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Ceramic Nanofibers by Electrospinning Technique — A Review

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Nanofibers are solid-state linear nanomaterials with diameters <100 nm, an aspect ratio >1000 and are characterized by high surface area to volume ratio. Nanofibers, due to their high surface area to volume ratio are potential candidates for a large number of applications such as separation of liquids and gases, as sensors, photovoltaic applications, insulation, ultrapurification of water, drug delivery etc. In recent years, electrospinning technique has been successfully used for the preparation of nanofibers. Initially, polymer nanofibers are prepared using this technique. Recently, this technique has also been successfully extended for the preparation of ceramic nanofibers. This paper reviews the electrospinning process, application of electrospinning process for the preparation of ceramic nanofibers and their possible applications.

[Keywords : Electrospinning, Nanofiber, Sol-gel, Alumina, Zirconia and Ceramic oxides]

Introduction

Nanoscience and nanotechnology are becoming more and more popular among researchers worldwide. Nanomaterials are expected to exhibit significantly improved properties due to their small size almost close to the corresponding atoms and molecules. Nanofibers belong to this class of nanomaterials with diameters <100 nm, an aspect ratio >1000 and are characterized by high surface area to volume ratio (Fig. 1). Examples of the materials of nanofibrous structure are plenty in nature. Some of the examples are : double helix strand of DNA molecules (2 nm), structure of wood, silk, hair, connective tissues, bones, blood vessels, etc. Due to the combination of high surface area to volume ratio and structural flexibility, nanofibers are potential candidates for large numbers of engineering applications.[1–3]

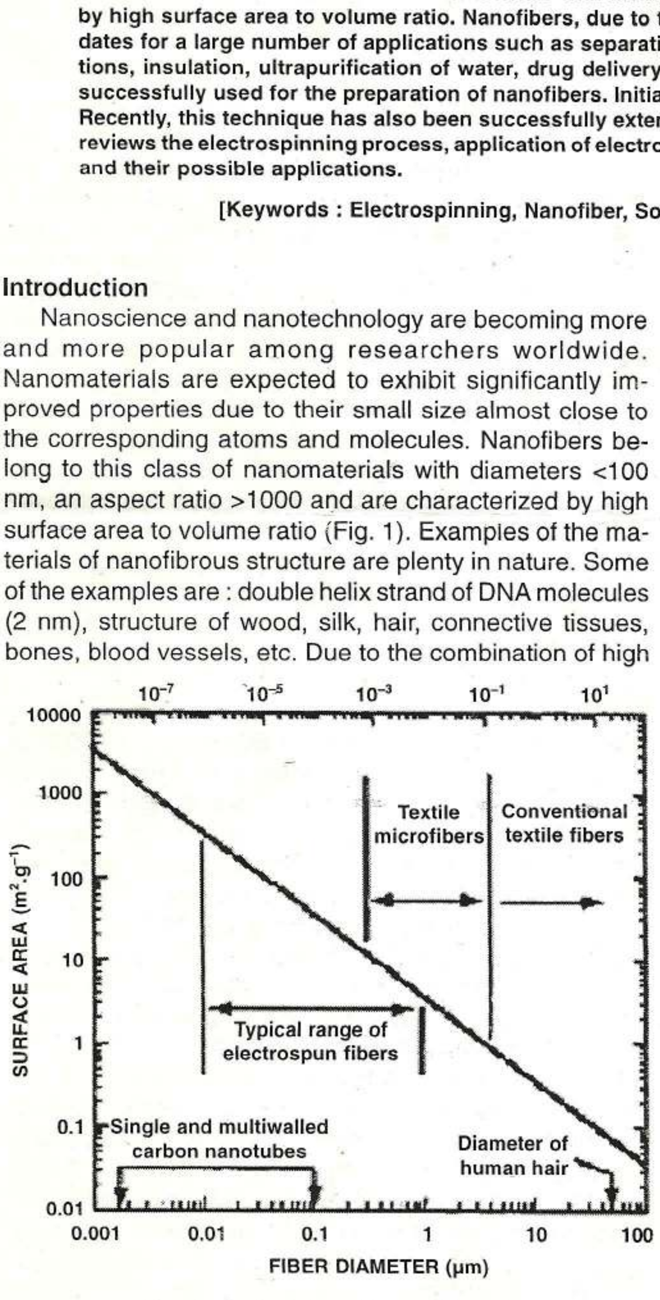

Fig. 1 – Surface area vs fiber diameter.

The fiber or whisker form of ceramic materials such as alumina, mullite, silicon carbide, silicon nitride etc is widely used for structural applications due to their high thermomechanical properties such as high strength and high fracture toughness. These fibers / whiskers are dense, defect free, crystalline orderly structures prepared by various routes such as melt spinning, chemical vapour deposition (CVD), sol-gel process, extrusion, hydrothermal / solvothermal technique etc. Due to high strength and toughness, these fibers are used as reinforcements for fabrication of composites, mainly ceramic matrix composites (CMC) and metal matrix composites (MMC) for various structural applications. In contrast, ceramic nanofibers prepared by electrospinning technique are generally porous. Their thermo-mechanical properties as well as their suitability for structural applications are yet to be established. However, these nanofibers are potential materials for a large number of applications such as separation of liquids and gases, sensors, photovoltaic applications, insulation material, ultrapurification of water, drug delivery, etc due to their high surface area to volume ratio.

Considering the importance of future applications of ceramic nanofibers, an attempt is made to review electrospinning processes with particular attention to study the critical process parameters.

Electrospinning Process

Electrospinning is a very simple and versatile technique that has been successfully used for the preparation of fibers or fiber mats from a broad range of organic polymers. Although the first patent on electrospinning process was awarded in 1934,[4] there has been little interest on this process till the nineties. In the last few years, thanks to the resurgence of nanoscience and nanotechnology,

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electrospinning has become popular for preparation of nanofibers.[5-13] The process involves the application of a strong electrostatic field to a capillary connected to a reservoir containing a polymer solution or melt. Under the influence of the electrostatic field, a pendant droplet of the polymer solution at the capillary tip is deformed into a conical shape (Taylor cone). If the voltage surpasses a threshold value, electrostatic forces overcome the surface tension, and a fine charged jet is ejected. The jet further divides itself into millions due to high repulsive force generated from the accumulation of similar charges. The jets move towards a ground plate, which acts as a counter electrode. The result is the deposition of nanofibers on a substrate located above the counter electrode. The solvent evaporates as the jet travels; and the evaporation rate is very high because of the high surface area created due to splitting of the jet. Therefore, dry nanofibers of diameters in the range of 20-1000 nm are produced. A schematic drawing of an electrospinning setup is presented in Fig. 2.

Initially, polymer nanofibers were prepared using this technique.[6, 14–16] In recent years, ceramic oxide fibers such as silica, zirconia, titania, nickel oxide, barium titanate, lead zirconate titanate etc have also been prepared.[7, 17–36] Interestingly, the nanofibers formed could be aligned (parallel and cross patterns) when an insulated cylinder attached to the axel of a DC motor is used as the substrate.[37] Li *et al.*[38] prepared polymeric and ceramic nanofibers as axially aligned arrays by the use of a collector consisting of two pieces of electrically conductive substrates separated by a gap. Katta *et al.*[39] used copper wires spaced evenly in the form of a circular drum as a collector of the electrospun nanofibers.

Electrospinning of Polymer Nanofibers

Ceramic fibers are always electrospun with a polymer phase because as such the ceramic phase is unsuitable for electrospinning. Therefore, it is important to identify a suitable combination of ceramic-polymer-solvent system that can form a viscous homogeneous solution required for successful electrospinning. Some polymer-solvent systems used for electrospinning are presented in Table I and a few popular systems are discussed below.

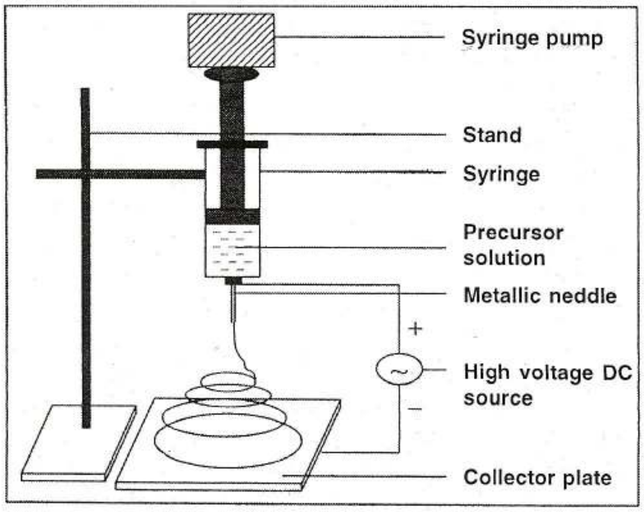

Fig. 2 – Schematic diagram of an electrospinning setup.

Table I : Compatible polymer and solvent systems

Polymer	Solvent	Reference no.
Polyvinyl alcohol, PVA	DI water	40, 41
Polyethylene oxide, PEO	DI water	42
Polyethylene glycol, PEG	Chloroform	43
Polycarbonate, PC	DMF, THF	44
Polyvinyl pyrrolidone, PVP	Ethanol	7, 45, 46
Polycaprolactone, PCL	Chloroform and methanol	47, 48

PVA-Water System

PVA is a semi-crystalline, non-toxic biocompatible hydrophilic polymer. It forms homogeneous sols with many salt solutions and solvents, and therefore, is used for electrospinning. Koski *et al.*[40] studied the effect of molecular weight and concentration of polyvinyl alcohol (PVA) for successful electrospinning. They observed that there is a concentration range for every molecular weight that can be electrospun into fibers. This concentration range shifts towards lower concentration with increase in molecular weight. The fiber diameter increases with molecular weight and the fiber cross-section shifts from circular to flat shapes. Ding *et al.*[41] prepared nanoscale PVA fiber (100-500 nm) aggregates with an electrospinning technique and then chemically crosslinked them. The results showed that the properly crosslinked PVA fiber aggregates had better resistance to dissolution in water and better mechanical properties than the non-crosslinked PVA fiber aggregates. A typical SEM picture of PVA (12 wt%) nanofiber is presented in Fig. 3a.

PEO-Water System

Deitzel *et al.*[42] electrospun polyethylene oxide (PEO) fibers using a 10 wt% solution of PEO (mol. wt. = 400,000) in water. They controlled the deposition of PEO fibers by using an electrostatic lens element and biased collection target. They could eliminate the beading instability associated with conventional electrospinning experiments. They also studied the effect of concentration and voltage on fiber morphology. They could electrospun PEO fibers from 4 to 10 wt% concentration. The diameter of the electrospun PEO fibers was found to increase with solution concentration according to a power law relationship. They also observed that fibers spun from solutions at concentrations of 8 wt% and higher exhibited a bimodal distribution of fiber diameters. A typical SEM picture of PEO (12 wt%) nanofiber is presented in Fig. 3b. Similarly, Hua *et al.*[43] used polyethylene glycol (PEG) as the polymer in chloroform and Gibson *et al.*[44] used polycarbonate (PC) in DMF (dimethyl formamide) as the polymer-solvent systems for electrospinning.

PVP-Ethanol System

Polyvinyl pyrrolidone (PVP) is an important synthetic polymer with good adhesion properties, excellent physiological compatibility, low chemical toxicity, and reasonable

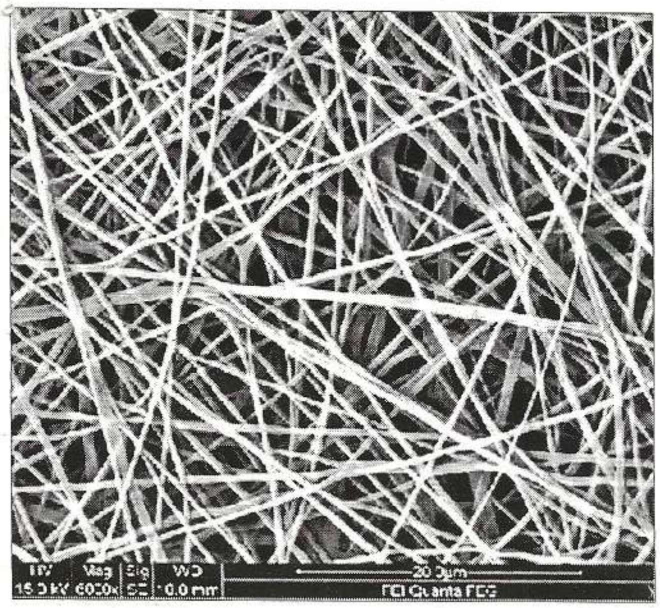

Fig. 3a – SEM picture of PVA nanofibers.

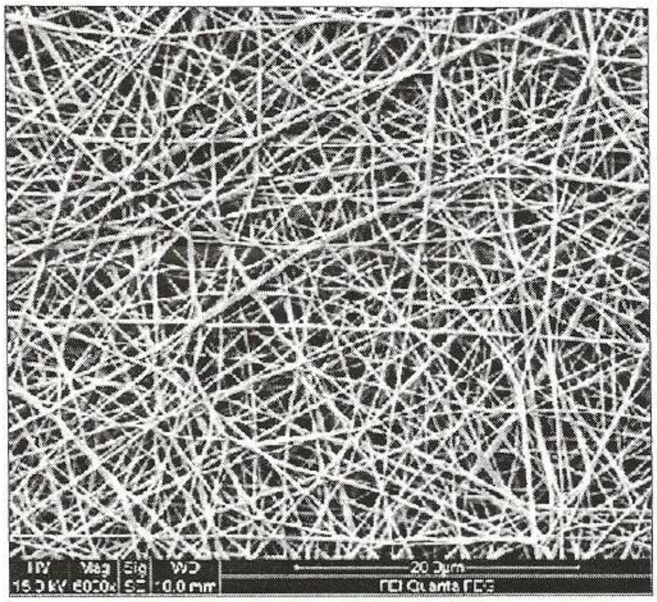

Fig. 3b – SEM picture of PEO nanofibers.

solubility in water and in most organic solvents. It is, therefore, widely used across many industries such as pharmaceuticals, cosmetics, beverages, adhesives, detergents, paints, electronics and biological engineering materials. The electrospinning of PVP fiber was first reported by Bognitzki *et al.*[45] Li and Xia[7] prepared composite nanofibers composed of PVP and TiO_2 (or SnO_2). Yang *et al.*[46] investigated the influence of solvents on the morphology of the PVP micro / nanofibers prepared by electrospinning. They observed that smooth PVP nanofibers were obtained with ethanol as a solvent although the size distribution of the fibers was somewhat broadened. Using a mixed solvent of DMF and ethanol in the ratio of 50:50 (w/w), they could produce PVP nanofibers with a diameter of about 20 nm. The formation of thin nanofibers is attributed to the combined effect of ethanol and DMF solvents that optimizes the solution viscosity and charge density of the polymer jet.

PCL-Chloroform System

Lee *et al.*[47] studied the electrospinning of polycaprolactone (PCL) using different combinations of solvents such as pure methylene chloride (MC), a mixture of MC and DMF, and a mixture of MC and toluene. They observed that high dielectric constant and good electrical conductive DMF help in electrospinning of fibers when added along with MC and the process effectively reduces the fiber diameter. Thus, MC and toluene combination is not good for electrospinning due to high viscosity and low electrical conductivity.

Hsu and Shivkumar[48] studied the effect of solution concentration and DC voltage on formation of PCL nanofibers as well as bead formation during electrospinning process. They observed that the solution concentration of PCL has significant effects on the morphology of electrospun polymer. At a solution concentration of <4 wt% PCL, the jet breaks down into droplets. At 4 wt% PCL concentration, transition of beads to fibers was observed. The fiber diameter increased from 510 to 850 nm with the increase in PCL content from 5 to 9 wt%.

Effect of Process Parameters

The morphology of the fibers generated by electrospinning method is influenced by (i) solution parameters, e.g. molecular weight of polymers, viscosity, conductivity, surface tension, (ii) electrospinning process parameters, e.g. hydrostatic pressure in the capillary, electric potential, the distance between the tip and the collection screen, and (iii) ambient parameters, e.g. temperature, humidity, air velocity in the spinning chamber.

Solution Properties

The solution must have a concentration high enough to cause polymer entanglements yet not so high that the viscosity prevents polymer motion induced by the electric field. The solution must also have a surface tension low enough, a charge density high enough, and a viscosity high enough to prevent the jet from collapsing into droplets before the evaporation of the solvent (Table IIa).

Processing Conditions

The syringe needle tip to collector distance (TCD) influences the morphology of the nanofibers. Bead formation can be minimized at a low electric field regardless of the concentration of the polymer in the solution. Therefore, increase in TCD decreases the electric field, hence, minimizes the bead formation (Table IIb).

Ambient Conditions

Among various ambient parameters, humidity is a key parameter, which influences the most on dry / wetness of the nanofibers collected. If the humidity is very high, the drying of the nanofibers is affected, particularly at very high humid conditions (>90%). Similarly, higher ambient temperature is desirable for drying of the nanofibers.

The influence of the various parameters on morphology of nanofibers as summarized by Sawicka and Gouma[49] is presented in Tables IIa and IIb as collected from various references.[42, 50–57]

Table IIa : Electrospinning solution parameters

Concentration of polymer	Directly proportional to the fiber diameter.[52] Power law relation to the fiber diameter.[42] Cube of polymer concentration proportional to diameter.[55] Parabolic – upper and lower limit relation to diameter.[56]
Ionic strength	Directly proportional to charge density.[57] Inversely proportional to bead density.[57]
Solvent	Effects volume charge density.[50] Directly related to the evaporation and solidification rate.[50]
Temperature	Inversely proportional to viscosity.[55] Uniform fibers with less beading.[55]
Viscosity	Parabolic relation to diameter and spinning ability.[56]

Table IIb : Electrospinning process parameters

Needle to collector distance	Exponentially inverse to the volume charge density.[50] Inversely proportional to bead formation density.[51,52] Inverse to the electric field strength.[50, 51] Inversely proportional to fiber diameter.[52]
Flow rate	Directly proportional to the electric current.[50] Directly proportional to the fiber diameter.[53] Inversely related to surface charge density.[50] Inversely related to volume charge density.[50]
Voltage	Inversely proportional to surface charge density.[50] Direct effect on bead formation.[42] AC potential improved fiber uniformity.[54] Inversely related to fiber diameter.[52]

Fiber Morphology

Generally, the fibers in the form of cylindrical shape are formed randomly in the form of mats. However, fibers in the form of beads, flat ribbon-like morphology or a combination of beads and fibers etc may form depending on electrospinning conditions. The beads may form when the jet at the end of the Taylor's cone splits into many mini-jets and each mini-jet disintegrates into small droplets. Koombhongse *et al.*[58] obtained branched fibers, flat ribbons, bent ribbons, ribbons with other shapes and fibers in different conditions. Studies on the properties of fibers with these cross-sectional shapes from a number of different kinds of polymers and solvents indicate that fluid mechanical effects, electrical charge carried with the jet, and evaporation of the solvent contributed to the formation of the fibers of different shapes.

Beading of Fibers

Fong *et al.*[59] reported that the beaded fibers came from a capillary breakup of the jet in the electrospinning, and that surface tension and viscoelastic properties are the key parameters for forming the beads. Lee and his co-workers[60] suggested that the beads occur only in a low viscosity polymer solution, and emphasized that the viscosity is the main reason for the formation of beads. Ryu *et al.*[61] reported that the addition of an organic salt, pyridinium formiate, to poly-L-lactide solution causes significant reduction of the bead formation in the electrospinning.

Addition of cationic surfactants improves the net charge density considerably, therefore, the jet stretches under stronger forces and prevents the formation of beads structures on the filaments. Increasing the concentration of cationic surfactant leads to thinner fibers. However, the presence of a non-ionic surfactant cannot stop the formation of bead fibers, but reduces the bead numbers and changes the fiber morphology.

The structure of the electrospun fibers can be modified by different additives, which changes solution properties such as electrical conductivity, dielectric constant, surface tension and viscosity. For example, DMF addition to the solution decreases the fiber diameter considerably. Fridrikh *et al.*[62] studied the stretching of a viscous charged fluid in an electric fluid and presented a model which suggests that there is a limiting diameter for the fluid jet attained during electrospinning. The final diameter of the fluid jet arises from a force balance between surface tension and electrostatic charge repulsion, which agrees with electrospun fibers produced from solutions of different polymers at various concentrations.

Ribbon shaped fibers are formed due to collapse of the nanofibers due to evaporation of the solvent.[59] Typical SEM pictures of 'beaded' and 'ribbon shaped' nanofibers are presented in Figs. 4a and 4b respectively.

Alignment of Fibers

The nanofibers collected by a general electrospinning process are in the form of randomly oriented non-woven

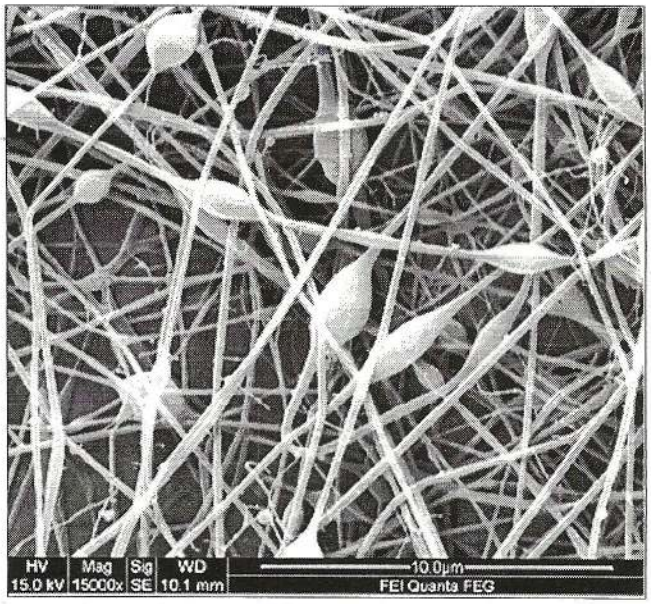

Fig. 4a – Beaded structure of PVA nanofibers.

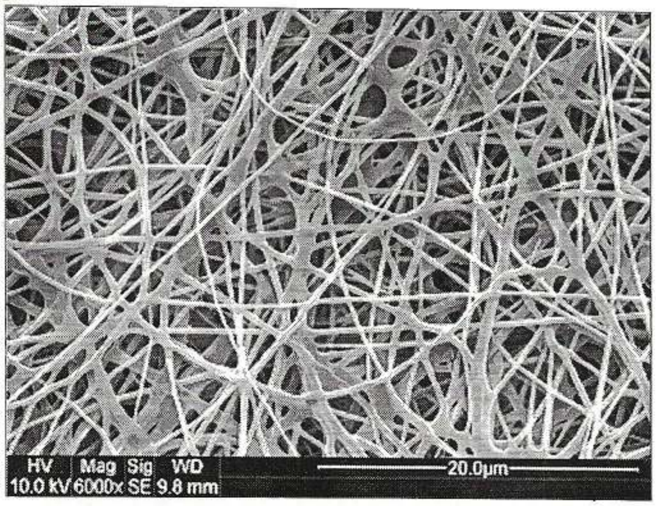

Fig. 4b – Flat (ribbon) structure of PVA nanofibers.

morphology. Although the non-woven forms are interested for most of the applications, aligned forms of fibers are required for a variety of applications. Efforts made by many research groups worldwide for alignment of fibers by using various techniques are summarized as follows.

Auxiliary Electrode / Electric Field

Li *et al.*[38, 63] aligned nanofibers uniaxially by collecting the electrospun nanofibers over a gap formed between two conductive substrates (Fig. 5a). As a result, the nanofibers are stretched to form a parallel array across the gap.

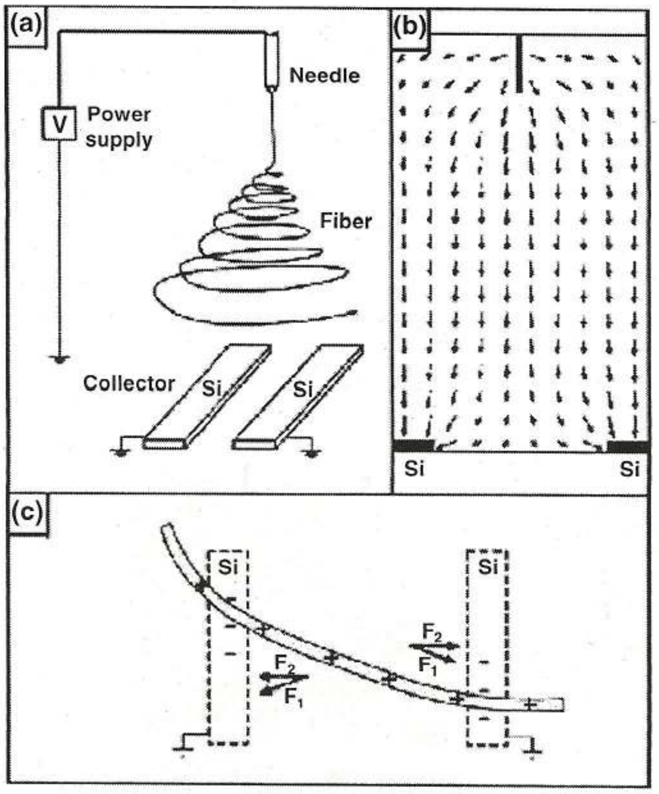

Fig. 5a – Alignment of nanofibers by auxiliary electrodes, adapted from ref. 38.

Frame Collector

Katta *et al.*[39] studied the alignment of nanofibers onto a wire drum collector consisting of copper wires spread evenly in the form of a circular drum (Fig. 5b). The fibers are aligned due to the electrostatic attraction of the copper wire close to the spinneret tip and also due to the gap between the copper wires. Dersch *et al.*[64] demonstrated the orientation of polyamide nanofibers on a metal frame as the collector (Fig. 5c). Theron *et al.*[65] used disc collector for alignment of nanofibers (Fig. 5d).

Hollow Nanofibers by Co-axial Electrospinning

Li *et al.*[8] demonstrated that long, hollow titania nanofibers with uniform, circular cross-sections could be directly fabricated by electrospinning of two immiscible liquids, i.e. ethanol and mineral solution of PVP and titanium isopropoxide (TIP) simultaneously with PVP as the core and TIP on the surface. The calcination of the electrospun fibers at 600°C or dissolution of the core in a solvent generated the hollow fibers of 20 nm wall thickness. A typical

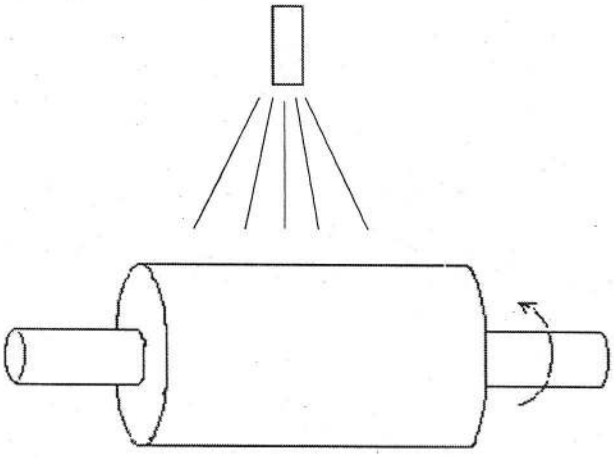

Fig. 5b – Alignment of nanofibers by rotating cylindrical drum, adapted from ref. 39.

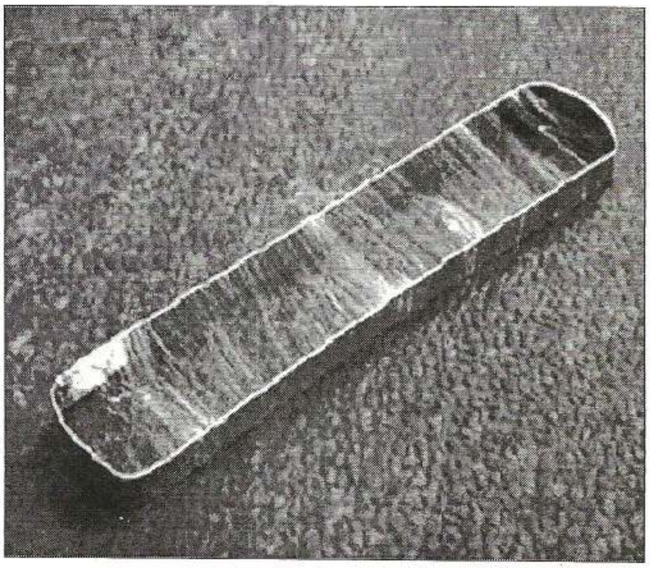

Fig. 5c – Aligned nanofibers by frame collector, adapted from ref. 64.

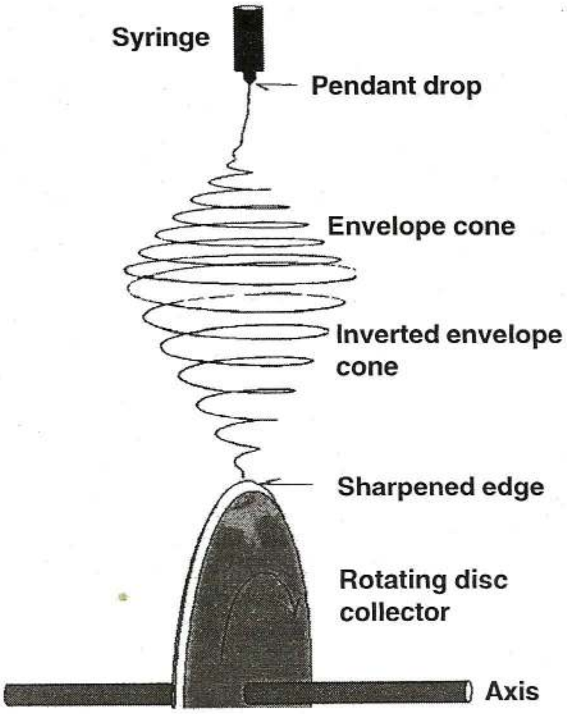

Fig. 5d – Aligned nanofibers by rotating disc collector, adapted from ref. 65.

picture of co-axial electrospinning spinneret and hollow nanofibers after calcination is presented in Fig. 6.

Preparation of Ceramic/Polymer Nanofibers

Preparation of Alumina/Polymer Nanofibers

Panda and Ramakrishna[66] prepared the alumina-polyvinyl alcohol (PVA) nanofibers by electrospinning a sol of PVA containing different precursors of alumina such as aluminium acetate and aluminium nitrates. The details of this process are presented below.

Polyvinyl alcohol (PVA) (M_n = 80,000-1,23,000) and polyethylene oxide (PEO) (M_n = 9,00,000) supplied by M/s Aldrich were used as the polymer precursors. Analytical grade hydrated aluminium nitrate, $Al(NO_3)_3.9H_2O$ and aluminium acetate supplied by M/s Aldrich were used as the source of alumina precursors. Based on initial experiments, PVA solution (10 wt%) and PEO solution (5 wt%) were selected as the optimum polymer precursor concentration. These solutions were prepared in hot water (for PVA) and in cold water (for PEO) while stirring well with a magnetic stirrer. Similarly, 20% aluminium nitrate or aluminium acetate solutions were prepared separately. The composite solutions of PVA or PEO and aluminium nitrate or aluminium acetate were prepared by mixing appropriate amounts with a magnetic stirrer. The homogeneous solutions thus prepared were used for electrospinning. The prepared viscous solutions of PVA/aluminium nitrate, PVA/aluminium acetate and PEO/aluminium nitrate were subjected to electrospinning by taking a small quantity of the solution in a syringe and connecting it to the positive terminal of the high voltage source. A grounded flat metallic stand covered with aluminium foil served as the counter electrode. The experiments were carried out by maintaining a 10 cm tip to collector distance (TCD). The solution flow rate was maintained at 1.3 $mL.h^{-1}$ and the humidity of the chamber was maintained in the range of 50-60%. The voltage was gradually increased till the liquid came out through the needle and split into web of fibers collected on the aluminium foil. The voltage was maintained in the range of 11-13 kV for pure PEO and PVA solutions. SEM pictures of the PVA and PEO fibers are presented in the Figs. 3a and 3b respectively. Similarly, the electrospinning of composite solutions were carried out at a voltage of 17-19 kV and their SEM pictures are presented in Figs. 7 (a and b) and 8 (a and b). The solution preparation methodology and electrospinning conditions are summarized in Table III.

In general, the electrospinning of both PVA and PEO was possible and was smooth in case of aluminium acetate precursor. In case of aluminium nitrate precursor, the resulted nanofibers were highly hygroscopic due to the presence of nitrate anions and their collection was extremely difficult because of the strong repulsion, probably originating from the concentration of similar charges. This might make the fibers to remain in vertical position on the collector or simply fly causing their collection difficult. Therefore, the PVA/aluminium acetate solutions are ideal for electrospinning.

In order to increase the alumina content in the fibers, three compositions of salt to polymer ratio of 10, 50 and 100 were electrospun. It was observed that the electrospinning was very smooth for 10 as well as 50% solid loading; typical morphologies of the fibers are presented in Figs. 8a and 8b respectively. The presence of beads was observed in case of low solid loading (10%), while the same was absent in higher solid loading (50%).

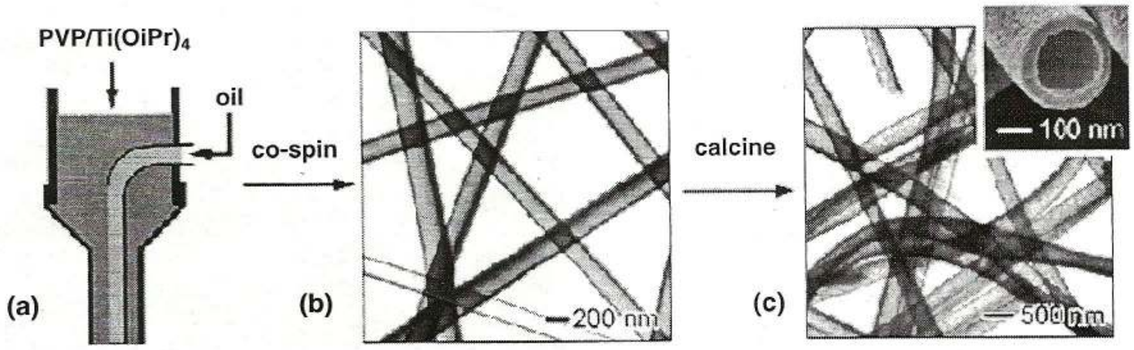

Fig. 6 – Co-axial electrospinning (a) to produce (b) composite nanofibers and finally (c) hollow nanofibers after calcination, adapted from ref. 8.

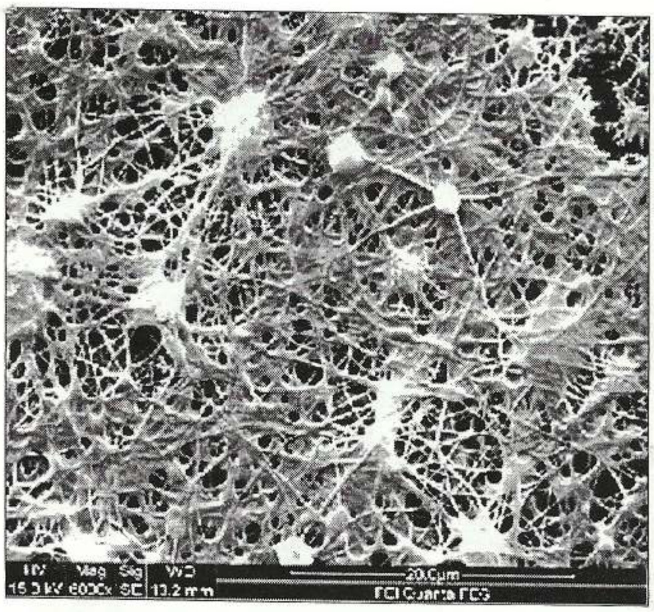

Fig. 7a – SEM picture of PVA/aluminium nitrate nanofibers.

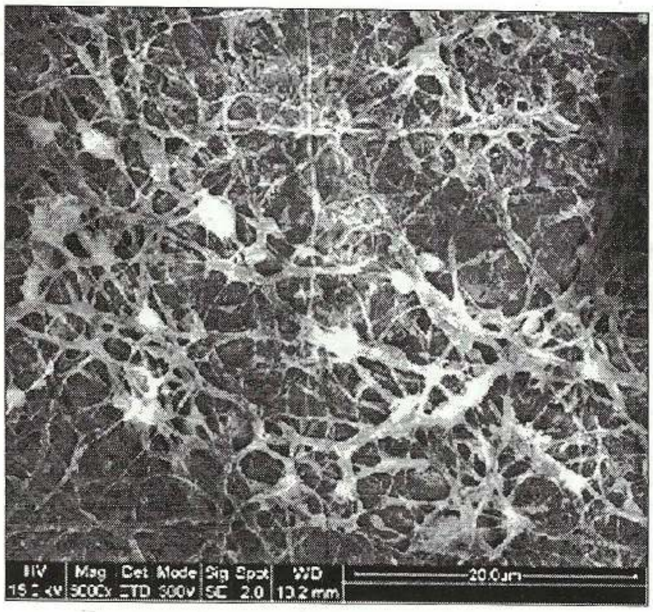

Fig. 7b – SEM picture of PEO/aluminium nitrate nanofibers.

The prepared nanofibers were heat-treated at 900° and 1300°C in order to remove the organics to generate pure alumina nanofibers. They are presented in Figs. 9a and 9b respectively. The XRD analysis of the calcined product at 1300°C confirmed the presence of pure α-alumina phase. From Fig. 9a it is observed that the nanofibers, heated at 900°C, are characterized by uneven surface due to the loss of organics, leaving porous un-sintered alumina phases. However, at 1300°C the diameters of the fibers were reduced to 20-500 nm range due to sintering (Fig. 9b).

Other Ceramic/Polymer Nanofibers

A recent development of the ceramic nanofibers prepared from compatible polymer-solvent systems is presented in Table IV.

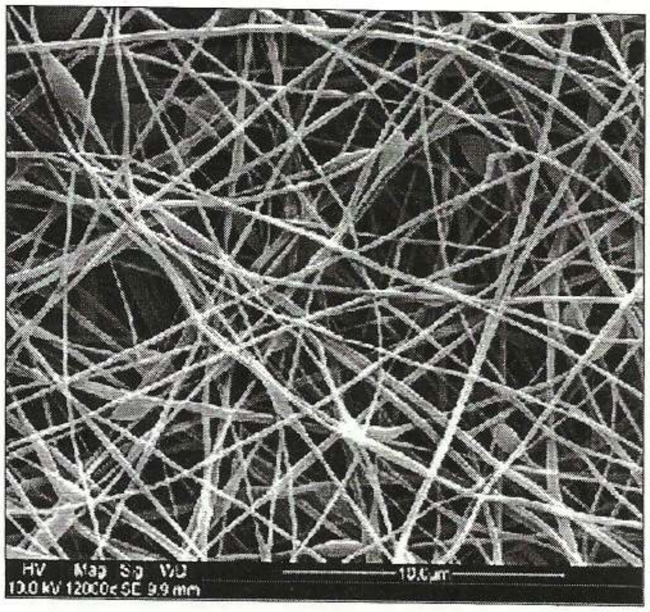

Fig. 8a – SEM picture of PVA/aluminium acetate nanofibers at 10% solid loading.

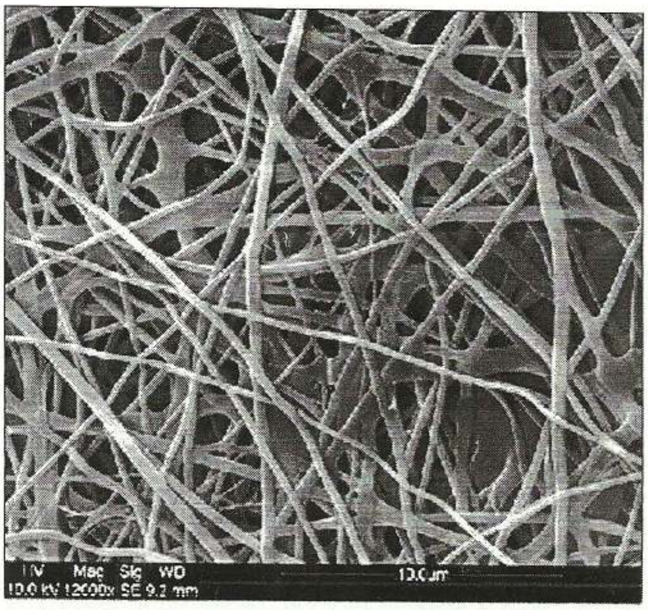

Fig. 8b – SEM picture of PVA/aluminium acetate nanofibers at 50% solid loading.

Choi *et al.*[31] studied the electrospinning of silica nanofibers using tetraethoxysilane (TEOS) as the precursor. They prepared silica sol by hydrolysis of TEOS in a mixture of water and ethanol and using HCl as the catalyst. Electrospinning experiments were carried out with a DC voltage ranging from 10 to 16 kV and a TCD of 10 cm. Shao *et al.*[67] prepared SiO_2 nanofibers using a combined solution of PVA and silica sol prepared by hydrolysis and sol-gel technique. The fibers were spun at a voltage of 18 kV and tip to target distance of 6 cm. The fibers were calcined at 800°C and obtained pure amorphous silica nanofibers of diameter 200-300 nm. They also prepared zirconia nanofibers by electrospinning a PVA/zirconium oxychloride composite solution and then calcining at 800°C.

Table III : Solution preparation methodology and electrospinning conditions of alumina

Chemical precursors	Preparation of solution	Electrospinning conditions
Polyvinyl alcohol (PVA)	10% PVA solution was prepared in hot water by heating at 80°C/12 h with magnetic stirring. Required amount of salt was added to PVA solution and were mixed for 5 h.	Nozzle dia (internal): 8.5 mm, Tip to collector distance (TCD) : 10 mm, Voltage : 11-13 kV (for pure PVA and PEO), Voltage : 19 kV (for polymer and salt solution), Humidity : 50-60%
Polyethylene oxide (PEO)	5% PEO solution was prepared in cold water by stirring well in a magnetic stirrer. Required amount of salt was added to PEO solution and were mixed for 5 h.	

By this process, pure tetragonal zirconia nanofibers of diameters in the range of 50-200 nm were obtained.

Li and Xia[7] generated nanofibers of TiO_2 (anatase) using PVP and TIP in ethanol. The electrospun fibers were heat-treated at 500°C and nanofibers of 20-200 nm diameter were obtained. The average diameter of the fibers are controlled by PVP : TIP ratio, strength of the electric field and feeding rate of the precursor solution. Tomer *et al.*[68] studied the electrospinning of Erbia modified electrospun nanofibers for selective infrared emitters. They electrospun a solution of tetra-isopropyl titanate (TPT) with a solution of polyvinyl pyrrolidone (PVP) at an electric field of 1 $kV.cm^{-1}$. The fibers were heat-treated at 900°C to produce rutile phase titania.

Dharmaraj *et al.*[19] prepared magnesium titanate nanofibers using magnesium ethoxide, titanium isopropoxide and polyvinyl acetate (18%) in DMF solution. Phase pure magnesium titanate has many applications such as in dew sensors, pigments, dielectric materials, etc. Dharmaraj *et al.*[20] also prepared nickel titanate/polyvinyl acetate (PVAc) composite nanofibers by preparing a sol of $NiTiO_3$ using nickel acetate and titanium isopropoxide precursors and mixing it with a solution of PVAc dissolved in DMF. The combined solution was electrospun at 15 kV DC voltage and the nanofibers were heat-treated at 900°C to obtain pure nickel titanate fibers.

Ding *et al.*[69] prepared electrospun TiO_2-SiO_2 nanofibers using a composite solution of PVAc, titanium isopropoxide (TIP) and tetraethoxysilane (TEOS) by sol-gel process. TiO_2-SiO_2 is a well-known material used in antireflective coatings, glasses, catalysis and as optical and chemical sensors.

Wang *et al.*[32] synthesized PZT (lead zirconate titanate) nanofibers by electrospinning using metalo-organic decomposition techniques. These electrospun fibers were calcined at 850°C to get PZT nanofibers. Fibrous PZT has potential for utilization in high performance hydrophones and ultrasonic transducer applications. This is because the fine fibrous geometry offers the possibility of composite fabrication where damping and reinforcement are the critical issues to be addressed.

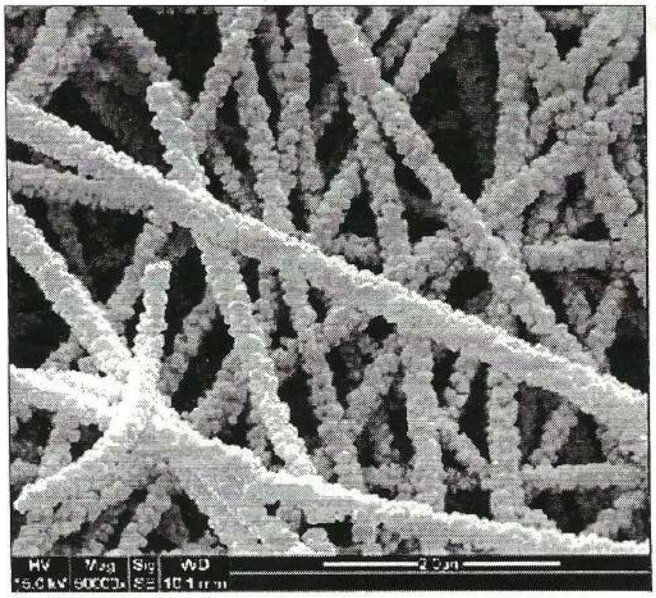

Fig. 9a – SEM picture of alumina nanofibers heat-treated at 900°C.

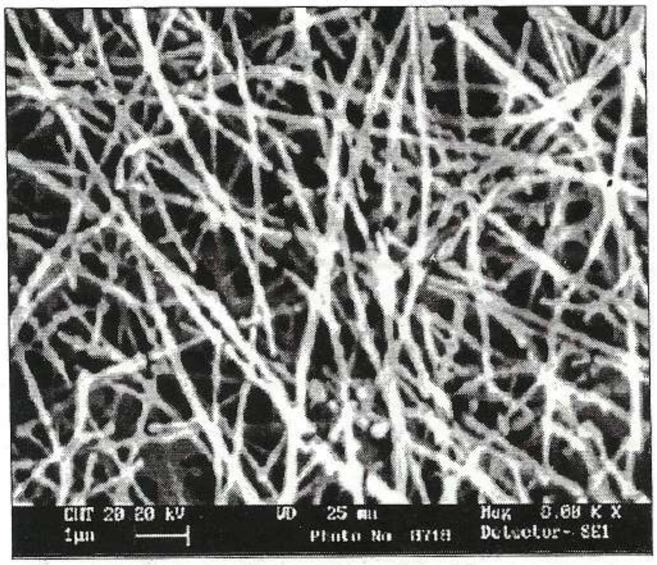

Fig. 9b – SEM picture of alumina nanofibers heat-treated at 1300°C.

Dharmaraj *et al.*[33] prepared PZT nanofibers by hydrolysis of a combined solution of PVAc (18 wt%) in methanol/ethanol (80/20 by wt).

Wu and Pan[70] prepared ZnO nanofibers using a combined solution of polyvinyl acetate and zinc acetate precursors by sol-gel method. The potential applications could be in light-emitting diodes, photo detectors, optoelectronic devices, varistors, gas sensors, solar cells, etc.

Wang *et al.*[32] prepared ultra-thin SnO_2 fibers having a rutile structure from a SnO_2 solution in a combined solvent of polyethylene oxide / chlorofom. Guan *et al.*[36] prepared $NiCo_2O_4$ nanofibers using water soluble nickel acetate, cobalt acetate and PVA as polymer precursor, by sol-gel method.

Table IV : Compatible polymer, ceramic precursor and solvent systems

Fiber	Polymer	Ceramic precursor	Solvent	Reference No.
Alumina	PVA	Aluminium acetate	DI water	66
Silica	PVA	TEOS	DI water	31, 67
Zirconia, YSZ	PVA	Zr-oxychloride	DI water	71, 72
In_2O_3	PVP	Indium nitrate	Water/ ethanol	73
NiO	PVA	Nickel acetate	DI water	17, 74
GeO_2	PVAc	Germanium isopropoxide	Acetone	24
Titania	PVP	Titanium tetra-isopropoxide	Ethanol	7, 68
Magnesium titanate	PVAc	Magnesium ethoxide, TIP	DMF	19
Nickel titanate	PVAc	Nickel acetate tetrahydrate, TIP, 2-methoxyethanol	DMF	20
Titania-silica oxide	—	TEOS, TIP	DI water/ isopropanol	69, 75, 76, 77
Mn_2O_3 and Mn_3O_4	PVA	Manganese acetate	DI water	78
NiO/ ZnO	PVA	Nickel acetate, zinc acetate	DI water	29
Nickel ferrite	PVP	Alkoxides of Ni, Fe	DI water/ ethanol	17
CeO_2	PVA	Cerium nitrate	DI water	22
Cobalt oxide	PVA	Cobalt acetate	DI water	26
Zinc oxide	PVA	Zinc acetate	DI water	79, 80, 81, 82
Vanadium pentoxide	PVAc	Vanadium isopropoxide	Ethanol/ water	83
Copper oxide	PVA	Copper acetate	DI water	84
Niobium oxide	PVAc	Niobium ethoxide	Acetone	27
Alumina borate oxide	PVA	Aluminium acetate, boric acid	DI water	85
Tin oxide	PEO	Dimethyldineo-decanoate tin	Chloroform	86
Palladium oxide	Polycarbonate (M_n= 23000) (11 wt%)	Palladium acetate	DMF	87
Tantalum pentoxide	PVAc	Tantalum isopropoxide	DMF	88
PZT (lead zirconate titanate)	—	Zirconium n-propoxide, titanium isopropoxide and lead 2-ethylhexanoate	Xylene	32

Applications of Ceramic Nanofibers

Ceramic nanofibers are potential candidates for applications as membranes for purification and separation of gases or liquids, as photocatalyst for generation of electrical energy from light energy, for miniaturization of electronic devices, as super capacitors, actuators, etc. A list of potential applications either already identified or projected for future applications is presented in Table V. Few of them are discussed below.

As Ferroelectric and Piezoelectric Materials, Devices and their Miniaturization

PZT nanofibers by virtue of their fibrous nature are potential candidates as reinforcements for development of

Table V : Projected applications of ceramic nanofibers

Fiber	Applications
Zirconia	Transparent optical devices, electrochemical capacitor electrodes, oxygen sensors, fuel cells, catalysis, synthesis of advanced ceramics etc.[71, 72]
NiO	Catalysis, battery cathodes, gas sensors, electrochromic films, magnetic materials.[17, 74]
Titania	Environmental cleaning and protection, photocatalysis, gas sensing, fabrication of solar cells and batteries.[7, 68]
Magnesium titanate	Dew sensors, pigments, dielectric application for electrical/electronic industries, high frequency capacitors, temperature compensating capacitors etc.[19]
Nickel titanate	Electrodes of solid oxide fuel cells (SOFC), metal-air barriers, gas sensors, tribological coating to reduce friction and wear in high temperature applications.[20]
Silica	Nanodevices, optoelectronic devices, chromatographic supports etc.[31, 67]
Titania-silica	Optical chemical sensors and catalysts.[69, 75–77]
Zinc oxide	Low-voltage and short-wavelength, electro-optical devices (light emitting and laser diodes), gas sensors and varistors.[79–82]
Vanadium pentoxide	For good electrical transport properties.[83]
Copper oxide	Gas sensors, magnetic storage media, solar energy transformation, semiconductors and catalysis.[84]
Niobium oxide	Capacitors, wave-guides, oxygen sensors, electrochromic devices, energy efficient windows etc.[27]
Aluminium borate	High temperature applications.[85]
PZT	Hydrophones and ultrasonic transducer applications.[32]
Tin oxide	Conductive electrode, anti-reflective coatings in solar-cell, gas sensor.[86]
Palladium oxide	PdO is a p-type semiconductor, as catalysis, sensors, photoelectrolysis etc.[87]
Nickel cobaltite ($NiCo_2O_4$)	Nickel cobaltite is a type of spinel oxide used as electrode for oxygen reduction and water electrolysis.

composites with optimum damping characteristics. Barium titanate nanofibers are useful in miniaturization of devices for dielectric and non-volatile memory applications.

As Emitters for Thermo-Photovoltaic Applications

A thermophotovoltaic (TPV) system consists of a source of thermal energy, an emitter, and an IR photovoltaic cell, which serves as the collector. Ideally, emitters should be isothermal and efficient in producing light that can be absorbed and converted to electricity by the photovoltaic collectors. The nanofibers, due to their high surface area, are useful for maximization of net emission to the collector, while, due to their low volume, minimize the light, reaching the collector, by re-absorption in their high surface area. A nanofiber is essentially an isothermal surface with very little volume. Isothermal nanofiber-based selective emitter structures with high ratios of surface area to volume should significantly increase the performance of the TPV system. This technology is ideal for power generation in space, in remote locations on the earth's surface, etc.

As Thermal Insulation/Protection System

Higher amount of porosity is desirable to increase the level of insulation. Usually, high porosity in an insulation brick is created by addition of sawdust, starch or other organic additives. In case of ceramic nanofibers by electrospinning process, the polymer phase helps in electrospinning as well as generates nanosized pores after heat-treatment. Therefore, miniaturized insulation bodies with nano porosity can be easily prepared in the form of mats, sheets, etc, which can be used as insulation / heat sinks in electronic devices. Additionally, as prepared ceramic hollow fibers should further enhance the insulation properties.

As Transport Medium for Drug Delivery System

The general practice of drug delivery is to inject the drug into the body with the help of a fine metallic needle (dia. ~0.5 mm) attached to a syringe containing the drug and the process is painful. Use of ceramic hollow nanofibers could avoid this problem due to their fineness. In addition, very small amount of drugs can also be delivered with the help of a nano pumping system. Therefore, a miniaturized drug delivery system consisting of a sensor to measure the level of blood sugar in case of a diabetic patient, a ceramic hollow nanofiber based needle, and a suitable micro/nano pump could be the right solution. It will be attached to the body of the patient conveniently to ensure the supply of the insulin as and when required depending upon the level of blood sugar. In this connection, ceramic hollow nanofibers should be preferred over their polymer counterparts because of high strength and rigidity.

Conclusions and Future Perspectives

Based on the above study, it could be concluded that electrospinning is a very simple, straightforward and versatile technology useful for the preparation of a large number of ceramic oxide nanofibers. The important aspect is the identification of a suitable ceramic salt-polymer-solvent system and application of sol-gel technique for the preparation of homogeneous and high viscous sol suitable for electrospinning. Various processing parameters, e.g. viscosity of solution, concentration, electrical conductivity; electrospinning conditions, e.g. DC voltage, tip to collector distance (TCD), flow rate; ambient conditions, e.g. humidity, temperature, etc affect the morphology of the fibers. Similarly, the fibers can be collected in the form of randomly oriented mats or in the aligned / parallel manner using various techniques.

Electrospinning technique is going to be more and more popular because a large number of salts of ceramic oxides as well as compatible polymers are available for the preparation of the homogeneous composite sol suitable for electrospinning. However, there are few challenges for the researchers. They are :

Preparation of High Density Nanofibers

For structural applications, it is essential that the density of fibers should be close to their theoretical density to derive the maximum thermo-mechanical properties. Currently, the ceramic fibers produced by electrospinning process are highly porous due to the loss of organic matrix during heat-treatment. To produce high density nanofibers, the following points are to be looked at:

(a) Minimization of the organics in the composite sol for electrospinning

(b) Optimization of heat-treatment temperature and time

(c) Addition of suitable sintering aids etc.

Preparation of Ceramic Hollow Nanotubes

Ceramic hollow nanofibers are potential materials for large number of applications such as drug delivery, insulation materials, for miniaturized components, etc. The preparation of hollow fibers has been demonstrated using co-axial electrospinning. More experiments have to be carried out for the preparation of large number of hollow nanofibers.

Large Scale Preparation of Ceramic Nanofibers

Ceramic nanofibers may be prepared in large scale for various applications. A large number of research groups have demonstrated this (Fig.10).[89] The environmental pol-

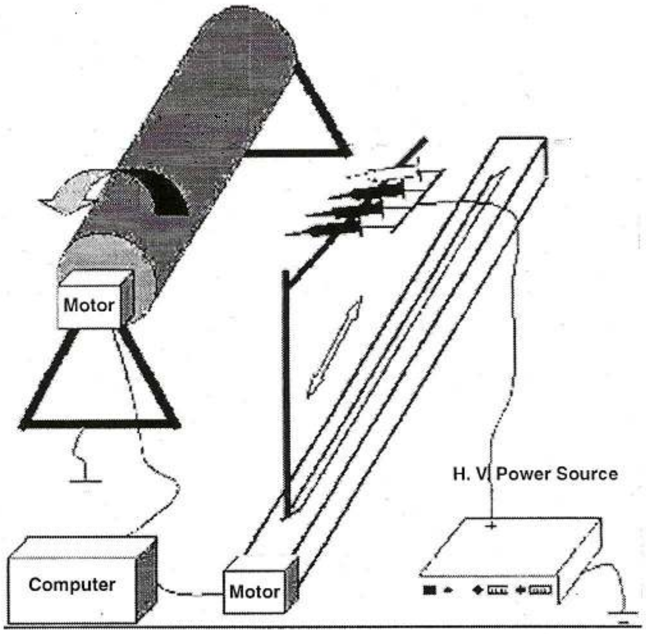

Fig. 10 – Multiple electrospinning, adapted from ref. 89.

lution and health hazards associated with large scale production have to be addressed.

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