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Green Synthesis of Nanofiber and Its Affecting Parameters

Dan Bahadur Pal and Deen Dayal Giri

Abstract

Nanofibers, the widely applied in various field of science research, is one of the important area in nanotechnology research. Nanofibers can be classified into polymeric, ceramic and composite nanofibers depending upon the material used. A variety of nanofibers are applied in field of energy storage, biotechnology and healthcare industry, environmental engineering, as well as security and defense. The wide uses of nanofibers are mainly due to low density, high porosity, tight pore size and large surface area per unit mass. Synthesis of nanofibers depends upon various parameters of solution like molecular weight of polymer, concentration, electrical conductivity, surface tension and viscosity. The process parameters affecting nanofibers synthesis are distance between needle tip and collector, feeding rate of polymer material and electric field.

Keywords: green synthesis, nanofibers, solution parameters, process parameters

1. Introduction

The basic purpose of the green chemistry is to diminish waste generation by complete consumption of material in the processes, or eliminate the generation and avoiding the processes that hazardous waste for human health [1]. Industrial and academic researchers are now more focusing on 'green' polymers from nature, instead of polymers derived from petroleum because of their sustainable environment-friendly nature, easy biodegradability and less energy need for renewing [2]. Fibers having diameters ~ 100 nm or lower exhibit special features are called nanofibers. These fibers have unique high surface area with respect to the mass compared to conventional fibers. They have high surface area ~ 1000 m²/g, high porosity, tight pores and low density. These features of materials are desirable for their application in different fields [2]. Some fields in which polymeric, ceramic and composite nanofibers are used include healthcare industry, biotechnological applications, environmental engineering, defense, security and energy storage. Researchers are interest to synthesize nanomaterials with special physical and chemical features for their application in the above mentioned fields. The extensive improvement has been recorded in the area of nanoparticles, nanotubes, nanofibers, nanolayers, nanodevices and nano-structured biological materials.

Providing clean drinking to public and improving their general health status is an important field of research and application of nanomaterials. Nanomaterials adsorb metals from the water on their surface and detoxify it [3]. The nanomaterials with large surface area naturally have high sorption capacities and less disposable waste generation. In nanostructures more unsaturated surface atoms get exposed, proximal

functional groups enhance reactivity and show nanoscale effect with decrease in particle size <20 nm diameter. A nanoparticle can have high adsorption for a selected metal [3]. Oxides of aluminum, iron, manganese and titanium have been investigated for their potential heavy metal adsorption from water. Titanium dioxide (TiO₂) anatase has been applied in many industries. Bulks as well as nanoparticles of Titanium dioxide (Titanium dioxide (TiO₂)) were able to degrade and remove organic compounds in presence of UV light and redox reactions in water [3].

The suitability of the sorbent for treating an inorganic pollutant depends on the cost effectivity and technical applicability. It is always necessary to develop an efficient and cheap adsorbent for the removing heavy metals from the industrial effluents, especially in the economically weak developing countries. Polymeric ceramic nanofibers are good option in this regard. For unit mass ceramic nanofibers harbor extraordinary high surface area and porosity. These low cost fiber show excellent structural and mechanical properties like high axial strength and extreme flexibility for a low basis weight [4].

Iijima (1991) discovered carbon nanotubes (CNTs) having excellent properties and applications. Depending upon layers of carbon atom in the wall, the tubular sheets of graphite are called single-walled CNT or multi-walled CNT [4]. Many heavy metals (Cr, Cu, Cd, Ni and Pb,) have been removed from waste water using CNTs [4]. The actual mechanisms by which metal ions get adsorbed onto CNTs is little bit complicated, however, possible it involves electrostatic attractive forces, sorption-precipitation or other chemical interaction between the metal ions and functional groups on the CNT surface.

The polymers applications are generally limited due to their poor mechanical strength and low antimicrobial resistance. A modification of polymers rectifies the limitations and improves wound healing property. A prominent biopolymer polylactide (PLA) has been exploited immensely in biomedical field due to biodegradability and biocompatibility [5]. Scaffolds of PLA temporary provide structural support to cells and tissue during healing by modulating cellular response that is helpful tissue engineering [6]. Wounds, cuts and damages skin heal rapidly in absence of germ because microbes on such surface trigger the immune response of our body and inflammation damage tissue leading to compromised self-healing. If such polymer scaffolds could contain antimicrobial agents capable to prevent opportunistic microbe on the wound surface, the healing process could be accelerated. When silver nanoparticles (AgNPs) impregnated into the polymer matrix, they impressive impart antimicrobial activity to scaffold in addition to improving mechanical, chemical, catalytic activity. Biomedically Ag-NPs have been applied in wound dressing material and in diagnosis of cancer [7] and sutures [8]. In addition to the antimicrobial activity, non-toxicity AgNPs are utilized in the fabricating non-infectious scaffolds. AgNPs are synthesized by using reducing chemical agents such as sodium borohydride [9], hydrazine etc. However, they have been extensively synthesized by use of medicinally important plant extracts [10]. The colloidal AgNPs has been synthesized using extracts of *Coccinia indica* [11], *Carica papaya* [12], *Brassica rapa* [13], *Aloe vera* [14], *Melia dubia* [15], *Citrus* sp. [16], *Acalypha indica* [17], *Prunus amygdalus* [18].

It is the cationic property that gives Chitosan (CHT) the ability to penetrate mucous layers in biomedical applications, perform an antimicrobial function in food preservatives, and trap dyes and metals in waste water [19]. It is also being used in technical applications such as packaging and decontamination, because of its physico-chemical properties, such as hydrophobicity, thermal stability, and mechanical performances [20]. These properties, unique to CHT, combined with high porosity and surface area by its nanosize, render it important for a range of different functional systems.

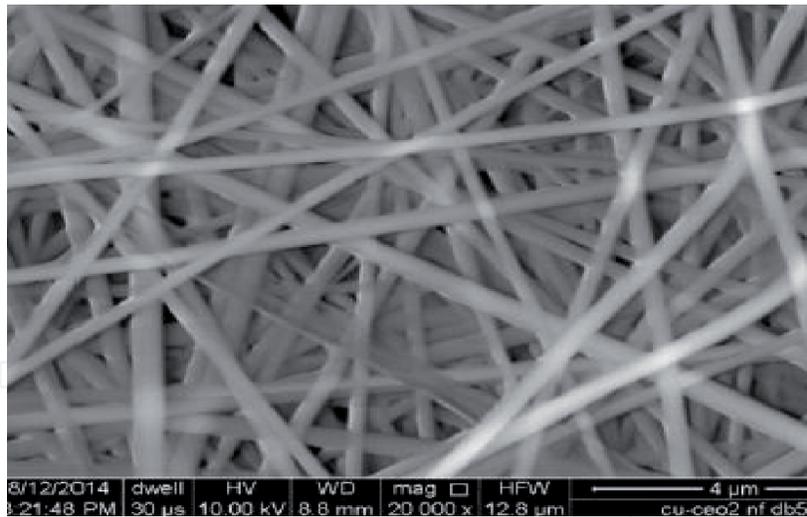


Figure 1.
Scanning electron micrograph of composite nanofibers synthesized from the PVP polymer by electrospinning process.

Hard and inert ceramic materials have excellent mechanical and thermal properties, in addition to superb chemical and corrosion resistance. These characteristics make them suitable for being used in electrodes, photonic devices, electronic and sensors, catalyst supports, drug delivery system and environmental science. The nanoribbons, nanorods, nanotubes, nanowires nanowhiskers and nanofibers are important nanostructures that are predominantly being synthesized in field of nanotechnology. These one-dimensional ceramics are interesting due to their unique optical, thermal, electrical, magnetic, gas sensing and or catalytic property. Such property of nanomaterial develop due to specific surface morphology and very small dimension compared to the same material in bulk. Among these nanostructures, highly porous, low density and high surface area containing nanofibers have been potentially applied in various fields [21]. A scanning electron micrograph of composite copper ceria nanofiber synthesized is given below in **Figure 1**.

2. Preparation methods of nanofibres

A number of methods have been used for fabricating nanofibers. Some of them are template synthesis [22], self-assembly [23, 24], phase separation [23], melt-blown [25] and electrospinning [26, 27]. Each process has its own challenge in preparing nanofibers. Selection of process for producing nanofibers depends on materials, fibers alignment, production rate and most importantly investment cost. Some of them are discussed below and only electrospinning process has been covered in details.

2.1 Template synthesis

The method employs a template or mold of desired material and structure is used to synthesize nanofibers. Generally, a templet of metal oxide membrane of nano-dimension pores is allowed to pass the polymer solution through it by applying water pressure from one side. The nanofibers extrude from the other side of the membrane. The generated fiber comes in contact with solidifying solution. Small sized nanofibers few micrometers length are generated. The fiber diameter is determined by the membrane pore size [28, 29]. The technique is very advantageous in fabricating nanofibers of various diameter by changing templates membrane.

2.2 Phase separation

In this method phases separate because of the physical incompatibility. The phase of the solvent then extracted from the solution while the other phase remain. This method consists mainly of four basic steps:

- i. Homogeneous polymer solution is prepared by dissolved the polymer in a suitable solvent.
- ii. Gelation of the solution to produce nanofiber matrixes. It is the most difficult step controlling porosity and morphology of the nanofiber. Gelation varies depending upon concentration of polymer and ambient temperature.
- iii. Extraction of the solvent from the gel.
- iv. Freezing and freeze drying.

The process is not equipment extensive in fabricating nanofiber matrix. The mechanical properties of matrix can be adjusted changing concentration of polymer [30]. By increasing polymer concentration, fiber mechanical properties are improved and porosity gets decreased [29].

2.3 Self-assembly

In self-assembly small building blocks spontaneously organized to build-up the stable nanofibers of very thin diameter. In such nano-material fabrication, building block molecules organize and arrange itself into definite patterns or structures due hydrophobic and electrostatic interactions and hydrogen bonding [31]. The inter-molecular forces bring units together to macromolecular nanofiber. The technique produce minute nanofibers of >100 nm to micrometers length. This nanofiber fabrication is complex, long, and extremely elaborate associate with limitation of low yield and uncontrollable fiber dimensions. Further, this method can be used to prepare nanofibers from selected molecules having capability of self-assemble themselves or under an external stimulus [29, 32].

2.4 Freeze drying

The technique is also known as ice segregation-induced self-assembly or solid-liquid phase separation. The technique comprises of following steps-

- i. Freezing- polymer solution is frozen at a low temperature
- ii. Primary drying- removal of water from frozen material by sublimation in a chamber have reduced pressure of few millibars and
- iii. Secondary drying- removal of unfrozen water from the polymer material by desorption.

Important advantages of freeze drying over other techniques of nanofibers fabrication is its ability to produce the porous structures of controlled sizes directly from polymers (e.g. chitin), without addition of structure directing additives and pre-treatment.

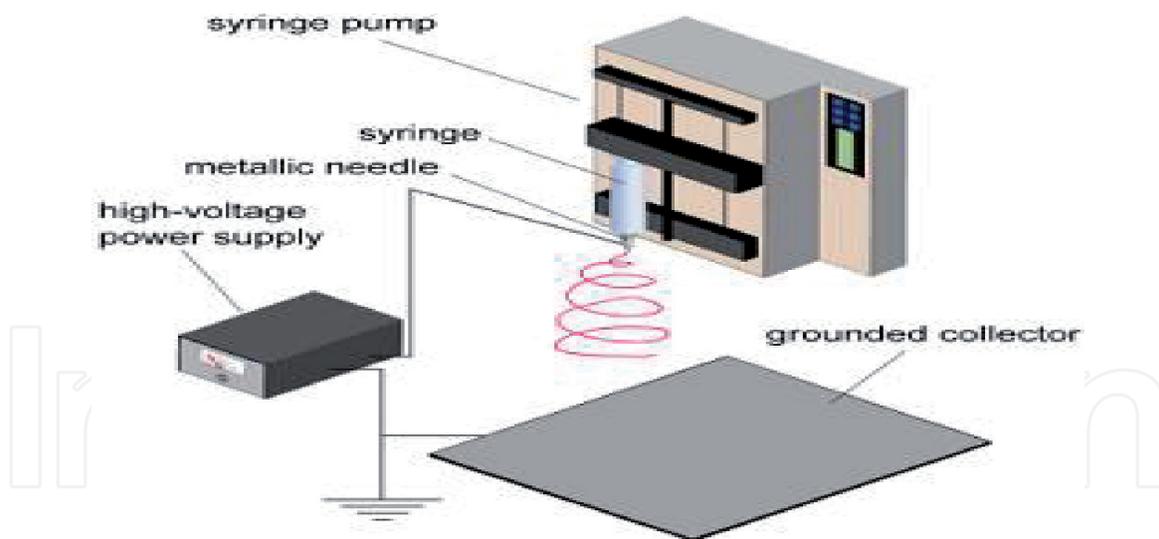


Figure 2.
Schematic representation of the electrospinning.

2.5 Electrospinning (ES)

In the field of nanotechnology electrospinning is the most promising remarkably simple processes for generating nanofibers from polymers solution. In combination with conventional sol-gel process, it offers a versatile technique for producing solid, porous, or hollow structured ceramic nanofibers. The technique has earned enormous attention because of its easy use and flexibility in controlling diameter in range of nanometers to micrometer and alignment of nanofibers as well as continuous nanofibers production capability. Electrospinning is peculiar in the sense that can be useful in producing fine nanofibers from different solution or melt of polymer, ceramic material and composite material for fast synthesis of nanofibers at industrial scale.

Formhals patented a process in 1934 for an experimental setup describing nanofiber production from polymer solution using electrostatic force, termed as electrospinning [33]. Now days, electrospinning is explored as a high efficiency method for the generating ceramic nanofibers [34]. In the generic design, an electrospinning setup consists of a high-voltage power supply, a metallic needle called spinneret, a piece of aluminum foil or silicon wafer acting as an electrically conductive collector and a syringe pump. A plastic syringe loaded with the polymer solution and connected to the metallic needle is often connected to a syringe pump for constant and adjustable feeding rate of the solution. In some cases, especially for electrospinning of ceramic nanofibers, the setup needs to be placed in a closed box for controlled humidity variation.

The collector can be constructed in different configuration from various materials depending on the end use of nanofiber. The electrospinning process is generally performed at room temperature at atmospheric conditions [35]. The ES system continuously need a high voltage (10-40kV) power supply of 40 kV, syringe pump, syringe, metallic needle and an electrically conductive collector plate during nanofiber synthesis. The electrospinning setup is schematically represented in **Figure 2** given below.

3. Parameters affecting the performance of electrospinning

Many parameters affecting ES process can be classified broadly into solution parameters, process parameters, and ambient parameters. Molecular weight,

concentration, conductivity, viscosity and surface tension are then solution parameters whereas feeding or flow rate, tip to collector distance and electric field are important process parameters. All these parameters individually and synergistically affect the final fibers morphology. Researcher used to adjust the above mentioned parameters to synthesize nanofibers of desired diameter and morphology and alignment [36]. Further, ambient environmental parameters like the temperature and humidity also affect electrospinning process and nanofiber morphology and diameter [37].

3.1 Solution parameters

3.1.1 Solution concentration

Nanofiber synthesis by ES process needs a minimum concentration of polymer in the solution for continuous nanofiber synthesis, the concentration below it, result in mixture of beads and fibers. The increase in concentration of solution the beads shape changes from spherical to spindle fibers and further increase in concentration synthesis uniform fibers with broad diameters due to the high viscosity resistance [38–41]. The range of concentration synthesizing continuous fibers is determined by surface tension and viscosity of solution. During ES process, solution concentration above optimum prohibits continuous fiber formation because of the inability to maintain the flow of the solution at the tip of the needle leading to the formation of larger fibers.

3.1.2 Molecular weight

Another important parameter is molecular weight of polymer that has strong influence on the morphology of electrospun nanofiber. Molecular weight of polymer affects rheology, electrical properties, conductivity, surface tension, viscosity and dielectric strength [42]. In ES process, generally high molecular weighted polymer offers the desired viscosity for the nanofiber synthesis whereas too low a molecular weighted polymer tends to form beads instead of fibers frequently. But very high molecular weighted polymers synthesize fibers of broad average diameters. Polymer's molecular weight and number polymer chain entanglements affect viscosity of the polymer solution. Polymer chain entanglement significantly determines the fiber synthesis in the electrospinning process.

3.1.3 Solution viscosity

Viscosity of solution is detrimental for the size of fiber and morphology during ES of fiber from polymer solution. The polymer solutions with very low viscosity lack continuous fiber formation whereas polymer solutions having very high viscosity results in difficult ejection of jets of polymer solution from the needle. So, an optimum viscosity is needed for ES process. Viscosity was shown to affect silk nanofibers synthesis by Sukigara and colleagues [43]. In the low viscosity solutions, surface tension becomes dominant factor. The increase in solution viscosity or concentration results in large sized fibers of uniform diameter [38].

3.1.4 Surface tension

Surface tension plays a critical role in the ES process. Surface tension of a solution is more likely a function of solvent compositions. So, the surface tension of polymer solution can be altered by using different solvents. The formation of

droplets, bead and fibers depends on the surface tension of polymer solution. If the surface tension of polymer solution is high, jet will be instable and the droplets will be sprayed from the tip of the needle leading to inhibition of ES process [44]. The reduced surface tension of a polymer solution will synthesize nanofibers without beads. The polymer solution with surface tension can of the spinning solution helps in ES process to occur at a relatively low electric field.

3.2 Process parameters

3.2.1 Voltage applied

Applied voltage in the ES process is a crucial process parameter. The applied voltage should attainment of threshold value for starting synthesis of fiber formation. The voltage induces the necessary charge and electric field on the solution to initiates the ES process. In the most cases, a high voltage greatly stretch of the solution because of greater columbic forces in the jet and a strong electric field that result in reduced fiber diameter and rapid evaporation of solvent from the fibers. Thus voltage influences fiber diameter at an extent, but the level of significance varies with the polymer solution concentration and on tip to the collector distance [45].

3.2.2 Feed rate/flow rate

The feed rate of the polymer solution is another important process parameter influencing velocity of jet from needle tip and the material transfer rate. Low feed rate is almost always desirable for getting enough time for evaporation of solvent from the polymer solution during fiber synthesis [46]. The spinning polymer solution should have a minimum flow rate for ES process to occur. Greater polymer solution flow rates forms beaded fibers due to improper smaller drying time period before reaching to the collector.

3.2.3 Types of collectors

A collector in ES process is a conductive substrate on which nanofibers are deposited. Collector is an important process parameter. Aluminum foil is one of the most common collectors in the ES process. To overcome the difficulty to transfer of collected fibers and necessity of aligned fibers for different applications, other collectors could also be conductive paper or cloth, rotating rod or wheel, pin, wire mesh parallel or gridded bar [47].

3.2.4 Distance between tip to collector

Fiber diameters and morphology could be controlled by manipulating the tip to collector distance. However, a minimum distance between collector and needle tip is essential for giving sufficient time for fibers dry before being deposited on the collector. The beads are frequently observed in the cases where tip to collector distance are either too close or too far. The optimum distance between the tip and collector are adjusted depending upon the polymer solution used for proper evaporation of solvent from the nanofibers [37].

3.3 Ambient parameters

In addition to the solution and process parameters, there are some ambient parameters such as humidity, temperature etc. which influence the ES process.

Increase in ambient temperature yield fibers of relatively decreased diameter which can be attributed the decrease in the viscosity of the polymer solutions at high temperatures. In the very low humidity environment, a volatile solvent will rapidly evaporate from synthesized fiber. However, too fast evaporation could be problematic in ES process when solvent get evaporated from the polymer solution just after emission from the tip of the needle. In such condition, ES process is stopped due to clogging of needle tip within few minutes operation of ES process [48]. It has been advised that the high humidity can help in the discharge of the synthesized nanofibers.

4. Preparation of nanofibres using electrospinning method

Well-controlled and high-quality ceramic nanofibers can be generated in ES process by following procedures

1. Preparation of a sol with suitable inorganic precursor and its proper mixing with a polymer solution to get the right rheology for electrospinning
2. Electrospinning of the solution to obtain inorganic/organic composite fibers under appropriate conditions, and
3. Calcination of the as-prepared composite fibers in air to yield pure metal oxide fibers. One of the attractive features associated with this method is that the nanofiber mats thus prepared possess high surface areas and small pore sizes [49].

4.1 The electrospinning solution

Ceramic nanofibers can be obtained by direct electro-spinning of sol of only inorganic precursor metal alkoxides or metal salts dissolved in a solvent. Notable examples are synthesis of nanofibers of CeO_2 [50–52], Titanium dioxide (TiO_2) [53] and $\text{Al}_2\text{O}_3/\text{ZnO}$ [54]. However, such synthesis shows inappropriate rheological properties and the rapid hydrolysis rates of metal alkoxides or metal salts, pose difficulties in controlling the ES process. To resolve such problems, one has to introduce a polymer matrix are added into the solution to adjust the rheological properties and catalyst is supplemented to control the hydrolysis rate of the used precursor [54]. Thus a typical spinnable precursor solution composed of metal salt or an alkoxide precursor, a polymer, an additive, and an easily volatile solvent like chloroform, ethanol, iso-propanol, water and dimethyl-formamide. The catalysts added into the solution usually stabilize the precursor and facilitate smooth electrospinning process. The catalyst are required in minute quantity but their addition in spinning solution play an key role in stabilizing the solution and the jet from the needle. The acid catalyst like acetic or hydrochloric or propionic acid is employed for adjusting both the hydrolysis and gelation rates to prevent blocking the needle mouth by solution and ensuring a continuous nanofiber synthesis [49].

At present we are discussing nanofiber synthesis using casting solution comprising precursor cerium nitrate hexahydrate and copper acetate monohydrate, PVP polymer, glacial acetic acid (3-4drops) and a solvent ethanol and water that was used for preparing green nanofibers through ES process. The details of procedure used for preparing the casting solution and green nanofibers are discussed below.

4.2 The precursor and polymer solution

The precursors in the present nanofiber synthesis were cupric acetate monohydrate ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$) and cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and polyvinyl pyrrolidone (PVP) was the base polymer. The PVP has a remarkably large molecular weight and high solubility in polar solvents. The solvent used in the process was ethanol and de-ionized water added as co-solvent [55, 56]. The aqueous precursor solutions was prepared in dissolving $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and cerium nitrate hexahydrate in 4 ml of deionized water and this solution was mixed ethanolic PVP solution (4 ml) for final 10% (w/v) of PVP. The mixed solution stirring continuously till complete dissolution. The 2–3 drops of acetic acid was added during magnetic stirring of solution for about 3 h at room temperature to preparing homogeneous solution for final spinning.

4.3 Electrospinning of composite nanofibers

The prepared polymer spinning solution or sol–gel solution was immediately loaded in plastic syringe of 5 ml capacity and a blunt ended 20-gauge stainless steel needle fitted in it. The nozzle equipped syringe was attached to the syringe pump. The positive electrode of high voltage power supply capable of generating DC voltages up to 40 kV attached with the needle whereas negative electrode was connected to the aluminum foil covered collecting plate. The ground electrode of the power supply was attached to a piece of flat aluminum foil used as the collector plate [57, 58]. The needle tip to collector distance was 10 cm to collect the nanofibers. The ES process was conducted in ambient air at room temperature ($25 \pm 2^\circ\text{C}$) having relative humidity of $65 \pm 5\%$. A solution feeding rate was set to 1 ml/h with the help of a syringe pump. The steady deposition of nanofibers on the collector plate was ensured by frequent cleaning of nozzle clogging intermittently. The experiment was conducted by applying positive high voltage of 18 kV across the needle and the collector plate. At such

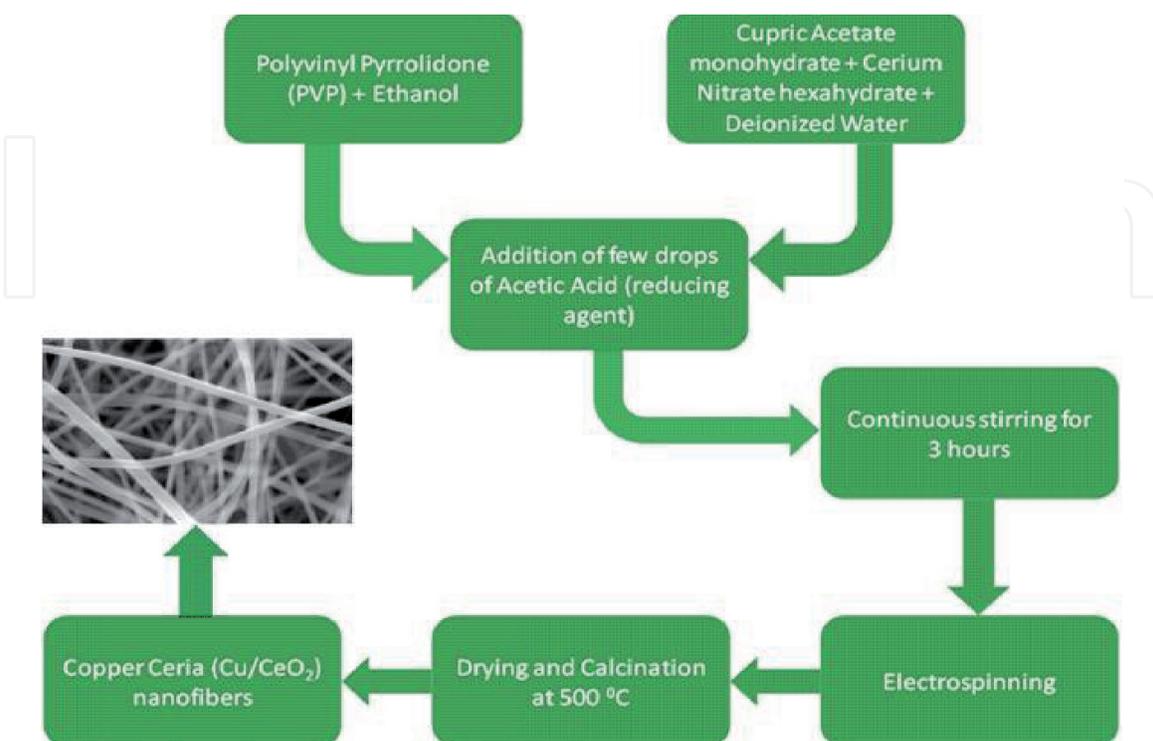


Figure 3.
Process flowchart for the preparation of nanofibers by electrospinning method.

environmental condition fluid jet ejected continuously from the nozzle and accelerated jet moved towards the collector plate. During this movement of jet the solvent get evaporated leaving ultra thin fibers on the collector plate. The ES process continued until all the solution in the syringe was exhausted. The complete sequence of spinning solution preparation and nanofiber synthesis, its calcination and final morphological feature are schematically represented in **Figure 3**.

4.4 Calcinations of green nanofibers

To complete the formation of CuO/CeO₂ nanofibers, the composite fibers prepared as above were left exposed to ambient moisture for 5 hr. to allow complete hydrolysis, then electrospun polyvinyl pyrrolidone (PVP) /cerium nitrate hexahydrate (CN)/copper acetate monohydrate (CA) fiber mats were removed from the aluminum foil. These composite fibers were placed on a ceramic crucible able to withstand high temperature and consequently calcined (500°C, 3 hr) in a muffle furnace in presence of air for eliminating the organic constituents and activating crystallization of Cu-Ce oxide.

5. Potential utilizations of nanofibers

Now a days, scientists and researchers have shown strong interest to develop the electrospun ceramic nanofibers in different field. The most significant characteristic of nanofibers are their long length, high porosity and large surface area. The features are makes them widely applicable in electric and optical devices, optoelectronic components, optical waveguides, gas storage units, fluidic devices, tissue engineering scaffolds and bioreactors. In this century, exciting and important research areas for nanofibers application are in energy technology, catalysis and environmental science [59]. Such applications of nanofibers are briefly discussed below. The basic nanofiber application shown in **Figure 4**.

5.1 Nanofibers application as catalysis

Highly porous and large surface area bearing electrospun nanofibers prominently used as solid supports in catalysts. Nanofibers of some materials having excellent semiconducting property make them suitable in photo-catalysts for removing

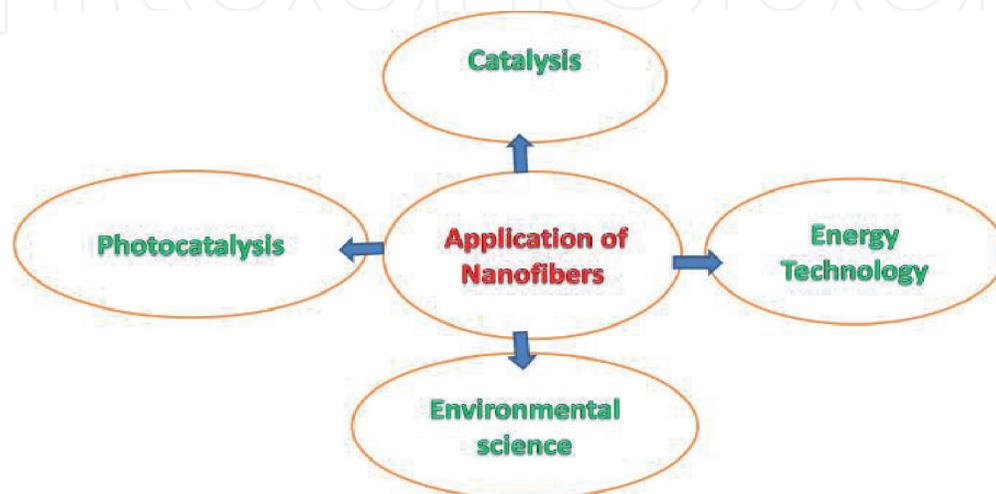


Figure 4.
Basic applications of nanofibers.

organic molecules from air flow or aqueous solution. The extent of catalysis and its efficiency is governed by surface area of the catalyst. Ceramic nanofibers possess extraordinarily high specific surface area are nice materials for their application as catalyst for chemical reaction. The ceramic nanofibers mats of Titanium dioxide (TiO₂), zirconium dioxide (ZrO₂) and tin dioxide (SnO₂) have been employed as support material for loading noble metal nanostructures catalysis in different applications [60]. The membranous catalytic system have distinctive benefit over other process in terms of its operation in a continuous flow mode, relatively short reaction time and even more importantly it need not separation of product after completion of reaction. In addition to large surface area, the support material should also be stable and good conductor of electron. The nanoparticles catalyst of noble-metal Pt, Pd, Rh etc. are homogeneous spread on solid support of carbon black for maximizing possible surface site availability [61]. The Pd-coated Titanium dioxide (TiO₂) nanofibers performed well in cross-coupling reaction [62]. It is interesting that the ceramic nanofiber substrate can pointedly influence noble-metal catalyst deposition [63].

5.2 Nanofibers application in energy technology

Energy shortage is one of the most serious issues of the 21st century because of limited natural energy resources like crude oil, natural gas, coal and uranium that are fulfilling the energy need for everyday life at presented. For rapid economic growth, will require subsequent increase in energy demand mean but the rate of oil production will no longer be adequate. This is evident from the rising price of crude oil. Presently, large volumes of carbon dioxide emitted by industrial burning of fossil fuels are deteriorating climate of the globe. So, it is necessity of the time to identify alternate environmentally friendly new sources of energy that are able to replace current energy supply. The people are trying to converse energy from renewable sources such as the sun, wind, and tides. The most promising energy conversion/storage devices likely to fulfill the need are based on photovoltaic cells, lithium batteries, and fuel cells. For example, Mai and colleagues demonstrated high performance lithium ion battery electrode based on electrospun vanadium oxide nanofibers [64]. They were able to prepare ultra-long hierarchical vanadium oxide nanowires of fine diameter (100–200 nm) and several millimeters using the low-cost starting materials by ES combined with annealing. The 1D characteristic of electrospun ceramic nanofibers have been widely explored as a new class of promising building blocks for fabricating the devices. Energy storage devices are becoming a very common in everyday life of public due to exponential expansion of digitization. Many devices need stored energy for their functions are electronic mobile, autonomous sensors and various kind of vehicle. So, the reliable energy storage devices with high power density and structural integrity are in demand for their use in various devices [65, 66]. Green flexible network of carbon nanofiber can be deriving from abundantly available but underutilized bioresources lignin. The PVA lignin nanofiber network showed has surface area of 1670m² per gram and excellent specific gravimetric capacitance of ~240 F per gram that was better than many nanostructured carbon or metal oxides [67]. The carbon based nanofibers have high specific electrical double layer capacitance at low cost [68].

5.3 Nanofibers application in environmental science

5.3.1 Nanofiber-based membrane for filtration

Electrospun ceramic nanofibers membranes are able to remove suspended particulate matter from air and other impurities dissolved in water. The highly

porous membrane structures, formed by entanglements of nanofibers facilitate material transport without causing resistant to gaseous stream flow or flow of aqueous solution; can be utilized for environmental applications. Dai et al. [50] prepared a hierarchically structured potassium manganese oxide (K_xMnO_2) / Titanium dioxide (TiO_2) mats for filtering Congo red dye from waste water. The membranes not only performance well but also showed high filtering efficiency and robustness survival against strong sheer force of solution flowing through it. In another investigation, Song and co-workers reported synthesis of ultrafine porous carbon nanofibers membrane efficiently removing sulfur dioxide (SO_2) from stream of gases. Doping of membranes with minute quantity of nitrogen is likely to improve their capacity, efficiency and durability [69].

5.3.2 Nano-sensors

Detection of threats to the environment is a key feature of environmental management strategy. The contaminants posing environmental threat could be detected with the help of sensors. Some semiconducting materials like Titanium dioxide (TiO_2), SnO_2 , zinc oxide (ZnO), tungsten oxide (WO_3), molybdenum oxide (MoO_3) have been shown to detect trace level of gaseous species in the parts per million levels [70]. The sensing ability of such materials could be enhanced by increasing specific surface area and porosity. The 1D architectures of nanofiber facilitate fast mass transfer near molecular interaction region and traverse of barriers by charge carriers. Nanofibers of Titanium dioxide (TiO_2), iron oxide (Fe_2O_3), SnO_2 , ZnO/SnO_2 , lithium chloride ($LiCl$)/ TiO_2 , Titanium dioxide (TiO_2)/ ZnO , potassium chloride (KCl)-doped- ZnO , and Co-doped- ZnO are successfully employed in sensing and enhanced limit of detecting gaseous species. The gases or vapors notably detected are hydrogen (H_2), carbon monoxide (CO), O_2 , nitrogen dioxide (NO_2), ammonia (NH_3), H_2O , methanol (CH_3OH), ethanol (C_2H_5OH) and toluene. Wang and colleagues reported very quick response of electrospun orthorhombic-phase WO_3 nanofiber's high sensitivity to different concentrations NH_3 [71]. The superior sensing performance of the material was attributed to high purity, preparation method, high surface area per unit volume and porosity for good accessibility of the gas. The electrospun ceramic nanofibers not only function as sensing materials, but also act as good support material for other sensing bodies derived from noble metal.

5.3.3 As photo-catalysts

Current environmental issue of air and water pollution motivate for sustained fundamental and applied research for remediation of different polluted ecosystem. The steadily growing field of nanoscience research is engaged in synthesizing nanostructured ceramics as photo-catalyst. The low cost and environmental friendliness compounds, ZnO and Titanium dioxide (TiO_2), have showed high catalytic activity are promising photocatalytic material. These small sized and extremely high surface area containing ceramic nanofibers provide channels for quick charge transfer due to its 1D nanostructure. Such ceramics nanomaterial could be potentially used in photo catalysis. Zhang and coworkers synthesized hybrid Fe-Titanium dioxide (TiO_2) /tin dioxide (SnO_2) nanofibers having high photo-catalytic activity and ferromagnetic properties at room temperature. It is supposed that this hybrid nanofiber can act new generation of visible light-excitable photo catalyst with easy recyclable and its potential predictable applications in water purifying and other pollution treatment [72]. Recently, Yoshikawa and colleagues showed Titanium dioxide (TiO_2) nanofibers potentially application as photo-catalysts for H_2 production [73]. The novel structured highly crystalline nanomaterial might be able to

reduce lattice defects to facilitate the electron transport for reactions with water adsorbed on their surface. During synthesis and producing of dyes, about 16% of the total global productions are lost with wastewater [74]. A variety of bioremediation techniques are utilized for dye elimination such as Enzymes, Microbiological decolorization. The common pollutants (organic/inorganic) present in aquatic atmosphere are due to the discharge of wastewaters from households as well as from the manufacturing sectors. These contaminants, organic molecules might be found in the land and surface water. The elimination of carcinogenic, non-biodegradable organic dyes and other chemicals from the surroundings is a central environmental problem [75].

5.3.4 Water and wastewater treatment

Pollution of ground and surface water across the world is now a critical issue. Heavy metals are the important pollutants that affect the physiology of living entities significantly. The heavy metals frequently reported in the polluted water bodies are As, Cu, Hg, Cd and Pb. The elements are released in industrial waste that are discharged and distributed in the environment and finally enter in water. e.g. Smelting of copper releases high quantities of Cd in its industrial wastewater. It is nearly impossible to eliminate some metal contaminants from water using conventional water purification procedures. Nanotechnology has greatly advanced water and wastewater treatment potential. They facilitate improved safe use of unconventional water sources. The limited surface area containing conventional adsorbents bears less active sites and also lacks selectivity. In contrast, nanosorbents with enhanced specific surface area and large number of available sorption sites, small intra-particle diffusion distance, tunable pore size and surface chemistry facilitate better adsorption. In the future, suitable polymer nanofibers functionalized ceramic membranes can be used for fabricating affinity membranes for treating heavy metal-containing industrial wastewater [76, 77]. The discharge of heavy metals like arsenic, cadmium, chromium, cobalt, nickel, copper, silver, tin, titanium, lead and zinc into the environment of textile production is an immense concern all over the globe because these metals pose unfavorable effects on human health, the natural atmosphere and aquatic life.

6. Summary

Green synthesis of composite nanofibers can be successfully prepared using sol-gel and ES techniques using polymer solutions. Some of the characteristics of the synthesized green composite nanofibers are their controlled average diameter distribution in the desired range, remarkably straight fibers over several micrometers of length, uniform and smooth surface. Generally, viscosity of the casting solution plays the most important role in the fiber morphology and diameter. The green syntheses of nanofibers are affected by solution parameters, process parameters and ambient parameters. Nanofibers are at the forefront of nanotechnology due to their merits and suitability to a wide range of applications in the field of healthcare, biotechnology, energy storage, environmental engineering, defense and security.

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Conflict of interest

There are no conflicts of interest between authors. All the co-authors have seen the final manuscript and agreed for submission. No data or figures have been fabricated or manipulated. The authors agree to transfer copy right to book publishers. All the further responsibilities will be undertaken by the corresponding author.

Author details

Dan Bahadur Pal^{1*} and Deen Dayal Giri²

1 Department of Chemical Engineering, Birla Institute of Technology, Mesra, Ranchi, Jharkhand, India

2 Department of Botany, Maharaj Singh College, Saharanpur, Uttar Pradesh, India

*Address all correspondence to: danbahadur.chem@gmail.com

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