapor-growth carbon nanofibers (VGCNFs). This method has been around since the 1970s for producing different materials and has been enhanced for producing CNF more recently [24,25]. CNFs can be prepared by catalytic thermal chemical vapor in a quartz tube electric furnace with C_2H_2 as the carbon source, involving a complicated chemical and physical process. Several types of metal or alloys have been utilized as the catalyst, such as iron, cobalt, nickel, chromium, and vanadium to dissolve carbon to form metal carbide. Additionally, the molybdenum, methane, carbon monoxide, synthesis gas (H_2/CO), or ethane are used to provide the carbon sources in the temperature range from 700 to 1200 K [26]. The prepared catalyst powder was placed in a ceramic boat at a center of a quartz tube that has an inner diameter of 45 mm and a length of 1000 mm in an electrical furnace, in which a uniform heating zone was maintained. The boat was preheated in N_2 flowing at 100 mL min^{-1} from room temperature to 200°C in 1 h, with a heating rate of 5°C min^{-1}. Next, the second stream of C_2H_2 and H_2 gas at 20 mL min^{-1} was introduced into the reactor for 40 min. After injection of the carbon source, the temperature was further raised to the desired reaction temperature, 700 or 800°C, for 2 h to prepare the CNFs [27]. Finally, the sample was cooled down to room temperature under an argon stream. The CNFs were purified and stirred in 3 M

HNO_3 solution and refluxed for 24 h at 60°C. Then they were stirred in 5 M HCl and refluxed for 6 h at 120°C. The purified CNFs were washed using distilled water and isopropyl alcohol. The CVD technique is only fit for producing relatively short fibers that are difficult to align, assemble, and process into applications [28].

The growth mechanism of the CNF depends on the geometric surfaces of a metallic catalyst particle and the gaseous carbon feedstock that is introduced during CNF processing. Fig. 8.1 shows the growth mechanism of vapor-growth carbon nanofibers using catalytic CVD. Generally, the structures of the CNFs are usually dependent on the manufacturing techniques employed. The size of the catalyst particles is usually in the range of 10−100 nm, which determines the outer diameter of the CNFs produced [29]. CNFs from vapor-growth carbon nanofibers have a very special structure like annular rings. The advantage of vapor-growth carbon nanofiber structure is sp^2 graphite (one double bond, with two single bonds). The thickness of the fibers can be adjusted by the metal particle size and the orientation of the graphite plane that can be steered by the growth temperature and/or the nature of the metal, such as iron, which tends to give rise to parallel fibers, while nickel often leads to fishbone-type fibers. In addition, two types of CNF can be prepared by CVD, namely, cup-stacked CNFs and platelet CNFs. The cup-stacked CNFs, also called conical CNFs, were first discovered by Ge and Sattler [30]. Fig. 8.2 demonstrates the

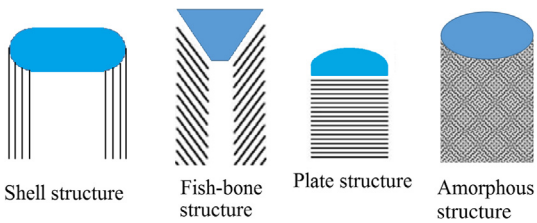

Figure 8.1 Growth mechanism of carbon nanofibers using catalytic CVD.

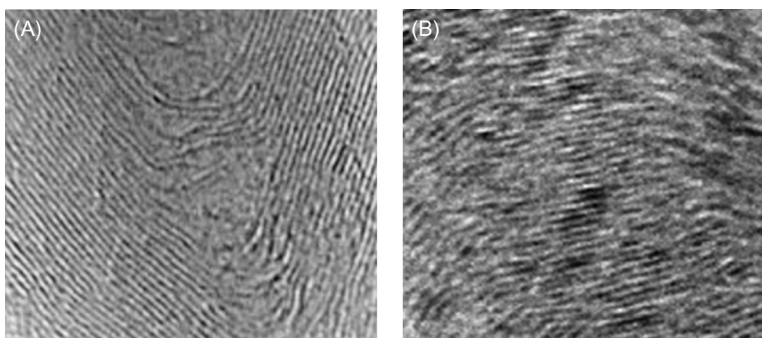

Figure 8.2 High-resolution transmission electron microscope (HRTEM) image of (A) cup-stacked CNFs and (B) platelet CNFs.

high-resolution transmission electron microscope (HRTEM) image of the cup-stacked CNFs and the platelet CNFs [31]. The structure of VGCNFs resembles graphene layers helically folded along the axis of the fiber, providing a hollow core. The graphitic layers are folded at an angle to the fiber axis, giving the appearance of cups that are layered, or "stacked" one on top of the other along an axis, as shown in the simplified diagrams of Fig. 8.3 [32,33]. Such a "cup-stacked" structure distinguishes them from CNTs, which have the appearance of a single cylinder or multiple concentric cylinders made of graphene layers oriented parallel to the CNT axis.

8.2.2 Electrospinning

Electrospinning is another widely used method for the preparation of CNFs. Electrospinning is an effective technique to produce polymeric nanofibers [34]. Owing to its advantages of ease of control and environmental compatibility,

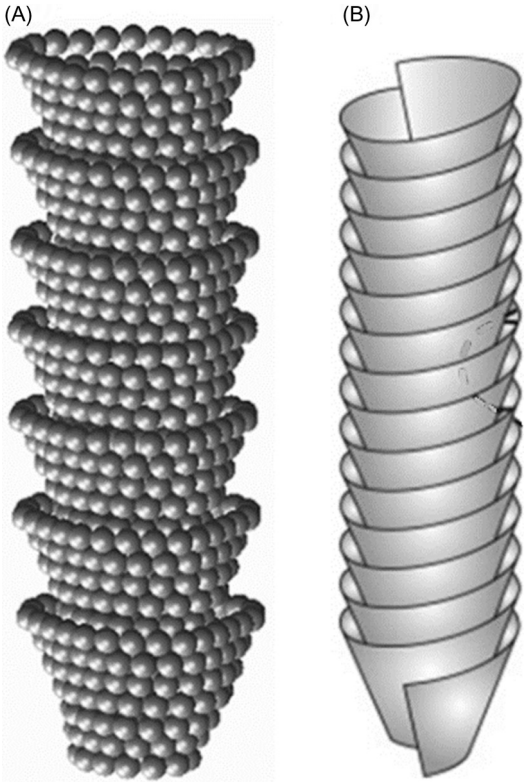

Figure 8.3 (A) 3D CAD rendering of cup-stacked graphene layers in a single CNF, and (B) simplified schematic of stacked-cup carbon nanofiber helical structure. *Poveda, R.L. and N. Gupta, Carbon Nanofibers: Structure and Fabrication, in Carbon Nanofiber Reinforced Polymer Composites. 2016, Springer International Publishing: Cham. p. 11–26.*

electrospinning is regarded as a flexible and powerful approach for the massive production of organic polymer or composite nanofibrous mats with diameters ranging from submicrons to nanometers, with good electrospinnability and fine stability [35]. It offers great opportunities to modify the fiber morphology, chemical composition, fibrous architecture, and functionality. The electrospinning process is schematically illustrated in Fig. 8.4. A typical electrospinning setup consists of a metallic spinneret, a syringe pump, a high-voltage power supply, and a grounded collector in a humidity-controlled chamber. A polymer solution, polymer melt, or a sol–gel solution is continuously pumped through the spinneret at a constant rate, while a high-voltage gradient is applied between the spinneret tip and the collector substrate [36]. High voltage is applied to the droplet at the tip of the needle, which causes the solution to spurt out from the needle to a target. When the surface tension is high enough for the solution to prevent breaking into a fine droplet, a fibrous structure is developed and collected at the target [37]. Polymeric precursors such as cellulose, phenolic resins, polyacrylonitrile, polybenzimidazol, and pitch-based materials have been electrospun to produce carbon nanofibers. During electrospinning, a polymer solution is stretched under a high electrical voltage into fine filaments, which deposit randomly on an electrode collector forming a randomly orientated nanofiber web [38]. The solvent continuously and rapidly evaporates while the jet stream is whipped and stretched by electrostatic repulsion forming solidified continuous nanofibers (diameters 50–500 nm) on the grounded collector. Improved electrospinning techniques have been able to produce aligned nanofiber arrays, nanofibers with porous surfaces, bicomponent cross-sectional configurations, and to generate nanofibers on a large scale [39–42].

Although such simple collectors are sufficient to obtain fibers, they may not produce a homogeneous fiber mat as more fibers are deposited in the center of the target, resulting in a variation in thickness through the mat, which may also affect the fiber morphology. In this regard, the rotating drum collector has been developed to allow the deposition of the fibers to occur homogeneously on the drum surface, resulting in a fiber mat with uniform thickness as shown in Fig. 8.5 [43,44]. Moreover, they can

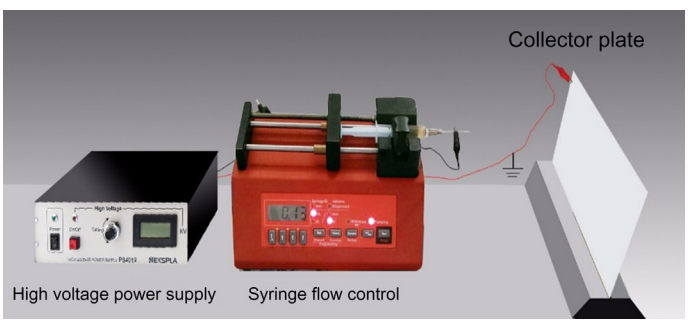

Figure 8.4 Schematic illustration of electrospinning components.

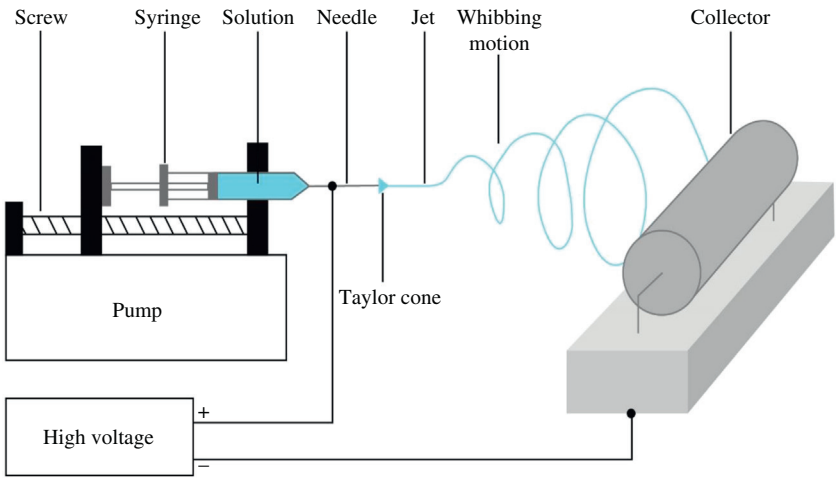

Figure 8.5 Schematic illustration of electrospinning components.

also be used to control fiber alignment as at very high rotation speeds, the fibers are aligned in the direction of rotation [45,46]. There are several parameters which affect the properties of the final CNFs such as types of polymer solution, solvent, capillary size, flow rate, working distance, and applied potential. Once the polymer nanofibers have been successfully prepared, a heat treatment will be applied to carbonize the polymer nanofibers to form CNFs. In addition, solution concentration, viscosity, and temperature have a great influence on fiber dimensions. Increasing the solution temperature can probably induce the formation of beta-phases in electrospinning [47]. Moreover, the diameter increases significantly as the solution concentration increases, and this increase follows a power law relationship [48–50].

8.2.3 Templating

There are other different techniques used for fabrication nanofibers such as drawing [9], template synthesis [51], phase separation [52], and self-assembly [53]. Carbon nanofibers are synthesized by a template technique used to make solid or hollow nanofibers of a diverse range of raw materials, including electronically conducting polymers, metals, semiconductors, and carbons. Nevertheless, production of one-by-one continuous nanofibers is not feasible by this technique.

8.2.4 Drawing

The drawing is another technique performed to produce one-by-one very long single nanofibers, and is a similar way to dry spinning in the fiber industry. However, only those viscoelastic materials which are able to tolerate strong deformations while pulling can be made into nanofibers through drawing.

8.2.5 Phase Separation

The phase separation is another technique consisting of dissolution, gelation, and extraction using different solvent, freezing, and drying methods, which finally results in the formation of a nanoporous foam. The whole process of conversion of the solid polymer into the nanoporous foam takes a relatively long period of time. The self-assembly is the process of self-arrangement of randomly dispersed preexisting components, thereby formation of an organized structure or pattern. Specifically, local interactions among the components themselves are the cause of such organization. This technique is the same as the phase separation and is time-consuming in the production of continuous polymer nanofibers. Thus, the electrospinning process is a suitable method for mass production of continuous nanofibers from various polymers [54].

8.3 COMPARISON OF VGCNFs AND ECNFs

The CVD process typically tends to yield ultrahigh modulus CNFs. However, a significant amount of catalyst residue, relatively lower product yield, and use of expensive equipment are limitations of the CVD process [55]. In addition, it produces fibers that are difficult to align without the use of electrophoretic methods or mechanical methods [56,57]. Electrospinning takes advantage of its manufacturing process, which facilitates production, assemblage, and alignment [58]. The two methods of CNF production are always developed to efficiently produce higher CNF yields for mass production.

8.4 PROPERTIES OF CARBON NANOFIBERS

The mechanical properties of CNF, such as strength, stiffness, fracture behavior, and toughness of materials rely upon the microstructure, processing procedures, and the fiber diameter. The tensile strength of CNFs ranges from 1.5 to 7 GPa, while Young's modulus is between 228 and 724 GPa [59]. Alaa M. et al. [60] synthesized a new composite nanofiber system containing polyacrilicnitrile polymer (PAN) and multiwalled carbon nanotubes (MWCNTs) to improve the mechanical properties of CNFs. The result indicates that the mechanical properties exhibit improvements in tensile strengths, and elastic modulus by 38% and 84%, respectively. Therefore, CNFs may improve the tensile strength, compression strength, Young's modulus, interlaminar shear strength, fracture toughness, and vibration damping of the base polymer.

The degree of change is dependent upon the type of polymer, dispersion, and processing history [61].

Carbon nanofibers offer a promising solution to enhance the mechanical and electrical properties. Endo et al. [62] first reported the intrinsic conductivity of highly graphitic vapor-grown carbon fiber at room temperature to be $5 \times 10^{-5}\ \Omega\ cm^{-1}$, which is near the resistivity of graphite. During the cure process of an epoxy resin, CNFs are observed to rotate and align with the applied electric field, forming a chain-like structure. The results show that the addition of 1.6 wt% of aligned CNFs increases the electrical conductivity of such nanocomposites by about seven orders of magnitudes to $10^{-2}\ S\ m^{-1}$ and increases the fracture energy, G_{Ic}, by about 1600% from 134 to $2345\ J\ m^{-2}$ [63]. In addition, Gu et al. [64] studied the electrical conductive electrospun aligned carbon nanofiber membrane. The result indicated that the randomly oriented CNF membrane was isotropic and the average electrical conductivity was $13.27\ \Omega \cdot cm$ compared with the normal membrane $1.3\ \Omega \cdot cm$, where the discrepancy was about 10 times.

The thermal conductivity of the carbon nanofibers can be inferred to be $2000\ W\ mK^{-1}$, based on direct measurements of the parent classes of CNFs, or macroscopic vapor-grown carbon fibers. CNF and CNT composites were mixed in soy wax and paraffin wax at different concentrations to increase the thermal conductivities of the CNFs [65]. The result indicates that the thermal conductivities of the composites increased from 0.324 to $0.469\ W\ mK^{-1}$. Teng et al. [66] tested the thermal conductivities of the CNF/polylactic acid (PLA) and CNT/PLA-PLA composites. It was found that the CNFs are randomly distributed in the PLA matrix, and the thermal conductivity of the composite reached $1.2\ W\ mK^{-1}$. Other researchers have focused on the fire-retardant properties of the CNFs in thermoplastic materials. Composites loaded with carbon nanofibers and exposed to a flame exhibited delayed and lower peak heat release rates, lower smoke emissions, and no dripping or pooling of molten polymer [67]. Fig. 8.6 gives an overview of the properties of CNFs.

8.5 APPLICATIONS OF CARBON NANOFIBERS

In recent years nanofibers have been widely used in various applications due to their excellent properties that can be implemented in specific areas such as water treatment, filtration, packaging, nanocomposites, sensing, energy devices, tissue engineering, and drug delivery, etc. [68–83]. Fig. 8.7 illustrates the different areas of application of the publications dealing with electrospinning with the relative percentages.

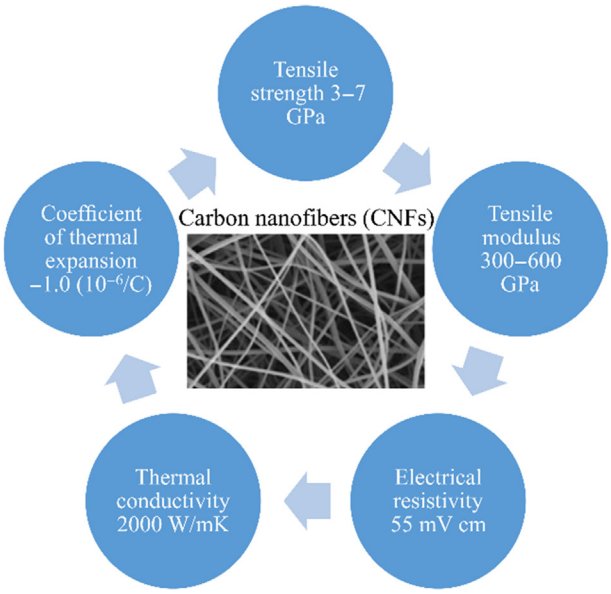

Figure 8.6 Overview of the properties of CNFs.

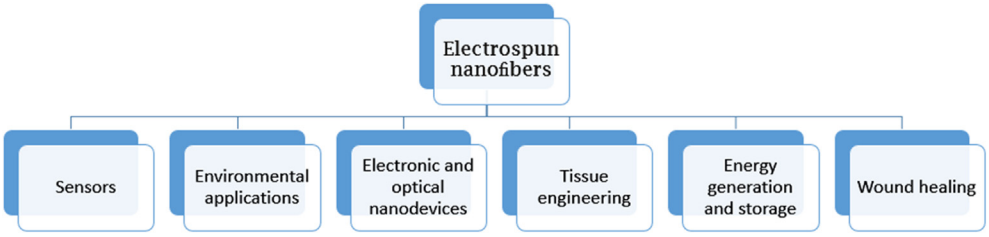

Figure 8.7 General application areas of electrospun nanofibers.

The overall problem on water and energy scarcity has prompted improvements in desalination technologies. Membrane distillation (MD) may address the weaknesses of reverse osmosis (RO) as MD can possibly use low-grade/waste heat, and solar energy with very high recovery for water purification and desalination. In this regard, Tijing et al. [69] fabricated nanofiber membrane containing CNTs for water distillation. It was found that the contact angle increased to superhydrophobic at 158.5 degrees upon the incorporation of 5 wt% CNTs in the nanofiber. The liquid entry pressure also increased when 5 wt% CNT was added compared to the neat PcH nanofiber membrane. The resulting flux of the 5 wt% CNT-incorporated nanofiber membrane (24−29.5 L m^{-2} h^{-1}) was consistently higher than the commercial PVDF membrane (18−18.5 L m^{-2} h^{-1}), with an average increase of 33%−59% depending on the feed water type (35 or 70 g L^{-1} NaCl solution) without compromising the salt rejection

(> 99.99%). In addition, poly(vinylidene fluoride-co-hexafluropropylene) (PVDF-HFP)/silica nanoparticles (SiNPs) flat-sheet hybrid membranes were fabricated for membrane distillation via electrospinning [68]. The electrospun membranes were tested through direct contact membrane distillation using 35 g L^{-1} NaCl solution as feed, and the highest permeate flux of about 48.6 kg m^{-2} h was obtained and the salt rejection maintained at 99.99%. The 240 h continuous desalination application demonstrated the stable permeability of the electrospun hybrid membrane, and the membrane hydrophobicity can also be maintained well with long-time immersion in salt solution.

Filtration membrane technology has already been utilized to remove different natural effluents produced from the leather, textile, food, paper, plastic, and mineral processing industries [71]. Polymeric nanofibers have been used in air filtration applications for more than a decade [84]. The small fiber diameter of less than 0.5 μm may enhance the filtration efficiency at the same pressure drop. The implementation of nanofiber networks as a filtering medium holds promising potential. Keeping in mind that the essential features of protective clothing are high atmospheric moisture transport, increased fabric breathability, and enhanced toxic chemical resistance, electrospun nanofiber membranes stand as good candidates for these applications.

Tissue engineering and drug delivery are another area where nanofibers have been employed. Nanofibers with a high surface area and porosity have huge potential for applications in engineering mechanically stable and biologically functional tissue scaffolds. The tissue scaffolding material must be selected carefully to ascertain its biocompatibility with the body cells. The biocompatibility depends on the surface chemistry of the scaffolds, which is dictated by the material properties [74]. The high surface to volume ratio of the nanofiber provides more space for the cell attachment than the regular fibers. The dimensions of these engineered scaffolds were in the comparable scale with those of the natural extracellular matrix. Electrospun biodegradable polymers are considered as suitable scaffolds for tissue engineering, with their large pore diameter and volume. The high porosity of the electrospun nanofiber scaffolds provides enough space for the cell accommodation and an easy passage for the nutrients and metabolic waste excretion. Mechanical properties, like elastic modulus and strain at failure, are important for the application of electrospun nanofibers as tissue scaffolds [76]. Moreover, nanofiber mats with their unique functional characteristics find application as drug carriers for the drug delivery system.

In addition, the self-sensing function of the CNF composites is realized by testing the variation of electrical properties that has resulted from a change in the external conditions, including stress/strain and the gas environment. The electrical conductivity of the CNF composites is able to be reversibly changed with the reversible change of the external conditions. Baeza [85] prepared CNF as strain-sensing and damage-sensing. CNF showed higher sensitivities (gage factor up to 191.8). Furthermore,

damage-sensing tests were run, increasing the applied load progressively up to the RC beam failure. Jang and Bae [86] was prepared with CNF/polypyrrole as gas sensors. In this study, the coating of CNF with polypyrrole provides a sensor of gases, such as ammonia (NH_3) and hydrochloric acid (HC1). In addition, Han et al. [87] fabricated a SWCNT-poly(methyl methacrylate) nanofiber onto IDE, which was used as a flexible sensing material to detect CH_3OH (600 − 3500 ppm). Apart from the strain/stress or gas sensing, the temperature, humidity, magnetic field, and light are all important factors that are required to be sensed in many applications.

8.6 CONCLUSIONS AND FUTURE PERSPECTIVES

The synthesis approaches for CNFs are discussed in this chapter. Catalytic chemical vapor deposition (CCVD) growth and electrospinning are the main effective pathways to fabricate CNFs. In the CCVD growth technique, some metals and alloys, including Fe, Co, Ni, Cr, and V, which can dissolve carbon to form metal carbides, were able to be chosen as the catalysts, and molybdenum, methane, carbon monoxide, synthesis gas (H_2/CO), and ethane are able to be used as carbon sources. Generally, the structures of CNFs are decided by the shapes of the catalytic nanosized metal particles. In the electrospinning process, the polymer types and the treatment process play the most important roles in the quality of the prepared CNFs. In addition, the difference in their structure reflects the difference in their properties. Surface modification can help in making CNFs compatible with the matrix polymer. For applications, the CNFs and their composites are able to be used in many fields, including sensors, tissue engineering, and environmental pollution.

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