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(54) **ELECTROSPINNING IN A CONTROLLED GASEOUS ENVIRONMENT**

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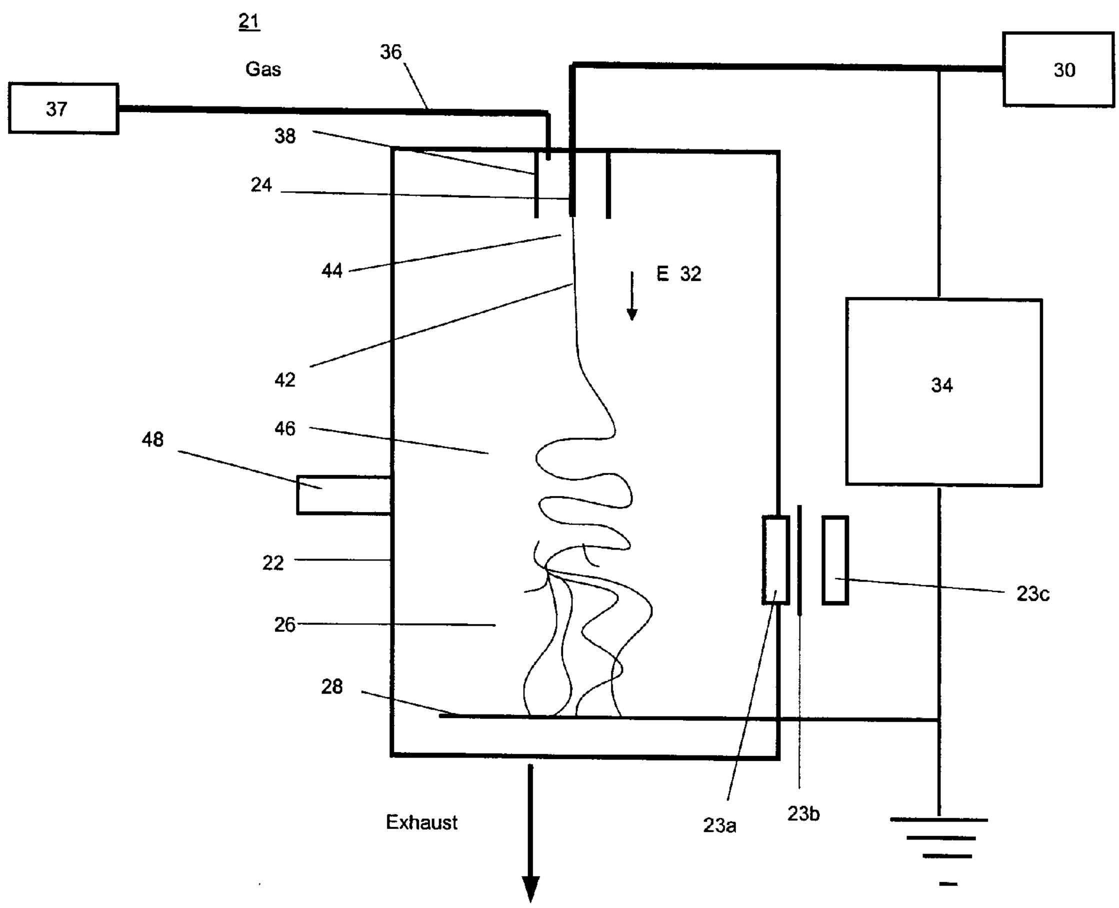
(57) **ABSTRACT**

Apparatus and method for producing fibrous materials in which the apparatus includes an extrusion element configured to electrospin a substance from which the fibers are to be composed by an electric field extraction of the substance from a tip of the extrusion element, a collector disposed from the extrusion element and configured to collect the fibers, a chamber enclosing the collector and the extrusion element, and a control mechanism configured to control a gaseous environment in which the fibers are to be electrospun. The method includes providing a substance from which the fibers are to be composed to a tip of an extrusion element, applying an electric field to the extrusion element in a direction of the tip, controlling a gaseous environment about where the fibers are to be electrospun, and electrospinning the substance from the tip of the extrusion element by an electric field extraction of the substance from the tip into the controlled gaseous environment.



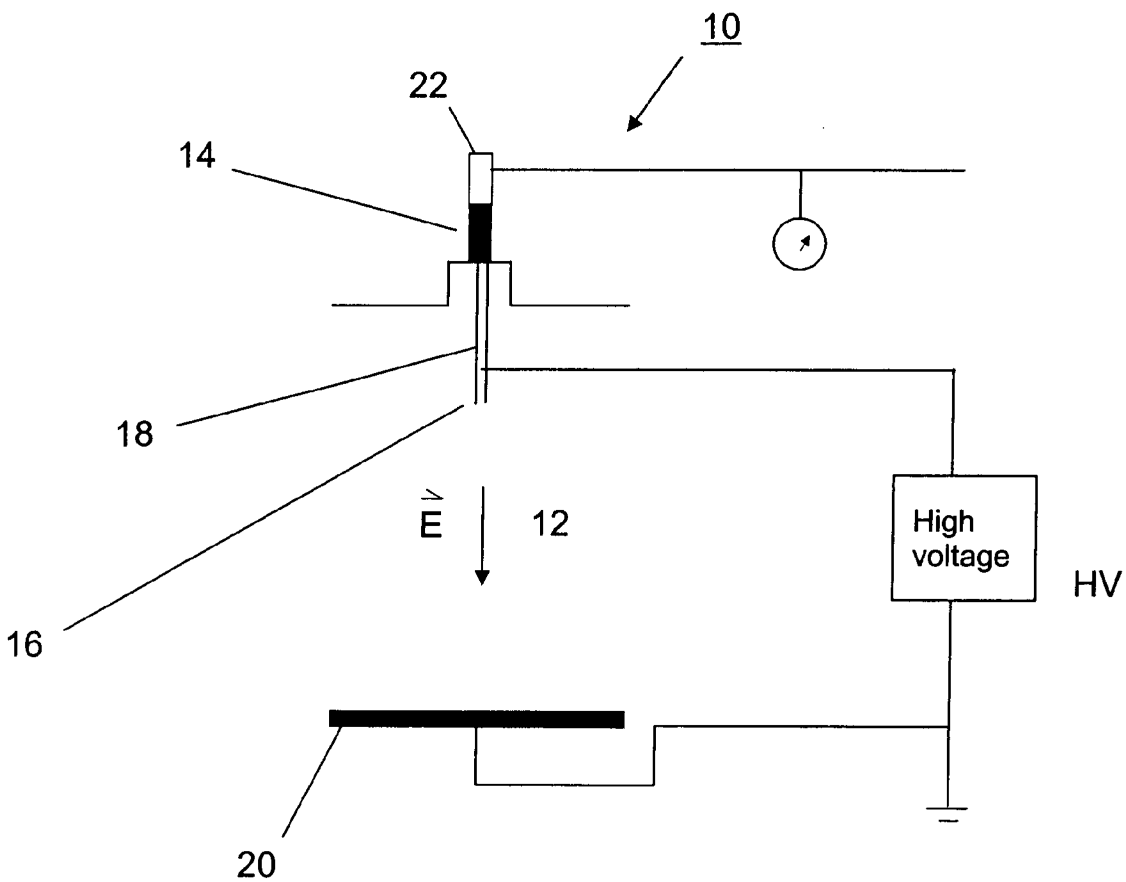
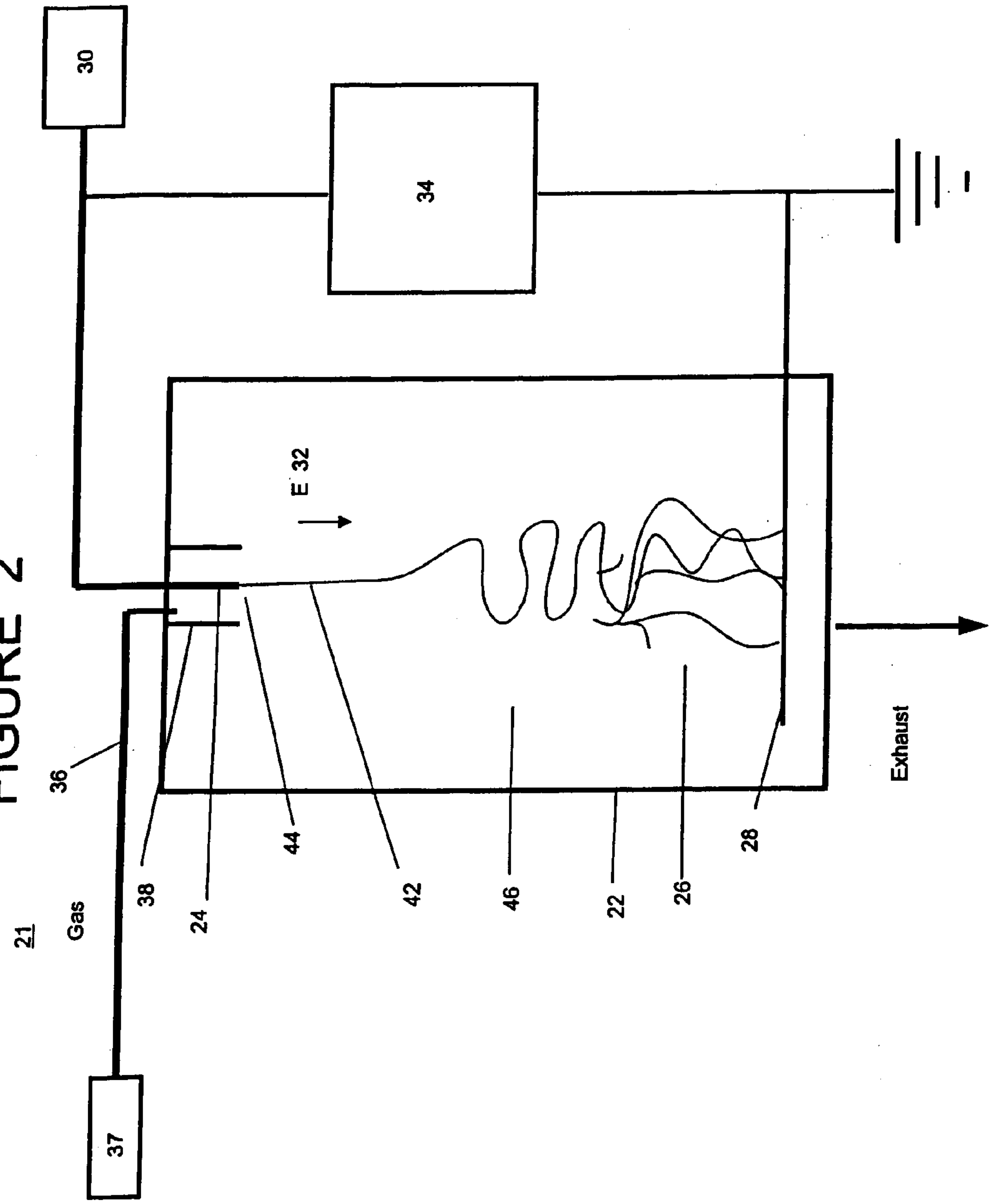


Figure 1

BACKGROUND ART

FIGURE 2



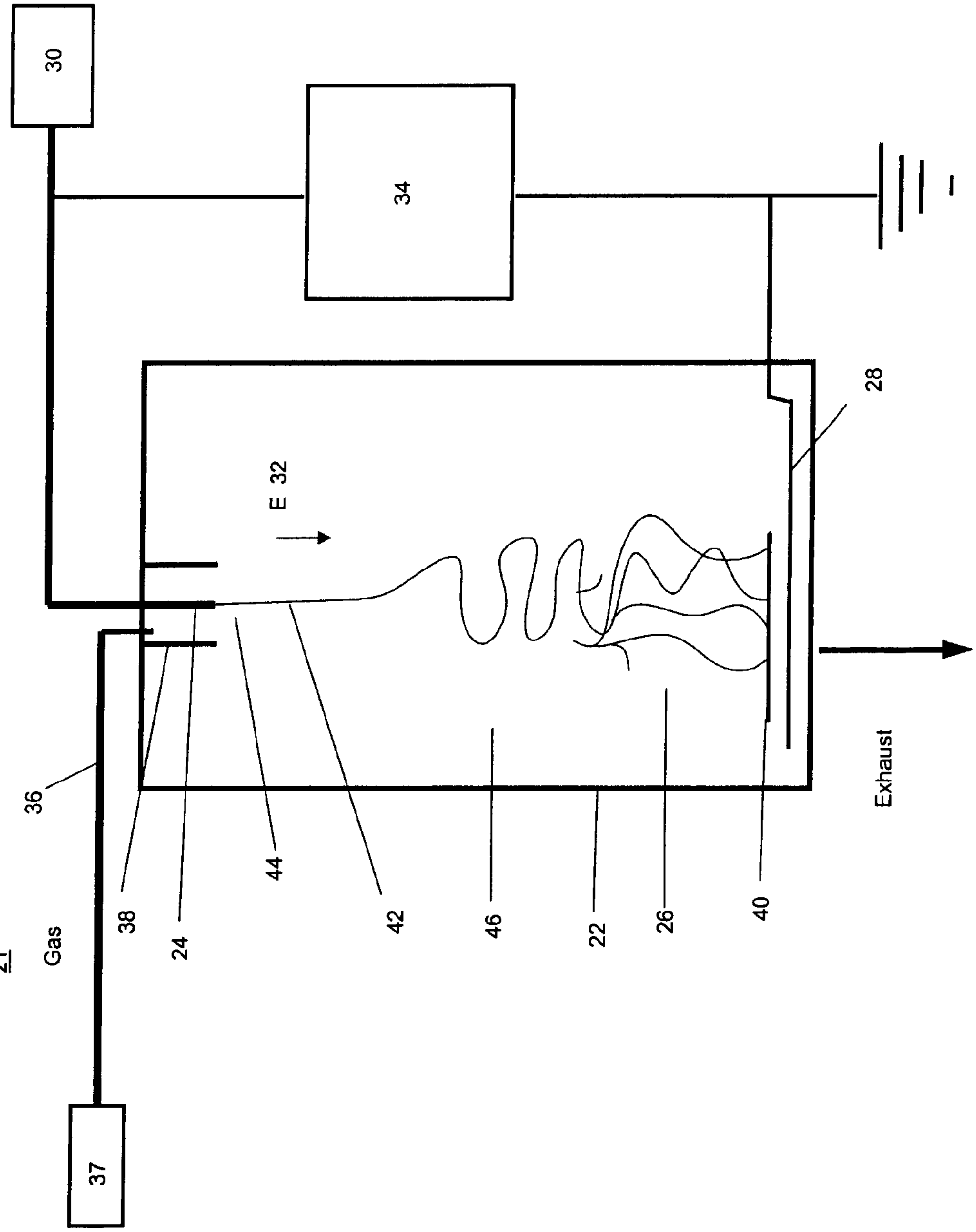


FIGURE 3

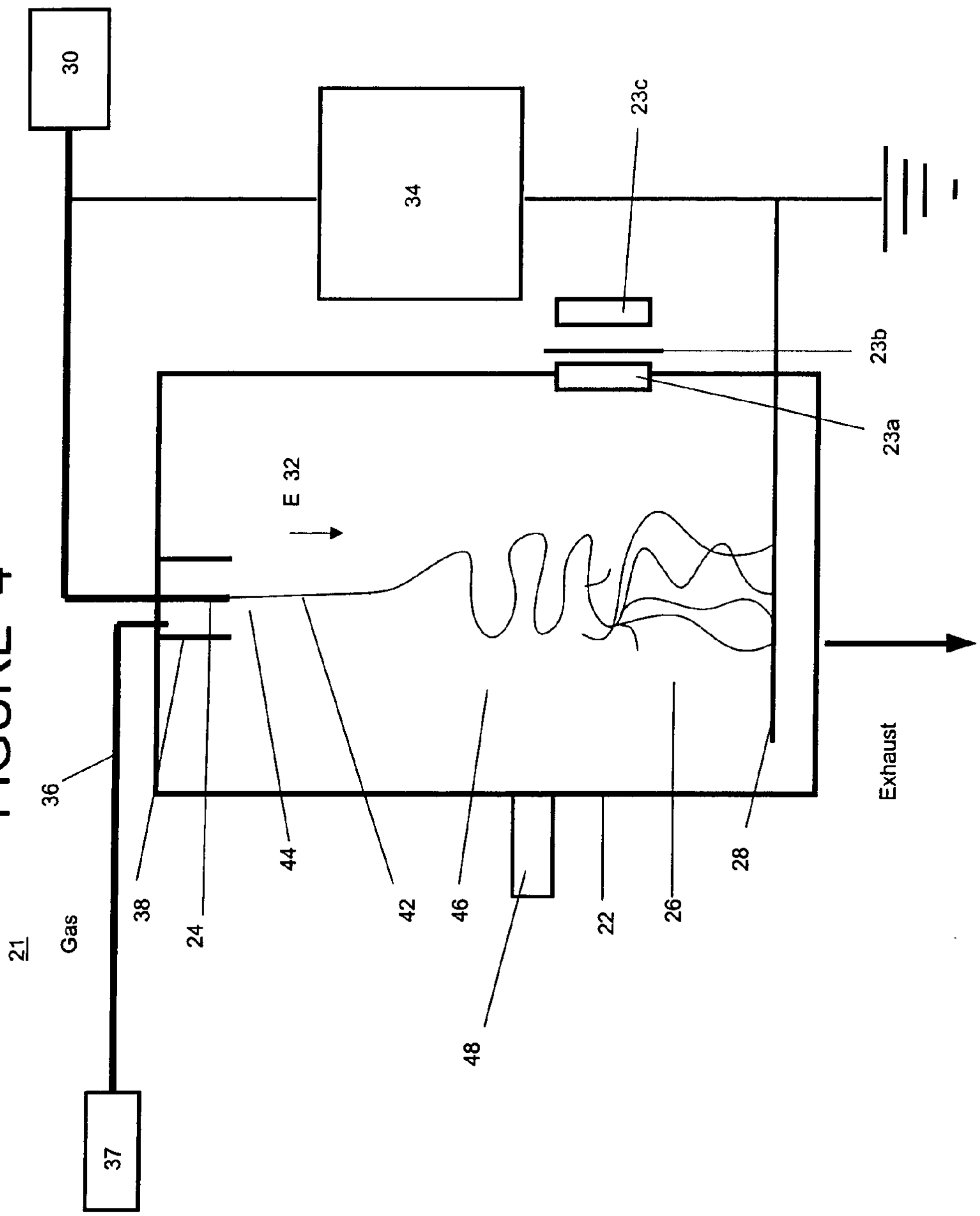

30
34
23c
23b
23a
E 32
Exhaust
36
38
24
44
42
46
22
26
28
21
Gas
48
37

FIGURE 4

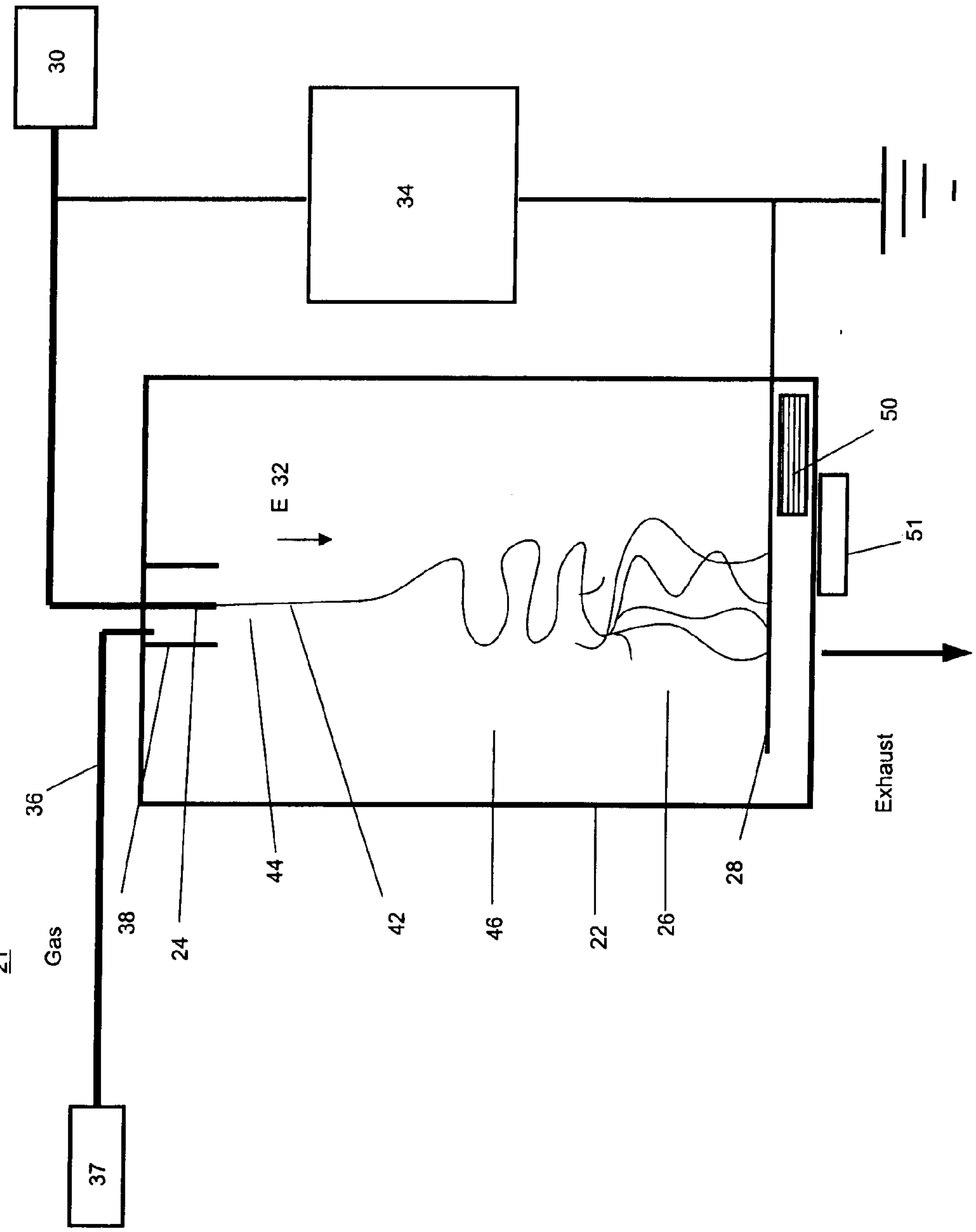
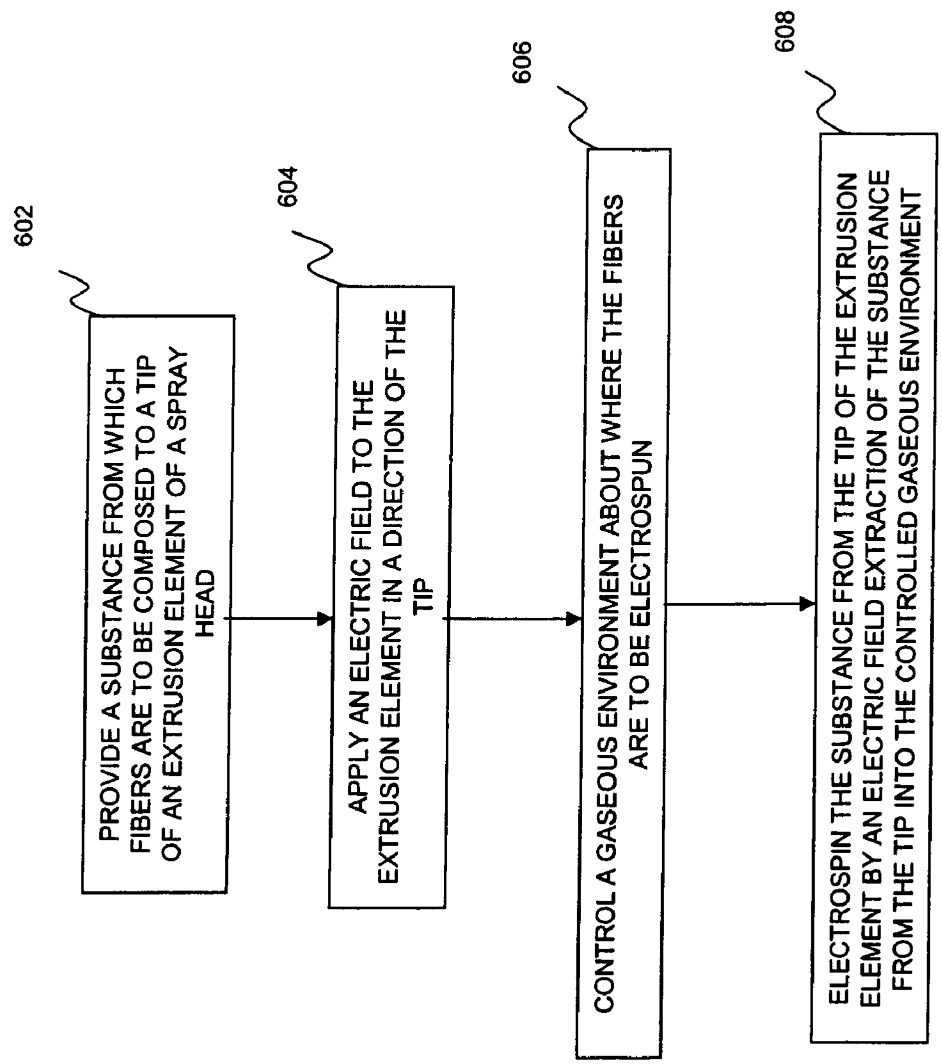


FIGURE 5

FIG. 6


602
PROVIDE A SUBSTANCE FROM WHICH FIBERS ARE TO BE COMPOSED TO A TIP OF AN EXTRUSION ELEMENT OF A SPRAY HEAD
604
APPLY AN ELECTRIC FIELD TO THE EXTRUSION ELEMENT IN A DIRECTION OF THE TIP
606
CONTROL A GASEOUS ENVIRONMENT ABOUT WHERE THE FIBERS ARE TO BE ELECTROSPUN
608
ELECTROSPIN THE SUBSTANCE FROM THE TIP OF THE EXTRUSION ELEMENT BY AN ELECTRIC FIELD EXTRACTION OF THE SUBSTANCE FROM THE TIP INTO THE CONTROLLED GASEOUS ENVIRONMENT

ELECTROSPINNING IN A CONTROLLED GASEOUS ENVIRONMENT

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application is a divisional of U.S. Ser. No. 10/819,945, filed Apr. 8, 2004 and the entire contents of which are incorporated herein by reference.

[0002] This application is related to U.S. application Ser. No. 10/819,916, filed on Apr. 8, 2004, entitled "Electrospinning of Fibers Using a Rotating Spray Head," Attorney Docket No. 245015US-2025-2025-20, the entire contents of which are incorporated herein by reference. This application is also related to U.S. application Ser. No. 10/819,942, filed on Apr. 8, 2004, entitled "Electrospray/electrospinning Apparatus and Method," Attorney Docket No. 241013US-2025-2025-20, the entire contents of which are incorporated herein by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0003] The U.S. Government, by the following contract, may have a paid-up license in this invention and the right in limited circumstances to require the patent owner to license others on reasonable terms, as provided for by the terms of DARPA Contract No. 972-01-C-0058.

DISCUSSION OF THE BACKGROUND

[0004] 1. Field of the Invention

[0005] This invention relates to the field of electrospinning fibers from polymer solutions.

[0006] 2. Background of the Invention

[0007] Nanofibers are useful in a variety of fields from clothing industry to military applications. For example, in the biomaterial field, there is a strong interest in developing structures based on nanofibers that provide a scaffolding for tissue growth effectively supporting living cells. In the textile field, there is a strong interest in nanofibers because the nanofibers have a high surface area per unit mass that provides light but highly wear-resistant garments. As a class, carbon nanofibers are being used for example in reinforced composites, in heat management, and in reinforcement of elastomers. Many potential applications for nanofibers are being developed as the ability to manufacture and control the chemical and physical properties improves.

[0008] Electrospray/electrospinning techniques can be used to form particles and fibers as small as one nanometer in a principal direction. The phenomenon of electrospray involves the formation of a droplet of polymer melt at an end of a needle, the electric charging of that droplet, and an expulsion of parts of the droplet because of the repulsive electric force due to the electric charges. In electrospraying, a solvent present in the parts of the droplet evaporates and small particles are formed but not fibers. The electrospinning technique is similar to the electrospray technique. However, in electrospinning and during the expulsion, fibers are formed from the liquid as the parts are expelled.

[0009] Glass fibers have existed in a sub-micron range for some time. Small micron diameter fibers have been manufactured and used commercially for air filtration applications for more than twenty years. Polymeric melt blown fibers have more recently been produced with diameters less than a micron. Several value-added nonwoven applications, including filtration, barrier fabrics, wipes, personal care, medical and pharmaceutical applications may benefit from the interesting technical properties of nanofibers and nanofiber webs. Electrospun nanofibers have a dimension less than 1 μm in one direction and preferably a dimension less than 100 nm in this direction. Nanofiber webs have typically been applied onto various substrates selected to provide appropriate mechanical properties and to provide complementary functionality to the nanofiber web. In the case of nanofiber filter media, substrates have been selected for pleating, filter fabrication, durability in use, and filter cleaning considerations.

[0010] A basic electrospinning apparatus **10** is shown in FIG. **1** for the production of nanofibers. The apparatus **10** produces an electric field **12** that guides a polymer melt or solution **14** extruded from a tip **16** of a needle **18** to an exterior electrode **20**. An enclosure/syringe **22** stores the polymer solution **14**. Conventionally, one end of a voltage source HV is electrically connected directly to the needle **18**, and the other end of the voltage source HV is electrically connected to the exterior electrode **20**. The electric field **12** created between the tip **16** and the exterior electrode **20** causes the polymer solution **14** to overcome cohesive forces that hold the polymer solution together. A jet of the polymer is drawn by the electric field **12** from the tip **16** toward the exterior electrode **20** (i.e. electric field extracted), and dries during flight from the needle **18** to the exterior electrode **20** to form polymeric fibers. The fibers are typically collected downstream on the exterior electrode **20**.

[0011] The electrospinning process has been documented using a variety of polymers. One process of forming nanofibers is described for example in *Structure Formation in Polymeric Fibers,* by D. Salem, Hanser Publishers, 2001, the entire contents of which are incorporated herein by reference. By choosing a suitable polymer and solvent system, nanofibers with diameters less than 1 micron have been made.

[0012] Examples of fluids suitable for electrospraying and electrospinning include molten pitch, polymer solutions, polymer melts, polymers that are precursors to ceramics, and/or molten glassy materials. The polymers can include nylon, fluoropolymers, polyolefins, polyimides, polyesters, and other engineering polymers or textile forming polymers. A variety of fluids or materials besides those listed above have been used to make fibers including pure liquids, solutions of fibers, mixtures with small particles and biological polymers. A review and a list of the materials used to make fibers are described in U.S. Patent Application Publications 2002/0090725 A1 and 2002/0100725 A1, and in Huang et al., Composites Science and Technology, vol. 63, 2003, the entire contents of which are incorporated herein by reference. U.S. Patent Appl. Publication No. 2002/0090725 A1 describes biological materials and biocompatible materials to be electroprocessed, as well as solvents that can be used for these materials. U.S. Patent Appl. Publication No. 2002/0100725 A1 describes, besides the solvents and materials used for nanofibers, the difficulties of large scale production of the nanofibers including the volatilization of solvents in small spaces. Huang et al. give a partial list of materials/solvents that can be used to produce the nanofibers.

[0013] Despite the advances in the art, the application of nano-fibers has been limited due to the narrow range of processing conditions over which the nano-fibers can be produced. Excursions either stop the electrospinning process or produce particles of electrosprayed material.

SUMMARY OF THE INVENTION

[0014] One object of the present invention is to provide an apparatus and a method for improving the process window for production of electrospun fibers.

[0015] Another object is to provide an apparatus and a method which produce nano-fibers in a controlled gaseous environment.

[0016] Yet another object of the present invention is to promote the electrospinning process by introducing charge carriers into the gaseous environment into which the fibers are electrospun.

[0017] Still another object of the present invention is to promote the electrospinning process by controlling the drying rate of the electrospun fibers by controlling the solvent pressure in the gaseous environment into which the fibers are electrospun.

[0018] Thus, according to one aspect of the present invention, there is provided a novel apparatus for producing fibers. The apparatus includes an extrusion element configured to electrospin a substance from which the fibers are to be composed by an electric field extraction of the substance from a tip of the extrusion element. The apparatus includes a collector disposed from the extrusion element and configured to collect the fibers, a chamber enclosing the collector and the extrusion element, and a control mechanism configured to control a gaseous environment in which the fibers are to be electrospun.

[0019] According to a second aspect of the present invention, there is provided a novel method for producing fibers. The method includes providing a substance from which the fibers are to be composed to a tip of an extrusion element, applying an electric field to the extrusion element in a direction of the tip, controlling a gaseous environment about where the fibers are to be electrospun, and electrospinning the substance from the tip of the extrusion element by an electric field extraction of the substance from the tip into the controlled gaseous environment.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] A more complete appreciation of the present invention and many attendant advantages thereof will be readily obtained as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings, wherein:

[0021] FIG. **1** is a schematic illustration of a conventional electrospinning apparatus;

[0022] FIG. **2** is a schematic illustration of an electrospinning apparatus according to one embodiment the present invention in which a chamber encloses a spray head and collector of the electrospinning apparatus;

[0023] FIG. **3** is a schematic illustration of an electrospinning apparatus according to one embodiment the present invention having a collecting mechanism as the collector of the electrospinning apparatus;

[0024] FIG. **4** is a schematic illustration of an electrospinning apparatus according to one embodiment of the present invention including an ion generator which generate ions for injection into a region where the fibers are being electrospun;

[0025] FIG. **5** is a schematic illustration of an electrospinning apparatus according to one embodiment of the present invention including a liquid pool; and

[0026] FIG. **6** is a flowchart depicting a method of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0027] Referring now to the drawings, wherein like reference numerals designate identical, or corresponding parts throughout the several views, and more particularly to FIG. **2**, FIG. **2** is a schematic illustration of an electrospinning apparatus **21** according to one embodiment the present invention in which a chamber **22** surrounds an electrospinning extrusion element **24**. As such, the extrusion element **24** is configured to electrospin a substance from which fibers are composed to form fibers **26**. The electrospinning apparatus **21** includes a collector **28** disposed from the extrusion element **24** and configured to collect the fibers. The chamber **22** about the extrusion element **24** is configured to inject charge carriers, such as for example electronegative gases, ions, and/or radioisotopes, into a gaseous environment in which the fibers **26** are electrospun. As to be discussed later, injection of the charge carriers into the gaseous environment in which the fibers **26** are electrospun broadens the process parameter space in which the fibers can be electrospun in terms of the concentrations of solutions and applied voltages utilized.

[0028] The extrusion element **24** communicates with a reservoir supply **30** containing the electrospray medium such as for example the above-noted polymer solution **14**. The electrospray medium of the present invention includes polymer solutions and/or melts known in the art for the extrusion of fibers including extrusions of nanofiber materials. Indeed, polymers and solvents suitable for the present invention include for example polystyrene in dimethylformamide or toluene, polycaprolactone in dimethylformamide/methylene chloride mixture (20/80 w/w), poly(ethyleneoxide) in distilled water, poly(acrylic acid) in distilled water, poly(methyl methacrylate) PMMA in acetone, cellulose acetate in acetone, polyacrylonitrile in dimethylformamide, polylactide in dichloromethane or dimethylformamide, and poly(vinylalcohol) in distilled water. Thus, in general, suitable solvents for the present invention include both organic and inorganic solvents in which polymers can be dissolved.

[0029] The electrospray medium, upon extrusion from the extrusion element **24**, is guided along a direction of an electric field **32** directed toward the collector **28**. A pump (not shown) maintains a flow rate of the electrospray substance to the extrusion element **24** at a desired value depending on capillary diameter and length of the extrusion element

24, and depending on a viscosity of the electrospray substance. A filter can be used to filter out impurities and/or particles having a dimension larger than a predetermined dimension of the inner diameter of the extrusion element **24**. The flow rate through the extrusion element **24** should be balanced with the electric field strength of the electric field **32** so that a droplet shape exiting a tip of the extrusion element **24** is maintained constant. Using the Hagen-Poiseuille law, for example, a pressure drop through a capillary having an inner diameter of 100 μm and a length of about 1 cm is approximately 100-700 kPa for a flow rate of 1 ml/hr depending somewhat on the exact value of viscosity of the electrospray medium.

[0030] A high voltage source **34** is provided to maintain the extrusion element **24** at a high voltage. The collector **28** is placed preferably 1 to 100 cm away from the tip of the extrusion element **24**. The collector **28** can be a plate or a screen. Typically, an electric field strength between 2,000 and 400,000 V/m is established by the high voltage source **34**. The high voltage source **34** is preferably a DC source, such as for example Bertan Model 105-20R (Bertan, Valhalla, N.Y.) or for example Gamma High Voltage Research Model ES30P (Gamma High Voltage Research Inc., Ormond Beach, Fla.). Typically, the collector **28** is grounded, and the fibers **26** produced by extrospinning from the extrusion elements **24** are directed by the electric field **32** toward the collector **28**. As schematically shown in FIG. **3**, the electrospun fibers **26** can be collected by a collecting mechanism **40** such as for example a conveyor belt. The collecting mechanism **40** can transfer the collected fibers to a removal station (not shown) where the electrospinning fibers are removed before the conveyor belt returns to collect more fibers. The collecting mechanism **40** can be a mesh, a rotating drum, or a foil besides the afore-mentioned conveyor belt. In another embodiment of the present invention, the electrospun fibers are deposited on a stationary collecting mechanism, accumulate thereon, and are subsequently removed after a batch process.

[0031] The distance between the tip of the extrusion element **24** and the collector **28** is determined based on a balance of a few factors such as for example a time for the solvent evaporation rate, the electric field strength, and a distance/time sufficient for a reduction of the fiber diameter. These factors and their determination are similar in the present invention to those in conventional electrospinning. However, the present inventors have discovered that a rapid evaporation of the solvents results in larger than nm-size fiber diameters.

[0032] Further, the differences in fluid properties of the polymer solutions utilized in electrospraying and those utilized in electrospraying, such as for example differences in conductivity, viscosity and surface tension, result in quite different gaseous environments about electrospraying and electrospinning apparatuses. For example, in the electrospray process, a fluid jet is expelled from a capillary at high DC potential and immediately breaks into droplets. The droplets may shatter when the evaporation causes the force of the surface charge to exceed the force of the surface tension (Rayleigh limit). Electrosprayed droplets or droplet residues migrate to a collection (i.e., typically grounded) surface by electrostatic attraction. Meanwhile, in electrospinning, the highly viscous fluid utilized is pulled (i.e., extracted) as a continuous unit in an intact jet because of the inter-fluid attraction, and is stretched as the pulled fiber dries and undergoes the instabilities described below. The drying and expulsion process reduces the fiber diameter by at least 1000 times. In electrospinning, the present invention recognizes that the complexities of the process are influenced by the gaseous atmospheres surrounding the pulled fiber, especially when polymer solutions with relatively low viscosities and solids content are to be used to make nanofibers (i.e., less than 100 nm in diameter).

[0033] With reference to FIG. **2**, the electric field **32** pulls the substance from which the fiber is to be composed as a filament or liquid jet **42** of fluid from the tip of the extrusion element **24**. A supply of the substance to each extrusion element **24** is preferably balanced with the electric field strength responsible for extracting the substance from which the fibers are to be composed so that a droplet shape exiting the extrusion element **24** is maintained constant.

[0034] A distinctive feature observable at the tip is referred to in the art as a Taylor's cone **44**. As the liquid jet **42** dries, the charge per specific area increases. Often within 2 or 3 centimeters from the tip of the capillary, the drying liquid jet becomes electrically unstable in region referred to as a Rayleigh instability region **46**. The liquid jet **42** while continuing to dry fluctuates rapidly stretching the fiber **26** to reduce the charge density as a function of the surface area on the fiber.

[0035] In one embodiment of the present invention, the electrical properties of the gaseous environment about the chamber **22** are controlled to improve the process parameter space for electrospinning. For example, electronegative gases impact the electrospinning process. While carbon dioxide has been utilized in electrospraying to generate particles and droplets of material, no effects prior to the present work have been shown for the utilization of electronegative gases in an electrospinning environment. Indeed, the nature of electrospinning in which liberal solvent evaporation occurs in the environment about the extrusion elements and especially at the liquid droplet at the tip of the extrusion element would suggest that the addition of electronegative gasses would not influence the properties of the spun fibers. However, the present inventors have discovered that the introduction into the gaseous environment of electronegative gases (e.g., carbon dioxide, sulfur hexafluoride, and freons, and gas mixtures including vapor concentration of solvents) improves the parameter space available for electrospinning fibers. Suitable electronegative gases for the present invention include CO_2, CO, SF_6, CF_4, N_2O, CCl_4, CCl_3F, CCl_2F_2 and other halogenerated gases.

[0036] By modifying the electrical properties of the gaseous environment about the extrusion element **24**, the present invention permits increases in the applied voltage and improved pulling of the liquid jet **42** from the tip of the extrusion element **24**. In particular, injection of electronegative gases appears to reduce the onset of a corona discharge (which would disrupt the electrospinning process) around the extrusion element tip, thus permitting operation at higher voltages enhancing the electrostatic force. Further, according to the present invention, injection of electronegative gases and as well as charge carriers reduces the probability of bleeding-off charge in the Rayleigh instability region **46**, thereby enhancing the stretching and drawing of the fiber under the processing conditions.

[0037] As illustrative of the electrospinning process of the present invention, the following non-limiting example is given to illustrate selection of the polymer, solvent, a gap distance between a tip of the extrusion element and the collection surface, solvent pump rate, and addition of electronegative gases:

[0038] a polystyrene solution of a molecular weight of 350 kg/mol,

[0039] a solvent of dimethylformamide DMF,

[0040] an extrusion element tip diameter of 1000 μm,

[0041] an Al plate collector,

[0042] ~0.5 ml/hr pump rate providing the polymer solution,

[0043] an electronegative gas flow of CO_2 at 8 lpm,

[0044] an electric field strength of 2 KV/cm, and

[0045] a gap distance between the tip of the extrusion element and the collector of 17.5 cm.

[0046] With these conditions as a baseline example, a decreased fiber size can be obtained according to the present invention, by increasing the molecular weight of the polymer solution to 1000 kg/mol, and/or introducing a more electronegative gas (such as for example Freon), and/or increasing gas flowrate to for example 20 lpm, and/or decreasing tip diameter to 150 μm (e.g. as with a Teflon tip). With most polymer solutions utilized in the present invention, the presence of CO_2 gas allowed electrospinning over a wide range of applied voltages and solution concentrations compared to spinning in presence of nitrogen gas. Thus, the gaseous environment surrounding the extrusion elements during electrospinning influences the quality of the fibers produced.

[0047] Further, blending gases with different electrical properties can be used to improve the processing window.

[0048] One example of a blended gas includes CO_2 (at 4 lpm) blended with Argon (at 4 lpm). Other examples of blended gases suitable for the present invention include, but are not limited to, CO_2 (4 lpm) with Freon (4 lpm), CO_2 (4 lpm) with Nitrogen (4 lpm), CO_2 (4 lpm) with Air (4 lpm), CO_2 (7 lpm) with Argon (1 lpm), CO_2 (1 lpm) with Argon (7 lpm).

[0049] As shown in FIG. **2**, electronegative gases can be introduced by a port **36** which introduces gas by a flow controller **37** into the chamber **22** through a shroud **38** about the extrusion element **24**. The port **36** is connected to an external gas source (not shown), and maintains a prescribed gas flow into the chamber **22**. The external gas sources can be pure electronegative gases, mixtures thereof, or blended with other gases such as inert gases. The chamber **22** can contain the extrusion element **24**, the collector **28**, and other parts of the apparatus described in FIG. **2** are placed, and can have a vent to exhaust the gas and other effluents from the chamber **22**.

[0050] The present inventors have also discovered that the electrospinning process is affected by introducing charge carriers such as positive or negative ions, and energetic particles. FIG. **4** shows the presence of an ion generator **48** configured to generate ions for injection into the Rayleigh instability region **46**. Extraction elements **49** as shown in FIG. **4** are used to control a rate of extraction and thus injection of ions into the gaseous environment in which the electrospinning is occurring. For example, in one embodiment to introduce ionic species, a corona discharge is used as the ion generator **48**, and the ions generated in the corona discharge (preferably negative ions) would injected into the chamber **22**.

[0051] Similarly, the present inventors have discovered that exposure of the chamber **22** to a radioisotope, such as for example Po 210 (a 500 microcurie source) available from NRD LLC., Grand Island, N.Y. 14072, affects the electrospinning process and in certain circumstances can even stop the electrospinning process. Accordingly, in one embodiment of the present invention as shown in FIG. **4**, the chamber **22** includes a window **23*a*** having a shutter **23*b***. The window **23*a*** preferably made of a low mass number material such as for example teflon or kapton which will transmit energetic particles such as from radioisotopes generated in the radioisotope source **23*c*** into the Rayleish instability region **46**. The shutter **23*b*** is composed of an energetic particle absorbing material, and in one embodiment is a variable vane shutter whose control determines an exposure of the chamber **22** to a flux of the energetic particles.

[0052] Further, the present inventors have discovered that retarding the drying rate is advantageous because the longer the residence time of the fiber in the region of instability the lower the electric field strength can be while still prolonging the stretching, and consequently improving the processing space for production of nanofibers. The height of the chamber **22** and the separation distance between a tip of the extrusion element **24** and the collector **28** are, according to the present invention, designed to be compatible with the drying rate of the fiber. The drying rate for an electrospun fiber during the electrospinning process can be adjusted by altering the partial pressure of the liquid vapor in the gas surrounding the fiber.

[0053] For instance, when a solvent such as methylene chloride or a blend of solvents is used to dissolve the polymer, the rate of evaporation of the solvent will depend on the vapor pressure gradient between the fiber and the surrounding gas. The rate of evaporation of the solvent can be controlled by altering the concentration of a solvent vapor in the gas. The rate of evaporation also affects the Rayleigh instability. Additionally, the electrical properties of the solvent (in the gas phase) influence the electrospinning process. As shown in FIG. **5**, by maintaining a liquid pool **50** at the bottom of the chamber **22**, the amount of solvent vapor present in the ambient about the electrospinning environment can be controlled by altering a temperature of the chamber **22** and/or the solvent pool **50**, thus controlling the partial pressure of solvent in the gaseous ambient in the electrospinning environment. Examples of temperature ranges and solvents suitable for the present invention are discussed below.

[0054] For temperature ranges from ambient to approximately 10° C. below the boiling point of the solvent, the following solvents are suitable:

[0055] Dimethylformamide: ambient to ~143° C.

[0056] Methylene chloride: ambient to ~30° C.

[0057] Water: ambient to ~100° C.

[0058] Acetone: ambient to ~46° C.

[0059] Solvent partial pressures can vary from near zero to saturation vapor pressure. Since saturation vapor pressure increases with temperature, higher partial pressures can be obtained at higher temperatures. Quantities of solvent in the pool vary with the size of the chamber and vary with the removal rate by the vent stream. For a chamber of about 35 liters, a solvent pool of a volume of approximately 200 ml can be used. Hence a temperature controller **51** as shown in FIG. **5** can control the temperature of the liquid in the vapor pool **50** and thus control the vapor pressure of the solvent in the chamber **22**.

[0060] Hence, the present invention utilizes a variety of control mechanisms to control the gaseous environment in which the fibers are being electrospun for example to alter the electrical resistance of the environment or to control the drying rate of the electrospun fibers in the gaseous environment. The various control mechanisms include for example the afore-mentioned temperature controllers to control a temperature of a liquid in a vapor pool exposed to the gaseous environment, flow controllers to control a flow rate of an electronegative gas into the gaseous environment, extraction elements configured to control an injection rate of ions introduced into the gaseous environment, and shutters to control a flux of energetic particles into the gaseous environment. Other mechanisms known in the art for controlling the introduction of such species into a gaseous environment would also be suitable for the present invention.

[0061] While the effect of controlling the environment about an electrospinning extrusion element has been illustrated by reference to FIGS. **2-4**, control of the environment is also important in other electrospinning apparatuses, such as for example the apparatuses shown in related provisional applications U.S. Ser. No. ______, filed on ______, entitled "Electrospinning of Polymer Nanofibers Using a Rotating Spray Head," Attorney Docket No. 241015US-2025-2025-20, and U.S. Ser. No. ______, filed on _______, entitled "Electrospraying/electrospinning Apparatus and Method," Attorney Docket No. 241013US-2025-2025-20.

[0062] Additionally, control of the gaseous environment in one embodiment of the present invention while improving the process window for electrospinning also homogenizes the gaseous environment in which the fibers are being drawn and dried. As such, the present invention provides apparatuses and methods by which fibers (and especially nanofibers) can more uniformly develop and thus be produced with a more uniform diameter size and distribution than that which would be expected in conventional electrospinning equipment with uncontrolled atmospheres.

[0063] Thus, as depicted in FIG. **6**, one method of the present invention includes in step **602** providing a substance from which the fibers are to be composed to a tip of an extrusion element of a spray head. The method includes in step **604** applying an electric field to the extrusion element in a direction of the tip. The method includes in step **606** controlling a gaseous environment about where the fibers are to be electrospun. The method includes in step **608** electrospinning the substance from the tip of the extrusion element by an electric field extraction of the substance from the tip into the controlled gaseous environment.

[0064] In step **606**, at least one of an electronegative gas, ions, and energetic particles are injected into the gaseous environment. Alternatively or in addition, electronegative gases such as CO_2, CO, SF_6, CF_4, N_2O, CCl_4, CCl_3F, and $C_2Cl_2F_2$, or mixtures thereof can be injected into the gaseous environment. When injecting ions, the ions can be generated in one region of the chamber **22** and injected into the gaseous environment. The injected ions are preferably injected into a Rayleigh instability region downstream from the extrusion element.

[0065] Further in step **606**, the gaseous environment about where the fibers are to be electrospun can be controlled by introducing a vapor of a solvent into the chamber. The vapor can be supplied by exposing the chamber to a vapor pool of a liquid, including for example vapor pools of dimethyl formamide, methylene chloride, acetone, and water.

[0066] In step **608**, the method preferably electrospins the substance in an electric field strength of 2,000-400,000 V/m. The electrospinning can produce either fibers or nanofibers.

[0067] The fibers and nanofibers produced by the present invention include, but are not limited to, acrylonitrile/butadiene copolymer, cellulose, cellulose acetate, chitosan, collagen, DNA, fibrinogen, fibronectin, nylon, poly(acrylic acid), poly(chloro styrene), poly(dimethyl siloxane), poly(ether imide), poly(ether sulfone), poly(ethyl acrylate), poly(ethyl vinyl acetate), poly(ethyl-co-vinyl acetate), poly(ethylene oxide), poly(ethylene terephthalate), poly(lactic acid-co-glycolic acid), poly(methacrylic acid) salt, poly(methyl methacrylate), poly(methyl styrene), poly(styrene sulfonic acid) salt, poly(styrene sulfonyl fluoride), poly(styrene-co-acrylonitrile), poly(styrene-co-butadiene), poly(styrene-co-divinyl benzene), poly(vinyl acetate), poly(vinyl alcohol), poly(vinyl chloride), poly(vinylidene fluoride), polyacrylamide, polyacrylonitrile, polyamide, polyaniline, polybenzimidazole, polycaprolactone, polycarbonate, poly(dimethylsiloxane-co-polyethyleneoxide), poly(etheretherketone), polyethylene, polyethyleneimine, polyimide, polyisoprene, polylactide, polypropylene, polystyrene, polysulfone, polyurethane, poly(vinylpyrrolidone), proteins, SEBS copolymer, silk, and styrene/isoprene copolymer.

[0068] Additionally, polymer blends can also be produced as long as the two or more polymers are soluble in a common solvent. A few examples would be: poly(vinylidene fluoride)-blend-poly(methyl methacrylate), polystyrene-blend-poly(vinylmethylether), poly(methyl methacrylate)-blend-poly(ethyleneoxide), poly(hydroxypropyl methacrylate)-blend poly(vinylpyrrolidone), poly(hydroxybutyrate)-blend-poly(ethylene oxide), protein blend-polyethyleneoxide, polylactide-blend-polyvinylpyrrolidone, polystyrene-blend-polyester, polyester-blend-poly(hyroxyethyl methacrylate), poly(ethylene oxide)-blend poly(methyl methacrylate), poly(hydroxystyrene)-blend-poly(ethylene oxide)).

[0069] By post treatment annealing, carbon fibers can be obtained from the electrospun polymer fibers.

[0070] Numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

1. An apparatus for producing fibers, comprising:

an extrusion element having a tip, and configured to electrospin a substance from which the fibers are to be composed by an electric field extraction of the substance from the tip of the extrusion element;

a collector disposed from the extrusion element and configured to collect the fibers;

a chamber enclosing the collector and the extrusion element; and

a control mechanism configured to control a gaseous environment in which the fibers are to be electrospun.

2. The apparatus of claim 1, wherein the control mechanism is configured to control a drying rate of electrospun fibers.

3. The apparatus of claim 2, further comprising:

a vapor pool containing at least one of an inorganic and organic liquid; and

said control mechanism comprises a temperature controller configured to control a temperature of the liquid in the vapor pool.

4. The apparatus of claim 3, wherein the liquid comprises at least one of dimethyl formamide, methylene chloride, acetone, and water.

5. The apparatus of claim 4, wherein the temperature controller is configured to control a temperature of the liquid to provide a predetermined vapor pressure of the liquid to the gaseous environment.

6. The apparatus of claim 5, wherein the temperature controller is configured to control the temperature from an ambient temperature to 10° C. below a boiling point of the liquid.

7. The apparatus of claim 1, wherein the controller is configured to control an injection of species altering an electrical resistance of the gaseous environment in which the fibers are electrospun.

8. The apparatus of claim 7, wherein the control mechanism is configured to control the injection at least one of an electronegative gas, a vapor, ions, and energetic particles.

9. The apparatus of claim 8, wherein the chamber is connected to a supply of the electronegative gas.

10. The apparatus of claim 9, wherein the control mechanism comprises a flow controller configured to control a flow rate of the electronegative gas into the chamber.

11. The apparatus of claim 9, wherein the chamber is connected to a supply of at least CO_2, CO, SF_6, CF_4, N_2O, CCl_4, CCl_3F, and $C_2Cl_2F_2$.

12. The apparatus of claim 8, wherein the chamber comprises:

a shroud about said extrusion element, connected to a supply of the electronegative gas.

13. The apparatus of claim 12, wherein the control mechanism comprises a flow controller configured to control a flow rate of the electronegative gas into the shroud.

14. The apparatus of claim 12, wherein the shroud is connected to a supply of at least CO_2, CO, SF_6, CF_4, N_2O, CCl_4, CCl_3F, and $C_2Cl_2F_2$.

15. The apparatus of claim 8, further comprising:

a radioisotope source of the energetic particles,

the control mechanism comprises a shutter configured to control an exposure of the chamber to the radioisotope source, said shutter comprising an energetic particle absorbing material.

16. The apparatus of claim 8, further comprising:

an ion generator configured to generate the ions; and

the control mechanism comprising extraction elements configured to control a rate of extraction of the ions from the ion generator into the gaseous environment.

17. The apparatus of claim 16, wherein the ion generator is configured to inject ions into a Rayleigh instability region in which the fibers are electrospun.

18. The apparatus of claim 1, wherein the chamber is connected to a supply of gas.

19. The apparatus of claim 18, further comprising:

a flow controller configured to control a flow rate of the gas into the chamber.

20. The apparatus of claim 1, wherein the chamber comprises:

a shroud about the extrusion element, connected to a supply of gas.

21. The apparatus of claim 20, wherein the control mechanism comprises a flow controller configured to control a flow rate of the gas into the shroud.

22. The apparatus of claim 1, wherein the extrusion element comprises a plurality of extrusion elements.

23. The apparatus of claim 1, wherein the collector comprises at least one of a plate and a screen.

24. The apparatus of claim 1, wherein the collector comprises an electrical ground.

25. The apparatus of claim 1, wherein the collector is disposed 1-100 cm from said extrusion element.

26. The apparatus of claim 1, further comprising:

a power source electrically connected across said extrusion element and said collector.

27. The apparatus of claim 26, wherein the power source is configured to generate an electric field with a strength of 2,000-400,000 V/m between said extrusion element and said collector.

28. The apparatus of claim 1, wherein the extrusion element has an inner dimension in a range of 50-250 μm.

29. The apparatus of claim 1, wherein the extrusion element has an interior cross sectional area of 1,900-50,000 μm^2.

30. An apparatus for producing fibers, comprising:

an extrusion element having a tip, and configured to electrospin a substance from which the fibers are to be composed by an electric field extraction of the substance from the tip of the extrusion element;

a collector disposed from the extrusion element and configured to collect the fibers; and

means for injecting a species to alter an electrical resistance of a gaseous environment in which the fibers are electrospun.

31. The apparatus of claim 30, wherein the means for injecting comprises:

means for injecting at least one of an electronegative gas, a vapor, ions, and energetic particles.

32. The apparatus of claim 31, wherein said means for injecting an electronegative gas comprises:

a chamber about said extrusion element and configured to introduce the electronegative gas into the chamber.

33. The apparatus of claim 31, wherein said means for injecting comprises:

an ion generator configured to generate the ions.

34. The apparatus of claim 33, wherein the ion generator is configured to inject ions into a Rayleigh instability region in which the fibers are electrospun.

35. An apparatus for producing fibers, comprising:

an extrusion element having a tip, and configured to electrospin a substance from which the fibers are to be composed by an electric field extraction of the substance from a tip of the extrusion element;

a collector disposed from the extrusion element and configured to collect the fibers; and

means for controlling a drying rate of electrospun fibers in a gaseous environment in which the fibers are electrospun.

36. The apparatus of claim 35, wherein the means for controlling comprises:

a temperature controller configured to control a temperature of at least one of an inorganic and organic liquid in a vapor pool exposed to the gaseous environment.

37. The apparatus of claim 36, wherein the liquid comprises at least one of dimethyl formamide, methylene chloride, acetone, and water.

38. The apparatus of claim 36, wherein the temperature controller is configured to control the temperature from an ambient temperature to 10° C. below a boiling point of the liquid in the vapor pool.

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