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(54) Title: ELECTRO-SPINNING METHODS AND USES THEREOF

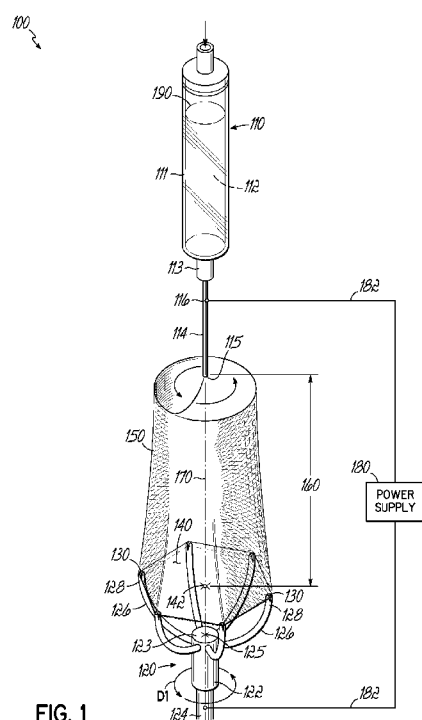


FIG. 1

(57) Abstract: A method of electrospinning a plurality of fibers (150) is provided. The method includes providing at least one collector (120) and a single extruder (110). The extruder (110) includes a channel (112) housing a precursor liquid (190). The method includes dispensing the precursor liquid (190) from the extruder (110), and in response to an electric field, collecting fibers (150) formed from the precursor liquid (190) by a collector (120) to form a hollow casing (210) of fibers (150).

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ELECTRO-SPINNING METHODS AND USES THEREOF

Government Rights

[0001] This invention was made with government support under government/contract number 1833345 awarded by the National Science Foundation. The U.S. government has certain rights in the invention.

Cross-Reference to Related Application

[0002] This application claims the benefit of U.S. Provisional Application Serial No. 63/297,026 filed on January 6, 2022. The disclosure of the above-listed Provisional Application is hereby incorporated by reference in its entirety.

Field of the Invention

[0003] The invention is directed to methods for forming electro-spun fibers using various starting materials. The electro-spun fibers, mats and randomly oriented fiber masses produced therefrom can be used in a range of applications, for industrial utility as well as for biomedical purposes.

Background of the Invention

[0004] Electro-spinning is a voltage-driven fabrication process governed by specific electro hydrodynamic phenomena wherein small diameter fibers are produced from a polymer - containing precursor liquid. The starting materials for a simple setup to practice this technique include a liquid typically retained in a reservoir such as a syringe, the syringe then being tipped with a blunt needle. Alternatively, the reservoir for dispensing the liquid can be needleless, utilizing a different aperture or apertures through which the liquid exits. Additional components include a pump, a high voltage power source, and a collector. An electric field is established between the reservoir/aperture and the collector by applying a specified voltage to the reservoir/aperture. The collector remains at ground potential. A pump which is connected to the reservoir is engaged to initiate a flow of precursor liquid at a constant rate. Upon applying a voltage to the appropriate components, an

electrostatic charge accumulates at the surface of the liquid as it begins to exit the reservoir. At the time when the electrostatic repulsion is larger than the surface tension of the liquid, the liquid meniscus forms into a conically shaped structure known as a Taylor Cone. Upon formation of the Taylor Cone, a charged liquid jet exits the needle tip or aperture and is conveyed towards the collector by electrostatic forces. The collector can be a flat plate, for example.

[0005] The liquid can be a mixture of a solid or semi-solid polymeric material with a solvent. It can also be a material which is normally a solid at room temperature, but is heated to a point above the melting point which would exit the needle tip or aperture as a liquid. The resulting fiber can be arranged in a uniform, linear fashion onto, for example, a rotating drum. Also, the fiber can take the form ultimately of a nonwoven fiber mat as a result of electrostatic forces causing the fiber to exit in a random whipping motion before reaching the collector.

[0006] The electro-spun fiber or mat can be used in a range of industrial and biomechanical applications. The diameters of the fibers are typically very small, on the order of between tens of nanometers to a few micrometers. Fibers of varying compositions can be prepared, such as those derived from polymeric starting materials. Also, for example, fibers can be formed from ceramic powders combined with a polymer material. As desired, a ceramic fiber with no residual organic component can be formed beginning with a blend of ceramic material with a polymer forming a fiber, then burning away the polymer component via a thermal treatment.

[0007] Typically, a high electric field is required to generate the electrostatic charge which is applied ultimately to the liquid. The thin jet of liquid which erupts from the Taylor Cone travels to the grounded electrode undergoing stretching and whipping motions when allowed to form a random mat. A more uniform electric field distribution produces finer and more homogeneous fibers. The electric field thus plays a very important role in the electro-spinning process and the final physical form of the fibers.

[0008] Though very fine diameter fibers are capable of being produced using electro-spinning, as well as random orientation mats, limitations attributed to the electric field distribution in the electro-spinning process affect the resultant nano fiber morphology. Also, the need to manage the output from the reservoir source tends to limit the volume of fiber and thus the dimensions of the fiber produced by the electro-spinning process.

Summary of the Invention

[0009] Described herein is a process, components, and final fiber product produced from electrospinning which addresses throughput challenges associated with the use of the electrospinning process. Single crystal fibers are produced with high throughput, the fibers having diameters of about 1 nm to about 5 μm , or diameters of about 600 nm to about 800 nm. The fibers are produced via electrospinning are typically prepared for commercial any biomedical applications, and can be modified by one or more subsequent thermal treatments. The fibers so produced have particular utility as scaffolds for the growth of animal and plant tissue, among other applications.

[0010] The precursor liquid may include a mixture of a polymer component with typically one or more solvents. This blend of components facilitates the preparation of a uniform mixture prior to passing the mixture through a spinneret employed as a component of the electrospinning apparatus.

[0011] The spinneret can be a syringe with an open end through which a precursor liquid of ceramic material, polymer and solvent or solvents would pass. The precursor liquid alternately can contain a mixture of polymer (or polymers) with one or more solvents, or can contain a polymer only, as in a circumstance where a solid polymer is heated to above a melting point prior to extrusion. Or, the spinneret can be an alternative device with an exit aperture through which the precursor liquid can flow. The spinneret must be capable of receiving an electrical charge which is then conducted into the precursor liquid. It is the so-charged precursor liquid which, upon exiting an aperture of the spinneret, travels towards an oppositely charged or grounded collector and is collected. Depending on the design of the collector, the precursor liquid converts into fibers before reaching the collector surface. The fibers may collect on the surface in an aligned arrangement. Or, the produced fibers may take the form of a fibrous mass similar in macro-structure to a cotton ball, wherein the individual fibers are not aligned.

[0012] In the electrospinning process, individual fibers are not formed from the aperture until a critical electric field intensity is achieved, at which time a polymer jet is formed. Upon collection of the formed fibers, one or more thermal treatments can be administered, for example, in the matter of extruding a ceramic fiber, which enable the conversion of one crystal form of the ceramic component to another.

Also, the processing conditions are configured so as to evaporate any solvents used when a polymer is part of the precursor mixture prior to reaching the collector, and also to decompose any polymer employed as a carrier for the ceramic component.

[0013] The invention includes a collector component which allows for the creation of both a randomly oriented fiber portion on the collector, and an oriented fiber portion. The collector consists of a centered disk or hub from which extends multiple fingers or spindles which extend outwardly from the hub, and may then curve upwardly. The ends of the spindles contain one or more tines to facilitate catching and holding the fibers exiting the extruder. The hub of the collector is connected to a shaft which can be rotated, causing the individual fingers to rotate equidistantly from the aperture on the spinneret. When the critical electric field intensity is achieved between the spinneret tip and the rotating collector, fibers formed by the electrostatic forces cause the exiting fibers to accumulate generally uniformly over the entire external surface of the rotating collector. The result of this collection process is that the fibers which collect along the external curved perimeter of the individual fingers tend to be highly aligned with each other, while the fibers accumulating at the top of the collector, on a plane directly above the individual tines, are randomly oriented. The randomly oriented fibers have end use applications distinct from the applications for the highly oriented fibers, such as in producing textile products.

[0014] Typically, the critical electric field intensity, identified by voltage differential is in the range of about 50 V to about 100 kV. The flow rate of the pump which causes the precursor to exit the spinneret will have a pump rate of about 0.1 mL/hr to about 10 mL/hr. The speed of rotation of the collector hub will be about 100 rotations per minute to about 1100 rotations per minute.

Brief Description of the Figures

[0015] The accompanying drawings, which are incorporated in and constitute a part of this specification, illustrate embodiments of the invention and, together with the general description of the invention given above, and the detailed description given below, serve to describe the invention.

[0016] Fig. 1 is system for electrospinning and collecting fibers from a precursor liquid.

[0017] Fig. 2 is a perspective view of a hollow casing formed on a collector from fibers electro-spun from a precursor liquid.

[0018] Fig. 3 is a side partially-broken-away-in-cross-section view of a hollow casing of electro-spun fibers formed on a collector.

[0019] Fig. 4A is a top view of an electro-spun hollow casing on a collector.

[0020] Fig. 4B is a micrograph of a zoomed-in portion of the top view shown in Fig. 4A.

[0021] Fig. 4C is a micrograph of a zoomed-in portion of the top view shown in Fig. 4A.

[0022] Fig. 5A is a side view of an electro-spun hollow casing on a collector.

[0023] Fig. 5B is a micrograph of a zoomed-in portion of the top view shown in Fig. 5A.

[0024] Fig. 5C is a micrograph of a zoomed-in portion of the top view shown in Fig. 5A.

Detailed Description

[0025] Referring to Fig. 1, in its broader aspects, the invention is directed to a method of electro-spinning a plurality of fibers 150 wherein the method includes providing at least one collector 150 comprising a hub 122 which is configured to rotate in a circumferential direction, D1 and a plurality of spindles 126 extending from the hub 122, the plurality of spindles 126 each including a spindle end 128 being a portion of the spindle positioned furthest from the hub 122, each spindle end 128 forking into a plurality of tines 130, each tine having a tip 132 that together define a plane 140, the plane 140 including a point 142 colinear with an axis 170 axially running through a center 125 of a face 123 of the hub 122; providing a single extruder 110 including a tube 111 defining a channel 112, the channel 112 housing a precursor liquid 190, and a spinneret 114 extending axially from the tube 111 and including at least one aperture 115 located at the spinneret 114 end, the spinneret 114 in fluid communication with the channel 112 [we need to define spinnerets in the spec]; positioning the point 142 a distance 160 from the at least one aperture 115;

applying a voltage differential between the spinneret 114 and the at least one collector 120; dispensing the precursor liquid 190 from the spinneret 114 via at least one aperture 115; and rotating the at least one collector 120 in the circumferential direction D1 to collect fibers formed from the precursor liquid dispensed from the spinneret 114 via the at least one aperture 115, the collection of the fibers forming 150 a hollow casing 210 of fibers 150, wherein the hollow casing 210 comprises a top face 212 and a circumferential face 214.

[0026] The collector 120 which is rotating to receive the fibers 150 formed after the precursor liquid 190 exits the spinneret 114 is rotating at a speed between 100 rpm (rotations per minute) and 1100 rpm. Though other numbers of spindles 126 may be included as elements of the collector, a typical number of spindles 126 is six. To create sufficient voltage differential between the spinneret and the at least one collector to cause formation of the Taylor Cone and formation of a jet of precursor liquid which exits the extruder, the voltage potential is between 50 V and 100 kV. As an alternative method for electro-spinning fibers, the system may include a plurality of apertures with precursor liquid dispensed from each of those apertures. The precursor liquid, which ultimately forms fiber, is uniformly mixed by the time that liquid exits the spinneret. The precursor liquid may be a polymer in molten form, which will harden upon exiting the spinneret. Alternatively, the precursor liquid is a mixture of the fiber component and at least one solvent. For example, the fiber component may be a polymer, or alternatively a combination of a ceramic material, with a polymer, and one or more solvents. The precursor liquid upon exiting the spinneret will lose the solvent component to evaporation and hardened into a fibrous form by the time that material reaches the collector.

[0027] Representative fiber components of a polymeric nature include polyvinylpyrrolidone (PVP) cellulose acetate (CA), polyaniline, polypyrrole, polylactic acid (PLA), polyglycolide (PGA), and other natural and synthetic polymers.

[0028] Representative solvents used in connection with preparing the precursor liquid include ethanol, acetone, acetic acid, water, formaldehyde, dimethylformamide (DMF), and isopropanol.

[0029] The fibers produced in the electro-spinning process are generally randomly distributed, uniaxially aligned, or present in both forms. The fibers have an average diameter between 1 nanometer (nm) and 3 micrometers (μm).

[0030] The average length of the fibers 150 is in part a function of the distance 160 between the spinneret 114 from which the precursor liquid 190 exits, and the collector 120. The distance 160 between the spinneret 114 and the collector 120 is generally between 10 cm and 2 m. Dispensing rates for the precursor liquid 190 from the spinneret 114, per aperture 115, is generally 0.1 mL/hr and 10 mL/hr. It is possible to utilize multiple collectors 120 to receive the fibers 150. Depending on the location on the collector 120 whereupon the fibers 150 collect, the fibers 150 may be generally aligned with each other, or they will be more randomly oriented. Random orientation is defined herein as adjacent fibers being greater than 30° relative to each other in the collected bundle.

[0031] Using the collector 120 described herein, the generally aligned fibers 150 will be found along the circumferential face 214 (shown in Fig. 2) of the hollow casing 210 of fibers 150, and the randomly oriented fibers 150 will be found on the top face 212 of the hollow casing 210, see Figs. 4A – 4C. Generally aligned fibers 150 are defined herein as adjacent fibers being less than or equal to 30° relative to each other in the collected bundle.

[0032] With reference to the figures, Fig. 1 displays a system 100 including a system 100 including an arrangement of extruder 110 and collector 120 with precursor liquid 190 loaded into the extruder 110, which includes a tube 111 and a channel 112. In an embodiment, the precursor liquid 190 is forced from the extruder 110 via a pump (not shown). In another embodiment, the voltage differential between the spinneret and the collector elongates a droplet of the precursor liquid 190 located at the aperture 115 to form a jet of fiber 150.

[0033] Precursor liquid 190, with pressurization from the pump or elongation from the voltage differential, travels through the extruder coupling 113 and into the spinneret 114. A voltage differential is applied to the spinneret 114 from a power supply 180 and connected to the system 100 by wires 182, by means of clips on one side at the spinneret 114 and on the other at the shaft 124 coupled to the collector 120. With a sufficient voltage differential, precursor liquid 190 at the aperture 115 collects sufficient charge to form what is known as a Taylor Cone, from which a jet of liquid will pass from the aperture 115 in the direction of the collector 120.

[0034] To collect fibers originating from the precursor liquid 190 at the collector 120, the collector 120 is rotated at the hub 122 via the shaft 124 in a direction D1. The hub 122 is coupled to the shaft 124 and is attached to a motor (now shown).

During operation, the motor turns the shaft 124 which engages the hub 122 and rotates the collector 120. Spindles 126 extend from the hub 122 and terminate at ends 128 tipped with tines 130. Hub 122 terminates at its upper end at face 123. Above the center 125 of the face 123 is a point 142. The tines 130 at the ends 128 of spindles 126 terminate along a spatial plane 140 which generally runs perpendicular to the axis 170 including the aperture 115 and point 142.

[0035] With precursor liquid 190 being withdrawn from aperture 115, the collector 120 spinning, and the power supply 180 engaged to establish the voltage differential, fiber 150 is formed in the space between the aperture 115 and the plane 140 of the collector 120. The distance 160 between aperture 115 and plane 140 can be adjusted as preferred to ensure that fibers 150 have formed by the time they reach collector 120. Fig. 2 shows the collector 120 after a quantity of fiber 150 has been collected.

[0036] These fibers 150 which are formed and form a hollow casing 210. The fibers 150 are in two general orientations. These fibers 150 appearing on the circumferential face 214 of the casing 210 are generally aligned. See figures 5A, 5B, and 5C. The fibers 150 in figures 5B and 5C are shown as being generally aligned.

[0037] At the top of the casing 210 as shown in Figure 4A, above plane 140 are fibers 150 on the top face 212 of the casing 210. See also Figs. 2 and 3. The top face 212 fibers are shown in further detail in Figs. 4A, 4B, and 4C, wherein the fibers 150 are shown as being randomly oriented. The randomly oriented fibers 150 which include the top face 212 of the casing 210 can be collected in the general form of a fluffy mass which then is able to be used in a manner similar to that employed for use in textile processing natural and synthetic fibers such as cotton and rayon. These randomly oriented fibers 150 from the top face 212 then have applications in, for example smart textiles, wound dressings, and the like. The fibers 150 so produced can have electrical properties introduced into the fibers 150 by proper preparation of the precursor liquid 190, such as by the introduction of ceramic or other semiconductor producing compositions, which can be incorporated into a textile and used to provide sensing capability. For example, monitoring the medical condition of the wearer can be conducted.

[0038] Fibers 150 taken from the circumferential face 214 of casing 210 have applications in the formation of fibrous mats which in turn can be used to produce scaffolds with biomedical utility.

[0039] Depending on the composition of the precursor liquid, and the desired final use of the fiber 150, one or multiple thermal treatments can be performed on the fiber.

[0040] Various use applications can be performed with the fibers produced by the methods described herein, various of which are described below.

[0041] Electrospun fibers using cellulose acetate have utility as biomaterials. Cellulose acetate was derived from the acetylation of purified cellulose from cotton linters and wood pulp. A urinary bladder matrix (UBM) including of a cellular, multilayer arrangement with open porosity using micro and nano-size cellulose acetate fibers was prepared, the upper layers having open porosity, with a flat, dense bottom layer.

[0042] A scaffold of electrospun cellulose acetate was used in combination with explanted perfused arteries to function as an initial endothelial cell culture for evaluating the onset of angiogenesis.

[0043] Electrospun cellulose acetate operated as a scaffold with sintered hydroxyapatite at a 10% concentration by weight in the scaffold. The hydroxyapatite was present as globular and nanostructured nanograins. The precursor included of 10% hydroxyapatite with cellulose acetate in 100% acetone.

[0044] Fibrous mats of randomly oriented cellulose acetate were electrospun in a single step to produce an extremely hydrophobic mat. The apparent water contact angle was 154°.

[0045] Amyloid fibrils were embedded in electrospun cellulose acetate mats. The cellulose acetate had a molecular weight of 30,000, Daltons and the precursor was comprised of amyloid fibrils prepared from Bovine Insulin, acetic acid, and acetone, with the cellulose acetate. 2 mL of 15 wt% cellulose acetate solution was mixed with 1 mL amyloid fibrils. The electrospinning process was conducted at a 1 mL/hr flow rate, at a 7 cm working distance between extruder tip and collector, at a 20 kV voltage differential.

[0046] Electrospun foams based on a honeycomb cell structure were prepared from cellulose acetate and tungsten isopropoxide ($C_{18}H_{42}O_6W$) to produce self-supported tungsten oxide foams. The foams were synthesized using a combination of sol-gel, electrospinning and thermal oxidation processes. After electrospinning, the fibers were heat treated. Structural characterization of the processed foam-like monoliths confirmed a structure of cubic WO_3 nanoparticles in a continuous matrix.

Formation of self-assembly of composite nano-foams resulted from self- assembly of composite nano-fibers in the non-woven electrospun mats. The cubic WO_3 foams had a band gap of 2.53eV which demonstrated catalytic action when activated by visible light. The 3D scaffold upon external stimulation had catalytic properties.

[0047] Continuous single crystal nanowires of $\alpha\text{-MoO}_3$ were synthesized using a single step sol-gel processing and electrospinning. The nanowires obtained by this process had a high aspect ratio and defect free microstructures; this resulted in an order of magnitude improvement in gas detection sensitivity compared to sol-gel processed powder materials of the same diameter. While sol-gel-based sensors had a threshold of 50 ppb in detecting ammonia gas, the nanowire-based sensors may detect concentrations down to a few ppbs, which is more than sufficient to detect ammonia emitted from the body.

[0048] The process employed involved modifying the sols of metal oxides through their interactions with a carrier polymer. Upon being released from a metallic orifice under the force of an electrostatic field, which broke the surface tension of the liquid droplet of the solution mixture, the solvents evaporated in flight, leaving on the collector solid, continuous fibers, of a core-shell morphology-the core being the amorphous metal oxide. During calcination, and as the polymer was decomposing, a massive-type phase transformation converted the amorphous core to a continuous, single crystal, with nanoscale diameter and micro-scale length. Their dimensions were 10–15 nm in width and more than 2 μm long. The measured d-spacings for the nanowires were 6.944 Å, 3.9 Å, and 1.822 Å, corresponding to the (020), (100), and (230) planes of the orthorhombic $\alpha\text{-MoO}_3$ polymorph, respectively. The crystal belongs to the space-group Pbnm (62).

[0049] Continuous single crystal nanowire was formed using a hybrid polymer-metal oxide sol precursor and a single step process; The nanowire structures were of the thermodynamically stable $\alpha\text{-MoO}_3$ polymorph.

[0050] Electrospun foams based on a honeycomb cell structure were produced. Self-supported tungsten oxide (WO_3) foams were synthesized by a combination of sol-gel, electrospinning, and thermal oxidation processes. Mixtures of tungsten isopropoxide ($\text{C}_{18}\text{H}_{42}\text{O}_6\text{W}$)-based precursors and cellulose acetate (CA) were electrospun and subsequently heat-treated. Structural characterization of the as-processed foam-like monoliths confirmed that they consist of cubic WO_3

nanoparticles in a continuous matrix with open porosity. The formation of the self-supported nano-foams was a result of self-assembly of the composite nanofibers in the non-woven electrospun mats. The cubic WO_3 foams had a band-gap of 2.53eV and they demonstrated catalytic action when activated by visible-light.

[0051] A directed self-assembly process involved metal diffusion inside polymer nanofiber mats which were produced by means of electrospinning and the resulting formation of 3D macroscale mats. CuWO_4 is a metal oxide photocatalyst that utilizes longer light wavelength (band gap: 2.3eV) with high photostability in a neutral pH. CuWO_4 utilizes the $\bullet\text{OH}$ radicals formed through oxidation of water and hydroxyl ions by the electron-hole separation. These oxidizing species along with other reactive species, such as H_2O_2 are capable of degrading the polluting substance. The use of CuWO_4 along with CuO was found to give the best response for the decomposition of benzene in water under visible light. Tungstates of Cu changed the valence band with 3d orbitals, thus helping with absorption in the visible spectrum.

[0052] Cellulose acetate (MW $\sim$ 29,000) precursor solution (15 wt%) was prepared in 4:6 acetic acid: acetone mixture with 1 hour of ultrasonication. Electrospinning was carried out using a 10mL syringe with a 20 gauge stainless steel needle at applied voltage 19kV over a distance of 15 cm. The syringe pump was set to deliver the solution at a flow rate of 9.6 mL/h and all the spinning was carried out at ambient condition.

[0053] Sol gels for the solutions were made by adding water to 1.5g of tungsten isopropoxide ($\text{C}_{18}\text{H}_{42}\text{O}_6\text{W}$). The hydrolysis was done in a glove box in a controlled atmosphere and the resulting solution was mechanically agitated inside a glove box for 5 minutes. The solution was then ultrasonicated for 2 hours and then aged for 24 hours to ensure complete hydrolysis of the solution. 1.5g of WO_3 sol-gel was mixed with 3 mL of acetic acid and 3 mL of ethanol in a nitrogen-filled glovebox. Then the mixed solution was removed from the glovebox and added to 10% wt/vol polyvinylpyrrolidone (PVP) (Aldrich, MW $\sim$ 1,300,000) in ethanol, followed by $\sim$ 30 min of ultrasonic bath. The mixture was immediately loaded into a syringe fitted with a 22 gauge needle. The needle was connected to a high voltage power supply and positioned vertically 7 cm above a piece of copper mesh (TWP Inc., 200 mesh, wire dia. 51 μm) which acted as a ground electrode. The syringe pump was programmed to dispense 5 mL of PVP solution at a flow rate of 30 $\mu\text{L}/\text{min}$. Upon application of a high voltage (25 kV), a solution jet was formed at the needle tip. The solvent

evaporated during flight and a nonwoven mat of fibers was deposited on the Cu mesh. Thermal oxidation of the composite Cu mesh-nanofibers was carried out at 500 °C for 5h for complete calcination of PVP. The thermal oxidation process first drove CuO crystals into the PVP nanofibers, which already contain amorphous WO₃. As the thermal process evolved, crystals of WO₃ form between and among the CuO crystals. At about 500 °C, the PVP calcinated as it was determined by differential scanning calorimeter test results, leaving a network of "fibers" -similar to the CuO fibers. However these were made of crystals of WO₃ in contact with crystals of CuO. This network of metal oxide fibers, or "nanogrid," exhibited photocatalytic properties.

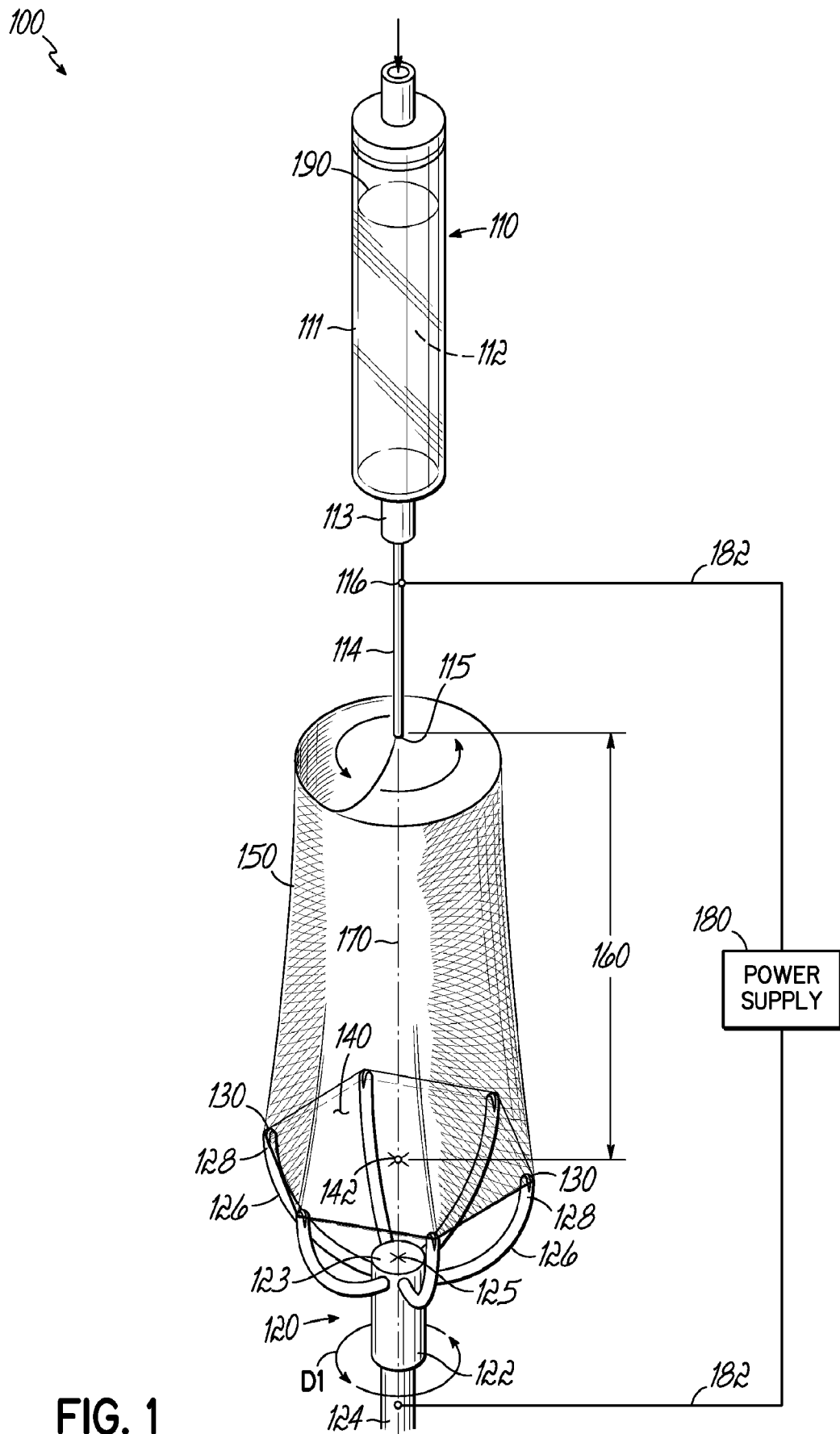
[0054] While the invention has been illustrated by the description of various embodiments thereof, and while the embodiments have been described in considerable detail, it is not intended to restrict or in any way limit the scope of the appended claims to such detail. Thus, the various features discussed herein may be used alone or in any combination. Additional advantages and modifications will readily appear to those skilled in the art. The invention in its broader aspects is therefore not limited to the specific details and illustrative examples shown and described. Accordingly, departures may be made from such details without departing from the scope of the general inventive concept.

WHAT IS CLAIMED IS:

1. A method of electrospinning a plurality of fibers, the method comprising:
providing at least one collector comprising:
a hub configured to rotate in a circumferential direction; and
a plurality of spindles extending from the hub, the plurality of spindles each including a spindle end being a portion of the spindle positioned furthest from the hub, each spindle end forking into a plurality of tines, each tine having a tip that together define a plane, the plane including a point colinear with an axis axially running through a center of a face of the hub;
providing a single extruder comprising:
a tube defining a channel, the channel housing a precursor liquid; and
a spinneret extending axially from the tube and including at least one aperture located at a spinneret end, the spinneret in fluid communication with the channel;
positioning the point a distance from the at least one aperture;
applying a voltage differential between the spinneret and the at least one collector;
dispensing the precursor liquid from the spinneret via the at least one aperture; and
rotating the at least one collector in the circumferential direction to collect the precursor liquid dispensed from the spinneret via the at least one aperture to form the fibers, the collection of the fibers forms a hollow casing of fibers, wherein the hollow casing comprises a top face and a circumferential face.
2. The method of claim 1, wherein rotating the at least one collector is performed at a rotational speed between 100 rotations per minute and 1100 rotations per minute.
3. The method of claim 1, wherein the plurality of spindles consists of six spindles.
4. The method of claim 1, wherein the voltage differential is between 50 V and 100 kV.

5. The method of claim 1, wherein the at least one aperture is a plurality of apertures and the precursor liquid is dispensed from each of the plurality of apertures.
6. The method of claim 1, wherein the at least one aperture is exactly one aperture.
7. The method of claim 1, wherein the precursor liquid comprises a solvent and a fiber component.
8. The method of claim 7, wherein the fiber component is selected from a group consisting of polyvinylpyrrolidone, cellulose acetate, polyaniline, polypyrrole, polylactic acid, and polyglycolide.
9. The method of claim 8, wherein the fiber component comprises the polyvinylpyrrolidone.
10. The method of claim 9, wherein the polyvinylpyrrolidone is present in the precursor liquid in a concentration of between 15 w/v and 20 w/v.
11. The method of claim 7, wherein the solvent is selected from a group consisting of ethanol, acetone, acetic acid, water, formaldehyde, and dimethylformamide.
12. The method of claim 1, wherein the fibers have an average diameter of between 1 nm and 5 microns.
13. The method of claim 1, wherein the distance is between 10 cm and 2 m.
14. The method of claim 1, wherein the fiber component is dispensed at a rate of between 0.1 mL/hr and 10 mL/hr.
15. The method of claim 1, wherein at least two collectors are provided.
16. The method of claim 1, wherein the fibers form a scaffold.

17. The method of claim 17, wherein the fibers comprise cellulose acetate.
18. The method of claim 1, wherein the hollow casing comprises the fibers generally aligned with each other along the circumferential face.
19. The method of claim 1, wherein the hollow casing comprises the fibers not generally aligned with each other along the top face.
20. The method of claim 1, wherein the spindles extend curvilinearly away from the hub.



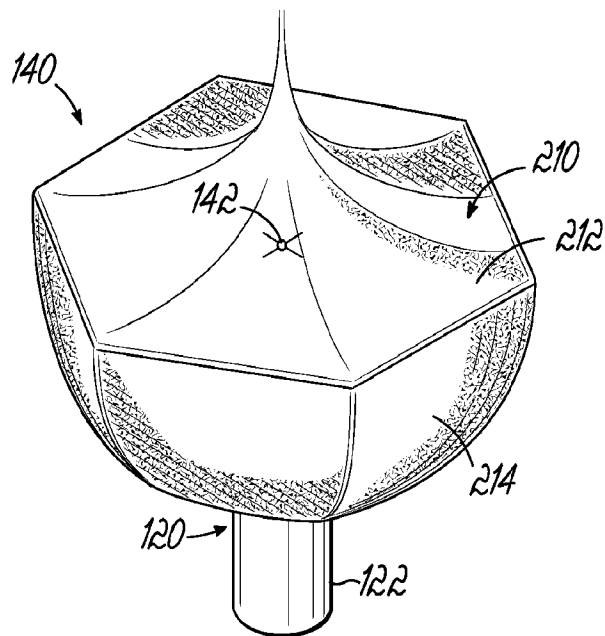


FIG. 2

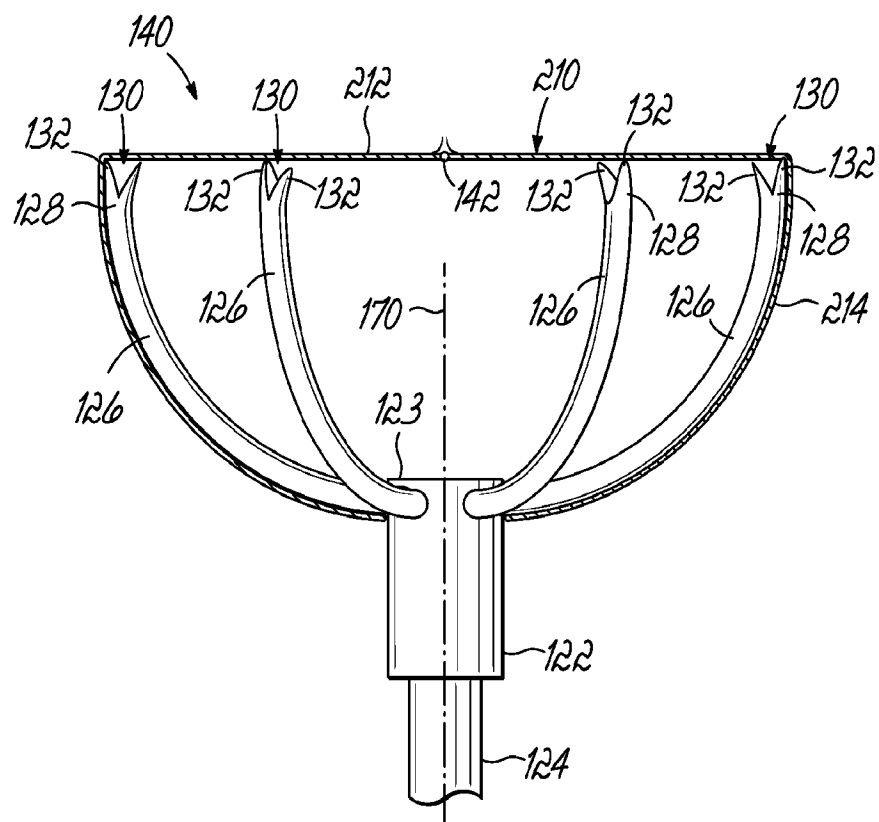
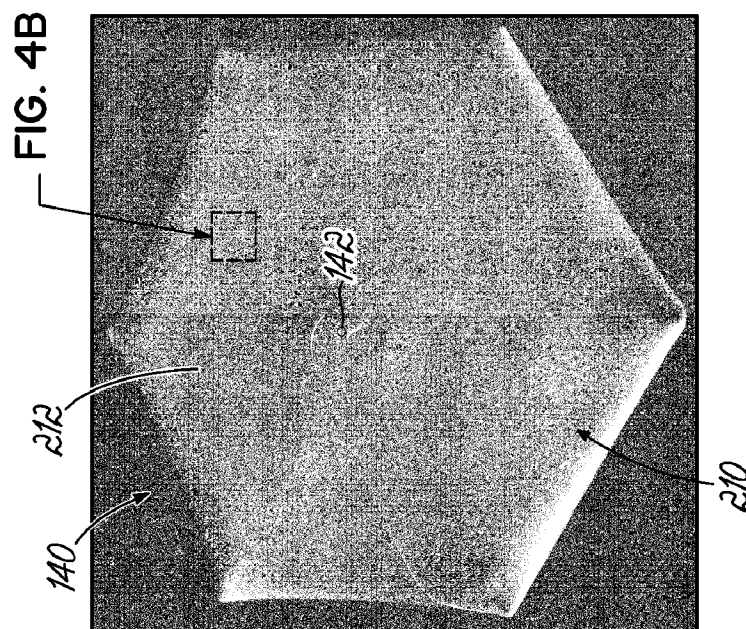
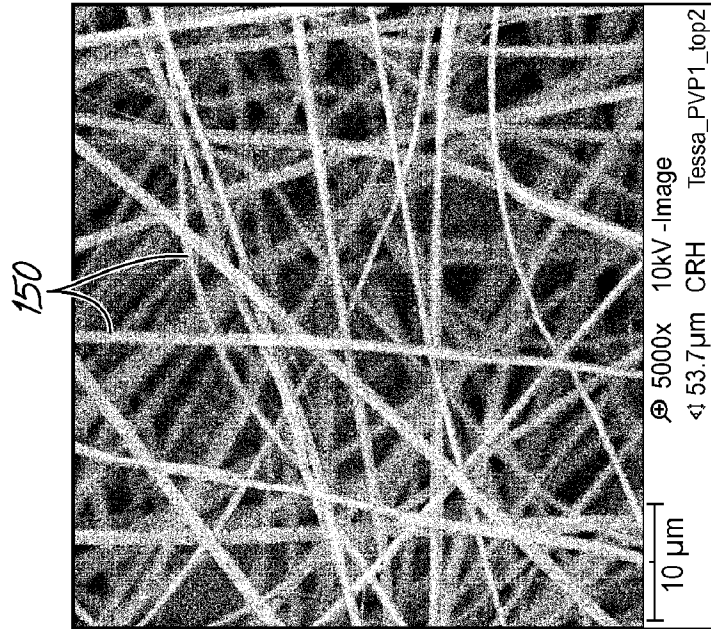
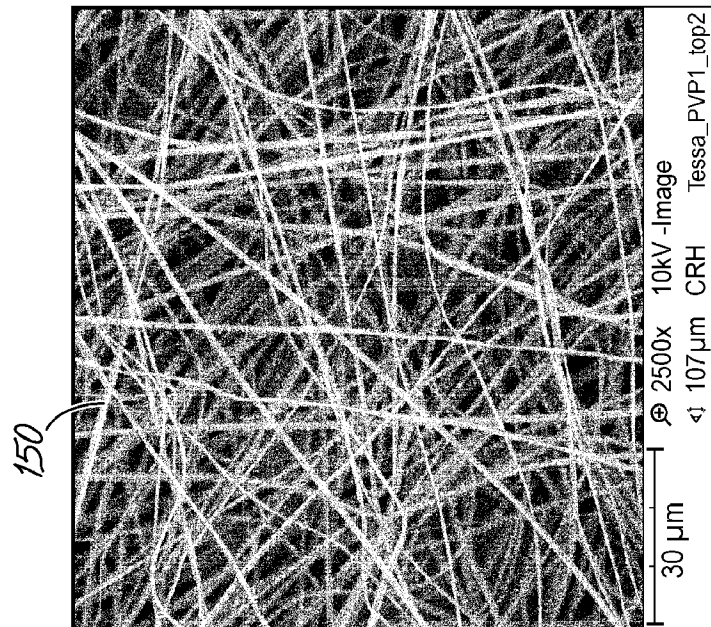


FIG. 3



SUBSTITUTE SHEET (RULE 26)



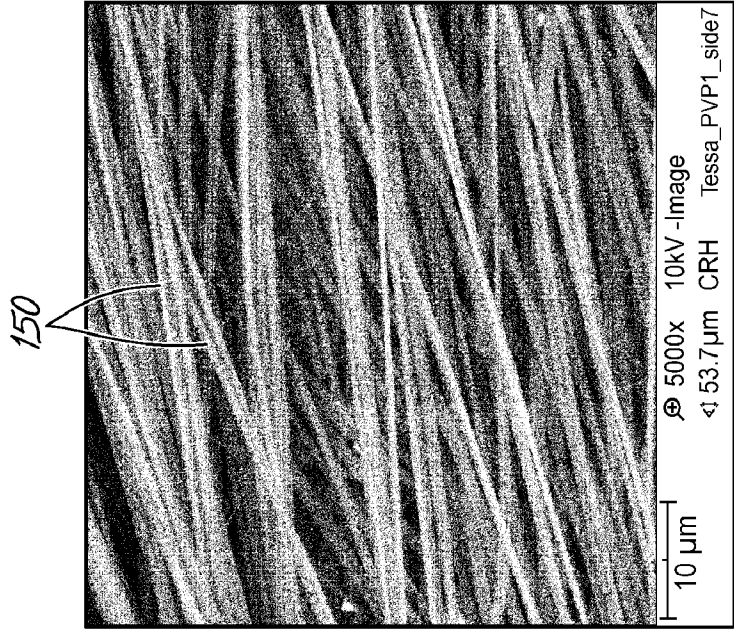


FIG. 5C

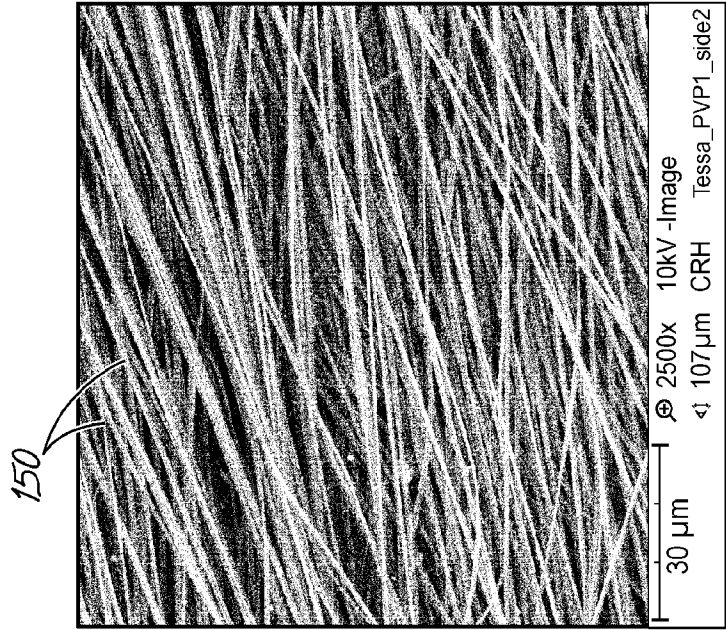


FIG. 5B

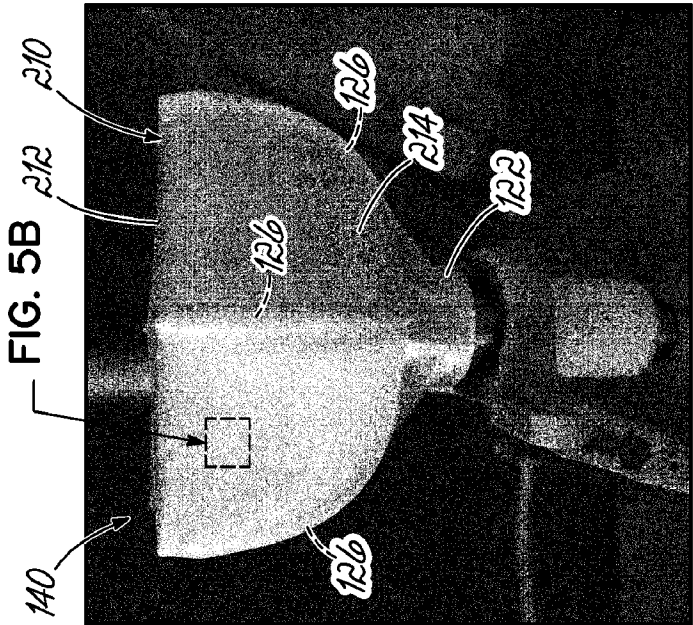


FIG. 5A

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2023/010335

A. CLASSIFICATION OF SUBJECT MATTER INV. D01D5/00 D04H1/728 D04H1/4382 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) D01D D04H		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2016/168754 A1 (MENON DEEPTHY [IN] ET AL) 16 June 2016 (2016-06-16)	1-8, 11-16, 18-20
A	paragraphs [0003], [0031], [0032], [0034], [0035], [0037], [0042], [0043], [0053]; figures 1, 3A, 3B, 3C; examples 1, 2, 3, 4	9, 10, 17
A	US 10 196 757 B1 (CHEN XING [US] ET AL) 5 February 2019 (2019-02-05) column 9, lines 17-42; figure 9; example 1	1-20
A	CN 203 007 507 U (TIANJIN WEICHER TECHNOLOGY CO LTD) 19 June 2013 (2013-06-19) abstract; figures 1, 2	1-20
	----- -/-	
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
30 May 2023		13/06/2023
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Van Beurden-Hopkins

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2023/010335

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 203 007 508 U (UNIV TIANJIN POLYTECHNIC) 19 June 2013 (2013-06-19) abstract; figures 1,3 -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2023/010335

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2016168754 A1	16-06-2016	US 2016168754 A1	16-06-2016
		US 2018274134 A1	27-09-2018

US 10196757 B1	05-02-2019	NONE	

CN 203007507 U	19-06-2013	NONE	

CN 203007508 U	19-06-2013	NONE	
