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(54) Title: THREE-DIMENSIONAL NANOSTRUCTURES CREATED BY ELECTROSPINNING

(57) Abstract: A method of manufacturing self-standing three-dimensional (3D) objects made of nanofibers is provided. Polyacryloni-
 trile (PAN), polyvinylpyrrolidone (PVP), Polycaprolactone (PCL), Cellulose Acetate (CA), and Polyvinylidene fluoride (PVDF) were
 produced as macroscopic 3D objects by 3D electrospinning printing (combination of 3D printing and electrospinning). In particular,
 the production of 3D carbon nanostructures was achieved by electrospinning polyacrylonitrile (PAN) nanofiber then the carbonising
 or calcination of the produced 3D nanofiber, in particular the 3D polyacrylonitrile (PAN) nanofiber.



THREE-DIMENSIONAL NANOSTRUCTURES CREATED BY ELECTROSPINNING

Field of the invention

The present invention relates to a method of manufacturing self-standing three-dimensional (3D) objects made of nanofibers. Polyacrylonitrile (PAN), polyvinylpyrrolidone (PVP), polystyrene (PS), polycaprolactone (PCL), cellulose acetate (CA), and Polyvinylidene fluoride (PVDF) were produced as macroscopic 3D objects by 3D electrospinning printing (combination of 3D printing and electrospinning). In particular, the production of 3D carbon nanostructures was achieved by electrospinning polyacrylonitrile (PAN) nanofiber then the carbonising or calcination of the produced 3D polyacrylonitrile (PAN) nanofiber.

Background

Nanofibers have enormous surface area per unit mass. This makes them useful for a large variety of industrial products and methods. Current methods for forming continuous nanofibers at large scales by electrospinning produce 2D structures.

The electrospinning process applies high voltage to solutions, suspensions or melts as they pass through a nozzle, converting the liquids into nanofibers. The high voltage charges the liquid as it passes through the nozzle. When the voltage is increased, the charge density on the liquid surface increases at the nozzle orifice, and a conically shaped jet is formed (Taylor cone). When the applied voltage is further increased, the charge density on the surface generates repulsive electrostatic forces that overcome the surface tension of the liquid. The resulting jet, dispensed from the tip of the Taylor cone, experiences electrical instabilities due to the strong electric field at that location, which causes it to elongate and bend. The drawn polymeric thread is directed to the oppositely charged or grounded collector, and solidification occurs, leaving only the polymer fibre on the collector mat. This allows production of 2D nanofibrous mats.

Rechargeable Li-ion batteries (LIBs) exhibit a high volumetric and gravimetric energy density of $\sim 700 \text{ Wh}\cdot\text{l}^{-1}$ and $\sim 250 \text{ Wh}\cdot\text{kg}^{-1}$ respectively. However, the use of organic liquid electrolytes limits their maximum energy density, safety and operating temperature, hindering their applications, e.g. in electric vehicles. The replacement

of the liquid electrolyte by safer solid electrolytes (SEs) is a considered as an alternative to overcome current limitations. In particular, solid polymer electrolytes (SPE) hold a promising prospect as they can be processed into thin membranes of 30-50 μm exhibiting conductivities of 10^{-3} - 10^{-4} S cm^{-1} at 70 $^{\circ}\text{C}$ and offer intimate
5 contact with electrodes.

Solid state batteries rely on the use of Li metal anode to achieve competitive gravimetric and volumetric energy density due to its high capacity of $\text{mAh}\cdot\text{g}^{-1}$. However, the use of Li metal entails several drawbacks such as high interfacial
10 resistance, lithium dendrite propagation or SE-lithium metal side-reactions, which currently hinder the deployment of this technology. Alternatives to replace Li metal electrodes are therefore sought.

Among available electrode alternatives to lithium, one-dimension structures such as
15 carbon nanofibers are highly desirable due to their enhanced surface-to-volume ratio, short lengths for ionic transport and efficient one-dimensional electron transport along the longitudinal direction. In addition, these materials show a potentially increased capacity as active materials compared to conventional intercalation mechanism (LiC_6) in graphite, due to their turbo-static storage behaviour. Several
20 reports have shown the performance of carbon nanofibers being similar or better than those of graphite in liquid electrolyte. The fabrication of carbon nanofibers can be obtained through several techniques; however, the complex processes required to fabricate them, limited availability and possible impurities during synthesis have been major drawbacks for their application.

25 When designing solid state electrodes, a robust ionic conductivity network must be ensured by the wetting of the active material with the solid electrolyte. The brittleness of carbon nanofibers hamper their processing into solid state electrodes.

30 There is therefore a need for flexible, solid state electrodes which offer a high surface area to provide an intimate contact with electrolytes, low interfacial resistance, avoid dendrite propagation and/or reduced electrode-electrolyte side-reactions.

There are also other applications for flexible electrodes, such as flexible photovoltaics, flexible displays or medical electrodes.

Summary of the invention

5 The inventors have developed a method that utilises electrospinning techniques and 3D printing methodologies to enable the generation of 3D nanostructures. CAD/CAM may then be used to create 3D shapes and designs. Further, a 3D electrospinning printer has been developed to allow this methodology to be used with nanofiber, for example polyacrylonitrile (PAN) nanofiber or other polymer as discussed herein, to
10 allow electrospun fabrication of 3D articles. The electrospun 3D articles formed of polyacrylonitrile (PAN), polyvinylpyrrolidone (PVP), polystyrene (PS), polycaprolactone (PCL), cellulose acetate (CA), and / or Polyvinylidene fluoride (PVDF) nanofiber are considered to be new. Further these can be carbonised, producing a 3D carbon nanostructure.

15 According to a first aspect of the present invention there is provided a method of producing a 3D structure, wherein the method comprises:

- a. providing a polymeric solution comprising a polymer, a solvent and a salt, acid or base additive to an electrospinning print head, wherein
20 the solvent/polymer/additive ratio is provided at approx. 200:30:1;
- b. electrospinning the polymeric solution from the print head onto a print bed to create a 3D fibre network by applying a voltage difference between the print head and a collector, optionally;
- c. annealing the fibre network in an inert/reducing atmosphere.

25 As would be understood by those of skill in the art, the solvent/polymer/additive ratio may be provided within an operational window in relation to viscosity and conductivity. Suitably the operational window may be approx. 15%, suitably approx. 10% variation of ratio 200:30:1, suitably about 7%, suitably about 5%, suitably about
30 3% variation of ratio 200:30:1. The skilled person would be able to provide suitable ratios to provide functionally suitable polymeric solutions with suitable viscosity and conductivity for use in the electrospinning method. Suitably the solvent/polymer/additive ratio may be 200:30:1. As would be appreciated in the art, 3

g polymer in 20 g solvent and 0.1 g HCl would provide a 30:200:1 ratio, or written as 200:30:1 ratio for the solvent/polymer/acid.

Suitably the acid is a strong acid. Suitably the base is a strong base. Suitably an acid has a pKa of less than 3.75. Suitably a base has a pKb of less than 4.77. Suitably an acid may have a pKa of less than 3, less than 2.5, less than or about 2. Suitably a base may have a pKb less than 4, less than 3, less than 2, less than 1, suitable about 0.2.

Suitably a polymer may be selected from PAN, PVP, PS, PCL, CA, PVDF or a combination thereof. Suitably a polymer may be selected from PAN, PVP, PS, PCL, CA, or PVDF. Suitably a polymer may be selected from PVP and PVDF. Suitably a polymer may be selected from PAN and PVDF. Suitably a polymer may be selected from PCL or CA. Suitably a polymer may be selected from PS or PAN. Suitably a polymer may be selected from PS or PVP. Suitably a polymer may be selected from PS or PCL. Suitably a polymer may be selected from PS or CA. Suitably a polymer may be selected from PS or PVDF. Suitably a polymer may be selected from PAN and PVP.

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Suitably the polymer or combination of polymers may be provided at 5 wt % to 25 wt % of the polymeric solution. Suitably the polymer may be PAN and may be provided in the range of about 5 wt % to 25 wt%, optionally 12 wt % to 15 % of the polymeric solution. Suitably the polymer may be PVP and may be provided in the range of about 10 wt % to 20 wt %, optionally 12 wt % to 18 wt % of the polymeric solution. Suitably the polymer may be PS and may be provided in the range of about 5 wt % to 25 wt%, optionally 12 wt % to 15 % of the polymeric solution. Suitably the polymer may be PCL and may be provided in the range of about 10 wt % to 20 wt %, optionally 12 wt % to 18 wt % of the polymeric solution. Suitably the polymer may be CA and may be provided in the range of about 10 wt % to 20 wt %, optionally 12 wt % to 18 wt % of the polymeric solution. Suitably the polymer may be PVDF and may be provided in the range of about 10 wt % to 20 wt%, optionally 12wt % to 15wt% of the polymeric solution. Suitably the polymer or combination of polymers may be provided at about 15 wt.% of the polymeric solution.

Suitably the solvent in the solution may be selected from a group consisting of DMF, MeOH, THF, ethanol, HFIP, DCM, or a combination thereof.

Suitably, the strong salt, acid or base additive may be selected from a group consisting of hydrochloric acid (HCl), phosphoric acid (H₃PO₄), lithium chloride (LiCl), lithium bromide (LiBr), potassium chloride (KCl), sodium chloride (NaCl) or sodium hydroxide (NaOH). Suitably the acid may be HCl. HCl provides enhanced shape fidelity of the 3D structure when compared to other acids, bases or salts. Without wishing to be bound by theory, it is considered the additive acid/base/salt dissociates and gives ions that can freely move in the solution (e.g. H⁺ and Cl⁻ in the case of HCl). These ions help polarise the nanofibers during the electrospinning process.

Suitably the voltage used in step b. (electrospinning step) is between about between 15-30 kV and the current is about 100 μ A. Suitably the voltage used in step b. (electrospinning step) is between about between 15-20 kV and the current is about 100 μ A. Suitably the wattage may be about 15 mW. Suitably step b. (electrospinning step) comprises electrospinning under about a 20-55 % relative humidity atmosphere, suitably wherein the relative humidity is about 30%.

Suitably electrospinning may be conducted at a temperature of about 0-70 °C. Suitably the electrospinning may be conducted at a temperature of about 25 °C. Suitably the atmosphere in which electrospinning is provided may be an Ar or N₂ atmosphere.

Suitably the carbonisation or calcination method may include an oxidation step first at a temperature between about 225 and 300 °C, preferably between about 250 and 280 °C for about 1 hour under air (ambient atmosphere). Suitably the method may include a carbonization step at a temperature between about 800 and 1000 °C, preferably between about 850 and 950 °C, most preferably 900 °C for about 1 hour under a flow of an inert atmosphere such as N₂ or Ar. The inventors have found that a temperature of about 900 °C is optimal as it provides a good ratio between the carbon and nitrogen atoms in the resulting structures (having sufficient nitrogen in the samples is important for battery anode applications). Suitably the temperature may be provided at a heating rate of 0.1 °C/min, 0.5 °C/min, 1 °C/min, at least 5 °C/min, at least 10 °C/min. Suitably a rate of heating may be provided which provides a 3D structure which resiliently deforms (i.e. one where a 3D structure may be compressed from a first shape to a second shape and, once the force is removed returns to approximately the same first shape over time. Suitably, a deformable structure may be provided when the heating rate is slower, for example 0.5 -1°C/min. Suitably, the temperature may be provided at a heating rate of 5 °C/min and at such a rate it is considered the 3D structure has a hard / brittle structure.

Suitably 3D polymers of the present invention which retain their charge over a long time (e.g. PAN) or are adhesive (e.g. PVP) may have decreased deformability.

Suitably in the method, the electrospinning may occur at a flow rate of about 5 mL/hour, the voltage applied may be in the range of about 15 to 30 kV, with a

working distance of about 5 cm. Suitably in the method, the electrospinning may occur at a flow rate of about 5 mL/hour, the voltage applied may be in the range of about 15 to 20 kV, with a working distance of about 5 cm.

5 Suitably movement of the print head provides layer by layer manufacturing of a 3D structure. Suitably the present method of 3D electrospinning can form macroscopic structures with a nanometer-scale resolution and without nozzle clogging as typically experienced with fused deposition modelling techniques. Suitably movement of the print head may be controlled by a computer aided design instruction file. This allows
10 structures with complex geometries to be generated. Suitably such structures may be used for tissue engineering, electrode formation, cell culturing or other bio-ink based forms.

The 3D electrospinning method is a non-contact printing technique that is suitable for
15 non-planar and complex surfaces of substrates. This can reduce damage from the nozzle touching the substrate during printing. Suitably the method provides for faster, at least twice as fast, at least 10 times as fast, at least 20 times as fast, at least 50 times as fast, at least 100 times as fast production of nanofiber 3D structures than other nanofiber printing technologies. Suitably the method provides more precise
20 printing that existing nanofiber technologies.

According to a second aspect of the present invention there is provided a 3D structure comprising carbon nanofibrous networks provided by the method of the first aspect of the invention.

25 Suitably the 3D structure may comprise carbon nanofibrous networks with diameters from about 150 to 1000 μm where the 3D structure is for example about 2 cm, about 3 cm, about 4 cm, up to 5 cm tall, up to 7.5cm tall, up to 10 cm tall or up to 12.5cm tall. Suitably the 3D structure may be a 3D structure comprising carbon nanofibrous
30 networks with diameters from about 150 μm where the 3D structure is up to about 10 cm tall.

Suitably a 3D structure of the second aspect can have a resistivity of around 1000 Ohms. Suitably the 3D structure can have a porosity of about 90-98%. Suitably the

3D structure can comprise nanofibers with an average cross section of about $0.74 \pm 0.01 \mu\text{m}$.

Advantageously nanofibers have enormous surface area per unit mass. The methodology of the invention which allows the combination of 3D printing with controlled electrospinning enables complex 3D nanostructures from CAD models to be provided.

Moreover, these 3D structures can be carbonised. This provides a carbonised 3D structure with a rare combination of electrical (e.g. conductivity, charge capacity), mechanical (e.g. stiffness, strength), and mass transport (e.g. permeability, diffusivity) properties. Suitably, a carbonised 3D structure may have a resistivity of around 400-1000 Ohms. Suitably the 3D structure can have a porosity of about 90-98%. Suitably the 3D structure can comprise nanofibers with an average cross section of about 300-800 nm. Suitably, the carbon content of the fibres can be about 84% of carbon via XPS analysis.

Suitably the polymeric solution may comprise additive nanoparticles, for example, silicon, carbon black, carbon nanotubes, graphene or graphite particles entrained into nanofibers to enhance their electrical conductivity. Suitably the energy density may be increased without the sacrifice of power density, by providing pseudocapacitive active materials (silicone, metal oxides, e.g. manganese oxide, or conductive polymers, e.g. polyaniline) onto the nanostructured carbon 3D electrode structures.

Where the polymer consists or substantially comprises PVDF, the resulting structure will be piezoelectric.

Suitably, the 3D structures may be functionalised for use as a cell culture substrate. Suitably the 3D structures may be provided by cryo-spinning. The polymer may be spun on a cooled surface – for example a mandrel at -70 to -90°C , suitably -70 to -80°C . Suitably cryo-electrospinning induces simultaneous deposition of ice crystals during the electrospinning. The ice crystals once sublimated can lead to more porous networks. Suitably the polymer may be polycaprolactone. Suitably the polymer may

be subsequently treated by O₂ plasma. Suitably such a cryo-spinning may provide an ultraporous nanofiber network.

Suitably the electrospun nanofiber network may be engineered to provide a designed degradation rate. Suitably the electrospun nanofiber network may provide a degradation profile suitable for substance or drug release. Suitably the electrospun network may be cell adhesive. Suitably the electrospun network may allow cell infiltration.

Details of creating 2D ultraporous and hydrophilic structures by cryo-spinning is provided in Formica et al., Adv. Healthcare Mater. 2016, DOI: 10.1002/adhm.201600867, which is herein incorporated by reference.

Suitably a carbonised 3D structure provides for handling high current densities, diminishing volume changes and strengthening the interphase between the electrode and electrolyte. This makes them particularly useful in solid electrolyte or liquid electrolyte batteries.

Where the polymeric solution comprises additional silicone, the porous 3D carbon nanostructures made by electrospinning can enhance the energy density by about factor of 10. Suitably, the 3D carbon nanostructures may be used with lithium batteries to increase the electronic and ionic conductivity, the cycle life and the lithium-ion diffusivity across the electrode/electrolyte interface.

Suitably, the 3D nanostructure may lead to improved physical interactions between an electrocatalyst and its support material.

According to a further aspect of the present invention there is provided a device to provide the method of the first aspect of the invention, wherein the device comprises an electrospinner with an electrospinner print head wherein the print head can be moved in X, Y and Z directions in relation to a print bed to allow electrospinning of a polymeric solution.

According to a third aspect of the present invention there is provided a 3D structure of the second aspect of the invention in an energy device such as a fuel cell electrode, a battery anode, or a solar cell, a supercapacitor, or a medical device electrode.

5

Suitably the 3D material can advantageously be used to provide electrodes for Li-ion batteries from porous structures of carbon made by electrospinning. It is considered these structures enhance the energy density by the increased surface area. Suitably the 3D material can increase the electronic and ionic conductivity, the cycle life and the lithium-ion diffusivity across the electrode/electrolyte interface. The 3D nanostructure can also lead to improved physical interactions between the electrocatalyst and its support material.

10

Suitably the 3D structure may be provided in a solar cell, a supercapacitor, a battery, a fuel cell.

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Suitably the 3D structure may be provided in a fuel cell electrode, a battery anode, or a medical device electrode.

Suitably the 3D structure may be provided in a filter material for example air / water filtration.

20

According to a fourth aspect of the present invention there is provided a 3D structure of the second aspect of the invention for use as a cell culture support, wherein the 3D structure was manufactured using cryospinning.

25

Embodiments of the invention will now be described, by way of example only, with reference to the accompanying figures in which

Figure 1 shows the photograph of the macroscopic of ca. 1 cm x 1 cm x 1 cm porous 3D carbon nanostructure that was fabricated using the method.

Figure 2 shows the nanostructure through scanning electron microscopy of the standard 2D (flat) PAN nanostructure.

Figure 3 shows the nanostructure through scanning electron microscopy of the 3D PAN nanostructure.

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Figure 4 shows the nanostructure of the carbonised 3D PAN.

Figure 5 shows (A) 3D electrospinning apparatus. (B) nozzle-free 3D electrospinning apparatus, (C) SEM image of 3D structures with scale bar showing increments in 1 cm (C) PS, (D) PAN, (E) PVP, (F) PCL (G) CA and (H) PVDA to show the diameter of the resultant nanofibers.

Figure 6 shows a resiliently deformable carbonised structure of the present invention.

Figure 7 shows a 3D electrospinning set up with humidity and temperature control, wherein the temperature is controlled by heated coils around a heat sink which can have hot air or nitrogen flowing inside them. Heating can be provided by electric heating tapes wrapped around copper tubes that formed a coil around 1-1 heat sinks. Hot gas can enter the 3D electrospinning setup from the top through a glass lid with holes (for example ~80 holes). In order to further control the temperature, the 3D electrospinning setup can have a heat-controlled collector bed (by applying electric heating in a silicon pad below the glass collector). A set of metallic rings charged to positive DC voltage (Eizel lens) can be installed directly below the nozzle, to focus the electric field, thus increasing the precision of the printer. Nozzles can be provided to allow co-axial and side-by side electrospinning. A camera can be installed for measuring the 3D build-up speed and monitor the process.

Figure 8 shows a 3D electrospun PVDF structure provided by the method.

Figure 9 shows (a) scanning electron microscopy imaging of carbonised 3D structures and their estimated thickness after calcination. (b) Adsorption isotherms with nitrogen (-196 °C), surface area and specific volume calculations. Structural characterization of carbonised 3D structures through (c) XRD and (d) Raman Spectroscopy.

Figure 10 shows a schematic representation of (a) liquid and (b) solid state cells using 3D electrospun carbon nanofibers of the present invention.

Figure 11 shows the galvanostatic cycling of the electrospun carbon electrode against a Li metal electrode, using a 50:50 EC:PC 1M LiPF₆ electrolyte. (a) rate capability test showing the charge-discharge capacity and coulombic efficiency as function of the cycle number from C/20 to 1 C and back to C/10. (b) voltage profiles at increasing C-rate from C/20 up to 1 C. (c) charge-discharge capacity and coulombic efficiency as function of the cycle number at 25 mA·g⁻¹.

Figure 12 shows galvanostatic cycling of the electrospun carbon electrode against a Li metal electrode, using a PEO:LiBOB (EO:Li 20:1) SPE separator. (a) charge-

discharge capacity as function of the cycle number under a constant current of 25 mA·g⁻¹, (b) voltage profiles at different cycles (25 mA·g⁻¹), (c) EIS profile of the cell at a discharged state before cycling and after 35 cycles, and (d) specific capacity as function of the C-rate.

5 **Figure 13** shows 3D electrospun structures of PS, PAN and PVP. (a.1) Top-view, (a.2) Side view, (a.3) SEM pictures and (a.4) High FPS camera picture during electrospinning of 3D PS. (b.1), (b.2), (b.3) and (b.4) are for 3D PAN. (c.1), (c.2), (c.3) and (c.4) are for 3D PVP.

Figure 14 shows a compression creep test on electrospun 3D PS. Most of the creep deformation is observed within the first 6 hours of loading, getting a deformation as high as 51.9%, 65.3% and 75.8% for the weights of 10, 20, and 50 g respectively.

Figure 15 shows a 3D PS structure electrospun with increasing working distance to generate tall structures. (a) Top-view of the 3D structure. (b) Side-view of the 3D structure.

15 **Figure 16** shows: **A**: PS 3D nanofibre structures of the present invention that were soaked in DMEM medium and seeded with MyC-Cap cells and successfully cultured for 72 hours and **B**: Fibroblast and osteoblast cells were successfully grown on CA and PCL scaffolds

Figure 17 shows impedance (resistance) testing at relaxed and compressed states shows that the conductivity increases as the material is compressed.

Figure 18 shows 3D fibrous PCL structures of the invention wherein PCL is polycaprolactone, CAD is Computer-aided design, and CA is Cellulose acetate.

Examples

25 **Example 1: Formation of a 3D structure**

Electrospinning was undertaken using polymeric solutions consisting of PS (molecular weight: 280,000), PAN (molecular weight: 150,000) or PVP (molecular weight: 360,000) in solutions of DMF, THF or MeOH, with additive amounts of HCl, H₃PO₄, HCOOH, H₂SO₄, NH₄OH or NaOH by dissolving 3 g of polymer in 17 g of solvent in a 100 mL bottle. When the solution was clear, between 2 µL and 200 µL of additive salt, acid or base were added to enable the 3D electrospinning.

During electrospinning, the DC voltage was applied in a range from +15 to +30 kV.

35 The flat collector, a 20 x 25 cm metallic plate covered with aluminium foil, was

grounded. The working distance, defined as the gap between the nozzle tip and the collector, was set to 5 cm. The flow rate was set at 5 mL.h⁻¹, a 20G syringe was used. The electrospinning time was set at 10 min, 3D build-up was observable within a minute of experiment. The experiment was done under ambient conditions, with temperature of about 20-25 °C and relative humidity of ~40-45%.

The 3D electrospinning was done with a moving nozzle following the pattern of a circle with a diameter of 5.5 cm. The movement speed was set at 12 mm.s⁻¹. The constant movement of the nozzle is critical to prevent any direct fibres bridging between the collector and the nozzle, which would cause a short circuit and stop the electrospinning process.

After electrospinning, nanofibers can be carbonized. For example PAN fibres were carbonized in a tube furnace in a Nitrogen atmosphere at 10 mL/min flow rate at 850 °C for 1h. A heating rate was 10 °C.min⁻¹.

In the present method it is considered that the top of the deposited mat gets negatively charged and then becomes the preferential deposition site. This attracts the positively charged jet ejected from the print head nozzle. As the fibres at the top of the layer have the charge, they naturally repel each other during build up and fabricate a non-compact “spongy” structure (Figures 5D-H and Figure 13). By applying additives such as acid, salt or base in the electrospinning solution, the polarizability of the electrospun fibres is increased, leading to repulsive forces between the fibres – this increases the space between the fibres and stabilises the structure.

As can be seen in Figure 13, the PS structure sharply followed the circular pattern of the nozzle head to produce a distinct cylinder. It had a height of 3.0 ± 0.1 cm and an average wall thickness of 2.4 ± 0.1 cm. The PAN 3D structure had the shape of a cone, 3.2 ± 0.1 cm in height, with a base thickness of 11.6 ± 0.2 cm and a top thickness of 3.1 ± 0.1 cm, and the PVP structure was made of several small cones, with a bigger one of 1.1 ± 0.1 cm in height, 4.5 ± 0.1 cm in base thickness and 2.0 ± 0.1 cm top thickness, located in the center of the electrospinning area. The circular motion of the nozzle forced the center of the electrospinning area to be continuously exposed to the electrospinning jet, which explains why the central cone is larger. The

average fiber diameters were $0.85 \pm 0.02 \mu\text{m}$, $0.74 \pm 0.01 \mu\text{m}$ and $1.04 \pm 0.2 \mu\text{m}$ for PS, PAN and PVP, respectively. The electrospinning time was set to 10 minutes, which translates to a layering speed of about $0.3 \text{ cm} \cdot \text{min}^{-1}$ for PS and PAN.

5 Without wishing to be bound by theory, it is considered a difference in shape between the PS, PAN and PVP structures can be provided due to wider whipping motion of the PAN and PVP jets compared to the PS, which lead to a higher deposition area and less control over the shaping of the 3D structures. Indeed, the whipping angle of the jet was measured to be $85 \pm 1^\circ$, $113 \pm 1^\circ$ and $125 \pm 1^\circ$ for PS, 10 PAN and PVP respectively, as shown in Figure 13. This correlates with increased polymer solution conductivity measured at $80.4 \pm 0.8 \mu\text{S} \cdot \text{cm}^{-1}$, $1.05 \pm 0.01 \text{ mS} \cdot \text{cm}^{-1}$ and $4.16 \pm 0.04 \text{ mS} \cdot \text{cm}^{-1}$ for PS, PAN and PVP respectively. An electrospun jet with more charge carriers is more susceptible to the external electric field and surface charge repulsion, which can, in turn, lead to a wider whipping motion. This may be 15 adjusted accordingly using e.g. different concentrations and types of additive or different polymers or blends of polymers.

Example 2 – Carbonised an Non-Carbonised Structures – Physical Stability and Resilient Compressibility

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A macroscopic (6cm x 3cm x 2 cm) porous 3D carbon nanostructure was fabricated by 3D electrospinning using PAN, wherein the PAN was dissolved in dimethylformamide, then 20 μl of hydrochloric acid was added. The sample was carbonised in a tube furnace in a nitrogen atmosphere at 10mL/min flow rate at 850 25 $^\circ\text{C}$ at a speed of 1 $^\circ\text{C}/\text{min}$. As shown in Figure 6, the carbonised 3D nanofibrous PAN was resiliently compressible. SEM imaging shows that the nanofibers are about 450nm in diameter.

Electrospun 3D PS of Example 1 demonstrated partial shape recovery on short-term 30 (5 min) compressive strength, developing a strain of about 20-30%, for all 3 weights examined: 10.0, 20.0 and 50.0 g. For all weights, it was observed that most of the deformation occurs within the first two hours; getting as high as 51.9%, 65.3% and 75.8% after 6 hours of compression for the weights of 10.0, 20.0 and 50.0 g, respectively. A total strain of about 56.6%, 78.0% and 95.4% was observed for the 35 same respective weights after 20 days of constant loading. This multiple-stage

deformation behaviour is due to the densification of the fibres, which increases their mechanical strength and resistance to compression. The results of the compression creep test can be seen in Figure 14.

- 5 3D polymers of the present invention which either retain their charge over a long time (e.g. PAN) or are adhesive (e.g. PVP) may not show resilient deformability or elasticity, and as such permanently lose their 3D feature after a light compression.

Example 3: Assessing the Effects of Different Additives

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Several PS, PAN or PVP solutions in DMF or MeOH with different amounts of acid or base additives were used to assess the effect of solution conductivity on the 3D build-up during electrospinning.

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As seen in Table 1, standard flat electrospinning was observed at solution conductivities of 0.24, 0.62, 3.15, 28.6, 32.3 and 48.0 $\mu\text{S}\cdot\text{cm}^{-1}$, which were obtained by using no additives, by adding 20 μL of NH_4OH , 2 μL of HCl , 20 μL of HCOOH , 5 μL of HCl and 10 μL of HCl , respectively. 3D electrospinning was achievable with solution conductivities of 4.04, 8.84, 32.2, 59.3, 73.1, 135.4, 140.3 and 206.0 $\mu\text{S}\cdot\text{cm}^{-1}$, which were prepared by adding 20 μL of H_3PO_4 , 40 μL of H_3PO_4 , 20 μL of NaOH , 15 μL of HCl , 20 μL of HCl , 40 μL of HCl , 100 μL of H_3PO_4 and 20 μL of H_2SO_4 , respectively.

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15 wt% PS (Mw 280k) in DMF				15 wt% PAN (Mw 150k) in DMF			
Additive	Amount (μL in 20 g of solution)	Conductivity ($\mu\text{S} \cdot \text{cm}^{-1}$)	3D Build- up (Yes/No)	Additive	Amount (μL in 20 g of solution)	Conductivity ($\mu\text{S} \cdot \text{cm}^{-1}$)	3D Build- up (Yes/No)
None	0	0.24	No	None	0	119	No
NH_4OH	20	0.62	No	HCl	200	1050	Yes
HCl	2	3.15	No				
H_3PO_4	20	4.04	Yes	15 wt% PVP (Mw 360k) in MeOH			
H_3PO_4	40	8.84	Yes	Additive	Amount (μL in 20 g of solution)	Conductivity ($\mu\text{S} \cdot \text{cm}^{-1}$)	3D Build- up (Yes/No)
HCOOH	20	28.6	No				
NaOH	20	32.2	Yes				
HCl	5	32.3	No				
HCl	10	48.0	No				
HCl	15	59.3	Yes	None	0	32.2	No
HCl	20	73.1	Yes	HCl	200	4.1×10^3	Yes
HCl	40	135.4	Yes				
H_3PO_4	100	140.3	Yes				
H_3PO_4	200	206.0	Yes				

Table 1. Polymer solution conductivity in the presence of various additives and whether 3D electrospinning was achieved or not. The electrospinning conditions were as follow: Applied voltage 20 kV, Working distance 5 cm, Flow rate 5 ml.L⁻¹.

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The results of Table 1 therefore assesses a wide range of conductivity from ~0.24 $\mu\text{S} \cdot \text{cm}^{-1}$ to ~140.3 $\mu\text{S} \cdot \text{cm}^{-1}$, however there is no direct correlation between 3D electrospinning and solution conductivity or a minimum solution conductivity before which 3D build-up initiates. As an example, 3D electrospinning is observed at solution conductivities of 4.04, 32.2 and 59.3 $\mu\text{S} \cdot \text{cm}^{-1}$ but not at the intermediate solution conductivities of 28.6 and 32.3 $\mu\text{S} \cdot \text{cm}^{-1}$. As such, solution conductivity alone is not the driving factor of 3D electrospinning.

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Without wishing to be bound by theory, it is considered that, where the outer surface of the deposited fibers is negatively charged due to polarization and electrostatic

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induction by the surrounding positive electric field, these negative charges favor fibers repulsion, which lead to a 3D structure instead of a flat mat.

In particular, it is interesting to note that the 3D structures are formed using HCl additives only after a minimal amount of HCl; 15 μ L in 20 g of PS solution. This is considered to be due to the high amount of charged particles, which would favor a strong polarization under the high electric field, which would increase the repulsive forces and the 3D buildup. It is interesting to note that HCOOH and NH₄OH, a weak acid ($pK_a = 3.75$ at 20°C) and a weak base ($pK_b = 4.767$ at 20°C) respectively, are unable to induce 3D electrospinning to the PS/DMF solution. This may be due to the lower amount of ions they can provide to the solution. It is therefore considered that the additive salt or acid must not be too weak (i.e. a pK_a of less than 3.75) or the base must not be too weak a base (i.e. a pK_b of more than 4.77).

Example 4: Printing Tall Structures

The effects of moving the printhead in the z direction away from the printhead during electrospinning were assessed. Figure 15 depicts a photograph of a tall 3D PS structure, built using the same PS mixture as Example 2 but steadily increasing the working distance by 1 cm every 2 min. Starting from a working distance of 5 cm, a final working distance of 10 cm was set after 10 min of 3D electrospinning. This taller 3D PS structure had a height of 5.0 ± 0.1 cm. However, it had an average wall thickness of 2.6 ± 0.1 cm, indicating a slight decrease in fidelity compared to methods with a fixed printhead height of 5 cm. More stray fibres are also present around the 3D structure. This small loss in resolution is considered to be due to the wider whipping motion occurring at a higher working distance as the 3D structure itself is not as attractive as the grounded collector. This incremental vertical movement allows for a slow and guided deposition of the electrospun fibres on top of the 3D structure, which enables the fabrication of tall 3D structures.

As will be appreciated, electrospinning with greater dynamic distance may cause the electrospun jet to no longer be attracted to the structure on the collector past a defined working distance as a weaker electric field will be provided at a higher working distance.

Example 5: Preparation and testing of solid and liquid electrolyte half cells using 3D structures of the present invention

3D structures of the present invention were used to prepare solid and liquid electrolyte half cells which were then duly characterised:

Preparation and characterisation of the electrodes

3D structures of PAN were prepared by the method of Example 1, oxidised (250 °C for 2 h under N₂) and carbonised (900 °C for Xh under N₂). The obtained carbonised 3D structures were a soft and flexible 3D sponge-like structures formed by smooth fibres.

When analysed by scanning electron microscope, the carbonised 3D structures presented homogeneous, straight and 1D structures (Figure 9a), without fibre ruptures or significant stress generated during oxidation. Fibre diameter was maintained between 300 and 800 nm.

Nitrogen adsorption analysis was performed to evaluate the surface area, micropore volume, total pore volume, and pore size distribution of the carbonised 3D structures (see Figure 9). The nitrogen adsorption isotherm in Figure 9b showed a type I isotherm, indicating that these samples are mainly composed of micropores, with low or null mesoporosity.

A total surface area of 385 m²·g⁻¹ and an average pore volume of 0.14 cm³·g⁻¹ was estimated for the carbonised 3D structure. The sample showed a narrow distribution of micropores with an average diameter of 0.5 nm, larger than the size of lithium atoms (0.115 nm) making them suitable for use in lithium ion batteries.

The X-ray diffraction (XRD) pattern of the carbonised 3D structures presented two weak and broad peaks at 23° and 43°, corresponding to the (002) and (100) diffraction modes (Figure 9c), characteristic of the disordered carbon material. In addition, the broad signal corresponded to large variations in the layer spacing of this structure, suggesting the large presence of disordered carbon. The interlayer

spacing (d_{002}) was calculated to be 0.370 nm, similar to that of lithium intercalating graphite (0.334 nm).

The ability for lithium-ion storage was qualitatively estimated through the simple empirical parameter R defined by Dahn et al., Carbon. 1996 Jan 1;34(2):193–200 which is herein incorporated by reference. According to the same authors, R decreases as the single layer content of the carbon increases, which shows a direct relation with the ability for lithium-ion storage. A value of $R = 2.3$ was obtained from the quotient between the height of and the background of the 002 peak. This indicates a partial degree of graphitization, thus, a concentration of the parallel single layers in carbon materials similar to other electrospun carbon nanofibers in the literature.

Raman spectroscopy was applied to yield detailed information on the degree of structural disorder of this material. The spectra from Figure 9d shows two characteristically vibrational bands at 1350 and 1600 cm^{-1} were observed; these bands were assigned to disordered carbon (D band) and graphitic carbon (G band) respectively. Unlike graphite, where a sharp peak is observed at 1600 cm^{-1} , both vibrational signals present a broad distribution, which requires a signal deconvolution procedure. This result confirms the presence of partially graphitized carbon, together with amorphous carbon. The intensity ratio of the de-convoluted D/G bands indicates the ratio of each carbon type, which in this material is found to be $I_D/I_G = 2.62$.

From all the above analyses, the porous carbonised 3D structures displayed optimal microstructural characteristics to be used as negative electrode materials in solid state batteries because of the graphitic structure of the pores and the high specific surface area available for the lithium intercalation during charging/discharging process.

Besides, the electrospun fibres present a mainly a disordered nature with partial graphitization, which will likely lead to an ion storage behaviour half way between of hard carbons and graphitic materials. In addition, from the structural and electrochemical point of view these materials are not only promising for lithium-ion storage, but also for other technologies such as Na-ion batteries.

Preparation of electrolytes

For the half-cell, a liquid organic electrolyte of EC:PC (1:1 wt/wt) with 1M Lithium Hexafluorophosphate (LiPF_6) was used.

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For the solid state cell, solid polymer electrolytes (SPE) separators were prepared from the mixture of poly(ethylene) oxide (PEO; $M_w = 5 \cdot 10^6 \text{ g} \cdot \text{mol}^{-1}$) and lithium bis(oxalato)borate (LiBOB). Both components were dried under vacuum at 50 °C before use to remove traces of moisture. The PEO-based solid electrolyte was prepared by mixing PEO and LiBOB in acetonitrile (ACN) with a weight ratio ACN:PEO of 30:1 and keeping a molar ratio EO:Li of 20:1. The solution was stirred overnight and then cast on a Mylar sheet at a blade gap of 1500 μm . The membrane was dried overnight in a vacuum oven at 50 °C to remove the solvent.

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Preparation of the half cells

Electrodes were prepared by punching 13 mm diameter disks of the carbonised 3D structure. For the liquid electrolyte cells, a glass fibre separator of 300 μm was impregnated with 200 μL of the liquid electrolyte solution. For the solid electrolyte cells, the PEO:LiBOB-CAN mixture was poured onto the carbonised 3D structure and then dried overnight at 50 °C under vacuum to remove the solvent prior to the cell assembly.

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The liquid electrolyte and solid-state cells were assembled in half-cell configuration in coin cells CR2032 using Li metal disks of 14 mm diameter and a thickness of 500 μm (Fig. 10a). For the solid state cells a solid electrolyte membrane of PEO:LiBOB-CAN with 16 mm diameter was used as the separator (Fig. 10b).

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Electrochemical characterization of the half-cells

The electrochemical characterization of the carbonised 3D structures was carried out in cells with liquid electrolyte and solid electrolyte separately. For the former approach, the carbonised 3D structures were assembled against Li^0 using a Celgard® separator. The electrolyte (EC:PC LiPF_6) was selected due to its high dielectric constant and SEI formation ability under reduction potentials. Rate

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capability and long-term cycling at $25 \text{ mA} \cdot \text{g}^{-1}$ are displayed in Figure 11. The rate capability test showed discharge capacity values of $360 \text{ mAh} \cdot \text{g}^{-1}$ at C/20 and remained as high as $200 \text{ mAh} \cdot \text{g}^{-1}$ at 1 C (Figure 11a), highlighting the potential of the 3D structures of the present invention as anode materials to be paired with high-voltage active material such as LiMn_2O_4 (CTh= $110 \text{ mAh} \cdot \text{g}^{-1}$) or $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (CTh= $165 \text{ mAh} \cdot \text{g}^{-1}$).

The polarization of the cell during charge and discharge steps increased with the increasing current, likely due to kinetic limitations (Figure 11b). A higher polarization was observed during the charging step indicated delithiation of carbonised 3D structures in comparison to the discharge, but this did not prevent the remarkable recovery of the cell at C/10, delivering $350 \text{ mAh} \cdot \text{g}^{-1}$ (Figure 11a). The CE remained at 99% for most of the cycles.

The capacity obtained for the carbonised 3D structures indicates that the maximum amount of lithium that can be stored agrees with the LiC_6 stoichiometry. Figure 11b shows the charge-discharge voltage profiles from C/20 up to 1 C. The Li^+ intercalation profile displays similarities between ordered and disordered carbon, which show the Li^+ intercalation exclusively below 0.5 V, and homogeneously at different voltages with a smoother initial slope, respectively (Figure 11). This is considered to be similar to Li^+ intercalation profiles of electrospun materials.

Regarding the solid electrolyte cell, the electrode material was tested using a PEO-based solid electrolyte. The replacement of the liquid electrolyte by a solid counterpart is a challenging endeavour mainly due to the larger solid-solid resistive interfaces, jeopardizing the performance of the cells owing to an increased polarization. In this work, the porous electrode of carbonised 3D structures was filled with a slurry containing PEO and the LiBOB salt. A self-standing membrane of PEO-LiBOB was used as SPE separator. LiBOB salt was selected over fluorinated lithium salts to avoid fluor-based decomposition products produced at low redox potentials.

Half-cells with the carbonised 3D structure composite electrode, a SPE separator and Li metal were assembled and conditioned at 70°C for 24 hours in order to minimize interfacial resistances by softening of the polymer. Inspection by scanning electron microscope (SEM) showed a cross-section of the cell after conditioning,

evidencing an excellent interlayer adhesion between carbonised 3D structure electrode, the SPE separator and the Li metal electrode. Moreover, the absence of pores at the cathode electrode evidence the full wetting of the electrospun fibres. Figure 12 gathers the galvanostatic cycling of the solid state cells.

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Figure 12a shows a large irreversible capacity during the initial cycles of the cell similar to the effect observed for the liquid-electrolyte cell. However, the irreversible capacity observed on the initial cycles of the SPE cell is higher than the observed in the liquid electrolyte cells, with 18% CE compared to the 50% of the liquid cell. The first discharge shows a flat plateau at 2 V attributed to solid electrolyte interphase formation and likely reduction of LiBOB to form lithium oxalate and lithium carbonate (Figure 12b).

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The CE increases up to 97% after the second cycle and the discharge profiles display a small flat plateau of 20 mAh g⁻¹ at ca. 0.5 V vs Li/Li⁺ followed by a sloping plateau. The average discharge capacity during the initial cycles is 300 mAh·g⁻¹ at C/20, with a stable CE above 96 %.

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Although the invention has been particularly shown and described with reference to particular examples, it will be understood by those skilled in the art that various changes in the form and details may be made therein without departing from the scope of the present invention.

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Claims

1. A method of producing a 3D structure comprising a fibre network, wherein the method comprises:
5 providing a polymeric solution comprising
 - a polymer,
 - a solvent, and
 - a salt, acid or base additiveto an electrospinner print head, wherein the solvent/polymer/additive ratio is
10 provided at approximately 200:30:1 by weight;
electrospinning the polymeric solution from the print head onto a print bed by applying a voltage difference between the print head and a collector to create the 3D structure.
- 15 2. The method of claim 1, wherein the method further comprises annealing the fibre network in an inert/reducing atmosphere.
3. The method of either claim 1 or 2 wherein the solvent/polymer/additive ratio is provided within 15% variance of ratio 200:30:1, optionally about 7%, 5% or 3%
20 variation of ratio 200:30:1.
4. The method of any one of claims 1 to 3 wherein the polymer or combination of polymers is provided at 5 wt % to 25 wt % of the polymeric solution.
- 25 5. The method of any of the previous claims wherein the polymer is selected from a polymer which can be electrospun.
6. The method of any of the previous claims wherein the polymer is selected from a polymer which can be electrospun to produce nanofibers from a polymer
30 solution.
7. The method of any previous claim wherein the polymer is selected from selected from a group comprising of: polyacrylonitrile (PAN), polyvinylpyrrolidone (PVP),

Polycaprolactone (PCL), Cellulose Acetate (CA), Polyvinylidene fluoride (PVDF), polystyrene (PS) or a combination thereof

- 5 8. The method of any previous claims wherein the polymer is selected from selected from a group comprising of: polyacrylonitrile (PAN), polyvinylpyrrolidone (PVP), Polycaprolactone (PCL), Cellulose Acetate (CA), Polyvinylidene fluoride (PVDF), or a combination thereof.
- 10 9. The method of claims 4 to 8 wherein A) the polymer is PAN and is provided in the range of about 5 wt % to 25 wt %, optionally 12 wt % to 15 % of the polymeric solution,
- 15 B) wherein the polymer is PVP and is provided in the range of about 10 wt % to 20 wt % of the polymeric solution optionally 12 wt % to 15 wt % of the polymeric solution,
- C) wherein the polymer is PCL and is provided in the range of about 10 wt % to 18 wt %, optionally 12 wt % to 15 % of the polymeric solution,
- 20 D) wherein the polymer is CA and is provided in the range of about 10 wt % to 18 wt %, optionally 12 wt % to 15 % of the polymeric solution, or
- E) wherein the polymer is PVDF and is provided in the range of about 10 wt % to 20 wt %, optionally 12 wt % to 15 wt % of the polymeric solution.
- 25 10. The method of claims 4 to 8 wherein the polymer or combination of polymers is at 15 wt.% of the polymeric solution.
- 30 11. The method of any one of the previous claims wherein a solvent in the polymeric solution is selected from a group comprising or consisting of DMF, THF, ethanol, MeOH, HFIP, DCM, or a combination thereof.
- 35 12. The method of any one of the previous claims wherein the acid or salt or base is a strong salt, a strong acid or a strong base, optionally wherein the acid or salt or base is selected from a group consisting of

hydrochloric acid (HCl) or phosphoric acid (H₃PO₄);
or lithium chloride (LiCl) or lithium bromide (LiBr) or potassium chloride (KCl) or
sodium chloride (NaCl);
or sodium hydroxide (NaOH).

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13. The method of any one of the previous claims wherein the strong acid is HCl.

14. The method of any one of the previous claims wherein the voltage used in the
step of electrospinning is between about 15-30 kV and the current is about 100
μA.

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15. The method of any one of the previous claims wherein the electrospinning step
comprises electrospinning under about a 20-55 % relative humidity atmosphere,
suitably wherein the relative humidity is about 30%.

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16. The method of any one of the previous claims wherein the electrospinning is
conducted at a temperature of about 0-70 °C.

17. The method of claim 16 wherein the electrospinning is conducted at a
temperature of about 25 °C

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18. The method of any one of claims 1-15 wherein the electrospinning is conducted
at about -70 to -90 °C.

19. The method of any one of the previous claims wherein the atmosphere of the
electrospinning step is an Ar or N₂ atmosphere.

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20. The method of any one of the previous claims wherein the 3D structure is a 3D
nanostructure comprising carbon nanofibrous networks with diameters from
about 150 nm and the 3D nanostructure is up to 0.5cm tall, 1 cm tall, 2 cm tall,
up to 3 cm tall, 5 cm tall, up to 7.5cm tall, up to 10 cm tall or at least 12.5cm tall.

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21. The method of any one of the previous claims wherein when the method
includes an oxidation step at a temperature of about 280 °C for 1 hour under air
(ambient atmosphere).

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22. The method of any one of the previous claims wherein when the method includes a carbonisation step at a temperature between about 800 and 1000 °C, preferably between about 850 and 950 °C, more preferably at about 900 °C for about 1 hour under an inert atmosphere, optionally an N₂ or Ar atmosphere.
23. The method of claim 21 or 22 wherein the temperature is provided at a heating rate of 0.5 to 1 °C/min.
24. The method of claim 21 or 22 wherein the temperature is provided at a heating rate of about 5 °C/min.
25. The method of claim 21 or 22 wherein the temperature is provided at a heating rate of about 10 °C/min.
26. The method of any one of the previous claims wherein the electrospinning occurs at a flow rate of about 5 mL/hour, the voltage applied is in the range of about 15 to 30 kV, with a working distance of about 5 cm.
27. A 3D structure comprising carbon nanofibrous networks provided by the method of any one of claims 1-26.
28. The 3D structure of claim 27 wherein the structure has at least one of
- a. a resistivity around 400-1000 Ohms,
 - b. a porosity about 90-98%.
29. The 3D structure of any one of claims 27 to 28 wherein the 3D structure comprises nanofibers with an average cross section of about 300-800 nm.
30. The 3D structure of any one of claims 27 to 29 wherein the carbon content of the fibres is about 84% of carbon via XPS analysis.
31. A fuel cell electrode, a battery anode, or a solar cell, a supercapacitor, or a medical device electrode comprising a 3D structure of any one of claims 27 to 30.

32. A purification system, such as an air or water purification system comprising a 3D structure of any one of claims 27 to 30.
- 5 33. A cell culture support structure comprising a 3D structure of any one of claims 27 to 30.

Figure 1

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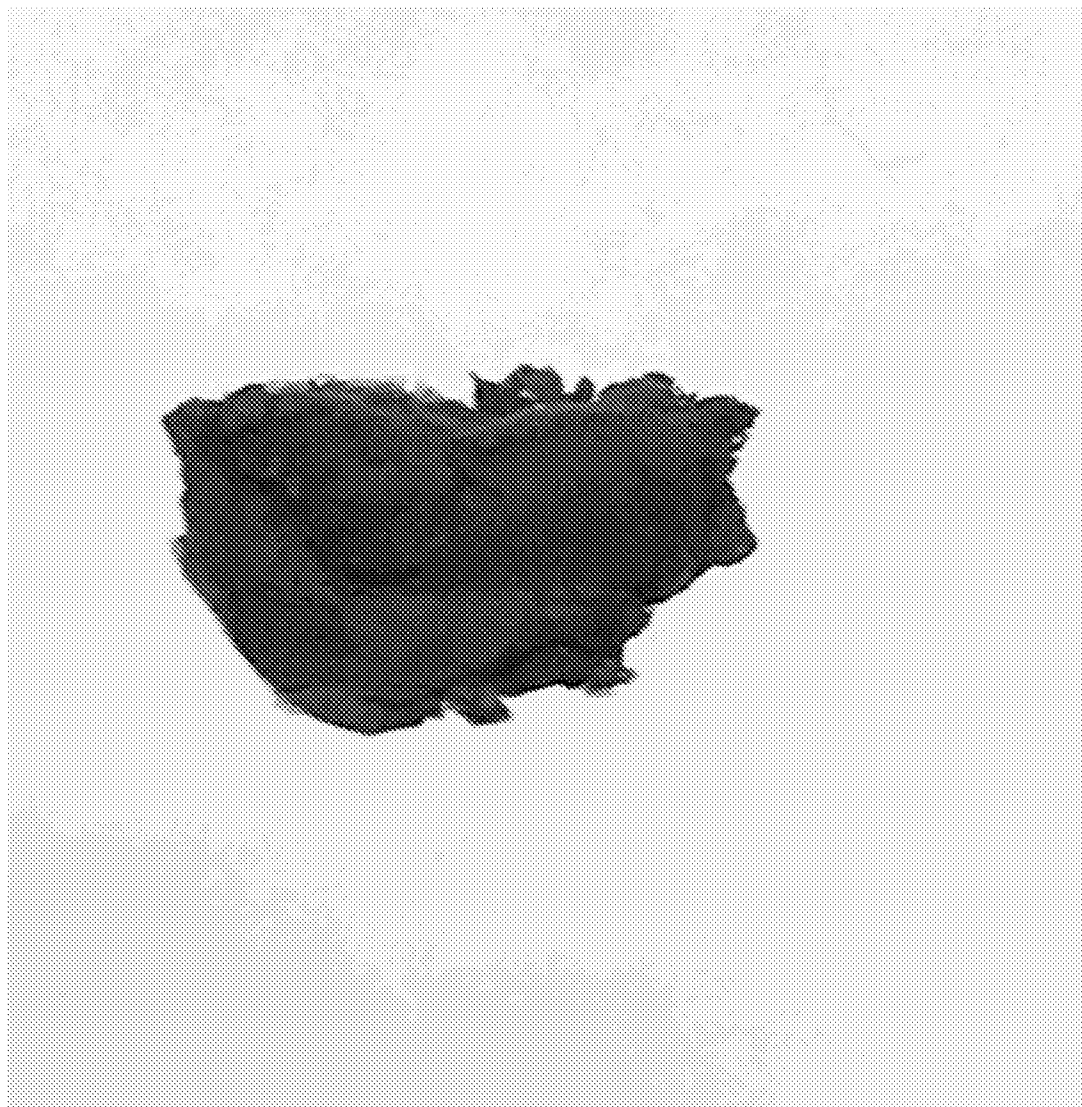


Figure 2

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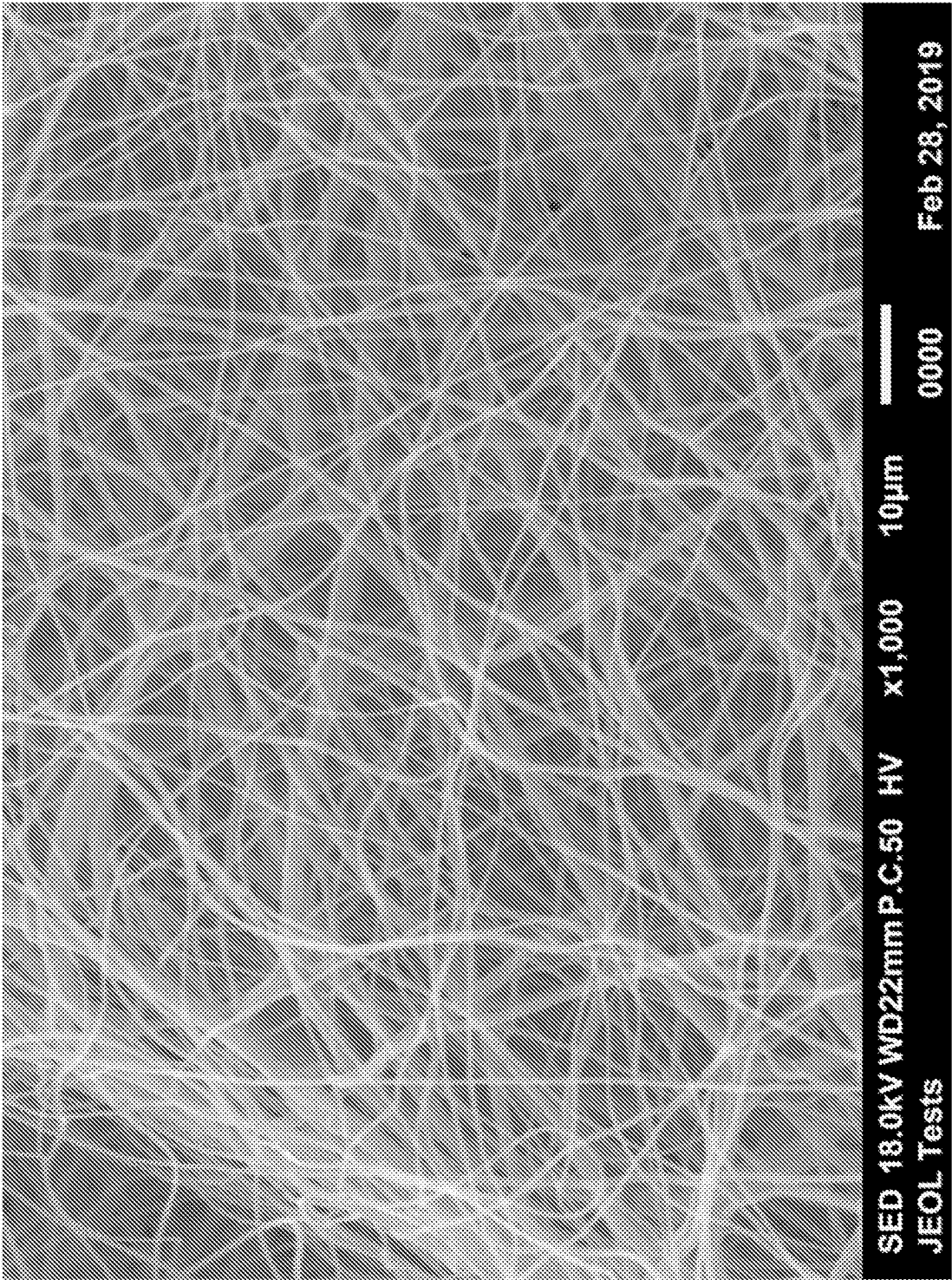


Figure 3

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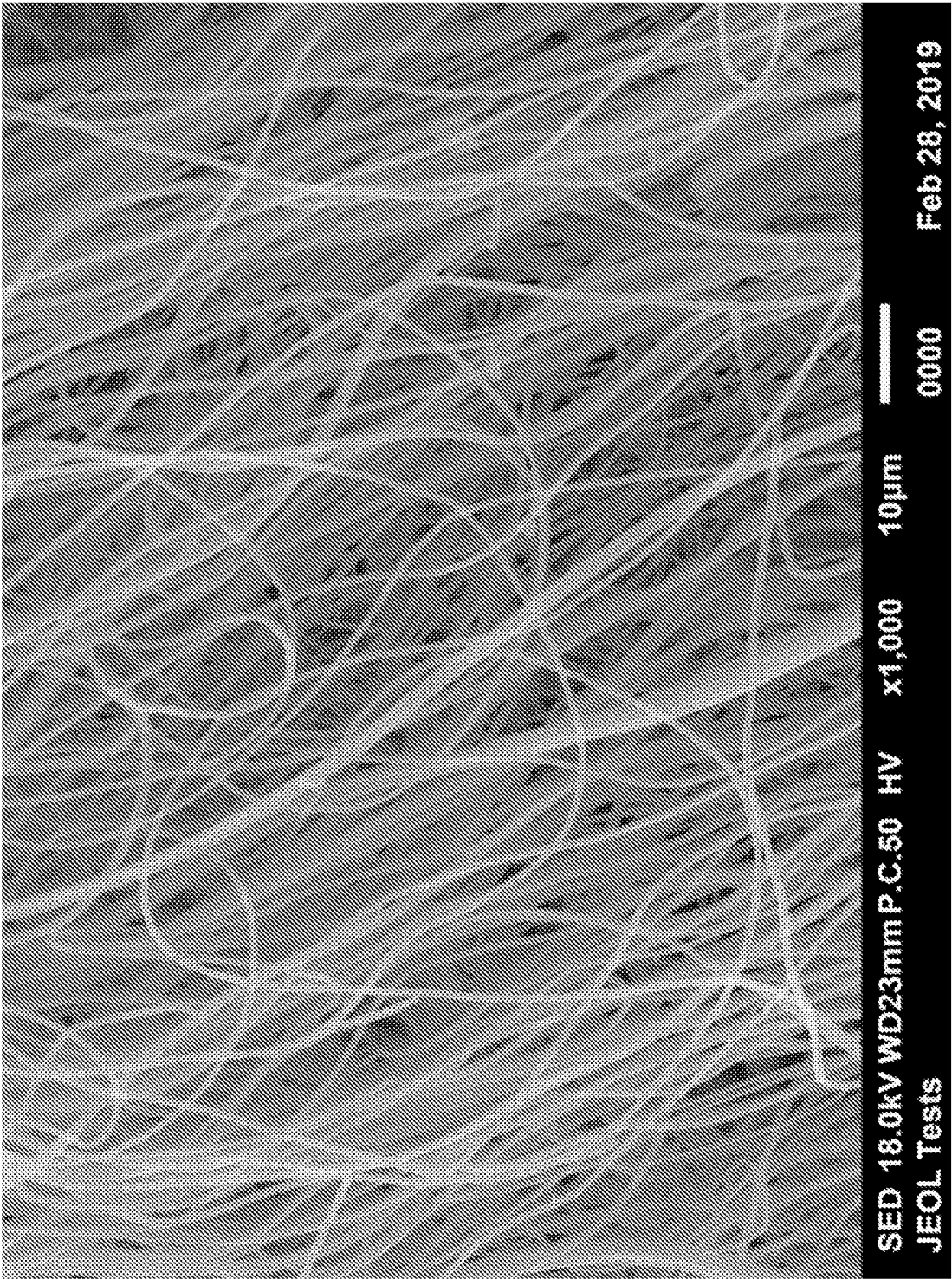
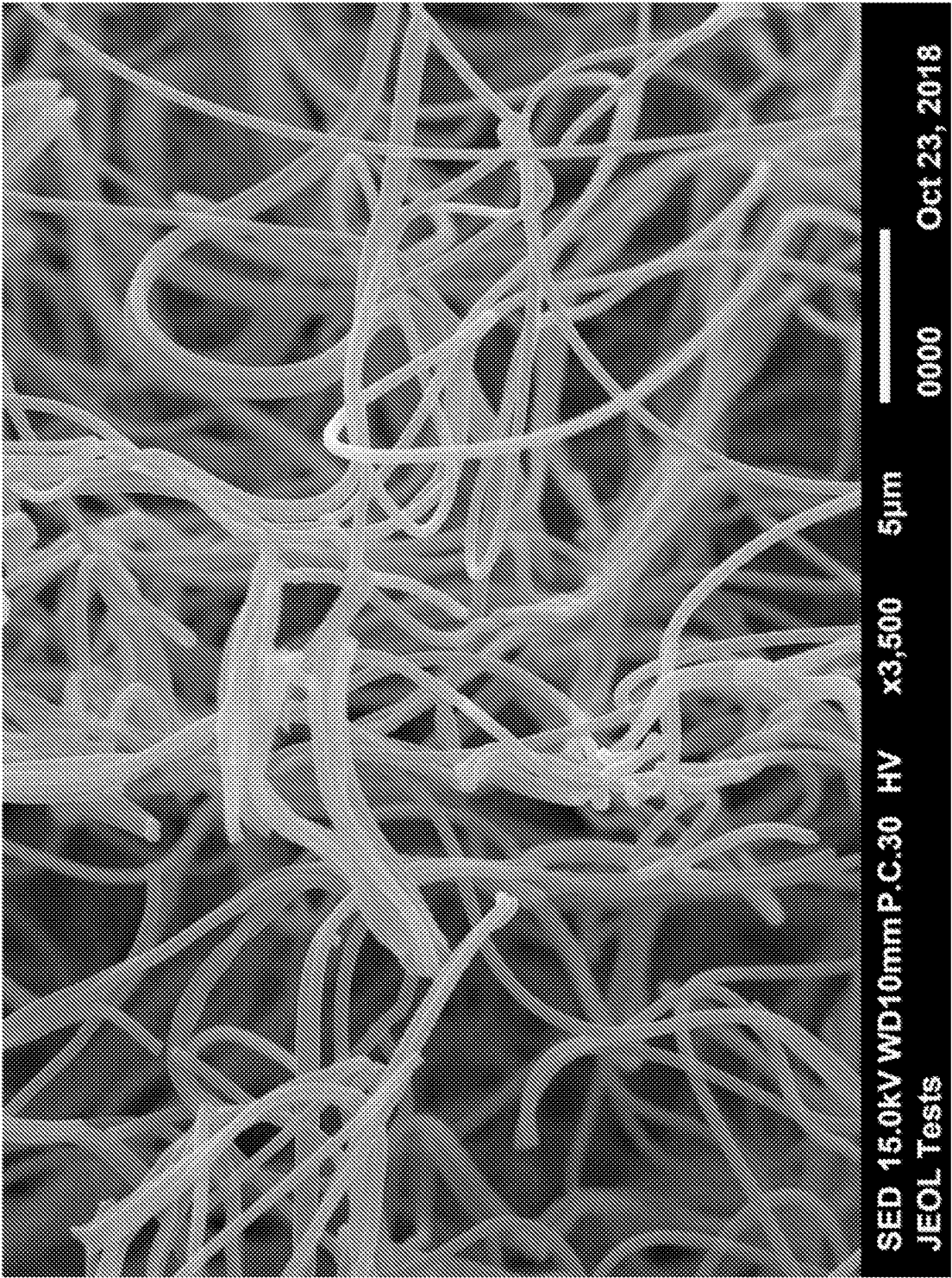


Figure 4

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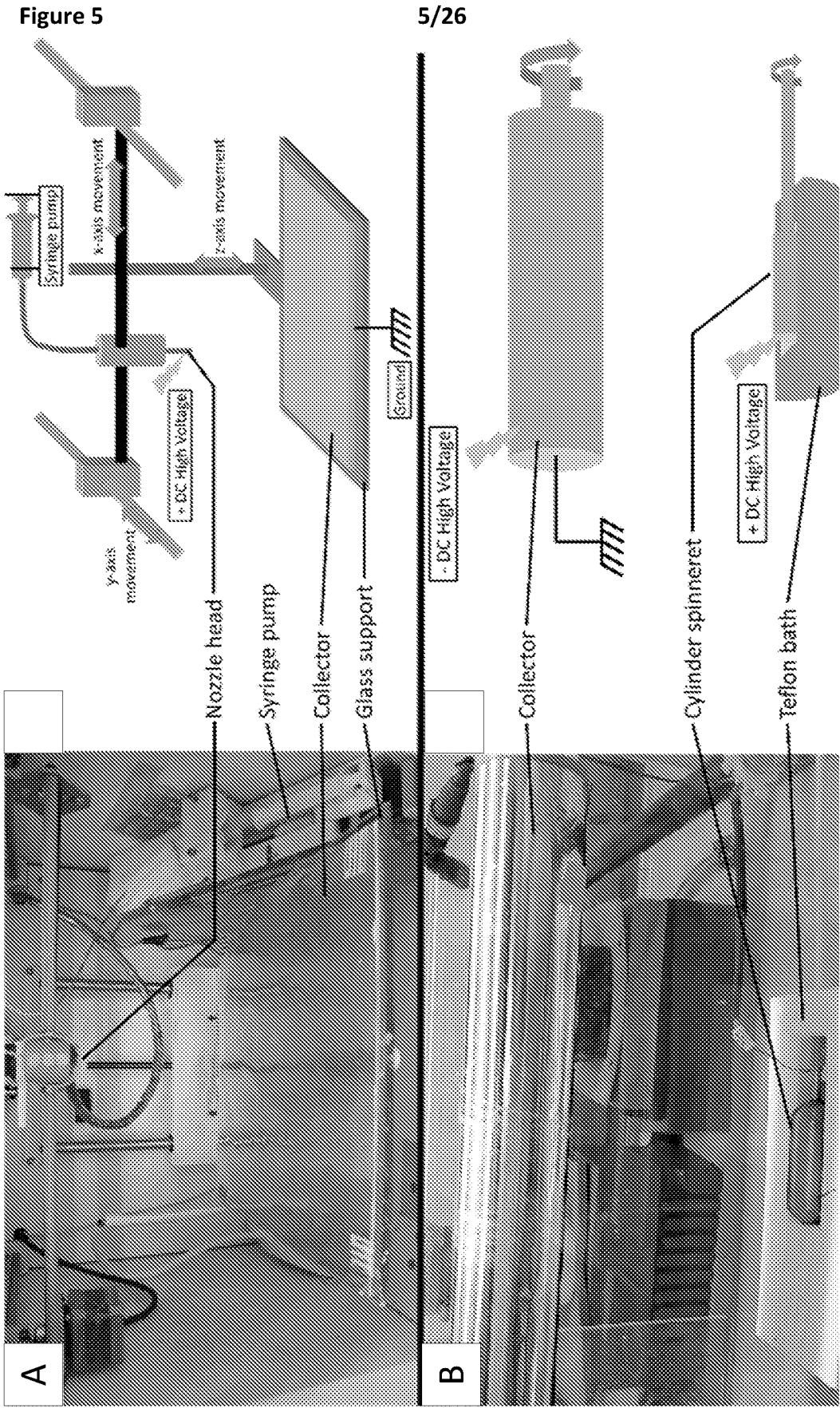


Figure 5 (Continued)

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C - PS

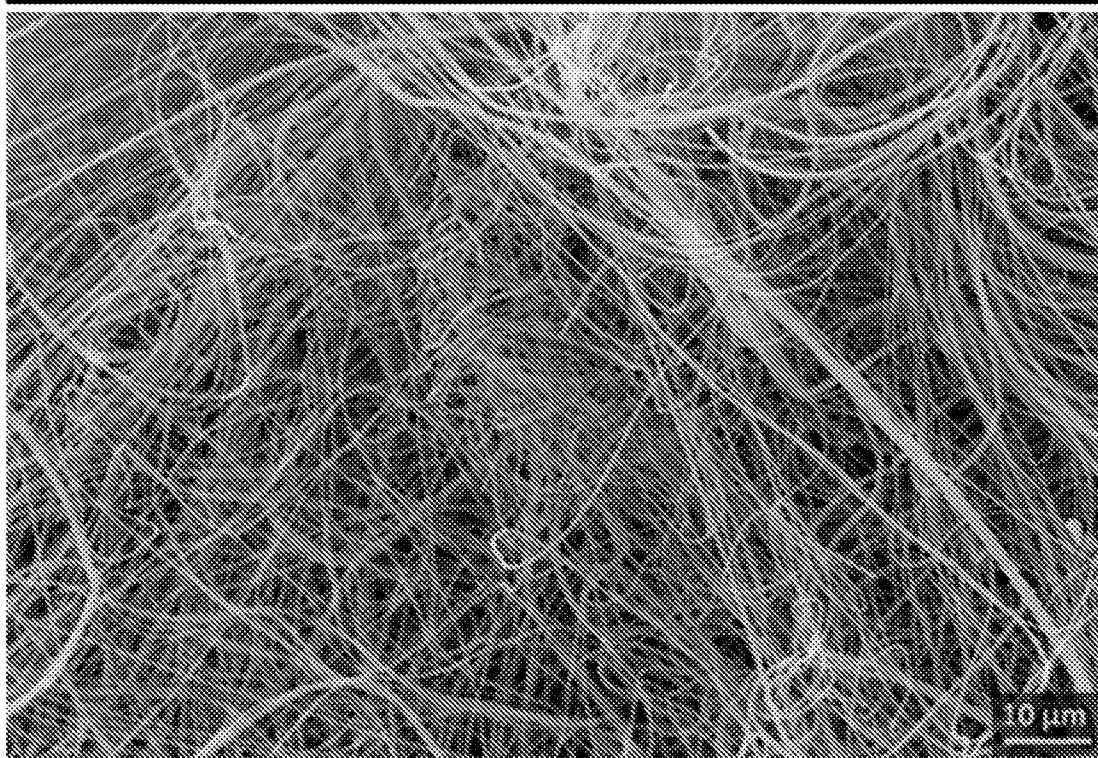


Figure 5 (Continued)

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D - PAN

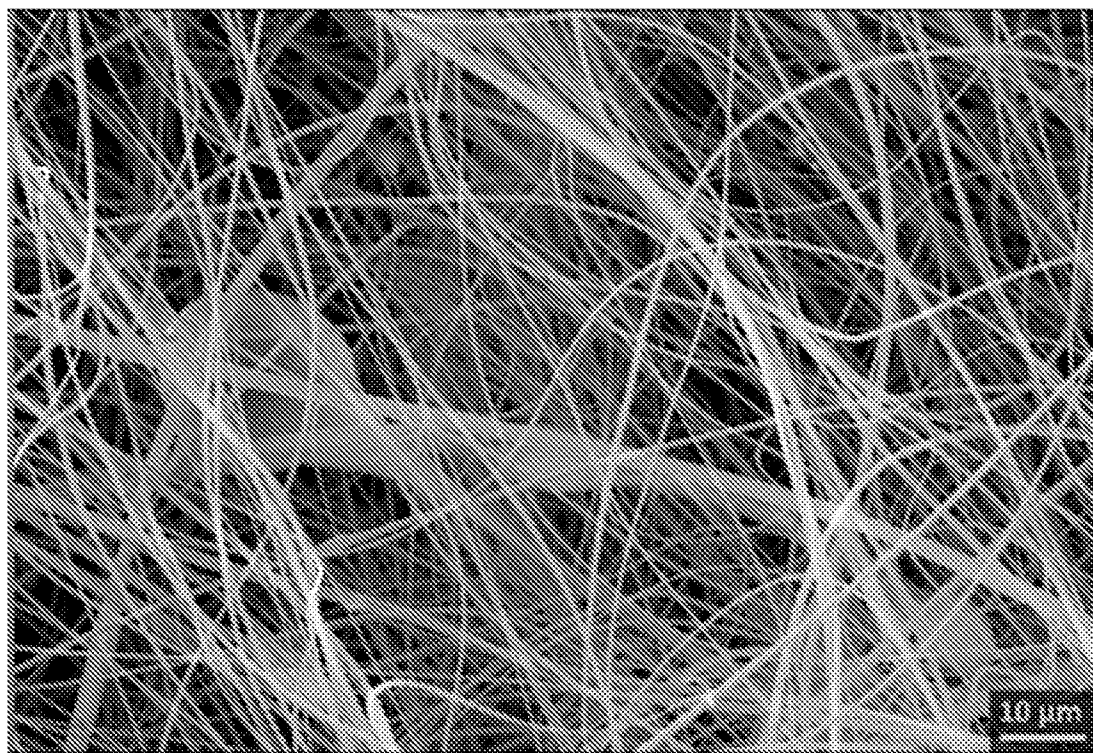
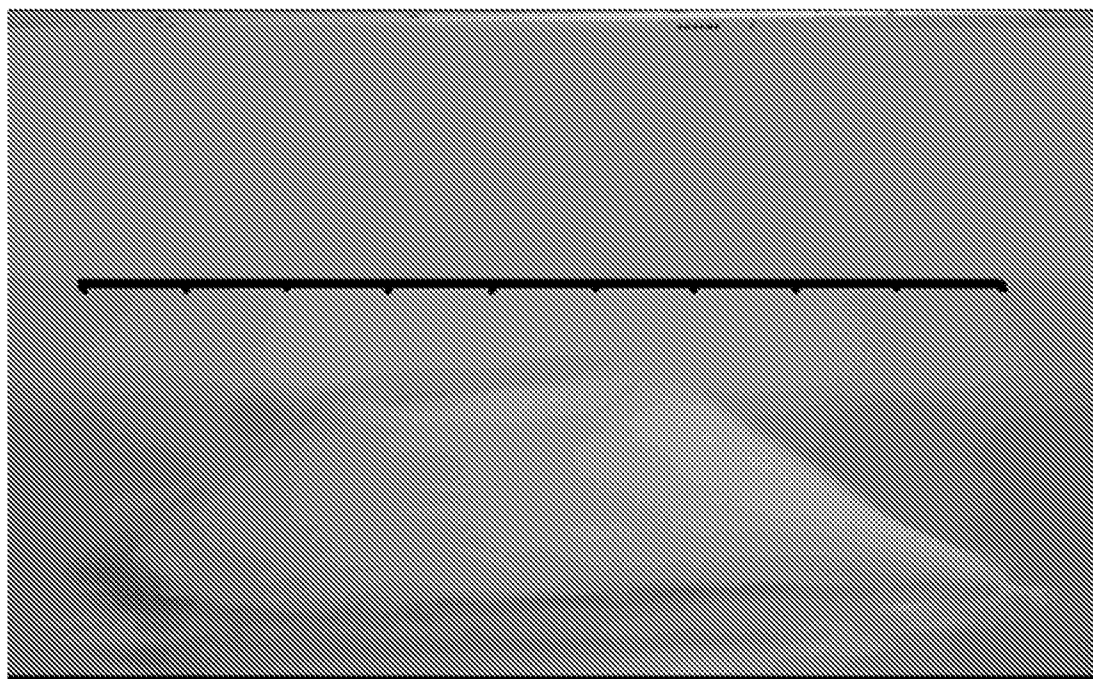


Figure 5 (Continued)

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E - PVP

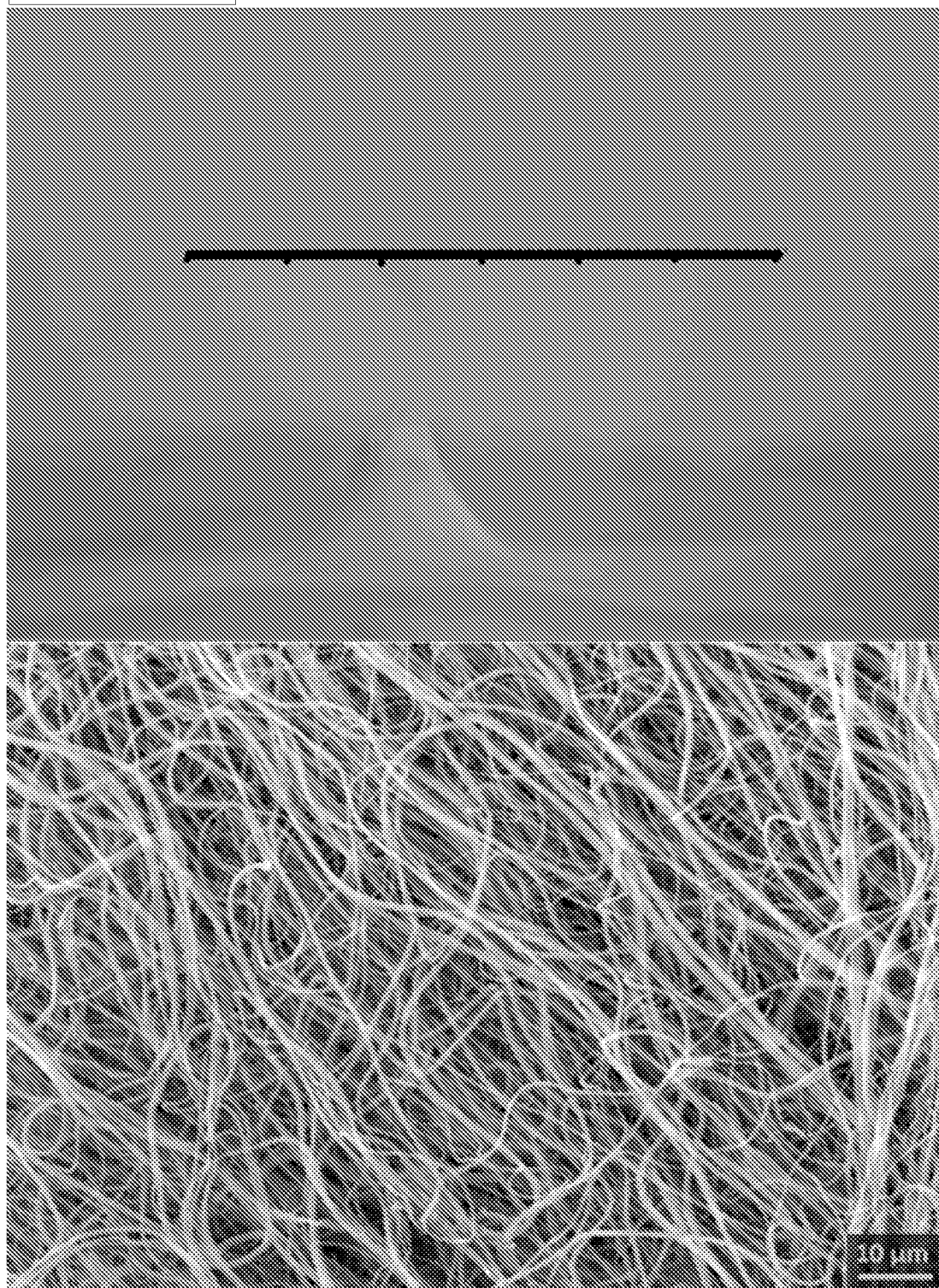


Figure 5 (Continued)

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F - PCL

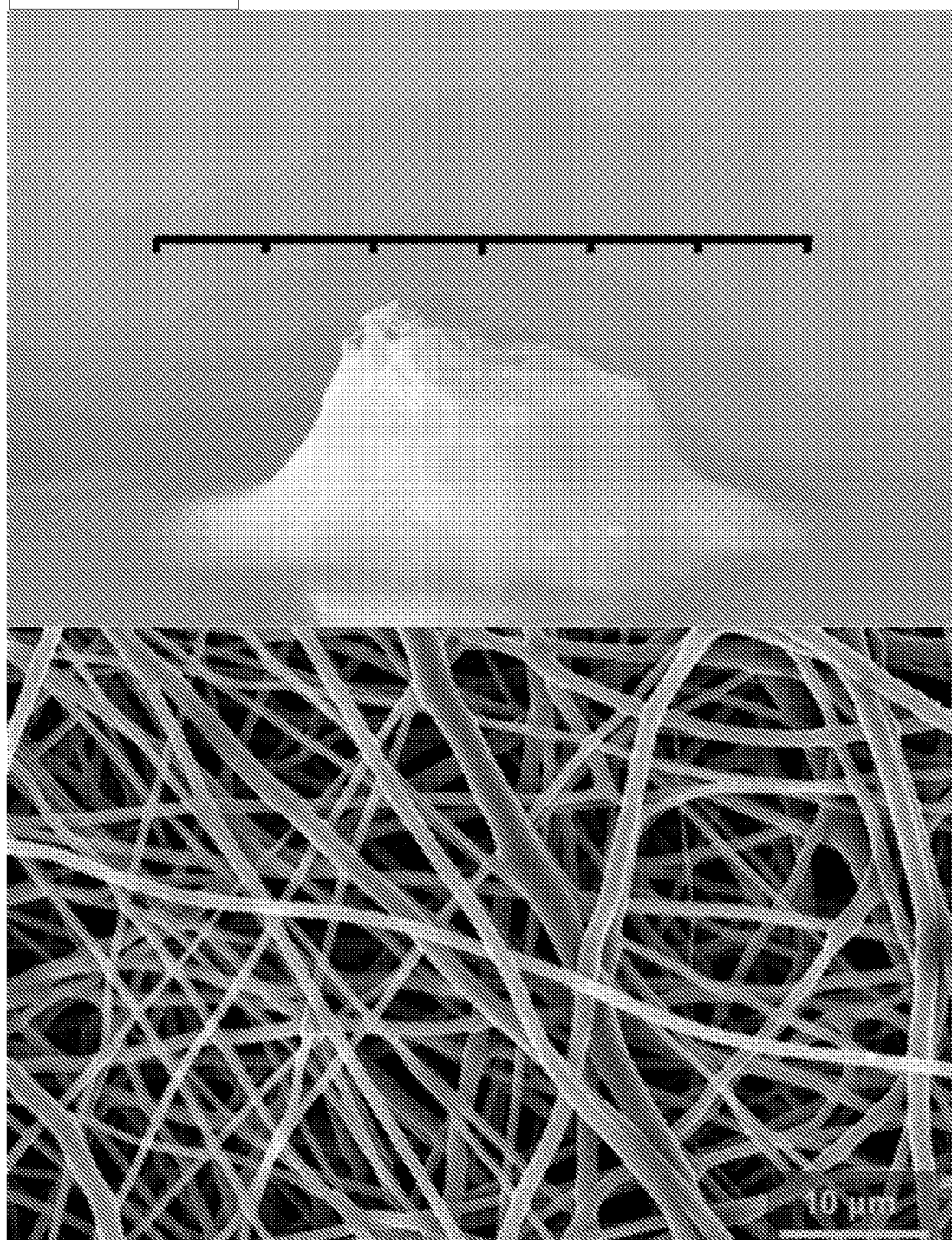


Figure 5 (Continued)

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G - CA

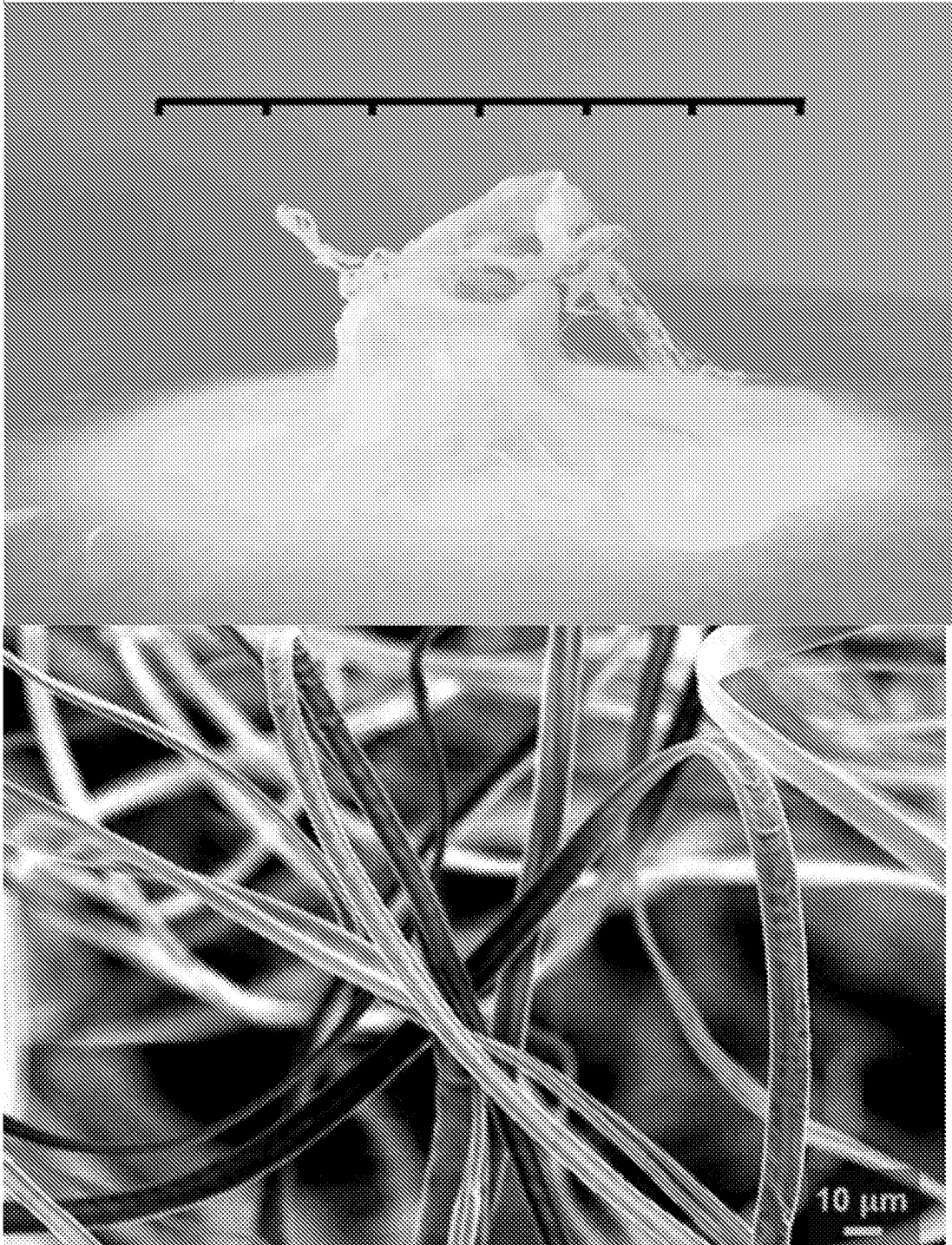


Figure 5 (Continued)

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H - PVDA

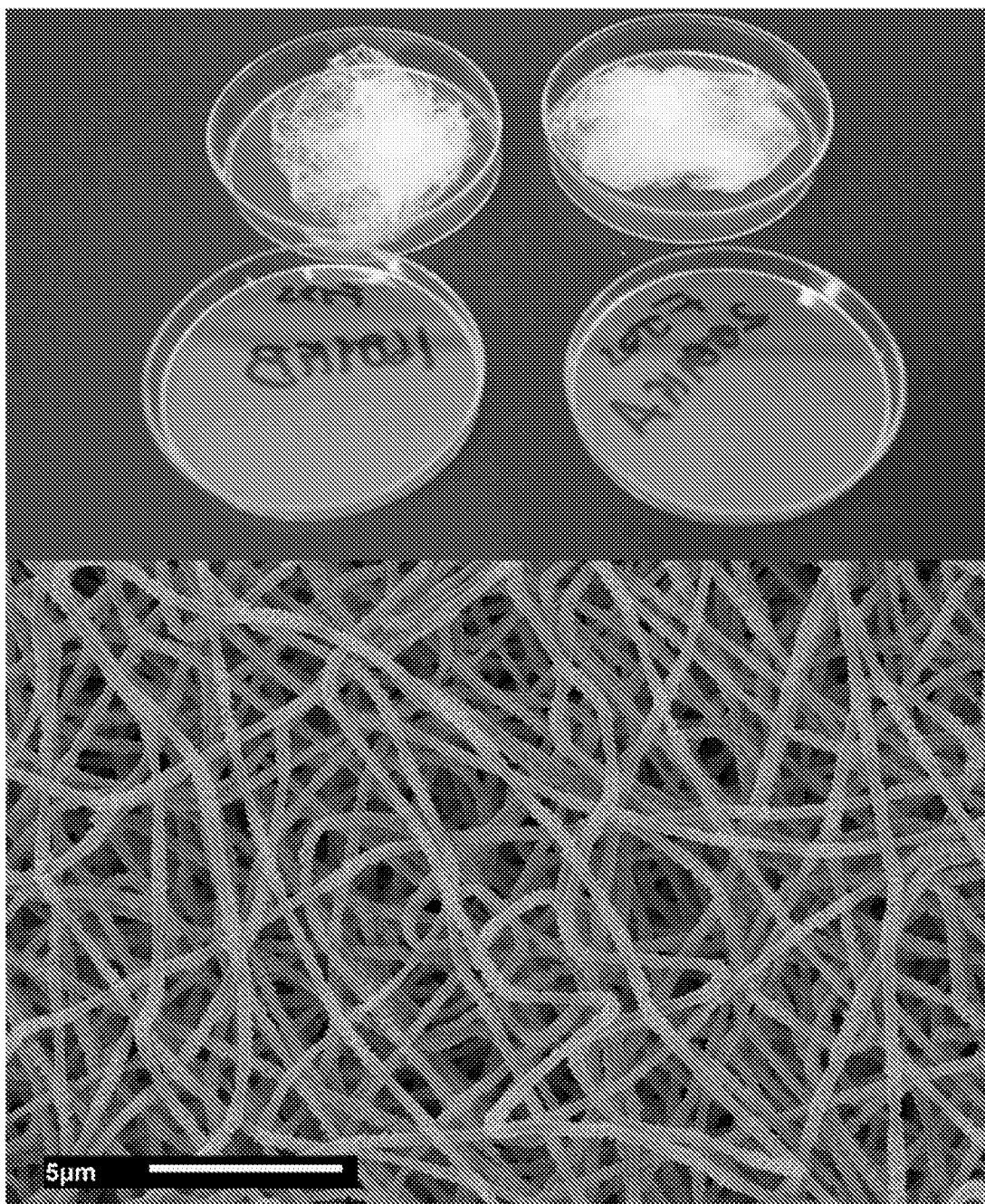


Figure 6

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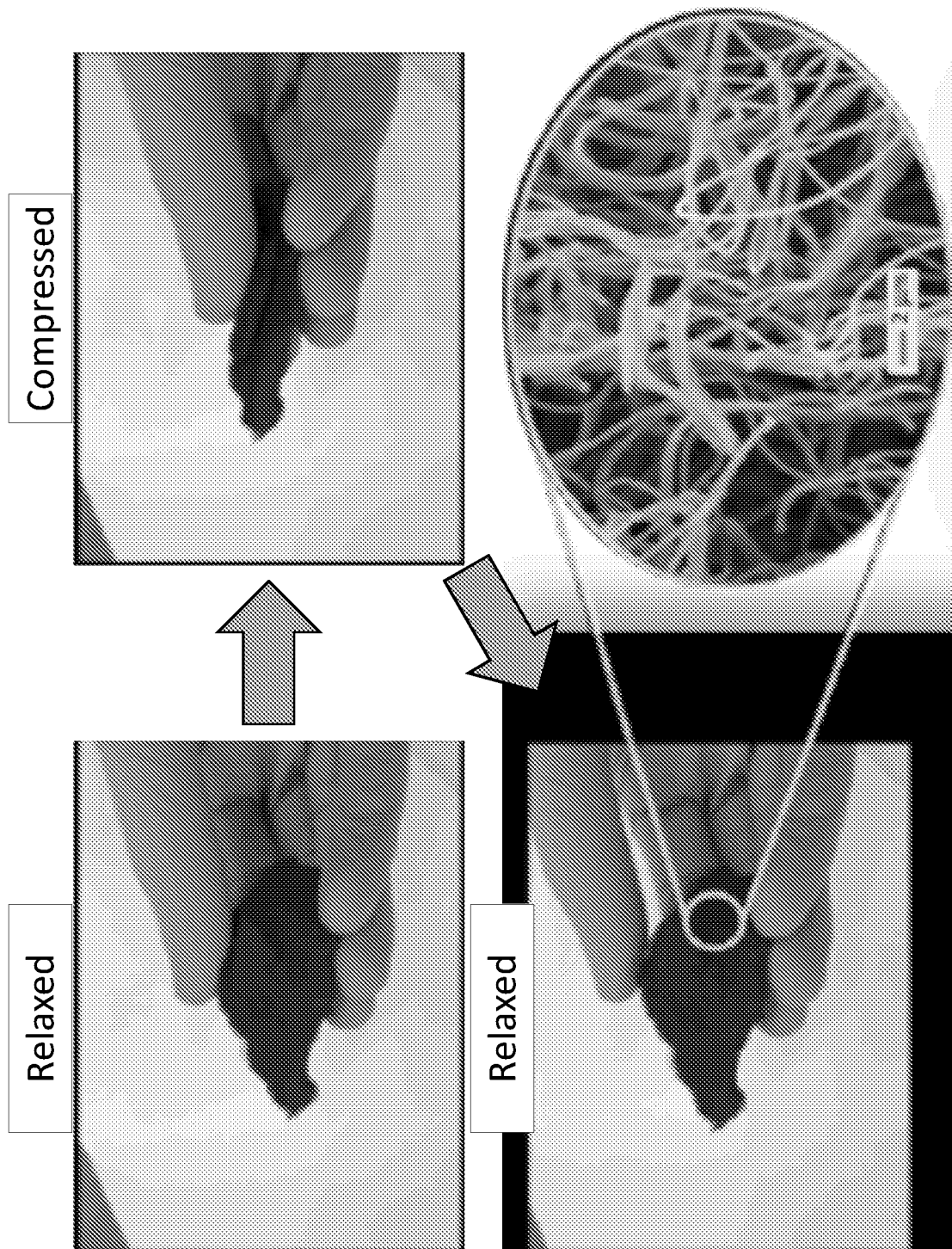


Figure 7

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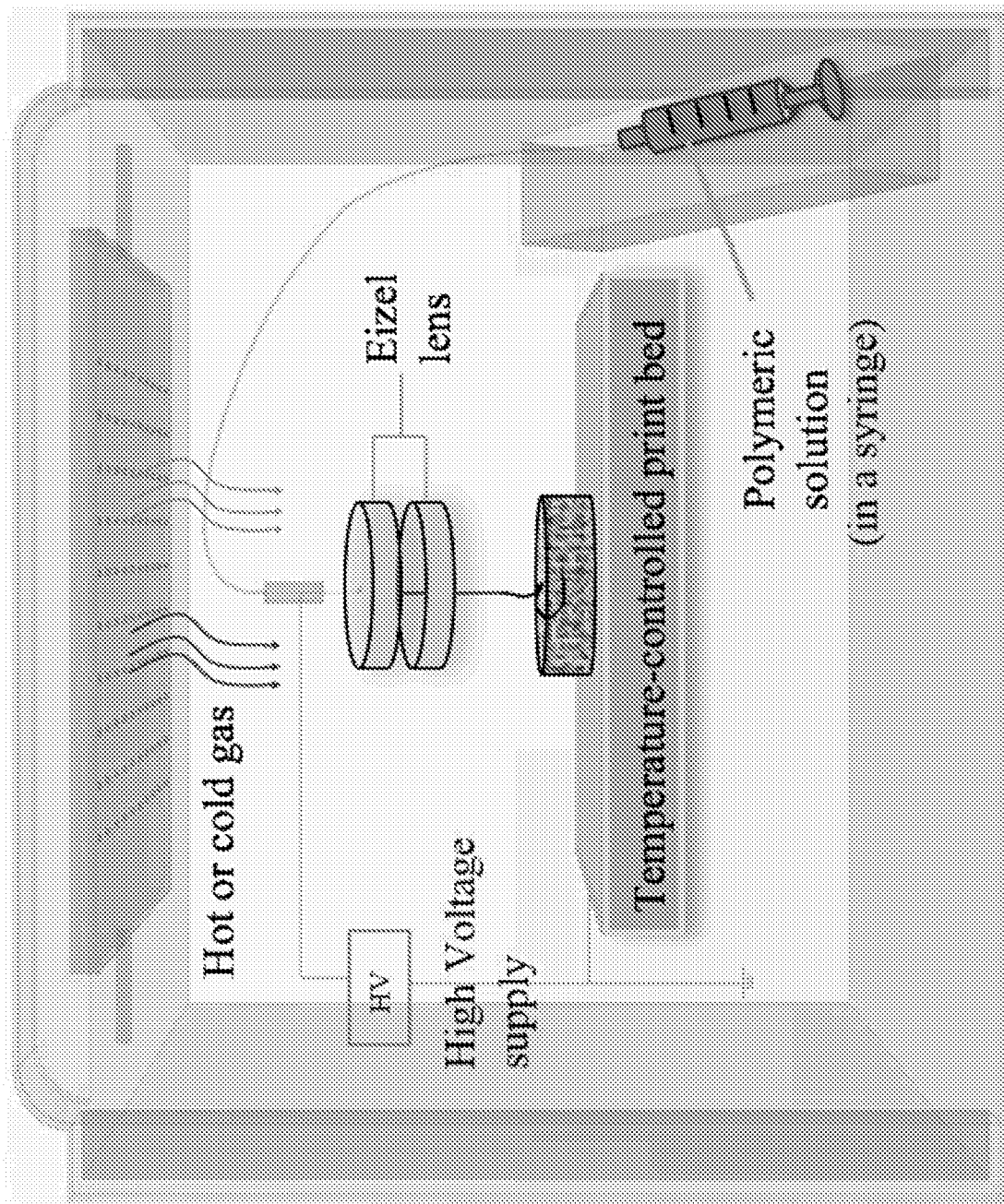


Figure 8

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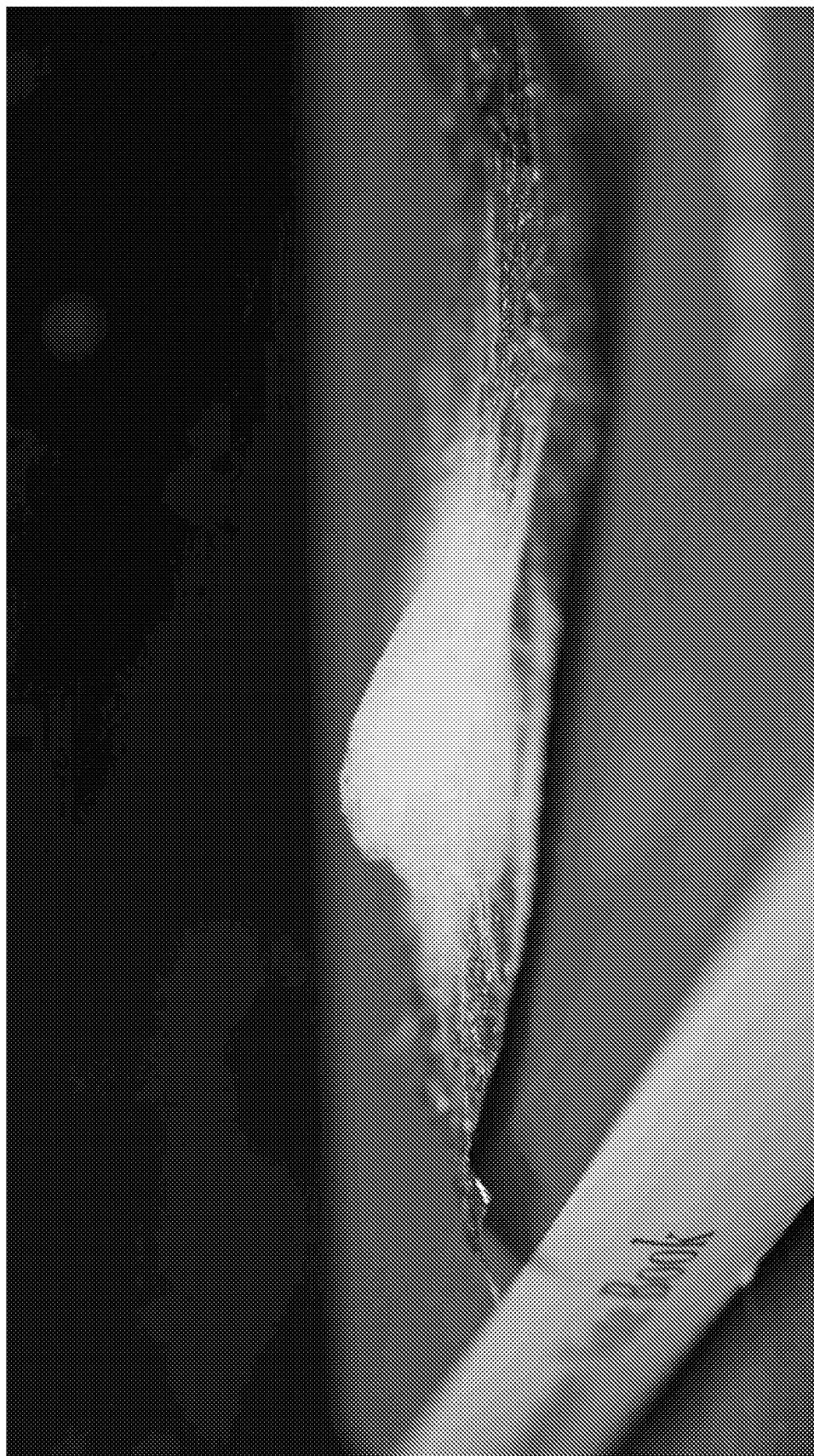


Figure 9

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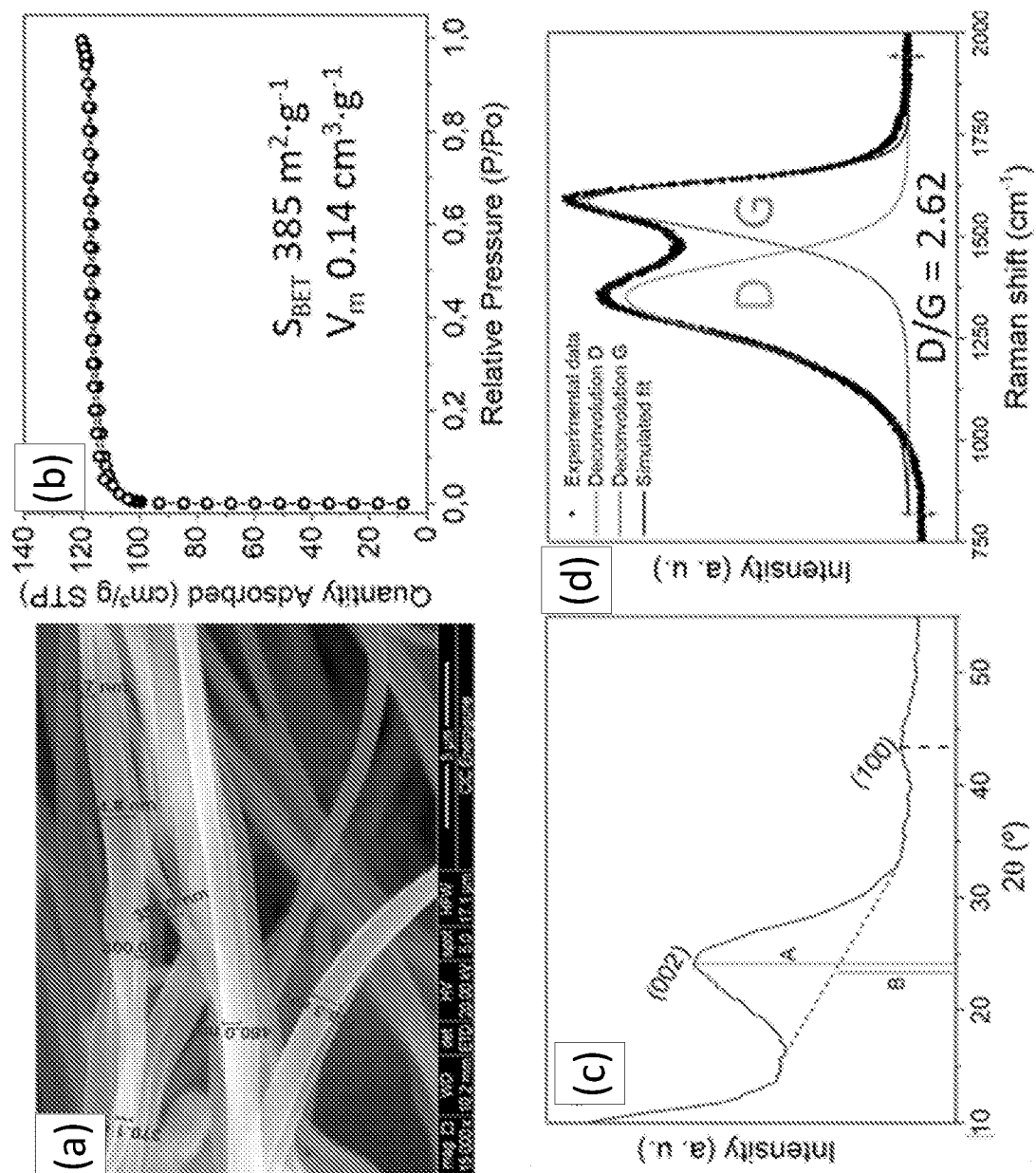
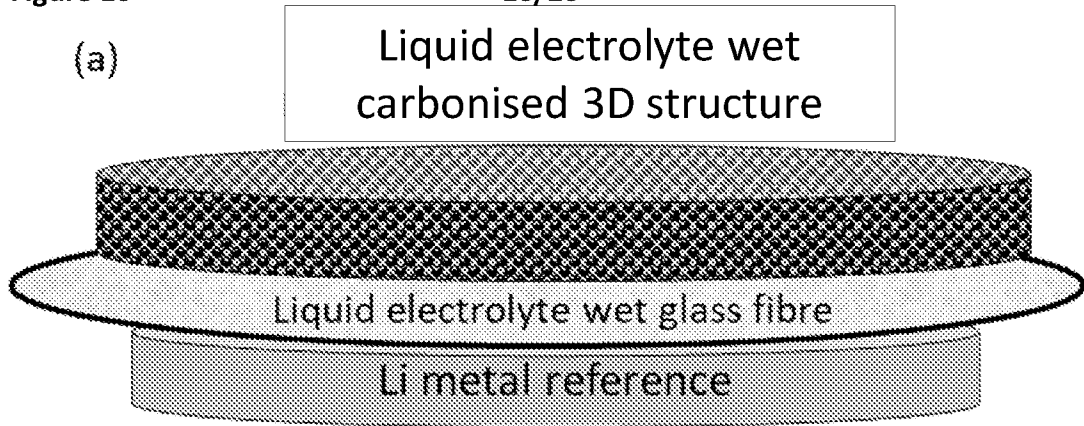
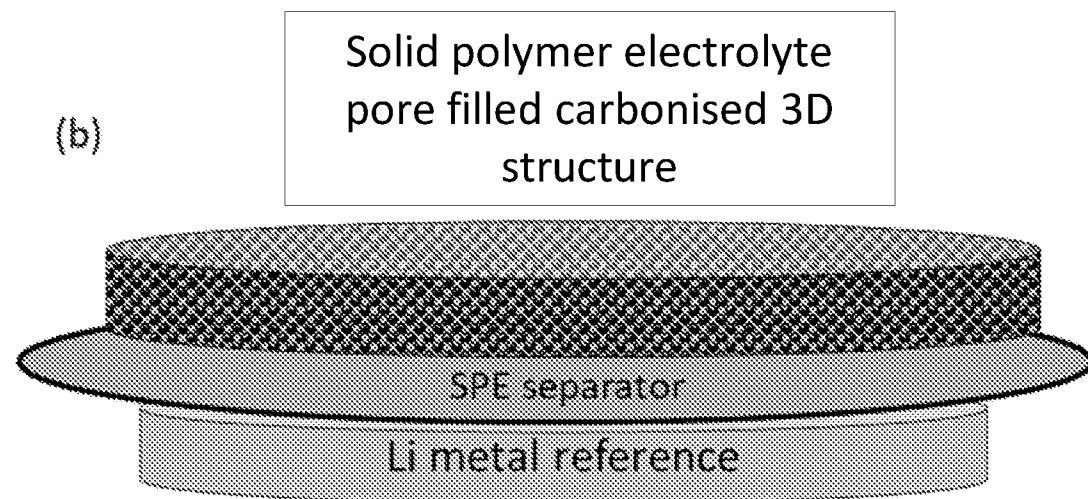


Figure 10

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Liquid electrolyte cell



Solid electrolyte cell

Figure 11

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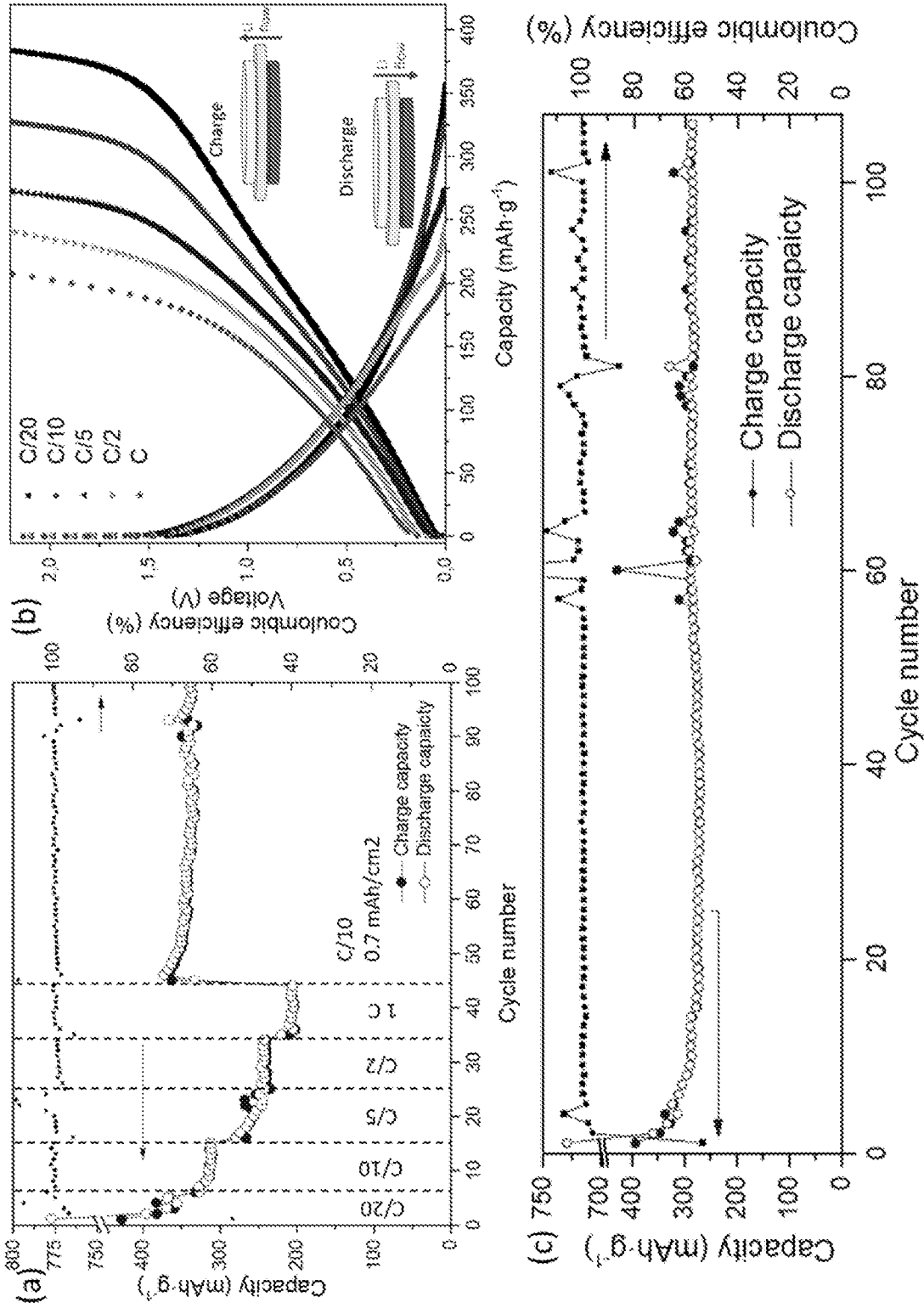


Figure 12

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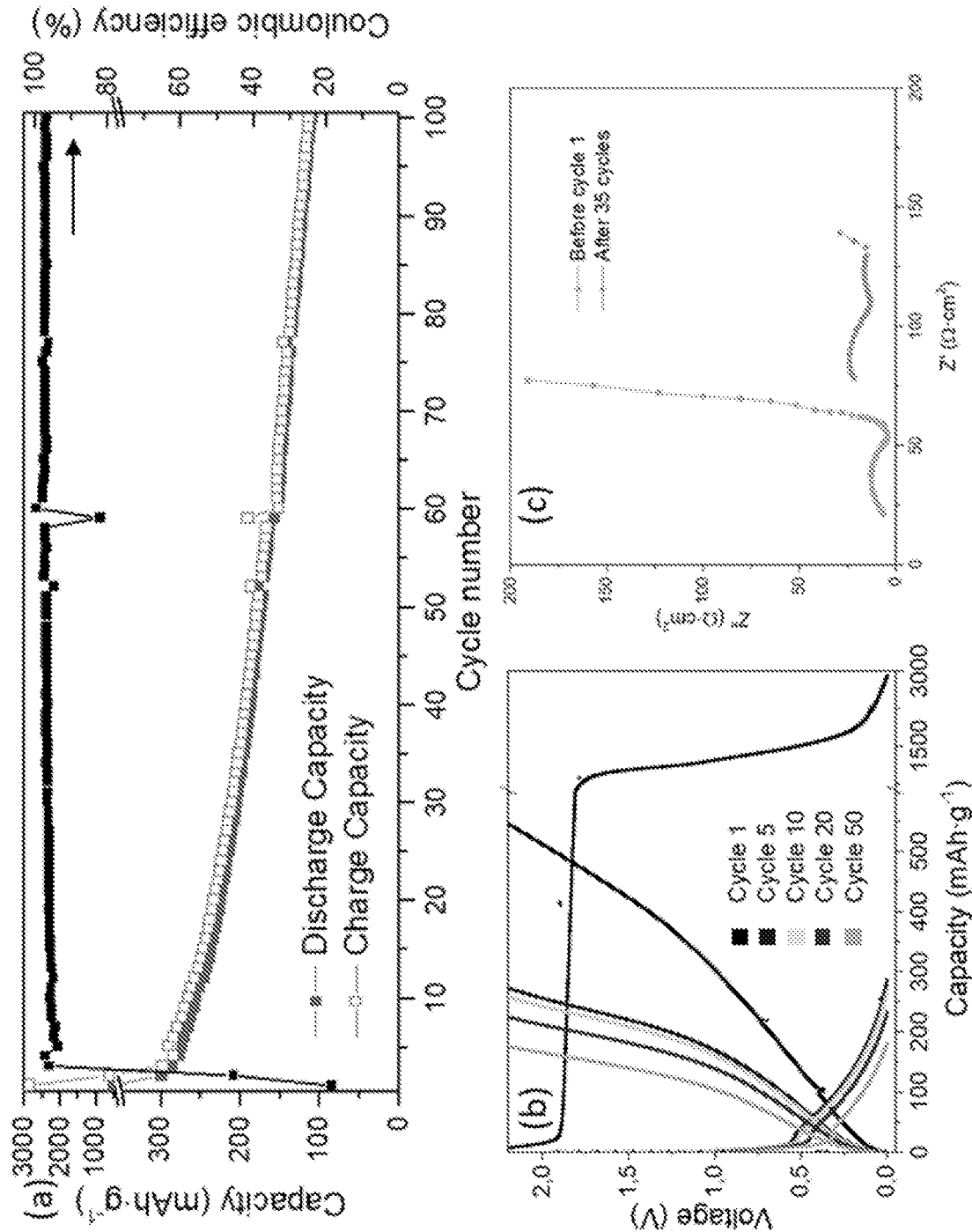


Figure 12 (continued)

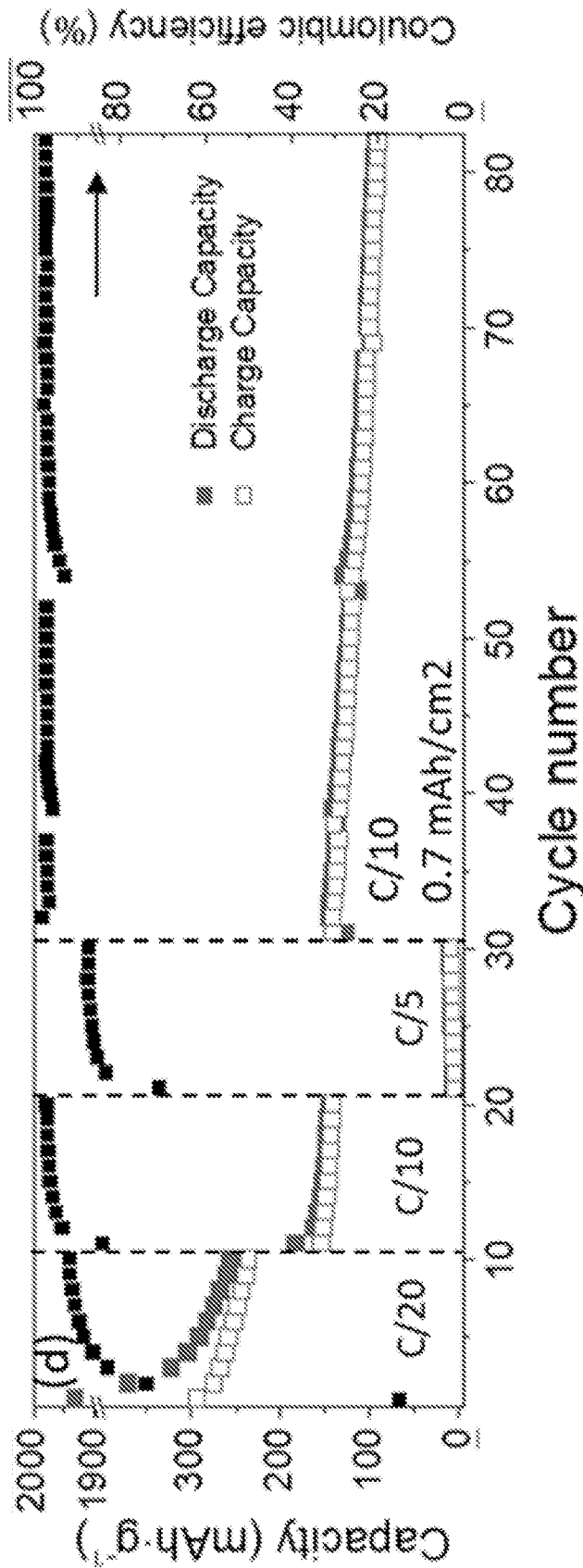


Figure 13

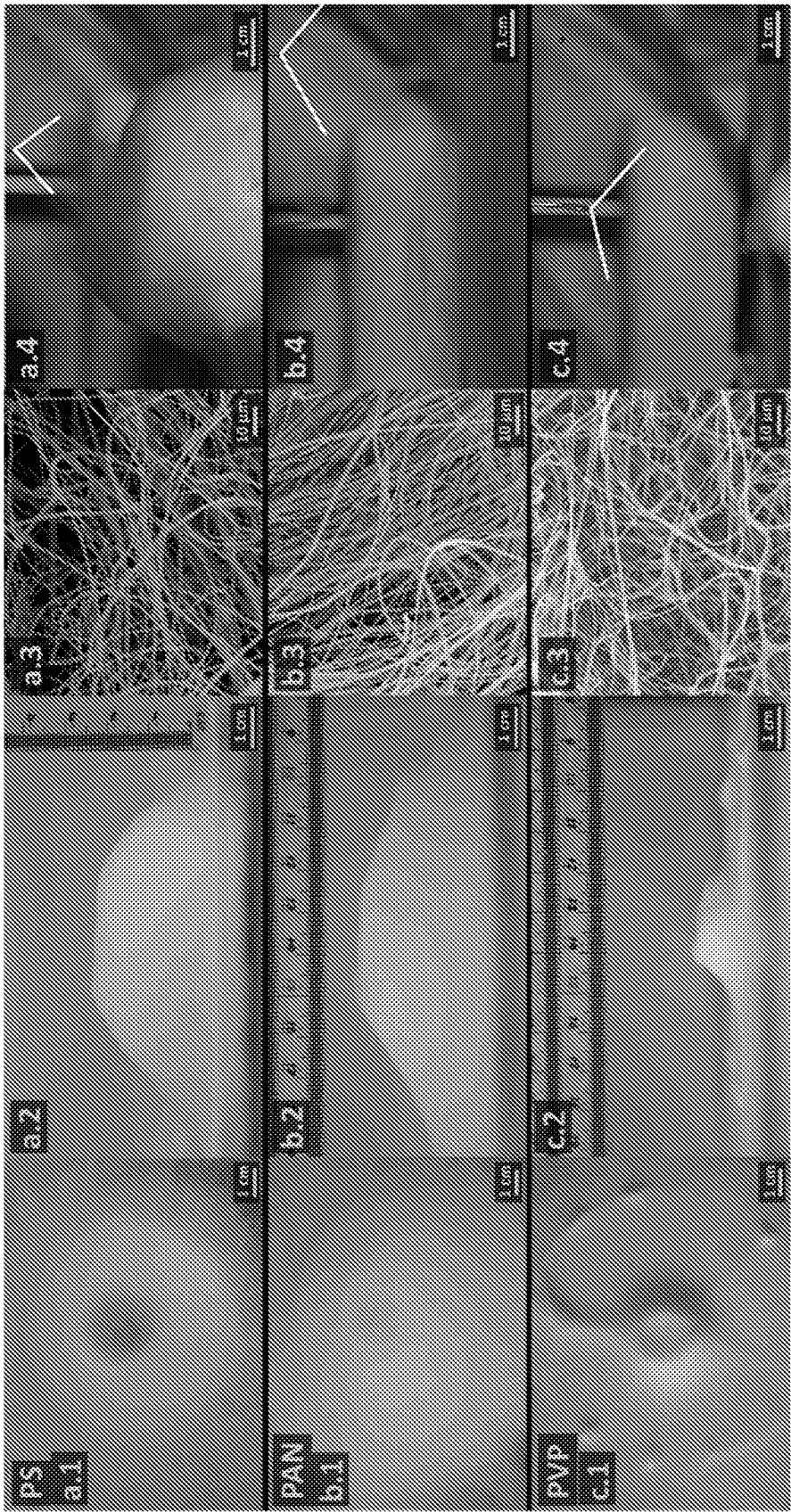


Figure 14

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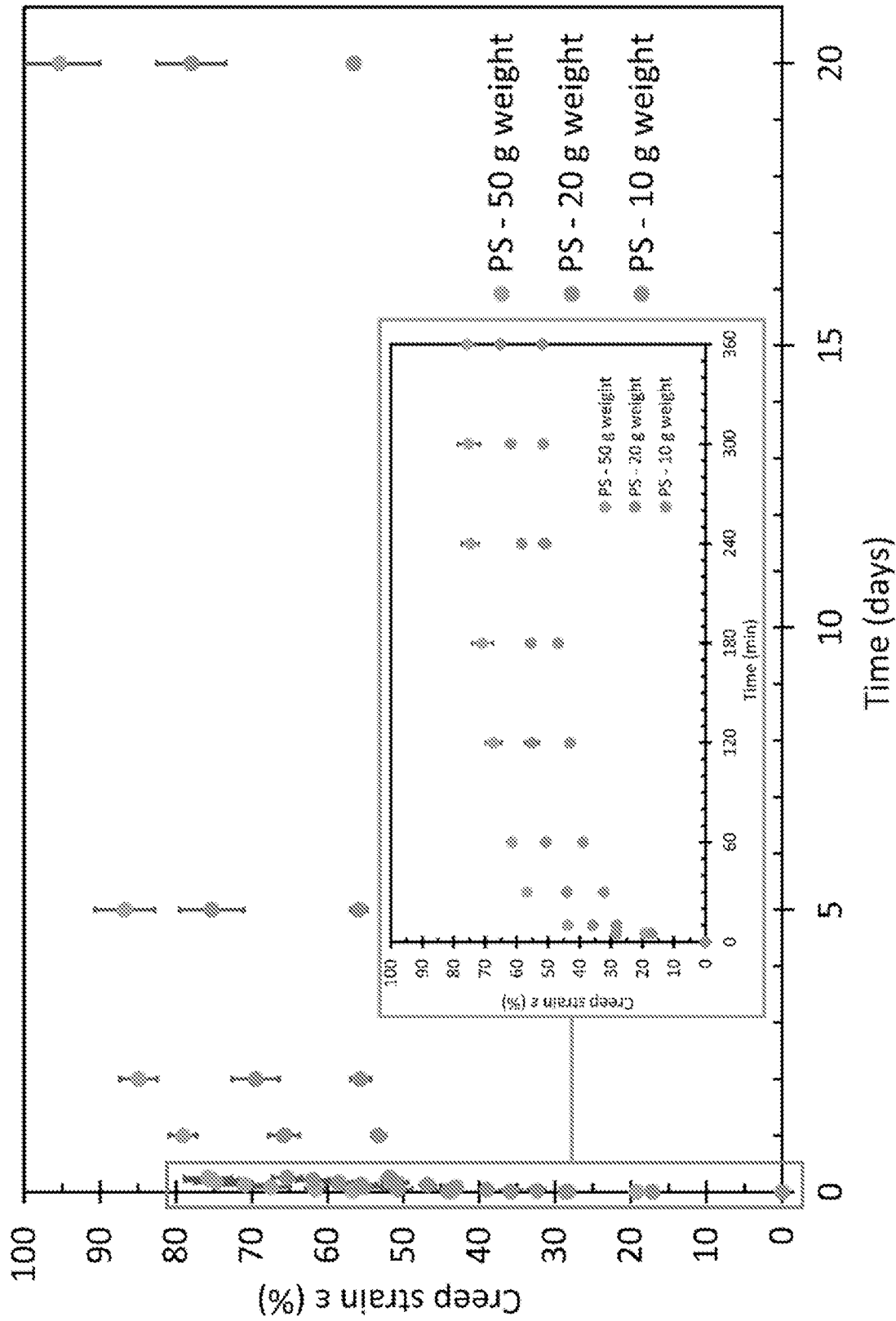


Figure 15

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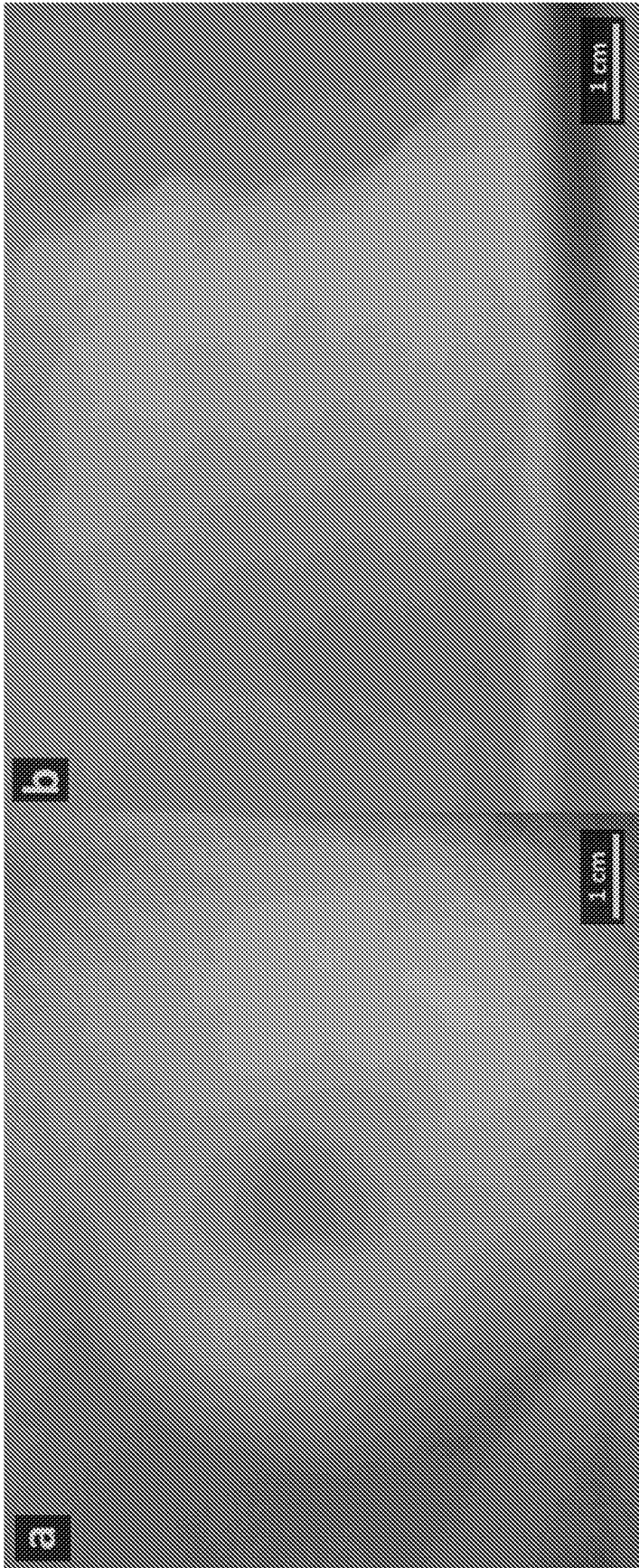


Figure 16

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A

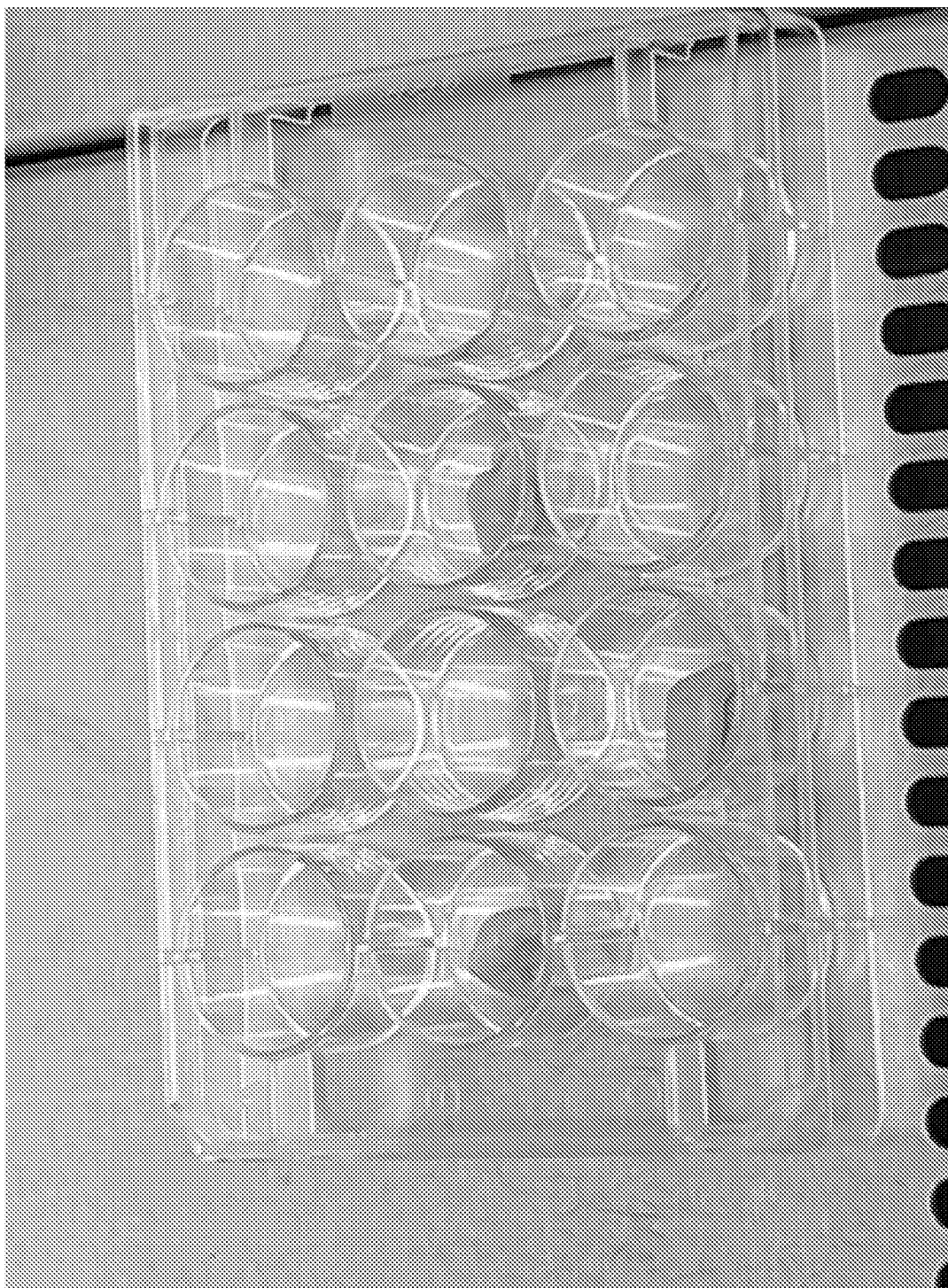


Figure 16 (continued)

B

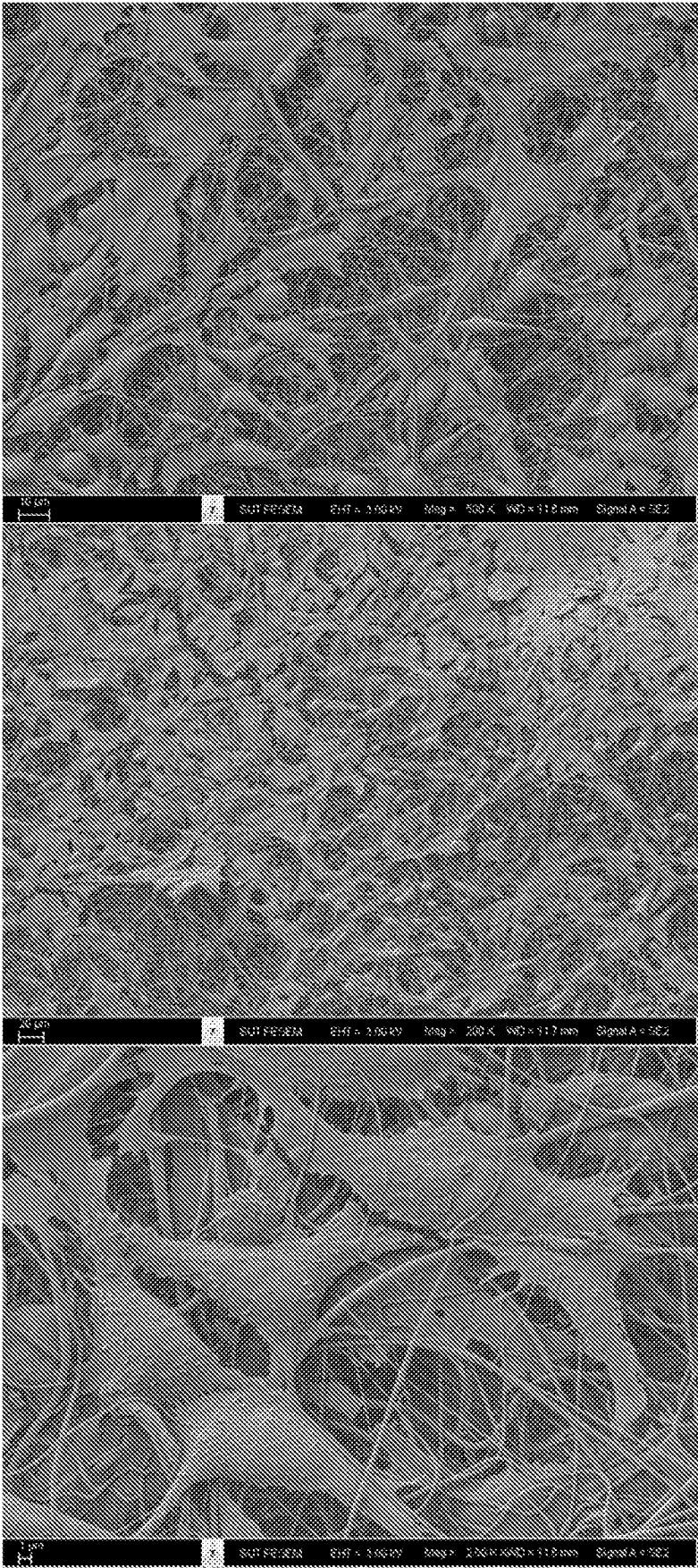


Figure 17

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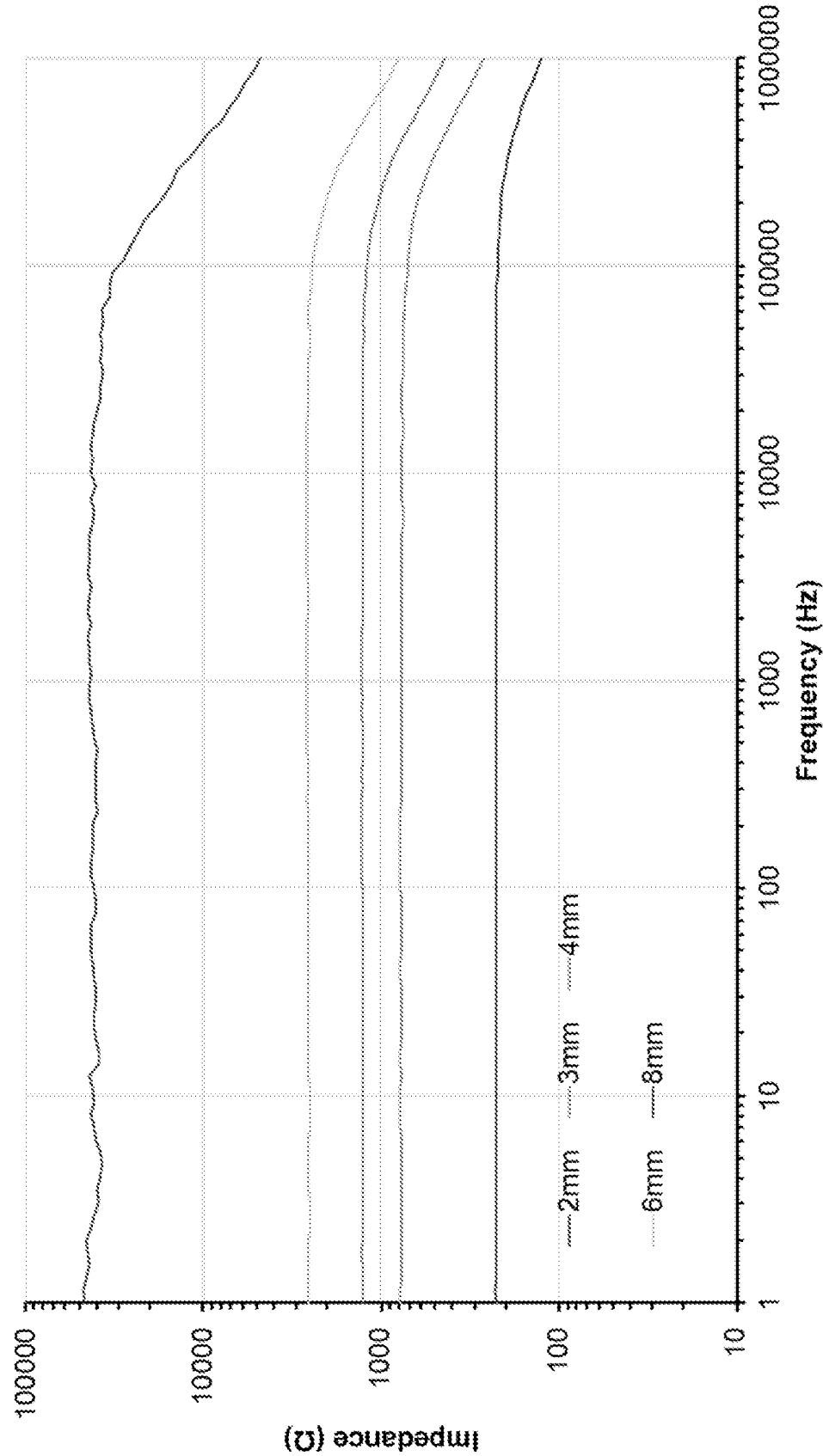
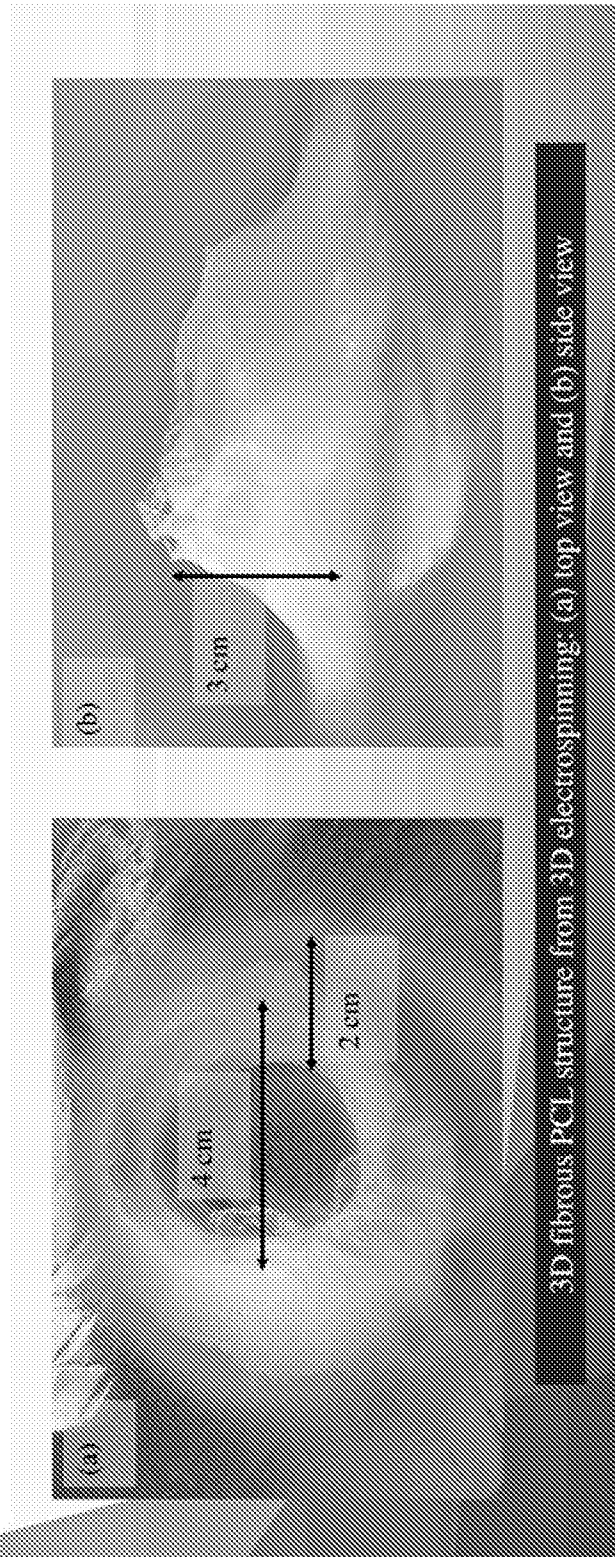


Figure 18

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3D FIBROUS PCL STRUCTURE

- ★ 12%wt of PCL solution dissolved in DCM:DMF
- ★ Flow rate of solution was 6 ml/h and extruder speed was 1 mm/s. The PCL solution was drawn under 14 kV of high voltage at 4 cm of an initial distance under 44% of humidity and 23°C of temperature.



INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2021/051601

A. CLASSIFICATION OF SUBJECT MATTER				
INV.	D01D5/00	B29C64/118	D01F9/14	B33Y10/00
	B33Y40/20	B33Y70/00	D01D10/02	B29C64/30
	B28B1/00	H01M4/1393	C12N5/00	B33Y40/00
				B29C64/371
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)				
B33Y D01D D01F B29C B28B H01M C12N				
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, WPI Data				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where appropriate, of the relevant passages			Relevant to claim No.
X	JUN-CHUAN WANG ET AL: "Preparation of active 3D film patches via aligned fiber electrohydrodynamic (EHD) printing", SCIENTIFIC REPORTS, vol. 7, no. 1, 8 March 2017 (2017-03-08), XP055715723, DOI: 10.1038/srep43924			1-12, 14-17, 19,21-26
A	abstract Material and Methods figures 1,2,4 ----- -/--			13
☒ 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	
17 August 2021			26/08/2021	
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 Fiocco, Marco	

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2021/051601

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LI MENG MENG ET AL: "Fabrication of Self-Assembled Three-Dimensional Fibrous Stackings by Electrospinning", JOURNAL OF METASTABLE AND NANOCRYSTALLINE MATERIALS, vol. 688, 1 January 2011 (2011-01-01), pages 95-101, XP055832405, CH ISSN: 1422-6375, DOI: 10.4028/www.scientific.net/MSF.688.95	1-12, 14-17, 19,21-26
A	abstract Experimental Section figures 1,2,6	13
X	----- SUN BIN ET AL: "Self-assembly of a three-dimensional fibrous polymer sponge by electrospinning", NANOSCALE, vol. 4, no. 6, 1 January 2012 (2012-01-01), page 2134, XP055832215, United Kingdom ISSN: 2040-3364, DOI: 10.1039/c2nr11782g	1-12, 14-17, 19,21-26
A	abstract Experimental figures 1-3	13
X	----- SUN B ET AL: "Advances in three-dimensional nanofibrous macrostructures via electrospinning", PROGRESS IN POLYMER SCIENCE, vol. 39, no. 5, 10 June 2013 (2013-06-10), pages 862-890, XP028648901, ISSN: 0079-6700, DOI: 10.1016/J.PROGPOLYMSCI.2013.06.002	1-12, 14-33
A	abstract figures 2f, 4d, 13 paragraph [03.1] paragraph [04.3] paragraph [05.2] paragraph [0007]	13
X,P	----- VONG MICHEL ET AL: "Ultrafast fabrication of Nanofiber-based 3D Macrostructures by 3D electrospinning", MATERIALS & DESIGN, vol. 208, 21 June 2021 (2021-06-21), page 109916, XP055832222, AMSTERDAM, NL ISSN: 0264-1275, DOI: 10.1016/j.matdes.2021.109916 the whole document -----	1-33