



## Polyacrylonitrile-based nanofibers—A state-of-the-art review

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### ABSTRACT

Polyacrylonitrile (PAN), a well-known polymer with good stability and mechanical properties, has been widely used in producing carbon nanofibers (CNFs) as these have attracted much recent attention due to their excellent characteristics, such as spinnability, environmentally benign nature and commercial viability. Among the various precursors to produce CNFs, PAN has been extensively studied due to its high carbon yield and flexibility for tailoring the structure of the final CNFs as well as the ease of obtaining stabilized products due to the formation of a ladder structure via nitrile polymerization. In view of this, they have applications in areas such as electronics, tissue engineering, membrane filtration and high performance composites. This review presents various combinations of PAN and PAN-based precursors in producing CNFs from the PAN homopolymer or its modified precursors, copolymers, blends and various composites. Various modifications of PAN and their future prospects in different scientific and technological disciplines are addressed.

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**Abbreviations:** (Na<sub>2</sub>O<sub>4</sub>), sodium cobalt oxide; [Pt(acac)<sub>2</sub>], platinum(II) acetylacetone; AAO, anodic aluminum oxide; ACNFS, activated carbon nanofibers; AFM, atomic force microscopy; CCVD, catalytic chemical vapor deposition; CNFs, carbon nanofibers; CR, Congo red; DMAc, dimethylacetamide; DMF, dimethylformamide; DMS, dimethylsulfone; DMSO, dimethylsulfoxide; DWNTs, double walled carbon nanotubes; EB, 1-(o-cyanostyryl)-4-(p-cyanostyryl)benzene; EDC/NHS, N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride and N-hydroxysuccinimide; EDLC, electrochemical double-layer capacitors; ER, 1,4-bis(o-cyanostyryl)benzene; Fe(Acc)<sub>3</sub>, Fe(acetylacetone)<sub>3</sub>; FE-SEM, Fourier transform scanning electron microscopy; FTIR, Fourier transform infra-red spectrometer; GNFS, graphite nanofibers; HRXRD, high resolution X-ray diffraction; MB, methylene blue; MWCNTs, multiwalled carbon nanotubes; NFs, nanofibers; PAN, polyacrylonitrile; PAN-*b*-PMMA, poly(acrylonitrile-*b*-methyl methacrylate); PAN-*b*-PS, poly(acrylonitrile-*b*-polystyrene); PANCAA, poly(acrylonitrile-*co*-acrylic acid); PANCAA, poly(acrylonitrile-*co*-acrylic acid); PANCMA, poly(acrylonitrile-*co*-maleic acid); PANOX, polyacrylamidoxime; PEO, polyethyleneoxide; PEU, poly(ester urethane); PL, photoluminescence; PMMA, poly(methyl methacrylate); Poly(AN-*co*-MMA), poly(acrylonitrile-*co*-methyl methacrylate); PU, polyurethane; PVdF, poly(vinylidene flouride); PVP, poly(vinylpyrrolidone); RS, Raman spectroscopy; RSM, response surface methodology; SERS, surface-enhanced Raman scattering; SiMoA, silicomolybdic acid; SiWA, silicotungstic acid; SWCNTs, single walled carbon nanotubes; TEM, transmission electron microscopy; THF, tetrahydrofuran; TMS, tetramethylsulfide; VGCNFs, vapor grown carbon nanofibers; WAXRD, wide angle X-ray diffraction; XRD, X-ray diffraction.

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## 1. Introduction

Polyacrylonitrile (PAN) and copolymers of PAN have been widely studied for almost a century for commercial/technological exploitations. PAN may be crosslinked, but also may exist without crosslinking. Crosslinking of PAN will impart some of its important physical properties, such as insolubility and resistance to swelling in common organic solvents. Recently, considerable efforts have been devoted to its processing and fiber forming technologies. Among the various precursors for producing carbon nanofibers (CNFs), PAN is the most commonly used polymer, mainly due to its high carbon yield (up to 56%), flexibility for tailoring the structure of the final CNF products and the ease of obtaining stabilized products due to the formation of a ladder structure via nitrile polymerization [1–5]. The chemistry of PAN is of particular interest because of its use as a precursor in the formation of CNFs for different applications, including porous structured CNFs of high surface area for electronics and energy storage applications as well as graphite reinforcement filaments for organic materials in high strength and high stiffness composites. The recent review by Inagaki et al. [6] describes the chemistry and applications of CNFs, restricted mainly to the research on scientific and technological developments in Japan. Barhate and Ramakrishna [7] published a review on nanofibers as a filtering media for tiny materials. Li and Xia [8] discussed about the trends in nanofibers with emphasis on electrospinning techniques to produce nanofibers. However, to the best of our knowledge, no review on the overall critical assessment of research activities on PAN-based CNFs prepared by different techniques and their numerous applications in a variety of areas as shown in Fig. 1. Various modifications of PAN as an efficient precursor and their future prospects in different scientific and technological fields as well as commercial applications are addressed in the following.

## 2. Polyacrylonitrile as a fiber

Even though acrylonitrile (AN) was known as far back as 1893, but PAN, because of difficulties in dissolving it for spinning, no progress was made in converting into a usable fiber until 1925. Acrylonitrile monomer was also useful as a copolymer with styrene, especially in a terpolymer with styrene and butadiene, known as ABS rubber. The homopolymer of PAN was developed for manufacturing of fibers in 1940, after a suitable solvent was discovered by

DuPont. PAN is soluble in polar solvents like DMF, DMSO, DMAc, dimethylsulfone, tetramethylsulfide and aqueous solutions of ethylene carbonate, as well as some mineral salts. PAN forms saturated solution with 25% dissolved in DMF at 50 °C, which is high solubility compared to other solvents [9]. PAN and its copolymers are predominantly white powders up to 250 °C, at which point they become darker due to degradation. Having a relatively high  $T_g$ , these polymers have low thermal plasticity and cannot be used as a plastic material. The high crystalline melting point (317 °C) of PAN, its limited solubility in certain solvents coupled with superior mechanical properties of its fibers is due to intermolecular forces between the polymer chains. Appreciable electrostatic forces occur between the dipoles of adjacent  $\text{—C}=\text{N}$  groups and this intramolecular interaction restricts the bond rotation, leading to a stiffer chain [10]. The properties of CNFs are strongly dependent on the microstructure of the stabilized PAN fiber [11–20].

## 3. Techniques to produce nanofibers and electrospinning

There are a number of methods to produce nanofibers, e.g., vapor growth [21], arc discharge [22], laser ablation and chemical vapor deposition [23]. However, these are very expensive processes due to low product yield and the expensive equipment required. On the other hand, the electrospinning method, invented in 1934, can generate fibers with diameters from 10 nm to 10  $\mu\text{m}$  [24,25] from a polymer solution under the application of an electrostatic force. The applied electric field and solution conductivity are important parameters that influence the fiber diameter during the spinning, in addition to parameters such as the jet length, solution viscosity, surrounding gas, flow rate, and the geometry of the collector assembly [26–30]. Fig. 2 displays the electrospinning process; these details can be found in published reports [31–33].

## 4. Carbon nanofiber

A carbon nanofiber (CNF) is a long, thin strand of material, about 10–1000 nm diameter composed mostly of carbon atoms bonded together in microscopic crystals and aligned parallel to the long axis of the fiber. The crystal alignment makes the fiber exceptionally strong for its size. The preparation of CNFs from PAN precursor involves three main stages; electrospinning, oxidative stabilization and carbonization. Adequate stabilization of the spun PAN

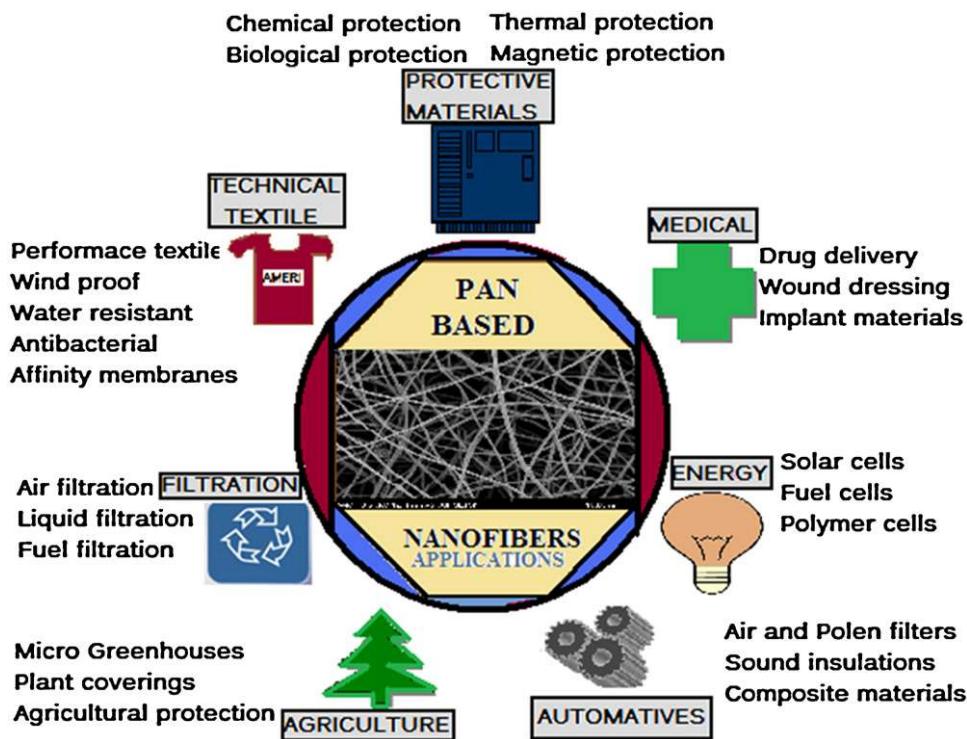


Fig. 1. Broad spectrum of PAN-based nanofiber applications in various fields.

fiber is necessary in obtaining good quality CNFs. Stabilization involves heating PAN fibers in an oxygen-containing atmosphere, inducing cyclization of nitrile groups ( $\text{C}\equiv\text{N}$ ) and crosslinking of the chain molecules in the form of

$-\text{C}=\text{N}-\text{C}=\text{N}-$ , a process that prevents melting during subsequent carbonization. In the second step, carbonizing the stabilized PAN fibers in an inert atmosphere [34–36] removes non-carbonized components selectively in the

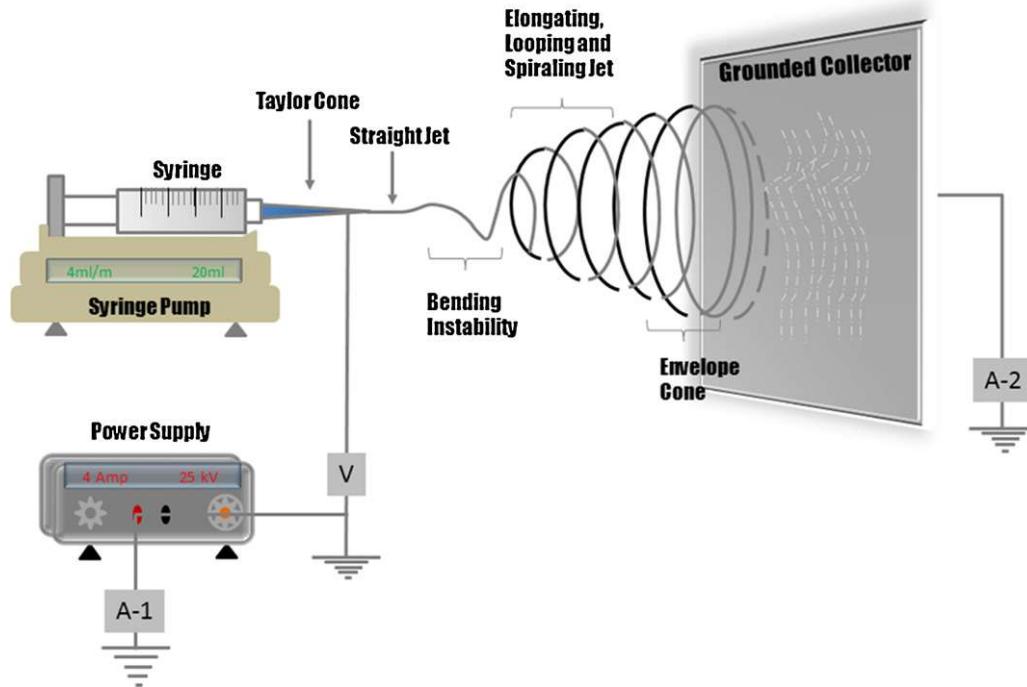


Fig. 2. Schematic diagram of electrospinning apparatus.

form of gases, such as  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CO}$ ,  $\text{HCN}$ ,  $\text{CO}_2$  and  $\text{N}_2$ , to give carbon fibers with a yield of about 50–57% of the mass of the original PAN.

#### 4.1. Porous CNFs

Carbon nanotubes (CNTs) and CNFs have attracted much attention in view of their unusual structural and electronic properties, useful in electrochemical double-layer capacitors (EDLC), batteries, catalyst supports, and field emission displays [37–42]. Among many techniques used for the synthesis of CNFs and CNTs, electrospinning and catalytic chemical vapor deposition (CCVD) are the most promising ones.

The polymer precursors used for making CNFs have shown poor mechanical properties giving very low carbon yields [43–50]. The three precursors that are used in large-scale production of CNFs are from PAN, rayon, and pitches [51], while other precursors are generally used if mechanical properties are not so important. Regular textile grade PAN contains 15% comonomers, but the amount of comonomers in PAN used for CNFs is less than 8%. Commercially available PAN precursors differ appreciably in their characteristics, such as molecular weight and its distribution, crystallinity, diameter, molecular orientation and impurities [52]. Since these characteristics will affect the mechanical and other properties of the final CNFs, many companies prefer to manufacture their own precursors using modified procedures, such as incorporation of certain additives to catalyze the cyclization reaction [53], resin coatings to suppress the cyclization exothermicity [54], post-spinning stretching in super-heated steam and nitrogen to improve the structure [55,56]. The modulus and strength of the final CNFs are directly related to stretch-ratio of the precursor [57,58]. When glycerol is used as the drawing medium, tensile properties are much improved, but since the carbon fiber properties depend upon the precursor properties; efforts have been made to improve the properties of PAN structure by modification, copolymerization, blending as well as in the composite form [59].

**Fig. 3** displays the schematic route of forming the carbonized structure of PAN. When the PAN fiber is subjected to the stabilization temperature, dense ladder-polymer structure begins to form above 200 °C by reacting with oxygen that prevents melting during subsequent carbonization [60]. Carbonizing involves the heat treatment of the stabilized PAN fibers to remove non-carbon elements in the form of different gases ranging from 700 to 1500 °C in an inert atmosphere. After carbonizing at 800 °C, denitrogenation takes place, resulting in the formation of a network structure. During this process, fibers shrink in diameter, losing approximately 50% of its weight.

##### 4.1.1. PAN homopolymer

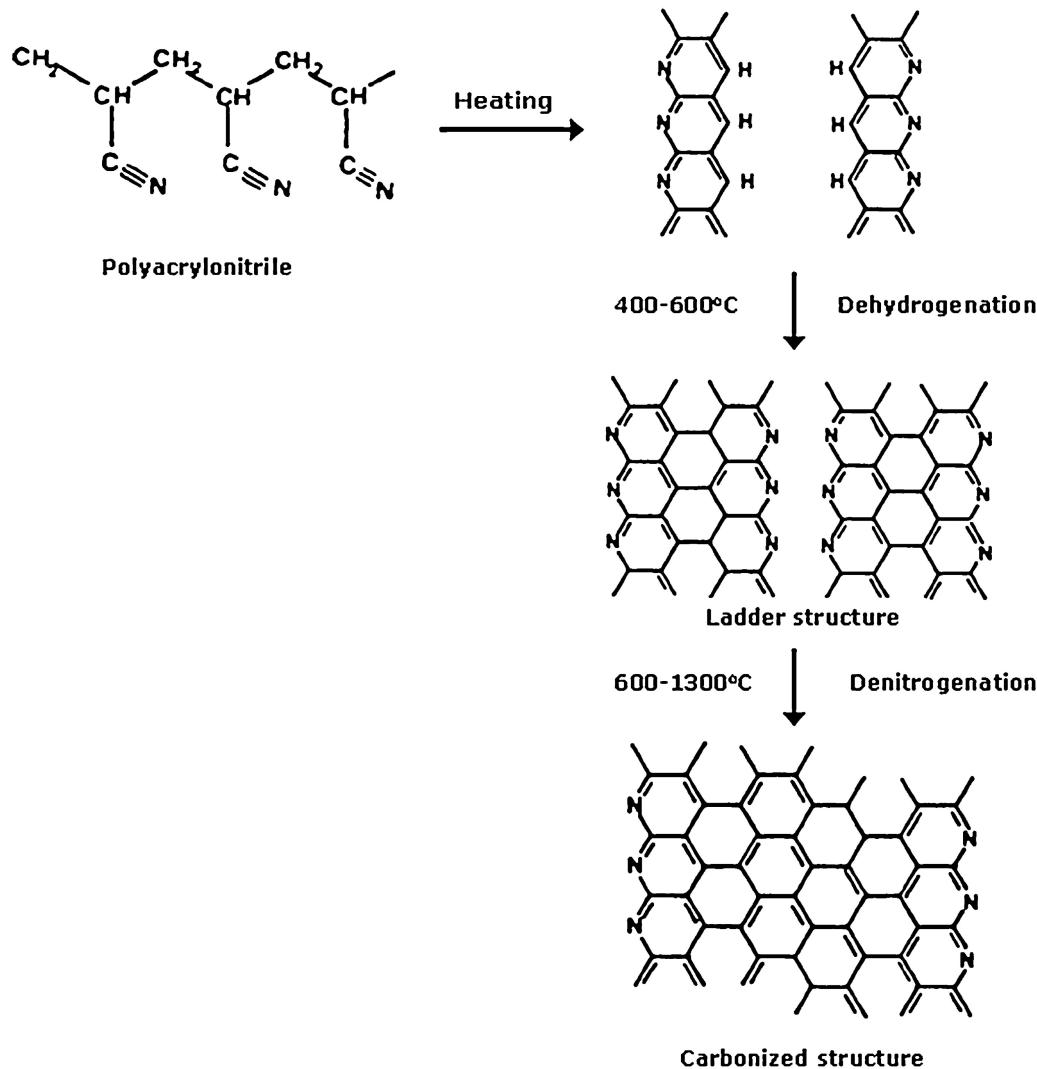
Chun and co-workers [61,62] were the first to prepare PAN nanofibers having diameters typically in the range from 100 nm to a few microns. Carbon polymorphs are the well-known Raman-active groups in these materials [63]. Due to their high specific surface areas, electrospun ultrafine fibers can be used as high performance filters or scaffolds in tissue engineering. For the same reason,

one may expect that chemisorbed gases may modulate electrical conductivity, leading to the fabrication of sensor devices.

MacDiarmid et al. [64] coated the PAN nanofibers evenly with a 20–25 nm thin layer of a conducting polymer with a polypyrrole by immersing PAN-based graphite NFs in an aqueous solution of polypyrrole. On the other hand, the PAN-based graphite NFs were obtained by Wang et al. [65] through electrospinning and subsequent pyrolysis. In that study, gold coated target of patterned Si-wafer substrate was used in place of a collector to accumulate PAN spun fibers for subsequent single fiber conductivity measurements. The graphitization of the PAN nanofiber led to a sharp increase in conductivity, to around 490 S/m. In another study [66], NFs were prepared from PAN/DMF precursor solutions using electrospinning and vacuum pyrolysis at temperatures from 500 to 1000 °C for 0.5, 2 and 5 h, respectively. The length and cross-section area of the NFs, evaluated by optical and scanning probe microscopes, respectively, were used to calculate the electrical conductivity. The conductivity increased sharply with pyrolysis temperature, increasing considerably with pyrolysis time at lower pyrolysis temperatures, viz., 600, 700 and 800 °C. By contrast, the conductivity varied less obviously with pyrolysis time at higher pyrolysis temperatures of 900 and 1000 °C due to thermally activated transformation. Gibson et al. [67] explored NFs as filtration membranes, while Ryu et al. [68] reported the fabrication of PAN-based CNFs using various activation methods that were characterized using low temperature nitrogen adsorption methods over the pressure range from  $10^{-6}$  to 1 Pa.

Feng et al. [69] developed a novel and simple method to synthesize PAN NFs using an anodic aluminum oxide membrane as a template and extruding PAN precursor solution of 18 wt.% of PAN in DMF. For this process, an anodic aluminum oxide membrane was used as the template (see Fig. 4). A clean and dry template was placed on a compact polytetrafluoroethylene (PTFE) film and the upper cavity was filled with PAN precursor solution. Extruding the precursor into a liquid for solidification using a pump at a pressure of 0.1 MPa resulted in the formation of PAN NFs.

The significance of pyrolysis temperature on carbon fibers at 1000 °C and above was examined to study the effect of various intermediate steps involved in carbonization of PAN [70]. SantiagoAviles and Wang [71] later performed conductivity and magneto-conductance measurements on CNFs prepared by using electrospinning and vacuum pyrolysis techniques. The precursor used was a commercial grade PAN, with 600 mg PAN dissolved in 10 mL of DMF. Silicon wafer substrates with a 150-nm thick film of silicon oxide were lithographically patterned with a 131-mm gold contact array. The as-spun PAN fibers were pyrolyzed at 1000 °C for 27 h in vacuum (10 Torr). The magneto-conductance of these materials was negative with a parabolic dependence on the transverse magnetic field and the conductivity was about 27535 S/m. A self-lubricating anodic film was developed by Zhao et al. [72] on aluminum by re-anodizing in oxalic acid and subsequently, carbon precursors were developed via polymerization of acrylonitrile within the pores of alumina film. CNFs were



**Fig. 3.** Schematics of the formation of carbonized structure from PAN nanofiber.

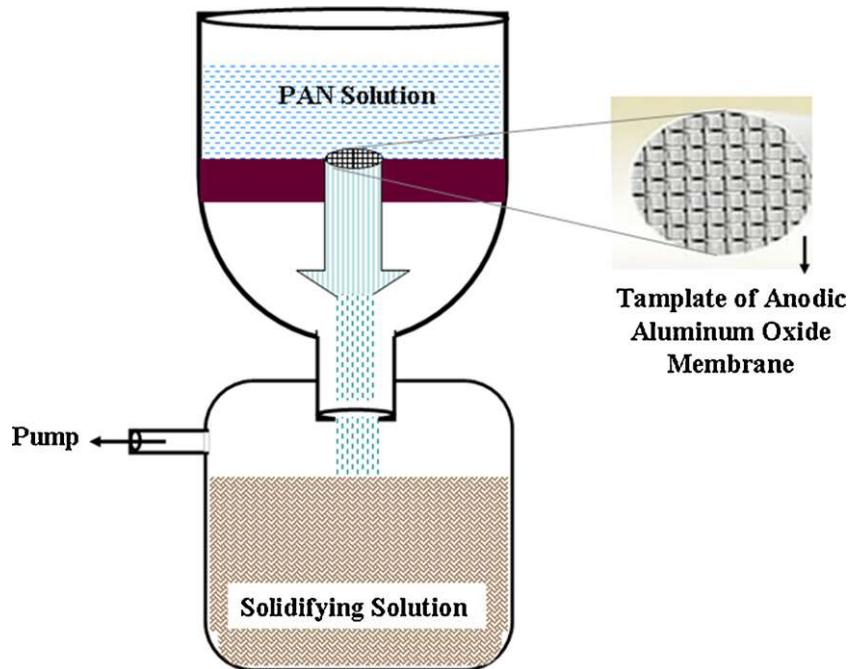
applied in the pores of the porous anodic oxide film (AOF) on aluminum to improve the wear properties of the alumina film.

Fernández et al. [73] used another method to prepare CNFs consisting of graphitization of previously formed PAN inside the nanosized pores of sepiolite. This natural microfibrous silicate contains structural pores extending throughout its volume able to contain acrylonitrile. Sepiolite powder was dehydrated at 140 °C in vacuum for 2 h to eliminate free water before mixing with the monomer. Then, 1 g of dehydrated sepiolite was added to 3 mL of AN, and the mixture was slowly sprayed onto a sepiolite sample using a syringe inside a glove box to avoid contact of any water from the atmospheric air with the sepiolite and AIBN was used as a radical initiator. After soaking for 24 h, the mixture was heated at 60 °C for 24 h in sealed bottles to induce polymerization, followed by heat treatment at 220 °C for 24 h in atmospheric air leading to yield sepiolite-PAN nanocomposite. Fig. 5 shows resulting solids that constitute a new class of conductive carbon-clay

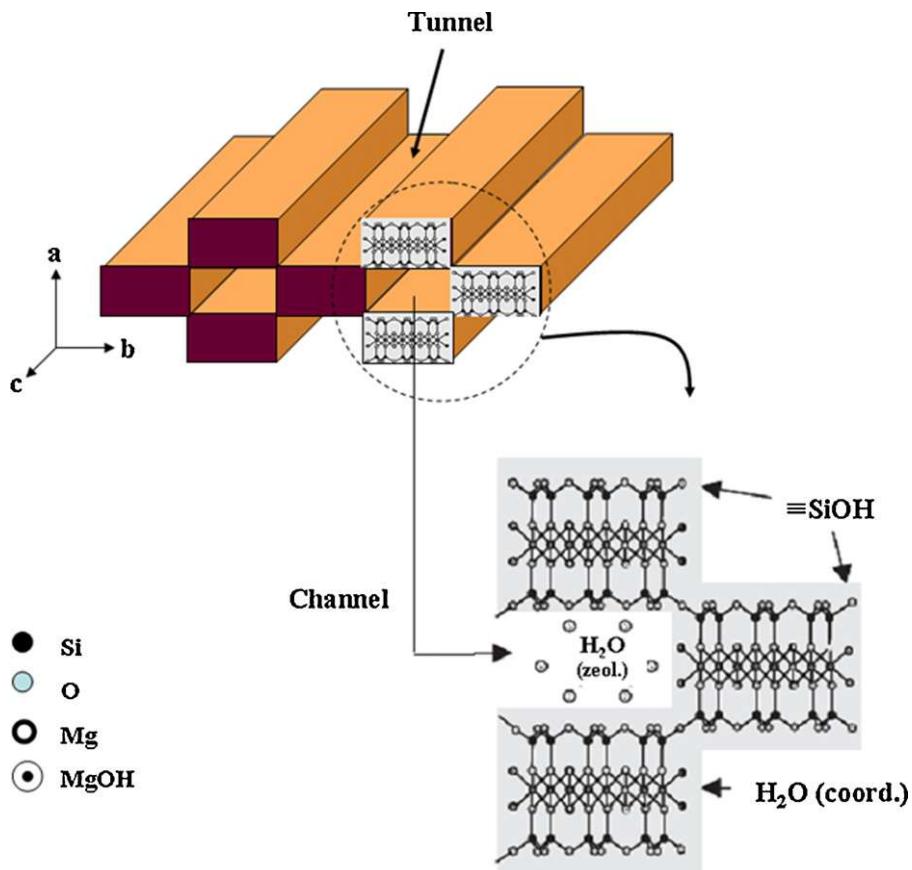
nanocomposites, useful for applications in diverse electrochemical devices such as lithium batteries, sensors, and/or electrocatalysts.

Jang and Bae [74] demonstrated a salt-assisted microemulsion polymerization technique to synthesize CNFs, in which iron(III) chloride coordinates PAN nanoparticles formed as spherical micelles in the microemulsion polymerization, followed by fiber formation with additional AN polymerization as shown in Fig. 6. Carbonization was done by heating PAN nanofibers up to 900 °C for 4 h under inert  $\text{N}_2$  atmosphere. The carbonized PAN nanofibers were used as conducting fillers for polymer composites to enhance the conductivity. CNFs were also produced from PAN/DMF precursor solution by electrospinning and vacuum pyrolysis at temperatures from 500 to 1000 °C by Wang et al. [66]. Further, their electrical conductivities were investigated [75].

Low-temperature electronic transport properties of electrospun PAN-based carbonized nanofibers have been reported [76], and their resistance was measured using



**Fig. 4.** Schematic drawing of the formation of PAN nanofibers [69].



**Fig. 5.** Structural model of sepiolite arrangements in the fibers [73].

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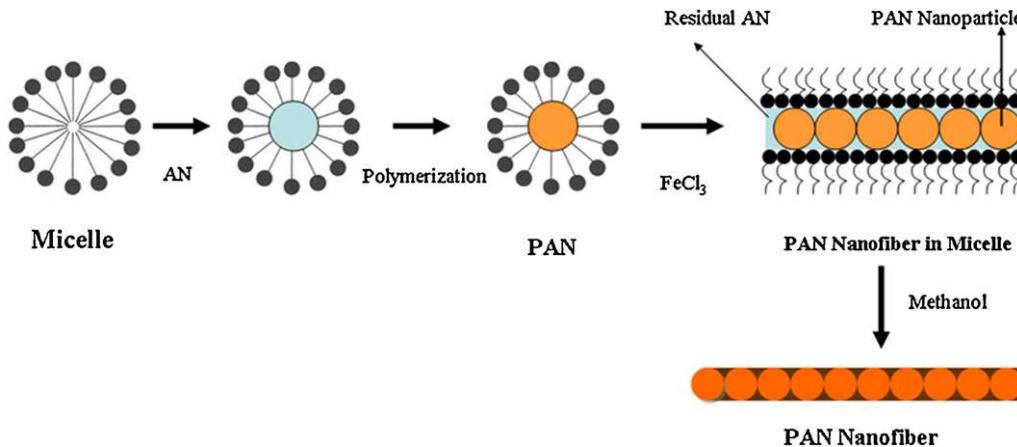


Fig. 6. Schematics of CNF preparation from PAN [74].

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a four-point probe method from 22 °C down to –260 °C. The semiconducting nature of CNFs was revealed by the positive temperature coefficient of conductance. However, Wang et al. [77] used Raman spectroscopy to characterize CNFs of PAN prepared from PAN/DMF precursor solution following the pyrolysis in vacuum at 600, 800, 1000 and 1200 °C. This study concluded with precise estimation of temperature dependent carbon and graphic disorder in the nanofibers.

Yang et al. [78] produced CNFs by electrospinning without a catalyst and reported useful electrical properties of the web. Kim and Yang [79] tested the activated CNFs of PAN that showed excellent performance as supercapacitors. Yang and co-workers [80] also reported the structural properties of PAN solutions in DMF. Electrical conductivity of the carbonized PAN CNF webs ranged from  $6.8 \times 10^{-3}$  and 1.96 S/cm by increasing the carbonization temperature of 700 and 1000 °C. Wang et al. [81] studied the effect of temperature on cone/jet/fiber morphologies during electrospinning of PAN/DMF solutions by varying solution properties and processing variables. The viscosity dependence of fiber (jet) diameter was studied to prepare uniform electrospun fibers, and the temperature dependence of the viscosity, conductivity and surface tension was investigated to obtain the corresponding activation parameters. Also, electrospinning was performed at various high temperatures, and temperature effects on cone/jet/fiber morphologies as well as birefringence and crystallinity of the collected PAN fibers were reported. The PAN NFs of this study have a 65 nm diameter and were readily obtained by electrospinning at 89 °C. A strong viscosity dependence of fiber diameter was obtained due to enhanced solution properties at higher temperatures, higher conductivity and lower surface tension.

Effect of concentration on the morphology of electrospun PAN/DMF solution was studied by Wang and Kumar [82] to reveal that individual beads may be produced at PAN concentration of as low as 2 wt%. The beaded fibers were electrospun from a solution of PAN (3–6 wt%); further increase of PAN concentration led to uniform size fibers as displayed in Fig. 7. Kalayci et al. [83] explored the issues

related to charging of polymer solution viz., charge quantification of electrospun fibers and different charge delivery designs taking PAN as a model. The authors reported a charge density of 30–50 C/m<sup>3</sup> for the electrospun PAN fibers and their theoretical charge density calculations compared well with the experimental observations.

#### 4.1.2. Modifications of PAN as a precursor

Acrylonitrile-based homopolymer and its copolymers have been widely used for electrospinning due to their superior fiber-forming properties. Table 1 gives details of PAN as a precursor in its pristine, blend and composite forms, as well as their applications in different fields. Chen et al. [84] reported the catalytic, electrospun, nonwoven nanofiber mats composed of polyacrylamidoxime (PANOx) blended with PAN. Oxime groups or oximate ions, among the most powerful nucleophiles, were reduced onto CNFs to obtain a stabilized transition state. PAN was modified via catalytic conversion of acrylonitrile groups to result in PANOx as shown in Fig. 8. PANOx fibers with diameters ranging from 10 to 300 nm were produced by electrospinning the blend solution of PANOx with PAN (1:1 by weight) in a mixture of DMF and DMSO in 85:15 ratios by weight. Such PANOx fibers have shown potential applications in self-detoxifying protective clothing.

There are many other developments. For example, a new method was developed [85] to obtain delustered polyacrylonitrile fibers, wherein fibers were formed by spinning a solution consisting of two copolymer solutions, one being polyacrylonitrile and the other a grafted ter-copolymer of acrylonitrile and styrene on rubber, such as butadiene or butadiene-styrene rubber-ABS-copolymer. This approach used low blending ratio of copolymers to act as dopant to yield different texture to nanofibers. Peng et al. [86] reported a novel strategy to prepare electrospun ultrathin CNFs from a blend consisting of a mixture of PAN and poly(AN-co-MMA) in DMF. Since the polymers were incompatible, phase separation occurred during electrospinning on evaporation of DMF, leading to the formation of microphase-separated fibers. After oxidation and carbonization, the copolymer domains were pyrolyzed and

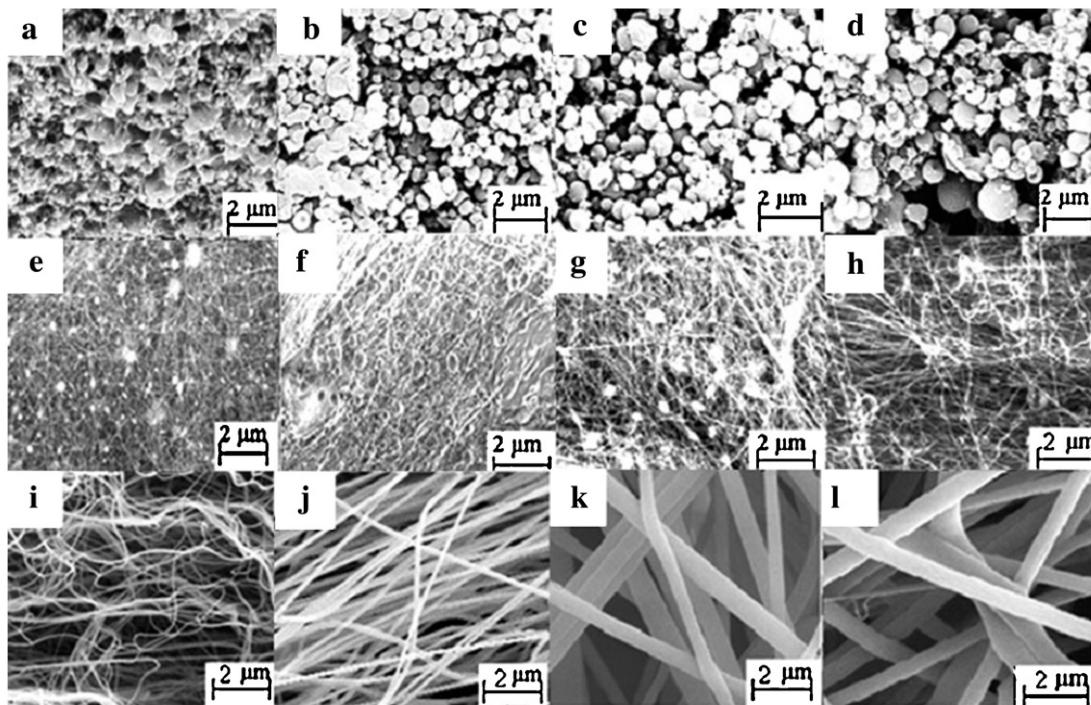
**Table 1**  
Details of PAN based precursors used in its different forms for the preparation of nanofibers.

PAN grade and form	Filler	Type of NF	Technique	Temperature	Fiber diameter	Applications	Ref.
PAN PAN $M_w = 86,200$	Tin dioxide and titanium dioxide	Ultrafine fibers Poros substrate	Electrospinning Electrospinning	600–1200 °C –	100 nm 100 nm	Electrochemical device Catalysis, sensing and photoelectric conversion applications	[65] [68]
PAN	–	Composite NF porous	Electrospinning	–	10–500 nm	In military/civilian protective clothing systems	[67]
PAN PAN $M_w = 125,000$	On silicon substrate Triethylbenzylammonium chloride (TEBAC) Dodecytrimethylammonium bromide (DTAB)	Composite Composite NFs	Electrospinning Electrospinning	1000 °C –	– 100 nm	Electronic devices Effect of needle on diameter	[71] [81]
PAN	–	Composite NFs	Electrospinning	–	100–1000 nm	–	[82]
PAN Modified PAN $M_w = 150,000$	Hydroxylamine hydrochloride and <i>p</i> -nitrophenyl acetate (PNPA)	Modified PAN nanofibers Porous carbon fibers	Electrospinning Electrospinning	20 °C –	600 nm 300 nm	Medical and filtration As key functional layers in a new generation of protective fabrics and filters	[83] [84]
PAN blend AN, AA, and vinyl porphyrin ter-copolymer PAN $M_w = 86,000$	Poly(AN-co-MMA) CNTs	Porous nanofiber Modified NFs	Electrospinning Electrospinning	600–1000 °C –	500 nm 180 nm	Electronic applications Supports for redox enzyme such as catalase immobilization	[86] [87]
PAN $M_w = 150,000$ PAN $M_w = 15,000$ PMMA-996,000 PAN-co-PANCAA $M_w = 83,200$	ER and EB whitening agents	Mechanical nanofibers	Electrospinning	800 °C	78–154 nm	Nano-photoluminescent fibers	[88]
PAN	–	Cone-shell fibers Composite NFs	Electrospinning Co-electrospin from co-annular nozzles,	700–1100 °C –	220–280 nm 0.5–5 μm	Mechanical applications As hollow nano/micro-fibers	[90,91,206] [95]
PAN	MWCNTs	Composite CNFs	Electrospinning	–	100–300 nm	For immobilizing redox enzymes, in bioprocess applications, biosensor	[96]
PAN	MWCNTs	Plain NFs	Electrospinning	1000 °C	100–120 nm	Nano-electrodes, supercapacitors and nano-sensors	[97,155,165,172]
PAN PAN $M_w = 70,000$	– MWCNTs	Composite NFs Mechanical nanofibers	Electrospinning Electrospinning and vibration-electrospinning	– –	200 nm 1000 nm	Viscoelastic performances Composites applications	[98,167] [98,167]
PAN $M_w = 86,200$	Polyester urethane	Blend nanofiber	Electrospinning	–	200–300 nm	As high strength mechanical applications	[99]
PAN blend	Polyurethane	Blend fiber	Electrospinning	–	240 nm	As nanotweezers, nanoactuators In antibacterial activities and medical applications	[102] [103]
PAN $M_w = 52,000$	Polyacrylonitrile- <i>co</i> -3-allyl-5,5-dimethylhydantoin copolymer LiCl, NaNO <sub>3</sub> , CaCl <sub>2</sub> and NaCl	Composite fibers	Two-stage wet spinning process	–	–	–	[108]
PAN $M_w = 75,000$ PAN $M_w = 75,000$ PAN $M_w = 75,000$ PAN	Polyacrylonitrile- <i>co</i> -3-allyl-5,5-dimethylhydantoin copolymer LiCl/DMF Platinum(II) acetylacetone	Porous composite Composite NFs Modified NFs Porous NFs	Electrospinning Electrospinning Electrospinning Polymerization of acrylonitrile in a porous anodic aluminum oxide template	– – – 700 °C	410–473 nm 555–880 nm 12–15 nm 80 nm	Composite applications Composite applications – As electrocatalysts for fuel cells	[109,110] [111,112] [113]

PAN	DMAc/iron(III) acetylacetone (AA)	Composite NFs	Electrospinning	900–1500 °C	150 nm	Gas diffusion electrodes and supercapacitor electrodes	[114]
PAN	NaY zeolite Fe(acetylacetone) <sub>3</sub> Fe(Acc) <sub>3</sub>	Porous NFs Porous NFs	Electrospinning Electrospinning	700 °C 700 °C	– 100–300 nm	As composite material Redox reaction electrodes and in nanoscale engineering	[116] [117]
PAN $M_w = 160,000$	Zinc chloride	Composite NFs	Electrospinning	800 °C	200–350 nm	Electrode in electrically double layered supercapacitor	[125]
PAN $M_w = 120,000$	PTFE substrate	–	Anodic Al <sub>2</sub> O <sub>3</sub> membrane extrusion in to solidifying solution method	–	206.7 nm	Composite applications	[126]
PAN $M_w = 120,000$	DMF	Porous NFs	Extrusion process with an anodic Al <sub>2</sub> O <sub>3</sub> membrane as the template	–	104.6 nm	Super hydrophobic surface applications	[127]
PAN	Porous anodic alumina	Composite NFs	Electrospinning/self lubrication	200–700 °C 800 °C	80 nm 20–200 nm	Aerospace and automobile products	[72,128]
PAN $M_w = 86,200$ $M_n = 22,600$	Sodium cobalt oxide (NaCo <sub>2</sub> O <sub>4</sub> )	Composite NFs	Electrospinning	–	–	In thermoelectric nanodevices	[129]
PAN $M_w = 60,000$ and $150,000$	PdCl <sub>2</sub> and AgNO <sub>3</sub>	Metal composite nanofibers CfCo composite nanofibers	Electrospinning	1000 °C	100–300 nm	Composite electronic applications	[130]
PAN $M_w = 86,000$	Cobalt acetate Co(CH <sub>3</sub> COO) <sub>2</sub>	–	Electrospinning	600 °C	100–300 nm	Anode material for high-power Li-ion batteries	[133]
PAN	Manganese acetate	Composite NFs	Electrospinning-activation	800 °C	250 nm	Toluene adsorption	[136]
PAN	Silver nitrate	Composite NFs	Electrospinning	2000 °C	100 nm	Catalytic applications	[138]
PAN	–	Ultrafine nanofibers	Electrospinning	–	200–1200 nm	Electrochemical applications	[142,205]
PAN $M_w = 100,000$	–	Mechanical nanofibers	Electrospinning	750–1600 °C	131 nm	Composite applications	[144,145]
PAN $M_w = 22,600$	MWCNTs	Composite NFs	Electrospinning	700–750 °C	100–300 nm	High strength applications	[156]
PAN $M_w = 86,000$	–	Porous nanofibers CNF/graphite-felt composite	Electrospinning Catalytic chemical vapor deposition (CCVD)	500–1100 °C 500 °C	149 nm 100 nm	Electronic devices	[159]
Commercial	Graphite felts	–	–	–	–	Catalytic applications	[162]
PAN-based CNFs	SWNT	–	–	–	–	In nanodevices and as AFM tips	[164]
PAN	MWCNTs	Anisotropic porous	Chemically vapor grown (CVD)	800–1000 °C	–	Electrodes in supercapacitors and fuel cells	[169]
PAN	Silica composite NFs	Ultrafine composite NFs Composite nanofibers	Electrospinning	–	200–300 nm	Composite applications	[173]
PAN	Graphite nanoplatelets	Composite NFs	Electrospinning	–	5–500 nm	Composite applications	[174]
PAN	Ceramic	Composite NFs	Electrospinning,	–	150–500 nm	High strength	[175]
PAN	–	Composite NFs	Electrospinning	–	130–280 nm	Composite applications	[177]
PAN	ZnCl <sub>2</sub> and KOH activation	Composite NFs	Electrospinning	1050 °C	200–300 nm	Hydrogen adsorption storage media	[180]
PAN $M_w = 250,000$ and $700,000$	Poly(acrylonitrile-co-methyl acrylate) copolymer $M_w = 100,000$	Blend NFs	Electrospinning,	–	30–3000 nm	Biomedical applications	[183]

Table 1 (Continued)

PAN grade and form	Filler	Type of NF	Technique	Temperature	Fiber diameter	Applications	Ref.
PAN $M_w = 180,000$	–	Porous nanofibers	Electrospinning	800 °C	200–300 nm	Adsorbents for removing toxic compounds	[184]
PAN $M_n = 80,000$	Cadmium acetate ( $\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ )	–	Electrospinning and gas-solid reaction	600 °C	100–800 nm	Optoelectronic and photonic devices	[190]
PAN $M_w = 200,000$	–	PAN/CdS composite	Electrospinning	–	270–290 nm	Composite reinforcement, membrane-based separation, sensing and tissue engineering	[198]
PAN $M_w = 100,000$ PAN $M_w = 100,000$	CNTs/DMAC	Composite NFs Composite NFs Composite NFs	Dry-jet-wet fiber spinning	–	60 nm 150–200 nm	In composite applications Mechanical applications	[200] [202] [206]
PAN blend	PMMA	Mechanical nanofibers Hollow NFs	Electrospinning Two stage co-electrospinning	750–1100 °C	200 nm–7 μm	For hydrogen storage	[211]
PAN $M_w = 150,000$	–	Porous nanofibrous scaffolds	Electrospinning followed by phase inversion technique	–	124–720 nm	As membrane filtration media	[214]
PAN	–	Hollow fibers	Electrospinning and phase inversion method	500–800 °C	300 nm–6 μm	As gas and liquid separation membranes	[217]
PAN 150,000	Lipase	Porous filtration fiber	Electrospinning	–	270–400 nm	As a filter media	[220]
PAN $M_w = 150,000$	Silver nitrate	Porous fibers composite NFs	Electrospinning	–	150–300 nm	For lipase immobilization As filters to protect the wearer from bacterial contaminants	[222]
PAN	–	Porous NFs	Electrospinning following UV-irradiation	–	100 nm	Medical applications	[223]
PAN IM7 fiber	CNTs	Composite fibers	Electrospinning and the pyrolysis of carbon-containing gases on an iron catalyst	500–1500 °C	–	500 nm	As filtration membranes
PAN $M_w = 150,000$	–	Porous nanofibers	Electrospinning	–	–	–	[224]



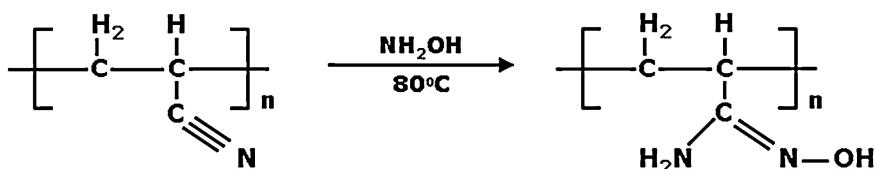
**Fig. 7.** SEM micrographs of the electrospun PAN copolymer fibers prepared in various concentrations: (a) 0.5, (b) 1.1, (c) 2.1, (d) 3.1, (e) 5.1, (f) 9.6, (g) 13.8, (h) 16.1, (i) 17.5, (j) 19.7, and (l) 20.3 wt.% [voltage = 22 kV; Q = 1 mL/h; distance between tip and the target was kept constant at 10 cm] [82]. Copyright 2006, John Wiley & Sons. Reproduced with permission

residual carbon fibers were interconnected with nanoscale dimensions throughout the surface as well as the interior. A copolymer of PAN and methyl methacrylate (MMA) was used instead of poly(methyl methacrylate) (PMMA) homopolymer as a second component in the polymer mixture to improve the compatibility of the second component with PAN in DMF solvent as well as the solution stability during electrospinning. It was found that PAN and poly(MMA-co-AN) formed transparent and homogeneous solution in DMF at a polymer concentration of <15 wt.%, regardless of the PAN/copolymer ratio. On the contrary, when PMMA was used as the second component the blend solution in the syringe phase separated during electrospinning. However, during oxidation, pyrolysis of copolymer domains produced a porous structure in the fibers that were preserved even after carbonization. Thus, ultrathin CNFs were obtained with high nanopore content throughout the surface as well as in the interior of fibers. The pores have diameter of 10 nm and were continuous, suggesting their potential in electrochemical applications.

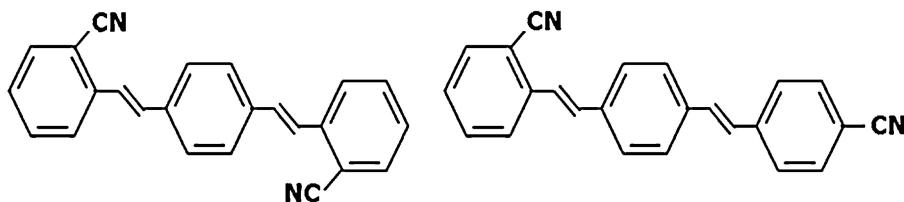
Wan et al. [87] explored acrylonitrile-based copolymers bearing porphyrin pendants, which were blended and elec-

trospun into nanofibers on which redox enzyme catalase was covalently immobilized. Rough surfaces as well as protruded parts induced by blending of CNTs were observed from the CNFs. Catalase was immobilized onto nanofiber surface through activation of carboxyl groups by *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride and *N*-hydroxysuccinimide (EDC/NHS). Results indicated that both the introduction of porphyrin pendants and CNTs improved the activity and stability of the immobilized catalases. Wang et al. [88] also prepared the PAN-based nanofibers composed of two kinds of fluorescent whitening agents viz., 1,4-bis(*o*-cyanostyryl)benzene (ER) and 1-(*o*-cyanostyryl)-4-(*p*-cyanostyryl)benzene (EB) as shown in Fig. 9. The variations in photoluminescence (PL) peak intensities between ER/PAN and EB/PAN nanofibers were related to their different structures and method of producing fibers.

Along with precursor modification, new routes to produce the desired properties of PAN-based system by process modification were attempted in a series of papers [89–94]. Of these, Doshi and Reneker [89] showed that as-spun fibers could be aligned parallel to each other when a



**Fig. 8.** Modification schematics of Polyacrylonitrile to polyacrylamidoxime [84].



**Fig. 9.** Structure of 1,4-bis(*o*-cyanostyryl)benzene (ER) and 1-(*o*-cyanostyryl)-4-(*p*-cyanostyryl)benzene (EB) [88].

drum rotating at a high speed was used as the collector. On the other hand, Zussman and co-workers [90,91] demonstrated a wheel-like bobbin as the collector to position and align the individual polymer nanofibers into parallel arrays. Because the edge of such a bobbin had to be relatively sharp, this technique is not feasible to form well-aligned nanofibers over large areas. Subsequently, Deitzel et al. [92] obtained yarns of aligned poly(ethylene oxide) fibers by introducing an electrostatic lens element to stabilize the liquid jet. Vaia and co-workers [93] fabricated aligned yarns of nylon-6 nanofibers by rapidly oscillating a grounded frame within the jet, but no detailed description and discussions were provided in their work. Recently, Wendorff and co-workers [94] reported the use of a metal frame as the collector to generate parallel arrays of polyamide nanofibers with an average diameter of 50 nm.

#### 4.1.3. PAN blends

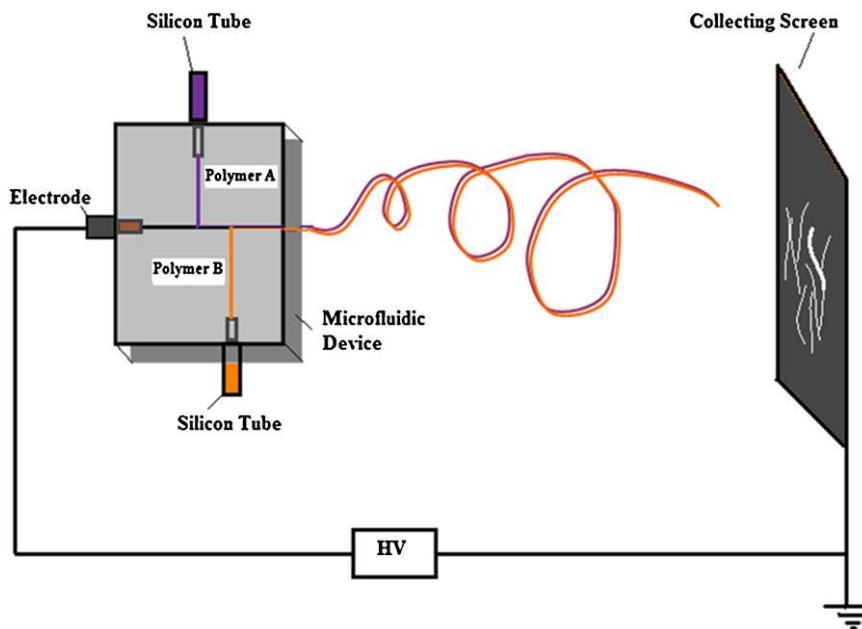
Bazilevsky et al. [95] developed a single-nozzle co-electrospinning technique to prepare CNFs from MMA/PAN blends dissolved in DMF, producing an outer diameter of 0.5–5 µm and a core-shell structure, similar to that obtained using co-annular nozzles. This technique was based on the precipitation of PMMA solution droplets trapped at the base of the Taylor cone issuing the PAN solution jet from its tip. The method was attractive for technological applications involving macroscopically long and radially inhomogeneous or hollow nano/micro-fibers. This concept was demonstrated by producing multichannel porous nanofibers via co-electrospinning of PAN and poly(AN-co-MMA) in DMF solution.

Novel conductive composite nanofiber mesh possessing the reactive groups was electrospun by Wang et al. [96] from solutions containing poly(acrylonitrile-*co*-acrylic acid) (PANCAA) and MWCNTs for redoxase immobilization, assuming that the incorporated MWCNTs would act as electron transfer agents during enzyme catalysis. PANCAA was blended with MWCNTs for electrospinning to facilitate the formation of charge transfer complexes between the negatively charged functional groups ( $-C\equiv N-$ ) and surface-oxidized MWCNTs, leading to enhanced electrical conductivity of the composite nanofiber mesh as well as the interfacial interaction between MWCNTs and the polymer chains. In case of PAN nanofiber, electrical conductivity was of the order of 1 mS/cm, while PAN/MWCNTs composite mesh without carbonization had a conductivity of 0.5–1.0 S/cm at ambient temperature [97]. PMMA/PAN blend nanofibers were electrospun with PAN as the core and PMMA as the shell wall by Yang and co-workers [98] for processing PAN as the continuous core and PMMA covering the nanofibers.

A crosslinkable elastomeric polyester urethane (PEU) was blended with a thermoplastic PAN and electrospun into nanofibers [99] to investigate the effects of PEU/PAN ratio and crosslinking reaction on the morphology and tensile properties of the as-spun fiber mats. The crosslinked PEU/PAN fibers were prepared by adding the crosslinker and catalyst to PEU/PAN solutions prior to electrospinning. At a polymer concentration of 9 wt.%, the nanofiber containing higher composition of PEU showed a slight decrease in average fiber diameter, but tensile strength, elongation at break and tensile modulus of the nanofiber mats were all improved. These tensile properties were further improved by a slight crosslinking of PEU component within the nanofibers.

Lazzari et al. [100] described a facile and low-cost method to prepare the CNFs from tunable wormlike micellar aggregates of PAN-based block copolymers and PAN blends. High incompatibility of PAN in block copolymers with less polar polymers facilitated phase-separation in bulk and micellization in block-selective solvents. For instance, poly[(acrylonitrile-*b*-polystyrene)] (PAN-*b*-PS) and poly(acrylonitrile-*b*-poly-(methyl methacrylate)) (PAN-*b*-PMMA) micelles were prepared by dissolution in a selective solvent for the second block. Jang and Zhao [101] discovered several electrical phenomena associated with CNFs due to a combination of potentially superconducting phases dispersed in CNFs microstructure.

Lin et al. [102] reported a different approach for electrospinning side-by-side bicomponent polymer nanofibers, using a microfluidic device as the spinneret, as shown in Fig. 10. Self-crimping nanofibers were obtained when fibers were prepared from elastomeric polyurethane (PU) and thermoplastic PAN. This technique provided even smaller nanofibers useful as a nano-mechanical chemical sensor, similar to micromechanical chemical sensors. The microfluidic device was prepared using three stainless-steel rods held together with a commercial cyanoacrylate glue to form the desired capillary channel structure. Two different polymer solutions were supplied separately from the syringes through the side channels. The PU half of the as-spun bicomponent PAN/PU nanofiber was removed by extracting the fibers with THF in an extractor for four days. The residual fiber mat was dried in a vacuum at ambient temperature for 6 h. Recent studies [103] have reported the silica/polyvinylpyrrolidone (PVP)-PAN coaxial composite NFs, which follows the co-electrospinning of two or more polymers mixtures to produce PAN-based composite silica nanofibers [104]. In a modified electrospinning set-up comprising two syringes having immiscible and miscible pairs of polymer solutions directed through a single needle to



**Fig. 10.** Schematics of microfluidic electrospinning device [102].

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generate, NFs with core/shell structures primarily comprising PAN as shell and conductive polymer species in the core.

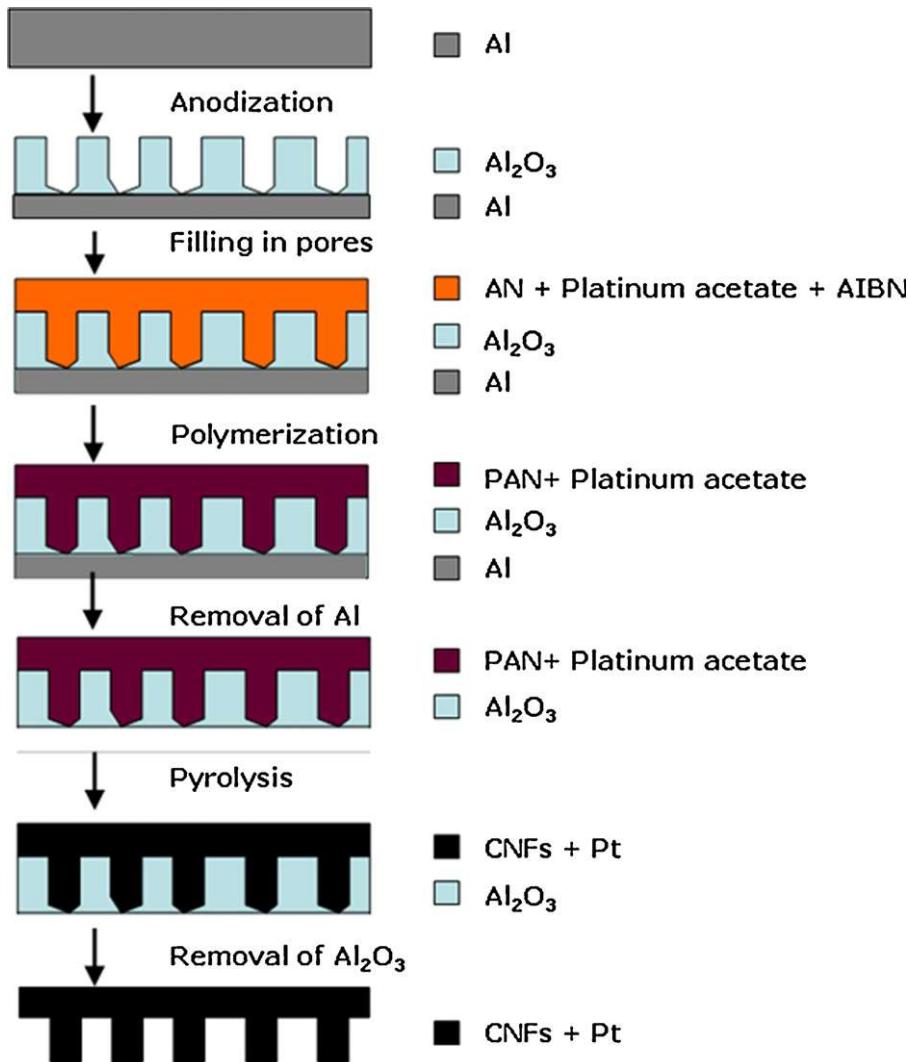
#### 4.1.4. Metal oxide incorporated PAN

Metal oxides are of immense interest to the scientific community due to their interesting chemical and electrical properties as well as their large interfacial area to enhance the desired properties. The interface is often composed of nanoparticles of metal oxide. In the case of dye-sensitized photovoltaic cells, an additional sintering step is required to ensure maximum electrical connectivity between the metal oxide particles [105,106]. Drew et al. [107] reported the fabrication of novel metal oxide-coated polymeric NFs by electrospinning, wherein PAN fibers were electrospun into a nonwoven fiber web, which was subsequently immersed in an aqueous solution of metal halide salts and halogen scavengers at ambient temperature to apply a metal oxide coating. Tin dioxide and titanium dioxide were applied as coatings by this method to obtain 100 nm diameter fibers with a 20–80 nm thick coating. Similarly, ultrafine PAN/silica nanofibers were prepared by Ji and Zhang [108] following a one-step electrospinning method in DMF. These PAN/silica NFs were used to produce composite or porous CNFs through carbonization and/or silica removal. This study elaborated the carbon content in silica/carbon composites obtained from silica/PAN composites with a maximum PAN loading.

The effect of salts such as LiCl, NaNO<sub>3</sub>, NaCl and CaCl<sub>2</sub> on the electrospinning of PAN polymer solution was investigated by Qin et al. [109], showing that the diameter and length of NFs depend on the amount of added salt. The conductivity of salt/CNFs varied in the order of added salt: LiCl > NaNO<sub>3</sub> > CaCl<sub>2</sub> > NaCl > pristine PAN as measured by the conductivity of the spinning solution. Qin et al. [110]

proposed allometric scaling laws for partial to fully charged fibers in electrospinning for PAN/DMF solutions, to assess the applicability of scaling laws, using LiCl in controlling the surface charge. This theoretical analysis showed that the relationship between radius,  $r$  of the jet and the axial distance,  $Z$  from the nozzle followed the relation:  $r \sim Z^{-0.5}$ . In case of fully charged surface, scaling exponent became larger during electrospinning. These experiments showed that the radius of the jet depends on salt content in the spinning solution. The predictions of theoretical analysis agreed well with the experimental observations. Qin et al. [111] also used PAN to study instability in fiber formation during electrospinning with varying amounts of LiCl precursors in the spinning solution. The decrease of the electrical potential of the fiber with increasing distance from the jet orifice was sharper with high content of LiCl than with low concentrations, thus causing the jet instability to occur at initial stage of jet formation with the higher LiCl content. Their data agreed well with the theoretical analysis. Recently, the interior structure of electrospun PAN nanofibers with LiCl was investigated to observe that diameter of CNF was increased by adding LiCl into the PAN matrix [112].

Lei et al. [113] prepared densely packed PAN nanofibers containing platinum(II) acetylacetone by polymerizing acrylonitrile in porous anodic aluminum oxide (AAO) template. Fig. 11 displays the schematics of the fabrication protocol. Anodic aluminum oxide templates were immersed in distilled acrylonitrile monomer ( $\text{CH}_3\text{CH}_2\text{CN}$ ) containing AIBN and platinum(II) acetylacetone [ $\text{Pt}(\text{acac})_2$ ]. Polymerization at 50 °C and cyclization at 220 °C were performed for 10 h in air. The PAN nanofibers were pyrolyzed at 700 °C under high vacuum for 6 h. Subsequent pyrolysis resulted in CNFs, wherein Pt(II) salt was reduced in situ to elemental Pt. High-resolution TEM showed that



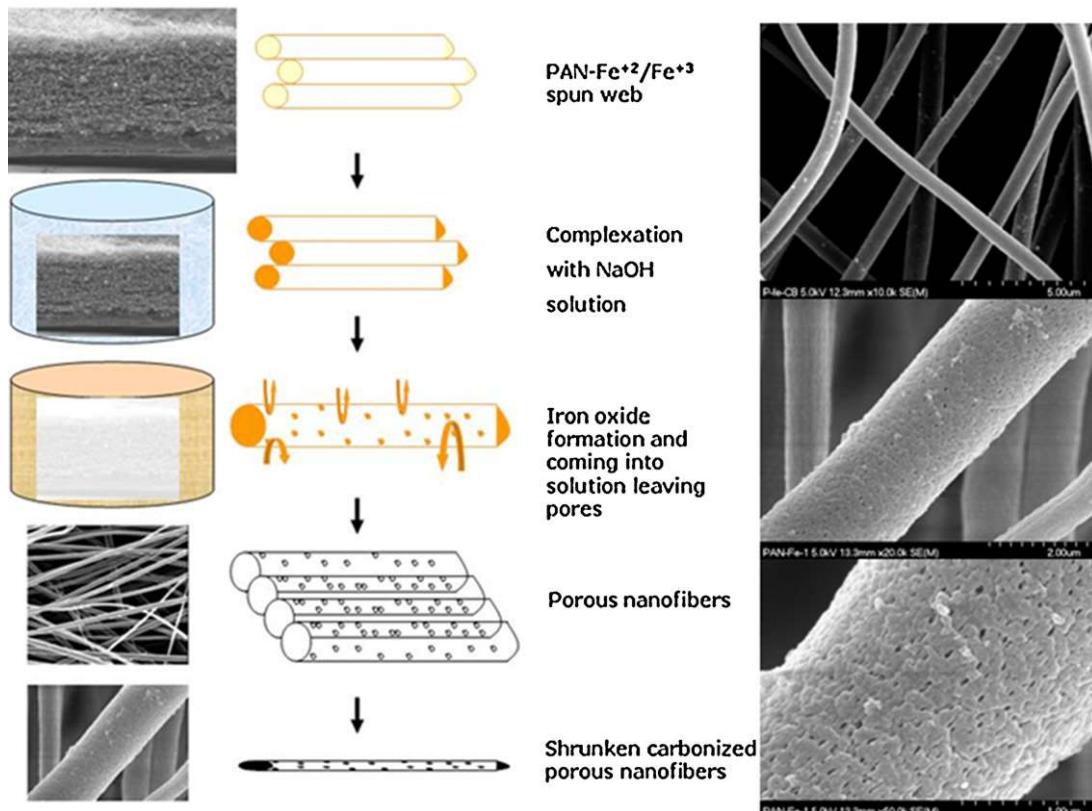
**Fig. 11.** Schematics of the fabrication process of Pt-CNFs using an anodic aluminum oxide (AAO) membrane template [113].

Pt nanoparticles were highly dispersed throughout the CNFs as single crystal sizes range from 1 to 4 nm. Rotating disc electrode voltammetry of these new composite materials has shown better electrocatalytic activity than similar materials fabricated via more complicated procedures. These materials were tested for fuel cell applications.

Park et al. [114] investigated the effect of iron complex on the carbonization behavior of PAN-based electrospun NFs using iron(III) acetylacetone (AAI) and DMAc in the temperature range 900–1500 °C in nitrogen atmosphere. Introduction of AAI promoted the formation of crystalline domains during catalytic carbonization. The electrical conductivity of CNF webs increased with increasing carbonization temperature and catalyst content. The authors claimed these materials as potential candidates for gas diffusion and supercapacitor electrodes because of their high electrical conductivity. Also, electrospun PAN nanofibers were carbonized with or without iron(III) acetylacetone to induce catalytic graphitization in the range 900–1500 °C,

resulting in ultrafine 90–300 nm diameter carbon fibers. It was established that the structure and diameter of CNFs can be controlled by selection of the catalyst, the carbon sources and the synthetic conditions [115]. CNFs produced without a catalyst showed amorphous structures with very low surface areas of 22–31 m<sup>2</sup>/g, but carbonization in the presence of a catalyst produced graphitic nanofiber (GNF). Hydrogen storage capacities of these CNF and GNF materials were also evaluated gravimetrically using magnetic suspension balance (MSB) at room temperature and at 100 bar pressure. The CNFs showed hydrogen storage capacities in the range of 0.16–0.50 wt.% with increasing carbonization temperature. Hydrogen storage capacities of GNFs with low surface areas of 60–253 m<sup>2</sup>/g were 0.14–1.01 wt.%.

In a recent study [116], the carbonization of PAN nanofibers and reduction of Fe<sup>3+</sup> were performed in a tubular high-temperature furnace through oxidative stabilization of the precursor nanofibers at 250 °C in air. Hou and



**Fig. 12.** Processing steps for fabrication of porous carbon nanofiber embedded with iron oxide (left) and FE-SEM images of CNFs carbonized at 1000 °C showing porous surface.

Reneker [117] prepared self-supported nanofiber sheets of PAN/Fe using PAN and Fe(Acc)<sub>3</sub> precursors with varying concentrations of Fe(Acc)<sub>3</sub> in PAN solution. The metallic particle size in resulting CNFs was controlled by varying the Fe(Acc)<sub>3</sub> concentration in the spinning solution. Carbonized nanofibers having reduced metal nanoparticles were then used as catalysts to grow CNTs on composite CNFs. This method resulted in obtaining CNFs/CNTs dense mats with unique properties useful for energy storage devices. In another study to produce CNFs using PAN incorporated with iron oxide particles (see Fig. 12), the authors suggested their applications as electrodes in electrical double layer supercapacitors [118].

Branching of carbon fibers was first introduced to overcome delamination problems in composites by Milewski [119]. Later, Downs and Baker [120,121] improved the process by growing carbon filaments on the surface of PAN and pitch-based carbon fibers via Cu/Ni catalyzed pyrolysis of C<sub>2</sub>H<sub>4</sub>. Specific surface area was significantly increased by branching, resulting in enhanced interfacial bonding between the fibers and the matrix. McAllister and Wolf [122] impregnated Ni on rayon fibers by using an incipient wetness method to grow branches under mild conditions, but a recent study by Hou and Reneker [117] reported homogeneously distributed nanofibers grown on PAN-based nanofibers. Fe(acetylacetone)<sub>3</sub>, (Fe(Acc)<sub>3</sub>), which is soluble in organic solvents, was used as a catalyst

precursor. PAN and Fe(Acc)<sub>3</sub> were both dissolved in DMF and the solution was spun into PAN precursor nanofibers that contained Fe(Acc)<sub>3</sub> nanofibers ranging in diameter from 100 to 300 nm. The iron catalyst used for nanofiber growth was mixed with the precursor of PAN fibers, which was produced by electrospinning. The size of the iron particles ranged from 10 to 30 nm, and the diameter of the secondary nanofibers was around 40 nm. Activated pitch-based carbon fibers were employed as substrates for the secondary NFs [123].

Ruthenium-embedded CNFs were prepared by stabilization, carbonation and activation after electrospinning the composite solution of ruthenium(III) acetylacetone and PAN in DMF [124]. Ru particles (size distribution of 2–15 nm) were embedded randomly into CNFs to increase the size from 2.0 to 2.5 nm. The specific capacitance of CNF without Ru loading was 140 F/g, while that with 7.31 wt.% Ru–carbon nanofibers increased to 280% for 391 F/g. This was due to the synergistic effect of electrical double-layer capacitance as a result of the expansion of average pore diameter as well as pseudo-capacitance by the well-dispersed Ru nanoparticles. Recently, Yang and co-workers [125] prepared a flexible, thin web consisting of intermingled long nanofibers by electrospinning of PAN solution containing zinc chloride, followed by high-temperature thermal treatment. The zinc chloride-incorporated PAN solution was successfully electrospun into thin white webs

consisting of long nanofibers 350–200 nm in diameter. The web was stabilized in air, changing its color from white to dark brown. Zinc chloride acted as a dehydrating agent, which enhanced the oxidation rate, giving a short stabilization time. Also, PAN-based composite nanofibers containing magnetic nanoparticles have been studied using PAN solutions [126].

Feng and co-workers [69,127] reported a novel method to prepare PAN nanofibers using anodic aluminum oxide membrane as a template. Compared to conventional template syntheses, this method was much simpler, to obtain nanofiber via extrusion of a PAN precursor solution into a solution of DI water under pressure where it solidified and polymerized as closely packed fibers; the template can be recycled after washing. Aligned CNF membranes with different diameters and densities were obtained by using templates of different pore diameters. CNFs prepared [128] by pyrolysis of PAN precursors in the interlayer space of taeniolite were used as electrode materials in lithium batteries.

Maensiri and Nuansing [129] were the first to use sodium cobalt oxide ( $\text{NaCo}_2\text{O}_4$ ) to prepare nanofibers of diameters ranging from 20 to 200 nm by electrospinning a precursor mixture of sodium acetate/cobalt acetate/PAN, followed by a calcination treatment of the electrospun composite nanofibers. This resulted in the formation of  $\gamma\text{-NaCo}_2\text{O}_4$  in sodium acetate/cobalt acetate/PAN composite NFs. Similarly, Wang and co-workers [130,131] fabricated PAN nanofibers from a precursor solution comprising  $\text{Ag}(\text{NO}_3)_3$  and  $\text{PdCl}_2$  and PAN using microwave irradiation and electrospinning techniques. The size of metal nanoparticles (Ag and Pd) was adjusted by varying the molar ratio of metal precursors in the PAN solution. This method offered a powerful platform to design and fabricate functional polymer/metal nanocomposite fibers with desirable properties. Other similar studies reported in the literature involved the fabrication of CNFs containing metal oxides [107,132] in the electrospun nanofibers to enhance the electronic properties of the composite CNFs.

In another study, the PAN-based carbon–cobalt (C/Co) composite nanofiber was fabricated [133] via electrospinning and subsequent low temperature thermal treatment. The incorporation of cobalt increased the interfacial surface area between carbon and liquid electrolyte to enhance the electrical conductivity for applications in Li-ion batteries. Luoh and Hahn [134] also successfully electrospun the nanocomposite fiber mats of PAN containing  $\text{SnO}_2$  nanoparticles as an optical sensor to detect  $\text{CO}_2$  gas. It was later demonstrated by Zhang and Hsieh [135] that such porous CNFs and metal oxide fibers can be readily synthesized via electrospinning. The nanoporous ultrahigh surface of the PAN fibers was fabricated by combining phase separation and electrospinning with the diameters ranging hundreds of nanometers with the pore diameter of 8–24 nm.

Recently, Oh et al. [136] prepared the manganese (Mn)-dispersed PAN-based composite CNFs by loading various amount of manganese salt for toluene adsorption to get higher toluene storage efficiency. Yang and co-workers [137] adapted a new route to incorporate Mg into PAN to produce porous CNF following two steps: the first one

includes the preparation of porous CNFs by incorporating magnesium acetate to increase the surface area, and the second step includes the coating of manganese oxide onto high surface area CNFs. This novel method served a dual purpose of producing high surface area and the coating of electrochemically active  $\text{MnO}_2$  thin layer onto the surface of CNFs.

Wang et al. [138] studied the dispersion of Ag nanoparticles (10 nm diameter) in PAN nanofiber film by electrospinning and by in situ reduction of silver ions in  $\text{N}_2\text{H}_5\text{OH}$  aqueous solution. Surface-enhanced Raman scattering (SERS) indicated that the structure of PAN was altered after Ag nanoparticles were dispersed in the PAN matrix. Controlled deposition of silver oxide nanoparticles on PAN/ $\text{TiO}_2$  composite nanofibers was also achieved through photocatalytic reduction [139] by a simple method to achieve controlled morphology with fiber diameter required in medical applications. Recently, Nataraj et al. [140] fabricated long and continuous composite nanofiber sheets of PAN incorporated with zinc oxide (ZnO). These CNFs exhibited enhanced physico-chemical properties. In a further study by Nataraj et al. [141], nickel nitrate was loaded into PAN to enhance the electrical and physico-chemical properties of the CNFs and these materials were proposed for their potential applications as catalyst supports in fuel cells and energy storage devices.

Gu et al. [142] produced PAN NFs using a stainless steel electrode immersed in a solution connected to a high voltage power supply. A flat metal plate covered with aluminum foil placed below the electrode served as the grounded counter electrode. The fibers were dried in flight and collected on the aluminum foil as nonwoven fabric. The molecular chains were oriented within the electrospun fibers during electrospinning; cyclization of PAN was initiated at lower temperature due to cyclization exothermic peak shift to lower temperature [143,144]. Ali and ElHamid [145] studied the electrospinning of PAN/DMF in a coagulating bath to produce CNFs with <100 nm diameter. Electrospun PAN fibers with diameters of 50–200 nm were also produced in an aqueous coating solution to deposit a continuous film of titanium dioxide on the surface [146]. Such PAN–metal oxide nanocomposites have applications as sensors, photovoltaic cells and catalytic surfaces. Yang and co-workers [147] recently developed electrically conducting CNFs obtained by incorporating different amounts of heteropolyacids (HPAs) viz., silicotungstic acid (SiWA) and silicomolybdic acid (SiMoA) in PAN. Microscopic studies confirmed cylindrical morphologies of CNFs with diameters of 100–300 nm after carbonization at 1000 °C, in addition to enhanced morphological and physico-chemical properties, such as the diameter, surface porosity and thermal degradation of the PAN nanofibers.

Composites of PAN with layered oxides undergo carbo-thermal reduction in an argon atmosphere at 1000 °C to give cubic carbides [148]. Formation of carbide begins at 800 °C and completes at 1000 °C. Thus, mesoporous carbons were synthesized from PAN using mesoporous templates [149]. The pores of the silica templates were infiltrated with PAN via polymerization of acrylonitrile from initiation sites chemically bonded to the template

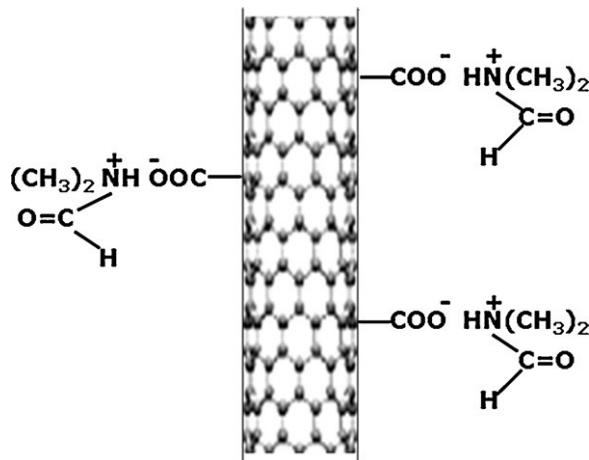
surface. These results have technological interest as the porous metal oxide–CNFs are promising candidates for a wide range of applications in which fiber morphology, lightweight and controlled pore structure as well as interfacial properties are desired.

#### 4.2. Composite PAN nanofibers containing CNTs

Single wall (SWCNT), double wall (DWCNT) and multi-wall carbon nanotubes (MWCNT) can be electrostatically assembled into nanofibers by electrospinning to increase the electrical property, strength and toughness of PAN-derived CNFs. It was found that the effectiveness of CNT in reinforcing PAN precursor is highly dependent on the dispersion and alignment of CNT [150–153]. Alignment was achieved during electrospinning by controlling the flow of polymer, electrostatic charge and diameter confinement. These results promise to produce the next generation of high performance CNFs. Composite papers of MWCNTs/PAN (20/80) without carbonization have electrical conductivities up to 0.5–1.0 S/cm at ambient temperature. PAN-based CNF papers are used as supercapacitor electrodes, where high capacitance of 173 F/g at 10 mA/g can be obtained, but power density will be poor due to the large electrical resistivity of PAN-based CNFs [79,154].

Ge et al. [97] prepared highly oriented, large area continuous composite nanofiber sheets made of surface-oxidized MWNTs and PAN by the electrospinning method. The preferred orientation of surface-oxidized MWNTs along the fiber axis was determined with TEM and electron diffraction. The extensive fine absorption structure detected via UV-vis spectroscopy indicated that charge transfer complexes formed between surface-oxidized nanotubes and the negatively charged functional groups in PAN during electrospinning led to a strong interfacial bonding between CNTs and the surrounding polymer chains. Thermal deformation temperature increased with increasing MWNT loading. In this aspect, a study [155] revealed the mechanical examination of hot pressed CNTs induced electrospun PAN nanofiber mat that showed better flexibility and ductile behavior than the nascent PAN.

The molecular orientation and microstructure of PAN precursors are strongly affected by incorporation of CNTs [156]. In one such a study, Hou et al. [157] prepared PAN nanofibers containing well-aligned MWCNT in concentrations from 0 to 35 wt.% as thick sheets of well-aligned nanofibers to demonstrate that at higher concentration, the MWCNTs are nearly parallel to the nanofiber axis. However, the heat shrinkage of the composite nanofiber sheet during carbonization was altered in the presence of the CNTs. For a CNT concentration of 35%, the sample shrank only 3% in the direction of the nanofiber alignment and about 11% in the direction perpendicular to nanofiber alignment, but electrical resistance, tensile strength and modulus of the nanofiber sheets were improved after the carbonization process. The model shown in Fig. 13 suggests an interaction between the DMF solvent and the carboxylic groups attached to the MWCNT surface. The MWCNT suspension in PAN–DMF solution was ejected from a spinneret connected with a solution reservoir under the driving force of high voltage. The PAN–MWCNT composite nanofibers



**Fig. 13.** Schematics describing the interaction of CNT surfaces with solvent molecules [157].

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were formed by evaporating the solvent. MWCNTs reinforced the PAN nanofibers to improve the tensile modulus by 144% at 20 wt.% MWCNTs loading, while tensile strength by 75% at 5 wt.% MWCNTs. The morphology and shape of the PAN–MWCNT composite nanofibers were maintained even after carbonization.

Lee and co-workers [158] successfully fabricated MWCNTs-embedded PAN nanofiber paper, for which the diameter of the nanofibers decreased with increasing CNT concentration. The electrical conductivity of the CNF web spun on aligned charged collector along the spinning direction was about three times greater than that of the randomly collected nanofiber mats; by contrast, CNFs without CNTs did not reveal anisotropy in electrical conductivity measurements. Thus, CNTs in PAN nanofiber preferentially aligned along the nanofiber axis are in excellent agreement with TEM observations.

Agend et al. [159] measured the electrical conductivity of PAN CNFs web to show that the conductivity of CNFs increased with increasing the pyrolysis temperature, concluding that at high temperature, reduction of the interlayer spacing, decrease in the void space and increase in the preferred orientation would facilitate compact and favorable microstructure to give increased electrical and thermal conductivity. Kim and Park [160] described a simple method to prepare activated carbon fibers (ACFs) coated with PAN-based graphitized nanofibers (GNFs). In their study, the low-pressure plasma mixed-gas (Ar/O<sub>2</sub>) treatment of ACFs led to the growth of GNFs on the surface. SEM and TEM revealed that GNFs were homogeneously coated onto ACFs, and that porous structures of ACFs did not sharply decrease even after GNF coating. The electrical resistivity of GNF-coated samples was slightly lower than that of as-received ACF sample, but was higher than commercial GNF. Thus, the GNF-coated ACFs are promising electrode materials. Kalayci et al. [83] observed a considerable increase in the accumulation of charge on electrospun PAN fibers at increased electric voltage resulting in enhanced repulsion between individual fibers. Such

fibers were later arranged in an orderly manner, offering increased permeability with uniform pore size distribution.

In another study [161], blend nanofibers of poly(acrylonitrile-co-acrylic acid) (PAN-co-PAA) were developed with charged  $[\text{Ru}(\text{bpy})_3]^{+2}$  immobilization in a controlled procedure to modify an electrode, which was tested using CV for range of scan rate (5–2000 mV/s) in electrochemical and electrochemiluminescent sensors.

Li et al. [162] prepared graphite-felt composite CNFs using the commercially available graphite felt composed of PAN-based graphite fibers as the substrate for in situ growth of CNFs by catalytic a chemical vapor deposition (CCVD) technique. The graphite felt was cut to pre-defined shapes and sizes. These graphite-felt CNF composites were used as catalysts in a probe reaction of oxidative dehydrogenation of ethyl benzene to styrene. The electron spin resonance characteristics of fibers derived from a PAN-based precursor, heat-treated between 1000 °C and 2800 °C were examined for structural characterization [163]. Kumar and co-workers [164] developed a novel approach to prepare SWNT/PAN composite CNFs by electrospinning using CNTs in the core surrounded with PAN as a shell in a continuous nanofiber filaments. These composite materials are expected to find applications in nanodevices as well as AFM tips.

An improved method was developed [165] based on X-ray diffraction studies for structural measurement and evaluation to obtain detailed information on fiber structure along with the evaluation of disordered fiber structures. Insights on ordered and disordered domain structures confirmed the absence of two-phase structures. Structural changes due to the addition of CNTs were studied, including helix-zigzag conformational changes in the alignment of CNTs in CNFs [166]. Changes were larger with gel-spun fibers than the solution spun fibers, mainly due to a decrease in PAN inter-chain spacing. In another study [167], MWCNTs were directly electrospun into PAN nanofibers by the traditional electrospinning and vibration-electrospinning methods. CNTs aggregated extensively in the fibers obtained by traditional electrospinning, while a good distribution and alignment was observed in PAN fibers obtained by vibration-electrospinning. These observations were further supported by Yang and co-workers [168], who suggested that using CNTs as fillers would offer property improvement in the derived CNFs.

MWCNTs-embedded PAN nanofiber paper was prepared [158] in which the diameters of PAN nanofibers decreased with increasing CNT concentration, but electrical conductivity of the carbonized NF paper along the spinning direction was three times higher than that normal to the spinning direction. However, carbonized PAN nanofiber paper without CNTs did not reveal anisotropy in electrical conductivity, suggesting that CNTs in PAN nanofiber are preferentially aligned along the nanofiber axis. In an attempt [169] to get high surface area CNFs suitable for energy storage applications, CNFs paper was prepared from PAN/camphor composite solutions, which upon carbonization resulted in submicron pore structures and high surface area. In a systematic approach from precursor to final fiber formation, Wan et al. [170] studied the

rheological properties of composite PAN precursor solution as well as the effect on electrospinning under the action of vibration, rheology and nonlinear mechanics, in which information could be obtained about rheological properties with respect to slow forces under the action of vibration.

In another study [171], composite nanofiber sheets of well-aligned PAN containing CNTs were prepared by electrospinning, wherein carbonization showed that higher concentration of CNTs effectively resisted the heat shrinkage of composite nanofiber sheet. Ge et al. [97] observed that orientation of CNTs within NFs was much higher than that of PAN. The composite CNTs/NFs of highly oriented, large area continuous sheets comprising surface-oxidized MWCNTs and PAN were developed by electrospinning. Surface tension, jet elongation and slow relaxation of CNTs in PAN nanofibers were the determining factors in the orientation of CNTs. Due to the highly anisotropic orientation and formation of complexes (PAN/CNTs), composite NF sheets showed enhanced electrical conductivity, mechanical properties, thermal deformation temperature, thermal and dimensional stability. Electrical conductivity of PAN/MWNT composite NFs containing 20 wt.% CNTs was enhanced to 1 S/cm. In a new approach [172], hot-stretched PAN/SWNT composite nanofibers were prepared in an oven to enhance the orientation and crystallinity, thereby resulting in enhanced electrical conductivity.

A simple one step pyrolysis was carried out by Beguin et al. [173] on the physically mixed CNTs/PAN nanofibers to achieve high capacitance. The authors used CNTs as minor electrode components to improve the electrical conductivity and mechanical properties of the composite nanofiber. Kaner and co-workers [174] used 7 wt.% PAN in DMF containing 1–4 wt.% graphite nanoplatelets relative to the weight of PAN to produce composite NFs that demonstrated a modest increase in thermal stability with increasing wt.% graphite nanoplatelets. It was shown that nanoplatelets can serve as alternative reinforcement materials. Li et al. [175] developed a new method to prepare uniaxially aligned nanofibers of organic polymers, ceramics and polymer/ceramic composites. Key to the success of this method was the use of a collector consisting of two pieces of electrically conductive substrates separated by a gap whose width could be varied from hundreds of micrometers to several centimeters. Materials used in these protocols include conventional organic polymers, graphite carbon and metal oxides [176].

In a theoretical and experimental approach by Gu et al. [177], ultrafine fibers were spun from PAN/DMF solution as a precursor of CNTs by electrospinning. Fibers with diameters from 200 nm to 1200 nm were obtained. A systematic understanding of process parameters was achieved by establishing a quantitative relationship between electrospinning parameters and average fiber diameter using response surface methodology to conclude that concentration of the solution was important to the diameter of the fibers. The applied voltage had no significant impact on the fiber diameter. It was suggested that concentration of the solution played the most significant factor in affecting the diameter of the fibers.

## 5. PAN-based nanofibers for electronic and energy storage applications

Because of their unique tailor-made properties, nanofibers attract much attention as these bear many potential applications in different fields of commercial interest. Their unusual structural and electronic properties make carbon nanostructures applicable in electrochemical double-layer capacitors (EDLC), batteries, catalyst supports, energy storage, fuel cells and different electronic devices. Many attempts have been made to produce PAN-based CNFs of high surface area for applications as supercapacitors that are intensely investigated as backup energy storage systems, since they carry high power and have long lifecycles. Their double-layer capacitance strongly depends on the type and form of electrode materials. In view of their scientific and technological importance at elevated temperature, the channel between carbon basal planes in PAN will be filled, resulting in a low surface area. Then, CNFs were treated in CO<sub>2</sub> at 880 °C for several min, the surface of CNFs was etched and the new pores formed enhanced the improved surface area, desired in electrochemical applications [178,179].

Microporous materials are promising as components for hydrogen storage. Im et al. [180] prepared PAN-based CNFs by electrospinning and subsequent heat treatment to obtain media for hydrogen adsorption storage. Chemical agents such as KOH and ZnCl<sub>2</sub> activations were done during carbonization in a pyrolysis chamber under the controlled atmosphere N<sub>2</sub> flow to increase the specific surface area and pore volume of CNFs. Yang and co-workers [124,125] reported a solution method to prepare porous and smaller-sized fibrous carbon in the form of thin webs using zinc chloride. Specific surface areas obtained for samples prepared from PAN containing 1, 3, and 5 wt.% ZnCl<sub>2</sub> were 310, 420, and 550 m<sup>2</sup>/g, respectively. Higher surface areas of fibrous materials exhibited higher specific capacitances. The CNF webs with 5 wt.% ZnCl<sub>2</sub> exhibited the largest specific surface area (550 m<sup>2</sup>/g) and highest capacitance (140 F/g). Park et al. [181] reported the electrochemical behavior of PAN nanofibers. The performance of hybrid supercapacitor with electrodes of carbon/RuO<sub>2</sub> in 6 M of aqueous KOH solution was investigated by Yang and co-workers [182]. The electrical conductivity of PAN-based activated carbon nanofibers (ACNFs) was increased from 0.42 S/cm to 0.98 S/cm by the dispersion of 3 wt.% of MWCNT. The capacitances of pristine PAN, MWCNT/PAN, RuO<sub>2</sub>/PAN, and RuO<sub>2</sub>/MWCNT/PAN-based ACNFs were 140, 180, 390 and 530 F/g, respectively. The capacitance was increased 4 times for 3 wt.% loaded MWCNT with a deposition of 20 wt.% of RuO<sub>2</sub>, even though specific surface area was reduced by the deposition of RuO<sub>2</sub> down to 1/3 of the original value.

PAN was electrospun in DMF solvent as a function of electric field, solution flow rate and polymer concentration. Fibers less than 350 nm in diameter contained beads, whereas beyond this diameter, bead-free fibers were obtained [183]. Carbonized and activated electrospun PAN fibers are attractive for supercapacitor electrodes, catalysis and other applications. Yang and co-workers [184] investigated the adsorption equilibrium, thermal desorption and

kinetics of organic compounds using PAN-based CNFs to assess their possibility as alternative adsorbent to commercial ACFs. Park and co-workers [185] electrospun the PAN nanofibers with or without iron(III) acetylacetone to induce catalytic graphitization in the range of 900–1500 °C, resulting in ultrafine carbon fibers with diameters ranging between 90 and 300 nm. Their hydrogen storage capacities were evaluated gravimetrically using a magnetic suspension balance. The CNFs showed hydrogen storage capacities that increased with increasing carbonization temperature ~1200 °C, but a storage capacity decreased for CNFs prepared at a temperature of 1500 °C. Hydrogen storage capacities of GNFs with low surface areas of 100–250 m<sup>2</sup>/g were 0.14–1.01 wt.%, while others [186,187] reported the effects of iron(III) acetylacetone (IAA) on the carbonization behavior of electrospun polyimide and PAN-based NFs, resulting in GNFs. In addition, carbonization of electrospun PVDF-based NFs with an average fiber diameter of 200–300 nm produced microporous CNFs with much higher surface areas than the PAN-based GNFs. Hydrogen storage capacity in SWCNTs was much lower than that of PAN-based GNFs [188]. A comparative analysis by Pittman et al. [189] on energy distribution functions provided significant information on the energetic and structural heterogeneities of CNFs. Furthermore, an investigation of adsorption equilibrium and kinetics of methylene blue (MB) and Congo red (CR) revealed that adsorption capacity and kinetics of MB were much higher and faster than that of CR.

Yang et al. [190] used PAN/CdS composite NFs as precursors to prepare carbon/CdS coaxial nanofibers. Their synthetic strategy involved the preparation of CdS/PAN composite NFs via electrospinning and gas-solid reaction. Subsequently, carbonization of these composites into carbon/CdS coaxial NFs, i.e., by immersing the as-spun PAN fibers into cadmium acetate aqueous solution, followed by reaction with H<sub>2</sub>S gas and carbonization produced materials for use in optoelectronic and photonic devices. In a microemulsion polymerization, the effects of surfactant properties such as concentration, chain length, ionic characters and polymerization temperature on the structure of the resulting polymer nanofibers have been investigated. Importantly, PAN-based nanofibers exhibited novel photoluminescence character as observed by Jang et al. [191] using electrospun PAN nanofibers as a template. The PAN-based CNFs were of high porosity after stabilization and carbonization at 200 and 700 °C, respectively. This temperature treatment sequence resulted in a uniform cross-section and a well ordered structure with a very low concentration of stacking faults, resulting in high porosity.

## 6. PAN-based mechanical nanofibers

Of all the mechanical tests, tensile test measurements of CNFs are the most challenging ones to perform because direct manipulation of a fiber is required. There are at least two difficulties that are to be overcome. First, proper specimen gripping is necessary to prevent the fiber from slipping from or breaking at the grips. Due to the small size of the samples, conventional mechanical grips are not suitable. Ko and co-workers [192,193] used AFM to

perform nano-indentation of electrospun PAN nanofibers. They assumed that indentation depth was of comparable size to the AFM tip and that the tip radius (5 nm) was small compared to nanofiber diameter (50–500 nm), such that the curvature of the fiber may be ignored. Earlier tests were also conducted on CNFs produced from both PAN and mesophase pitch [61] to examine the morphological changes associated with mechanical properties of CNFs. Nanofibers of PAN–PMMA were prepared in a core-shell confinement and used as-spun as well as post-drawn reinforced dental composites [194]. The post-drawn procedure enhanced the composite tensile strength and modulus of PAN nanofibers by several orders of magnitude.

One of the most important applications of traditional (micron-size) fibers, especially engineering fibers such as carbon, glass and Kevlar fibers, is to use them as reinforcements in composite developments. With these reinforcements, composite materials will provide superior structural properties such as high modulus and strength to weight ratios that are generally not achievable by other monolithic materials. It is anticipated that NFs will eventually find important applications in making nanocomposites because they have even better mechanical properties than micro-fibers of the same materials and hence, superior structural properties of nanocomposites can be anticipated [195]. For instance, if there is a difference in refractive indices between fiber and matrix, the resulting composite becomes opaque or nontransparent due to light scattering. This limitation can be circumvented when fiber diameters become significantly smaller than the wavelength of visible light. These nanofibers provide a higher ratio of surface area to mass than carbon fibers ordinarily used in composites. CNFs can also be useful in filters, as a support for catalysts in high temperature reactions, in composites to improve mechanical properties or for thermal management in semiconductor devices [196]. Nanopores in carbon fibers were produced using nitrogen gas saturated with water vapor.

Mordkovich [197] analyzed the prospects of introducing NFs into the market of high-strength and heat-resistant materials and realized the importance of partial replacement of PAN-based fibers by nanofibers, first and foremost, in the fields where the requirements for high strength are particularly stringent due to safety reasons. Thus, the CNFs are described as a new ultrahigh-strength material, superior to both ordinary carbon fibers and other high-strength materials. Formation of PAN-based nanofibers, the fiber spinning velocity and fiber draw ratio was measured for PAN solutions with DMF [198]. The ultimate strength and modulus of the twisted yarns increased with increasing angle of twist to a maximum of  $162 \pm 8.5$  MPa and  $5.9 \pm 0.3$  GPa, respectively, at an angle of  $9.3^\circ$ . Twisted yarns of highly aligned PAN nanofibers with twist angles between  $1.1^\circ$  and  $16.8^\circ$  were prepared.

Ye et al. [199] prepared CNT-PAN composite fibers by electrospinning using both SWCNT and MWCNTs for the reinforcement. The results showed that distribution of CNTs in polymer matrix and interfacial adhesion between nanotubes and polymers are the major factors responsible for the determination of the reinforcement effect of CNTs in the polymer fibers. Composite nanofiber sheets of well-aligned PAN nanofibers containing MWCNTs were

prepared by electrospinning MWCNT-suspended solution of PAN in DMF using a moving collector [156]. Carbonization showed that higher concentration of MWCNTs effectively resisted the heat shrinkage of the composite nanofiber sheet. Mechanical properties of the composite nanofibers were reinforced by MWCNT fillers, which were observed parallel and oriented along the nanofibers axes. PAN/CNTs composite fibers were spun from solutions in DMAc using SWCNTs, DWCNTs, MWCNTs and VGCNFs. The nanotubes contributed to property improvements in all cases. Chae et al. [200] observed a maximum increase in modulus of 75% and reduction in thermal shrinkage up to 50% in SWNT-containing composites and maximum improvement in tensile strength of about 70%, strain to failure of 110% and work of rupture of 230% were observed in MWNTs containing composites. Improvement in low strain properties such as modulus and shrinkage was attributed to PAN interaction with the nanotubes, while improvement in high strain properties, such as tensile strength, elongation to break, and work of rupture was correlated with the nanotube length.

The feasibility of co-electrospinning of vapor grown nanofiber (VGNF) reinforced PAN a fiber was demonstrated by Lam et al. [201]. A comparison of the processability and properties of the fibers reinforced with VGNF and CNT indicated that VGNFs are more processable than the smaller SWNT, DWNT and MWNT in terms of dispersion, resulting in higher mechanical strength properties. The better dispersed VGCF has lead to composite fibers having mechanical properties that are almost double than that of CNT-reinforced nanofibers. Multifilament yarns of uniaxially aligned nanofibers were obtained by electrospinning of PAN/DMF precursor [202]. These CNFs bundles have shown enhanced mechanical properties viz., modulus and tensile strength at break were 4575 and 178 MPa, respectively.

Electrospun PAN nanofibers were subjected to cold drawing in atmospheric conditions and at different strain rates. In this case, Naraghi et al. [203] observed ultimate strain of PAN nanofibers of 60–130%, varying monotonically with the strain rate. On the contrary, fiber tensile strength, ranging between 30 and 130 MPa varied non-monotonically, with the slowest drawing rate resulting in the largest ductilities and fiber strengths. At faster rates, large fiber ductilities originated in the formation of a cascade of ripples (necks), while at the slowest strain rate, nanofibers deformed homogeneously, allowing for the largest mechanical strengths and extension ratios. Recently, Dabirian et al. [204] introduced a new system capable of producing such continuous uniaxially aligned PAN nanofiber yarns by manipulating the electric field. The yarns were treated in boiling water under tension and their mechanical properties were comparable with those of the untreated ones. In a similar study, Gu et al. [205] measured the Young's modulus of a single electrospun PAN fiber using AFM cantilever.

In a study by Zussman et al. [206], CNFs were produced by pyrolyzing electrospun nanofibers from PAN having typical diameters of few hundred nm after pyrolysis, and these were characterized for structures as well as mechanical properties. The bending modulus of individual nanofibers was measured by a mechanical resonance method, with an

average modulus found to be 63 GPa. The fracture strength of the carbonized fibers was analyzed using the Weibull statistical distribution function based on the assumption that variation in strength is caused by the variation in stress concentration from a critical defect in a given volume of material. Zussman et al. [206] found that the stiffness and fracture strength of CNFs improved substantially by optimizing polymer precursor morphology and molecular orientation through the carbonization process. PAN fibers modified with cobaltous chloride at 1300 °C gave increased crystal size, crystallinity and orientation, resulting in an improved tensile strength by about 15–40% and modulus by 10–20% [207]. The formation of ladder structure in these modified PAN fibers shows slow and gradual transformation during the stabilization process. The resulting CNFs have better modulus than the pristine PAN-based CNFs.

A recent study [208] focused on the changes in physical properties and the capacity of dye adsorption using the regenerated ACNFs. The regeneration process led to a decrease in weight and loss in mechanical strength due to a change in the orientation of the structure during air reactivation. Adsorption and regeneration were carried out over several cycles, but fibers retained their mechanical properties even after the fourth regeneration [209].

## 7. PAN-based nanofibers as filtration membranes

Conventional fiber technologies have reached their limits for producing commercially available monofilaments and are likely to produce fibers in the range of 10–50 µm, while the nonwoven fibers produced by melt blown technology are in the range of 3–8 µm. In this situation, a major challenge is to overcome the apparent 3 µm particle filtration barrier for a fiber-based filter that has desirable high-capture efficiency at an affordable cost. Electrospinning produces nanofibers of unprecedented and unrivalled small diameter with a high surface area. Integrating such electrospun polymeric nanofibers with conventional filter media represents a unique opportunity to overcome the current threshold of filterable particle size barrier.

Since electrospinning would produce polymer fibers with diameters ranging from 3 to 1000 nm [210], experiments were performed to study the effects of co-precursors like Nylon 6, PAN and Ultem-1000 on PAN nanofibers filter media prepared by electrospinning to capture oil droplets as small as 0.3 µm, or even less. Thus, PAN electrospun nanofiber mats have been widely used in ultrafiltration, nanofiltration [211,212] and reverse osmosis [213] due to its good solvent resistivity.

Saufi and Ismail [214] reported PAN-based carbon hollow fiber carbon membrane and discussed various factors influencing the electrospun nonwoven fibrous membrane structure and their transport properties. Experiments and theoretical calculations showed that electrospun fiber mats are extremely efficient in trapping airborne particles and the high filtration efficiency is a direct consequence of the submicron-size fibers generated by electrospinning [67]. Also, the surface active nanofiber affinity membranes offer better separation properties compared to the traditional polymer membranes for high molecular weight cut off

[MWCO] applications involving dairy and beverage products [215].

Musale and Kumar [216] discussed the importance of PAN as a filtration media on nanoparticles, wherein they produced PAN fiber mats by electrospinning. Yun et al. [217] prepared the PAN fibers by electrospinning for use as a filter media with the mean diameters ranging between 270 and 400 nm and their performance was evaluated by measuring the penetration of monodisperse NaCl nanoparticles of <80 nm. The penetration of nanoparticles through electrospun filter media was minimized by increasing the fiber web thickness. Filter quality factors and single fiber collection efficiencies were found to be independent on the filter thickness. The penetration of nanoparticles through electrospun filters was in better agreement with the theoretical predictions than the measured penetration through a commercial filter.

Drew et al. [146] reported the fabrication of novel metal oxide-coated PAN nanofiber nonwoven fiber membrane using electrospinning. The membranes were subsequently immersed in an aqueous solution of metal halide salts and halogen scavengers to apply tin dioxide and titanium dioxide coating. The authors explored the potential of these membranes in highly reactive surfaces for improved catalysis, sensing and photoelectric conversion applications. These nano-scaled textiles meet the increasing demand of filter media with high filter efficiency in the sub-micrometer range [218]. Other interesting applications of such filtration nanofibers are as the effective barriers against bacteria of <0.3 µm, viruses and other microorganisms in gas/liquid, fiber reinforced composite materials and protective clothing.

Liu and Hsieh [219] prepared PAN nanofiber membranes from hydrophilic acrylic nanofibers by alkaline hydrolysis. Gibson et al. [67] summarized the information related to the transport properties of electrospun fiber membranes, both as single layers and as coatings applied to the existing military chemical/biological protective clothing systems. This study was an attempt to enlighten the information on water vapor diffusion and air permeability for protection from chemical and biological warfare agents.

Electrospun PAN-based NFs have shown excellent properties for immobilization of lipase, chymotrypsin, cellulose and lysozyme. Simple and effective enzyme immobilization system showing improved enzyme properties over the previous immobilized lipase systems using the same enzyme and substrate were prepared by Li et al. [220]. Enzyme immobilization requires inertness and hydrophobicity in the backbone, which was achieved by introducing acrylonitrile monomer functional groups into the main polymer backbone. The PAN nanofiber layer was supported on the nonwoven microfibrous substrate on which a water permeable coating of chitosan was applied. In another study, a PAN derivative viz., poly(acrylonitrile-co-maleic acid) (PANCMA) containing reactive carboxyl groups was synthesized and fabricated into NF membrane for lipase immobilization [221]. This lipase immobilization method showed the best performance among the various immobilized lipase systems using the same source of lipase and substrate when considering protein loading, activity retention, and kinetic parameters.

A comparative study of antimicrobial activity using three different electrospun CNFs incorporated with silver nanoparticles viz., CA, PAN and PVC was done by Lala et al. [222] in a DMF solvent. The antimicrobial activity of these functionalized CNFs showed that the combination of PAN in DMF containing 5 wt.% of  $\text{AgNO}_3$  and UV-irradiated for 30 min was found to be most effective. Grabinski et al. [223] studied the cellular effects of PAN-based CNFs with diameters ranging from micron- to nano-dimension, using mouse keratinocytes (HEL-30). This study focused on the role of dimension in dermal toxicity of CNTs and their use in the mouse keratinocyte cell line, HEL-30 cells, as a model for dermal exposure. Barhate et al. [224] investigated the structural and transport properties of electrospun PAN fiber web membrane in relation to processing parameters to understand the distribution, deposition and orientation of NFs as filtering media. The orientation of NFs in the electrospun mat and correlating the conditions of collection of the nanofibers with the structural and transport properties of the mat were found to be important.

## 8. Specialized applications and future prospects of PAN-based CNFs

The pace and development on electrospinning of PAN-based CNFs has been rapidly increasing over the past decade in flexible photovoltaic membranes and biomedical devices to serve as encapsulating tools [225,226]. Pittman et al. [189] found that vapor-grown CNFs during nitric acid oxidation have produced high strength materials than the PAN-based CNFs. Their wettability increased sharply on oxidation, but the PAN-based fibers exhibited a continually increasing surface area with a continuous weight loss by increasing oxidation time.

Lakshminarayanan et al. [227] studied the oxidation of PAN-based CNFs to show a continually increasing surface area with oxidation time using nitrogen BET measurements. However, the increases were very small considering the strongly oxidizing conditions to which these fibers were exposed (69–71 wt.% nitric acid, 115 °C) and the much larger surface area increase that occurred when the PAN-based CNFs were oxidized. Ligand molecules, biomacromolecules or even cells can be attached or hybridized with the nanofiber membrane for applications in protein purification and waste water treatment as affinity membranes, enzymatic catalysis or synthesis in membrane bioreactors. Research trends have shown that new ways in chemical analysis and in biosensor applications may be anticipated using the PAN-based CNFs. In addition, the CNFs can also form an effective size exclusion membrane for particulate removal from wastewater. Several studies are underway to check their efficiency in removing particles from polluted air.

From the forgoing discussions, it is realized that the PAN-based CNFs are increasing in the worldwide market covering a wide range of areas such as electrochemical devices, lithium batteries, sensors, electrocatalysts, conducting nanowires, atomic force microscopy tips, ballistic and chem-bio protection. However, the future research in this area depends on the development of in situ

methods of observing changes in nanostructures of a single polymeric nanofiber during stretching and developing methods of measuring viscoelastic properties of single polymeric nanofibers. When using such fibers as an engineering fiber, it is important to know that individual nanofibers that are stiff and strong enough to withstand the forces are required. Very few reports are available in the literature on mechanical nanofibers and not many tests have been done to characterize the single nanofibers. Such challenges have been isolated in handling individual nanofibers. In the future, one can expect more attention to the preparation and documentation of high strength nanofibers for numerous applications.

Other innovations of NFs and nano-structured surfaces are in gas and liquid filtration areas, fiber-reinforced composites materials, protective clothing, etc. Electrospun fiber coatings produce exceptionally lightweight multi-functional membranes for protective clothing applications that exhibit high breathability, elasticity and filtration efficiency. The high specific surface area of ultrafine fibers as high performance filters, scaffolds in tissue engineering, sensors, etc. have been envisaged. High porosity, interconnectivity, microscale interstitial space, and a large surface-to-volume ratio mean that nonwoven electrospun nanofiber meshes are excellent materials for membrane preparation, especially in biotechnology and environmental engineering applications.

## 9. Conclusions

PAN-based CNFs are seemingly a new class of materials used in a wide array of applications including filtration barriers, material reinforcements, garments, insulators, medical and energy storage devices, and many more. However, their unique properties make them perfect modern materials of choice across many disciplines covering engineering, medicine, and biology. The accelerating technologies of producing PAN-based nanofibers have now matured enough to overcome the drawbacks of low production rate of few grams per hour in laboratory environments to large industrial scale production. Nanofiber membranes comprising sheets of randomly oriented nanofibers show an extremely effective removal method with a high rejection rate of airborne particles by both physical trapping and adsorption. It is anticipated that the future will witness many more applications of PAN-based nanofibers in a wide variety of scientific disciplines.

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