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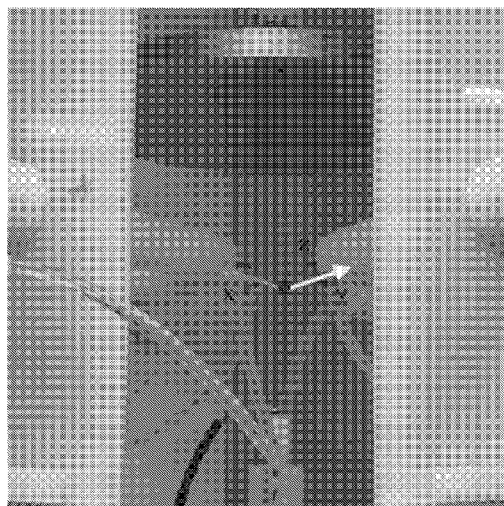


Figure 3

(57) Abstract: Methods and systems for electrospinning are provided. In a method of electrospinning, a solidifiable fluid is dispensed from a nozzle and biased at a first DC voltage. A fiber stream is drawn from the fluid using a collector biased to a second DC voltage. The fiber stream may be moved orthogonal to a direct stream path using a plurality of inter-electrodes biased to one or more midstream voltages (which may vary over time). The fiber stream is collected on the collector.



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METHODS AND SYSTEMS FOR ELECTROSPINNING

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Application No. 62/532,758,
5 filed on July 14, 2017, the disclosure of which is hereby incorporated by reference.

STATEMENT REGARDING FEDERALLY-SPONSORED RESEARCH OR DEVELOPMENT

[0002] This disclosure was made with government support under contract number DMR-
1120296 awarded by the National Science Foundation. The government has certain rights in the
10 disclosure.

FIELD OF THE DISCLOSURE

[0003] The present disclosure generally relates to methods and systems for
electrospinning. More particularly, the present disclosure relates to methods and systems for
depositing polymer fiber structures.

15 BACKGROUND OF THE DISCLOSURE

[0004] Electrospinning is a technique often used for the production of continuous
submicron diameter fibers composed of various polymers and ceramics. A typical
electrospinning setup utilizes a strong electric field to attract a charged viscous polymer solution
from a high voltage injection site, *e.g.*, a syringe needle, toward a grounded substrate. As the
20 solution is pumped into the electric field, molecular ionization forces positive charge to its
surface, causing it to bulge in a conical shape (Taylor Cone). When the electrostatic force
overcomes the surface tension, a charged jet (also referred to herein as a stream) is electro-
hydrodynamically emitted with an initial axial and radial velocity. As the viscosity of the
solution maintains continuity along the flight path, ion redistribution and space charge effects
25 make the jet increasingly unstable. While there has been some debate in the theoretical
community regarding the physics of these instabilities, three modes of operation have been well
examined: whipping, axisymmetric, and Rayleigh. These instabilities promote erratic
accelerations, driving the solution toward thinner diameters as it whips along the flight path.
During this time, the solvent begins to evaporate, thus solidifying the jet as the polymer chain
30 bends and buckles upon deposition due to its impingement velocity, diameter, density and final
viscosity. From this, a random distribution of continuous nanofibers is typically deposited along
the substrate in a matted form.

[0005] Electrospinning has garnered attention as a simple and cost effective method for advanced materials development. However, the inherently random distribution of nanofibers seen from a typical setup is somewhat limiting.

[0006] While the viscoelastic properties of the polymer jet help maintain continuity along the flight path, ion mobility/drag, surface tension, solvent evaporation, and space-charge-effects make the jet increasingly unstable. Past studies have shown multiple mechanisms which may contribute to these instabilities, including lateral perturbations between adjacent charges at the nozzle, changes in viscoelastic properties along the jet due to solvent evaporation, as well as bending/buckling of the polymer chain due to the impingement velocity upon deposition. As such, random fiber deposition is typically inherent to the electrospinning process and is the result of a complex system of instabilities, not only at the point of emission and along the jet trajectory, but at the point of deposition as well. Although random deposition patterns may be well utilized for some applications, a more structured and predetermined fibrous architecture is usually preferred for enhanced functionality.

[0007] Historically, controlled deposition of electrospun nanofibers has come in two common forms: mechanical and electrical. Mechanically, rotary motion has been successful in aligning electrospun fibers, having applications involving electroluminescent emitters for lab-on-a-chip technology, as well as cross-linked nanofiber junctions for zeptomole scale chemical reaction sites. Rotating drums running at high RPM have also been used to construct aligned scaffolding for tissue engineering applications. Such mechanical methods usually involve a grounded rotating collector, oscillating through the deposition path with rotational velocities comparable to that of the axial velocity of the emitted jet, *i.e.*, 0 – 5 m/s. Similarly, lower speed actuation has also been employed with the advent of near field electrospinning, which uses a linear mechanical stage to control a single nanofiber.

[0008] While mechanical motion compensates for deposition variability by disallowing fiber segments to accumulate at the same point on the collector (at short time intervals), electrical manipulation approaches the orientation problem by changing the underlying electrodynamics of the jet. This process has been previously demonstrated using a pair of stationary grounded conducting strips as collectors to deposit aligned nanofibers between them. Although this type of deposition is still randomly collected on each strip individually, the fibers between them are roughly parallel. Similar to this, two circular electrodes to collect a multi-filament yarn has been demonstrated. Likewise, it is also possible to manipulate the intermediate electric field between the point of injection and the collector. This method was demonstrated in the form of several DC focusing electric lenses, which create a kind of ion funnel to minimize

the point of deposition into a single spot with a diameter on the order of centimeters. However, controlling the deposition coordinates of the collected spot can be quite complicated. One way to do this is by analyzing the magnitude of movement of a spot using two DC auxiliary electrodes. Going one step further, a pair of alternating high-voltage steering electrodes, in addition to a DC lens, was used to draw a one-dimensional fibrous pathway between two points.

[0009] A charged polymer jet can be manipulated by novel substrate architectures, mechanical motion, and intermediary electric field manipulation. However, the tradeoff between morphology control and throughput has been inversely proportional. Although current systems do provide an ability to draw single fibers in one dimension, with relatively high throughput, the waste accumulation of random nanofibers at each point of deposition, as well as the inability to control fiber pathways in two and three-dimensions has been limiting. This has been somewhat of a deterrent for large-scale integration in an industry setting, *e.g.*, when repeatedly drawing predetermined 2D networks of electrospun nanofibers for chemical sensors in large quantities. Although current systems have provided some ability to draw fibers in one-dimension, they fall short in controlling the orientation and placement of fibers in two and three-dimensions, which is desirable for enhanced material performance in many applications. Therefore, it would be desirable to develop an electrospinning method to fabricate predetermined geometries with controlled morphologies in an efficient way.

[0010] Based on the foregoing, previous electrospinning techniques have drawbacks and limitations. Therefore, an improved electrospinning system and method is needed.

BRIEF SUMMARY OF THE DISCLOSURE

[0011] The present disclosure provides methods and systems developed for the controlled fabrication of, for example, 2D nanofibrous geometries, by continuously accelerating the jet (linearly and/or centripetally) along the flight path. For example, this is achieved using mechanical actuation and high-voltage AC switching to manipulate the applied electric field in a continuous manner. Using the methods/systems of this disclosure, various macroscopic nanofibrous geometries can be deposited at different velocities and the alignment of their respective morphologies can be correlated.

[0012] The electrospinning systems of the present disclosure can continuously accelerate a charged polymer jet (linearly and/or centripetally) fast enough to obtain predetermined two and three dimensional geometries with well-aligned morphologies. This is achieved using AC switching algorithms and electronics, alongside mechanical actuation, which accommodates consistent deposition for varied level of production.

[0013] The methods and/or systems of the present disclosure provides a means to stretch polymer fibers toward nano-diameters while redirecting them along continuous predetermined paths to fabricate novel 2D nanofibrous geometries. For example, this is done by continuously accelerating a charged polymer jet in a two-dimensional (x-y) plane that is perpendicular to its deposition (z-axis) trajectory. If centripetally and/or linearly accelerated fast enough, it is also possible to manipulate the underlying nanofiber morphology. Real-time adjustable electrode configurations and novel electronics involving high-voltage AC amplification with phase variability, frequency, and amplitude control are developed for controlled fiber deposition. While this disclosure provides examples based on polyethylene oxide (PEO), the disclosure is applicable to any polymers that can be electrospun, as well as polymer solutions involving exotic or encapsulated particles, *e.g.*, conductive, magnetic materials, DNA etc.

BRIEF DESCRIPTION OF THE FIGURES

[0014] For a fuller understanding of the nature and objects of the disclosure, reference should be made to the follow detailed description taken in conjunction with the accompanying figures.

[0015] Figure 1 shows (A) a typical electrospinning setup. (B) Random deposition of electrospun nanofibers.

[0016] Figure 2 shows (A) the overall setup used in the present disclosure, including the electronics that power the system, and (B) the injection chamber (*i.e.*, linear driving mechanism and stepper motors (1), collector plate (2), inter-electrodes (3), and syringe needle (4)).

[0017] Figure 3 shows the injection chamber with the chosen origin between the inter-electrodes.

[0018] Figure 4 shows the jet being accelerated before (left) and after (right) an amplifier is pulsed.

[0019] Figure 5 shows a few shapes that were drawn using different permutations of the six available electrodes. The star (A) is created by superimposing two triangles (B). The hexagon (C) is created by pulsing centripetally. Here, a 10 Hz frequency is used.

[0020] Figure 6 shows (A) a spot on the order of mm collected along the z-axis. Keeping the grid at negative voltage suppresses the current and keeps the DC potential high, which was unexpectedly able to create a similar effect to Deitzel's DC electric lensing experiment. (B) The nanofibers are collected for 166 ms before switching to the next x-y coordinate on the collector by pulsing each electrode at 1 Hz. The spots are then centripetally accelerated with respect to the z-axis.

[0021] Figure 7 shows the ability to transition from discrete point deposition to a more continuous deposition using higher frequencies (*e.g.*, 15 Hz).

[0022] Figure 8 shows (A and B) varying the diameter by changing the electrode displacements and collector voltage.

5 [0023] Figure 9 shows (A and B) varying the diameter by changing the frequency.

[0024] Figure 10 shows (left) an SEM image of one segment of a 45 Hz circle with a 1 cm diameter. (Right) An SEM image of a 45 Hz circle with a diameter of 2 cm. Notice that the tangential velocity is twice as high when doubling the diameter.

10 [0025] Figure 11 shows a sequence of circles drawn one after the other. (A) After the first circle is drawn, (B) the collector plate rotates as the next is deposited.

[0026] Figure 12 shows the nanofibers being directly deposited onto the inter-electrodes.

[0027] Figure 13 shows a short list of components used in the invention.

[0028] Figure 14 shows the overall system. Numbers refer to the parts listed in Figure 13.

[0029] Figure 15 shows determining the loads for each amplifier.

15 [0030] Figure 16 shows the circuit used for the high-voltage AC amplifier. This changes the voltage/electric field to accelerate the jet. Numbers refer to the parts listed in Figure 13.

[0031] Figure 17 shows the amplification from the pulsed signal from the function generator (top line) and the amplifier output pulse (bottom line). The actual voltage supplied to the amplifier is the middle line. This shows a 2 kHz signal, however, the amplitude, frequency, and pulse shape can be changed (*e.g.*, sinusoidal, square, etc.).

20 [0032] Figure 18 shows how the charged jet is accelerated by the amplifier when pulses arrive. (A) shows before the pulse arrives. (B) shows after the pulse arrives.

[0033] Figure 19 shows some of the printed 2D nanofibrous geometries that are possible using several amplifiers being pulsed in a sequential manner (*e.g.*, a hexagon, triangle, and star).

25 [0034] Figure 20 shows a CAD (computer-aided design) depiction of the emission chamber.

[0035] Figure 21 shows the wireframe perspective of how the electrodes (center) are driven by the stepper motors. Numbers refer to the parts lists in Figure 13.

[0036] Figure 22 shows the mechanism for driving each electrode back and forth/up or down.

30 [0037] Figure 23 shows an exploded view to construct the driving mechanism. Numbers refer to the parts list in Figure 13.

[0038] Figure 24 shows an exploded view of the driving mechanism for the emitter/needle and collector plate.

[0039] Figure 25 shows the dimensions required for the six electrodes to be spaced evenly (*i.e.*, each at 60 degrees from one another).

[0040] Figure 26 shows how the electrode driver is attached to the bottom plate.

[0041] Figure 27 shows how all six electrode mechanisms are attached to the top and bottom plate. The collector mechanism, similar to the syringe mechanism, is also attached.

[0042] Figure 28 shows the assembled system, including the stepper motors, outer plates, cylinders, driving mechanisms, electrodes, and collector plate.

[0043] Figure 29 shows (Left) a CAD depiction of a typical electrospinning setup, including the bending instabilities as known in the art. (Right) A scanning electron microscope (SEM) image of random electrospun nanofibers from a typical setup.

[0044] Figure 30 shows a CAD depiction of the injection chamber, as well as a spring and dashpot model of the deflected jet. The positively charged polymer jet is ejected from the positively charged nozzle toward the negatively charged collector. In this configuration, if the jet is deflected from five positively charged intermediate electrodes, while attracted toward one grounded electrode, an off axis deposition radius is obtained. By oscillating the ground point sequentially along the six electrodes, it is possible to centripetally accelerate the jet as seen in Figure 38. The x-y-z origin is shown in the plane of the intermediate electrodes.

[0045] Figure 31 shows the electronic circuit used for each high-voltage AC amplifier. A low-voltage oscillation at the grid of the vacuum tube can produce a high-voltage oscillation at the plate.

[0046] Figure 32 shows pulsing output capabilities of one amplifier. The actual voltage supplied to the amplifier is shown in green (left image), *i.e.*, ~ 5 kV. A 15 Hz square wave is supplied from a function generator to the grid of one vacuum tube amplifier, which causes a high-voltage oscillation on the plate. The high-voltage supply is connected to a 10 M load resistor (as seen in the circuit in Figure 31).

[0047] Figure 33 shows a jet is deflected before (left) and after (right) the amplifier is pulsed using the signals demonstrated in Figure 32.

[0048] Figure 34 shows (Left) keeping the grid at negative voltages suppresses the current and sets a DC high-voltage signal at each inter-electrode, which was unexpectedly able to create a similar effect to Deitzel's DC electric lensing experiment. Here, a spot with a diameter on the order of ~ 1 cm is collected along the z-axis. (Right) By pulsing each electrode at 1 Hz, the nanofibers are collected for $\phi_n = 166$ ms at one point, before switching to the next x-y coordinate on the collector. The spots are then centripetally accelerated from point to point with respect to the z-axis.

[0049] Figure 35 shows (Left) a screenshot from a digital oscilloscope sampling three 10 Hz pulses, each with a 33.3% duty cycle. The second and third pulses are 33.3 ms and 66.6 ms out of phase from the first, respectively. These pulses are supplied to the grid of the circuit in Figure 31. (Right) The corresponding triangular deposition pattern.

5 [0050] Figure 36 shows a star (Left) is created by printing two triangles. A hexagon (Right) is created by pulsing the electrodes centripetally. Here, a 10 Hz frequency is used.

[0051] Figure 37 shows the ability to transition to a more continuous deposition using higher frequencies 15 Hz, *i.e.*, spending less time, *i.e.*, $\phi_n = 11.1$ ms, depositing the polymer at each spot.

10 [0052] Figure 38 shows (left and right) varying the deposition radius by fixing the frequency and changing the voltages and distances.

[0053] Figure 39 shows (left and right) varying the deposition radius by changing the frequency alone.

[0054] Figure 40 shows an SEM comparison of the fiber orientation from the deposition

15 patterns in Figure 39. (Left) Corresponding fiber orientation at $\sim v_t = 2\pi r f = .14 \frac{m}{g}$ for a circle with a deposition diameter of $D_{Dep} = 1$ cm. (Right) Corresponding fiber orientation at $\sim v_t = 2\pi r f = .28 \frac{m}{g}$ for a circle with a diameter of $D_{Dep} = 2$ cm.

[0055] Figure 41 shows the cross-deposition of nanofibers. Each electrode is pulse 90° out of phase with its opposite, while all other inter-electrodes are held high.

20 [0056] Figure 42 shows (left and right) EM images of cross-deposited nanofibers generated in Figure 41.

[0057] Figure 43 shows the polymer being directly deposited onto the inter-electrodes.

[0058] Figure 44 shows the overall setup used in the present disclosure, including: two – P 6015A Tektronix high voltage probes; a Gamma DC High Voltage Research power supply (0 – 30 kV , 0 – 200 μ A); a Spellman SL40P150 DC power supply (0 V – 15 kV , 0 – 10 mA); a Spellman SL15P 300 Negative DC power supply (0 – 40 kV , 0 – 7.5 mA); a BK Precision 91225 DC power supply (0 – 60 V , 2.5 A); a Harvard Apparatus syringe pump 70 – 3005 with a $\pm 0.25\%$ accuracy; a Nintendo remote control, which drives the electrodes forward and backward; electronics for each stepper motor and remote control; six Tektronix AFG2000/3000 function generators; a Tektronix, 4-channel, digital oscilloscope; a Sony AFG30 function generator (to produce a 10 MHz clock signal to keep the function generators in time with one another). See Figure 46 for details involving the injection chamber, Figure 45 and Figure 31 for details involving the vacuum tube amplifiers.

30 [0059] Figure 45 shows determination of load lines for each amplifier.

[0060] Figure 46 shows the injection chamber with an electrospun hexagonal geometry deposited on a printed circuit board.

[0061] Figure 47 shows viscosity measurements of a 10% (w/w) mixture of deionized (DI) water and Polyethylene Oxide (PEO), with a molecular weight of $M_w = 600,000$, at 20 °C over 4 minute intervals at shear rates ranging between $(0-180)\frac{1}{g}$ using an Advanced Rheometer AR 2000.

[0062] Figure 48 shows measurements of the elastic modulus (G') of PEO 10% using a frequency sweep from 1 to 10 Hz, with 20 sample points, at 25 °C with a strain percentage of .6% using an Advanced Rheometer AR 2000.

[0063] Figure 49 shows a cross section of the three-dimensional voltage profile calculation for the experimental setup in Figure 30 used to obtain the results seen in Figure 38 (Left). The collector is at the top, the nozzle is at the bottom and only two inter-electrodes are shown, *i.e.*, one grounded (right) and one at 5 kV (left).

[0064] Figure 50 shows a cross section of the three-dimensional electric field line calculation for the experimental setup used to obtain the results seen in Figure 38 (Left). The collector is at the top, the nozzle is at the bottom and only two inter-electrodes are shown, *i.e.*, one grounded (right) and one at 5 kV (left).

[0065] Figure 51 shows scaled CAD depiction of the injection chamber (without dielectrics), and the trajectory of the electrospun polymer solution (shown as a spring and dashpot model as discussed above). This CAD model is imported into Comsol 5.3 to analyze the electric field strength between the intermediary electrodes (see Figures 48–49).

[0066] Figures 52A and 52B depict a system according to another embodiment of the present disclosure, wherein Figure 52B shows a detail view of the system of Figure 52A.

[0067] Figure 53 is a flowchart showing a method according to another embodiment of the present disclosure.

DETAILED DESCRIPTION OF THE DISCLOSURE

[0068] Although claimed subject matter will be described in terms of certain embodiments, other embodiments, including embodiments that do not provide all of the benefits and features set forth herein, are also within the scope of this disclosure. Various structural, logical, process step, and electronic changes may be made without departing from the scope of the disclosure.

[0069] Ranges of values are disclosed herein. The ranges set out a lower limit value and an upper limit value. Unless otherwise stated, the ranges include all values to the magnitude of

the smallest value (either lower limit value or upper limit value) and ranges between the values of the stated range.

[0070] The present disclosure provides electrospinning methods and systems. The present disclosure also provides articles of manufacture, which may be made by a system and/or method of the present disclosure.

[0071] In an aspect, the present disclosure provides electrospinning systems. For example, the present disclosure may be embodied as an electrospinning system **10** (*see, e.g.*, Figures 52A and 52B). A nozzle **12** is configured to dispense a solidifiable fluid as a fiber stream biased to a first DC voltage. The nozzle **12** may be, for example, a syringe needle. A collector **20** is spaced apart from the nozzle **12**. The collector **20** may be a plate or any other suitable shape as will be recognized by a person of skill in the art in light of the present disclosure. The collector **20** is biased to a second DC voltage which is selected to attract the solidifiable fluid biased at the first DC voltage. In this way, when a solidifiable fluid is dispensed from the nozzle **12**, a fiber stream biased at the first voltage will be drawn by attraction to the collector **20** due to the second voltage bias of the collector **20**. The fiber stream will travel from the nozzle **12** to the collector **20** in a flow direction. The collector **20** and nozzle **12** can have various arrangements. In an example, the collector plate and needle are vertically arranged. For example, the flow direction may be opposite the direction of gravity (*i.e.*, the collector **20** is arranged vertically above the nozzle **12**).

[0072] The system **10** further includes a plurality of inter-electrodes **30** arranged at a location between the nozzle **12** and the collector **20**. The plurality of inter-electrodes **30** may be arranged on a first plane where the first plane is orthogonal to a direct stream path (the path along the shortest distance between the nozzle **12** and the collector **20**—identified as ‘A’ in Figure 52A). The plurality of inter-electrodes **30** may be arranged circumferentially around a direct stream path A. The plurality of inter-electrodes may any number of inter-electrodes **30**, for example, any even number of inter-electrodes **32**. For example, the system **10** may include two to twelve inter-electrodes **32** or more. Figures 52A and 52B depict a non-limiting embodiment having six inter-electrodes **32** arranged circumferentially around the direct stream path A. The inter-electrodes **32** may be arranged symmetrically or asymmetrically. In an example, the electrodes are not directly connected (*e.g.*, disposed) on the collector.

[0073] The system **10** includes a voltage generator **40** in electrical communication with the plurality of inter-electrodes **30**. The voltage generator **40** is configured to apply a voltage to the inter-electrodes **32** (as further described in the sections marked as “Examples” below). The voltage generator **40** may comprise a plurality of voltage generators. In some embodiments, the

voltage generator **40** comprises a plurality of voltage generators corresponding to the number of inter-electrodes **32**, and each inter-electrode **32** may be in electrical communication with a corresponding voltage generator. In some embodiments, the voltage generator **40** may comprise a function generator.

5 **[0074]** The system **10** may include a plurality of actuators **34** configured to move the plurality of inter-electrodes **30**. Each actuator **36** of the plurality of actuators **34** is configured to move at least one inter-electrode **32**. For example, in some embodiments the number of actuators is equal to the number of inter-electrodes. In another example, each actuator may be configured to move two inter-electrodes, for example, two opposing inter-electrodes (on opposite sides of
10 the direct stream path. Embodiments of the present disclosure can comprise various actuators and/or combinations of actuators. In various examples, the actuators are linear driving actuators and/or stepper motors. In some embodiments, each actuator is configured to move one or more inter-electrodes closer to or further from the direct stream path *A* (*i.e.*, radially along the first plane). In this way, the effect on a fiber stream of a voltage potential applied to an inter-electrode
15 may be increased (moving the inter-electrode closer to the direct stream path *A*) or decreased (moving the inter-electrode away from the direct stream path *A*).

[0075] In some embodiments, the system **10** includes a stage actuator **22** configured to move the collector. For example, such a stage actuator **22** may be configured to rotate the collector **20** about an axis which is parallel to the direct stream path *A*. In some embodiments,
20 the stage actuator may be configured to translate the collector **20** closer to or further from the nozzle **12**. Such a stage actuator **22** may be configured to rotate and translate the collector **20**. In some embodiments, the system **10** may include a nozzle actuator **14** configured to move the nozzle **12**. For example, the nozzle actuator **14** may be configured to move the nozzle **12** closer to or further from the collector **20**.

25 **[0076]** The systems may be referred to as polymer accelerators. In some embodiments, the systems can provide continuous morphologies of aligned nanofibers.

[0077] Systems of the present disclosure can use various materials. In an example, the material includes a polymer. Any polymer that can be electrospun can be used. Examples of suitable polymers are known in the art. In an example, the material comprises deionized water
30 and polyethylene oxide. In various examples, the material is an aqueous polymer solution. In some examples, the polymer solutions of the material involve exotic or encapsulated particles, *e.g.*, conductive, magnetic materials, DNA, etc.

[0078] Systems of various first, second, and midstream voltages are disclosed herein in various examples and embodiments. One having skill in the art will recognize that said voltages

may be selected according to factors including, for example, the geometry of the system and/or the material chosen as the solidifiable fluid. In some embodiments, the first DC voltage is a positive voltage and the collector is 0 VDC or a negative voltage. For example, the first DC voltage may be selected as any value from +2,000 VDC to +20,000 VDC or greater, and the second DC voltage may be selected from any value from 0 VDC to -20,000 VDC or lower. In other embodiments, the first DC voltage is a negative voltage and the second DC voltage is 0 VDC or a positive voltage. For example, the first DC voltage may be selected as any value from -2,000 VDC to -20,000 VDC or lower, and the second DC voltage may be selected from any value from 0 VDC to +20,000 VDC or greater. In some embodiments, the inter-electrodes are biased to a voltage (which may vary) which is generally between the first DC voltage and the second DC voltage. The midstream voltage may be selected such that no material is collected on an inter-electrode.

[0079] In an aspect, the present disclosure provides electrospinning methods. The methods can be carried out using systems of the present disclosure. In an embodiment of a method **100** of electrospinning, a solidifiable fluid is dispensed **103** from a nozzle. The dispensed **103** fluid is biased at a first DC voltage. The method **100** includes drawing **106** a fiber stream from the dispensed **103** fluid along a direct stream path using a collector (as described above, along a path of the shortest distance from the nozzle to the collector). The biased fiber stream is drawn **106** to the collector by biasing the collector to a second DC voltage selected to attract the fluid. For example, the fiber stream may be biased to a voltage of 13,000 volts DC, and the collector may be at -2,600 volts DC (*e.g.*, grounded). In this way, the fiber stream dispensed from the nozzle is attracted to the biased collector. Other suitable voltages may be used as described above and within the examples below.

[0080] A midstream voltage is applied **109** to at least one electrode of a plurality of inter-electrodes causing the fiber stream to move. For example, the fiber stream may be caused to move in a direction generally orthogonal to the direct stream path. Using the example above where the first DC voltage is 13,000 VDC and the second DC voltage is -2,600 VDC, a midstream voltage may be applied **109** such that five inter-electrodes are biased to 5,000 VDC and one inter-electrode is at 0 VDC. In this way, a fiber stream may be moved in a direction towards the grounded inter-electrode and away from the inter-electrodes biased to 5,000 VDC.

[0081] In some embodiments, the plurality of inter-electrodes are arranged in a first plane, wherein the first plane is orthogonal to the direct stream path.

[0082] In some embodiments, the collector is moved **112** relative to the nozzle. For example, the collector may be rotated about an axis parallel to the direct stream path. In another

example, the collector may be translated in a direction orthogonal to and/or parallel to the direct stream path. The collector may be both rotated and translated.

[0083] In some embodiments, one or more inter-electrodes of the plurality of inter-electrodes may be moved **115** relative to the nozzle and/or the collector.

5 [0084] In some embodiments, the midstream voltage may be varied **118** over time. Using the above exemplary values, the midstream voltage may be such that all but one inter-electrode is biased to a voltage of 5,000 VDC, and a single inter-electrode is held at 0 VDC. Then, the inter-electrode held to 0 VDC is switched to a different one of the inter-electrodes. This may continue, for example, in sequence through each inter-electrode. The midstream voltage may be
10 varied **118** in any other way to collect desirable patterns of the material on the collector. For example, the midstream voltage may be oscillated. In some embodiments, the midstream voltages is a oscillating voltage, and the oscillating voltage is set to various amplitudes, phases, frequencies and duty cycles, as applied to each electrode independently or in combinations (groups).

15 [0085] In an example, a method of electrospinning comprises: biasing a collector plate; dispensing a material (*e.g.*, a material described herein) from a needle positioned apart from the collector plate, wherein the material is depositing on the collector plate after the dispensing; and positioning and/or biasing inter-electrodes disposed along a path between the needle and the collector plate.

20 [0086] The depositing may be adjusted by tuning at least one parameter selected from the group consisting of a distance between the nozzle and an origin (where the origin is located at the intersection of the inter-electrode plane and the direct stream path), a distance between the collector and the origin, a distance between each of the inter-electrodes and the origin, voltages of the nozzle and/or the collector, peak-to-peak voltages of the inter-electrodes, frequency, duty
25 cycle, and relative phases of each pulse.

[0087] The methods can be used to form various shapes of electrospun fibers. The fibers can be of different sizes (*e.g.*, diameters). In an example, the fibers are nanofibers having at least one nanoscale dimension (*e.g.*, a width/diameter of 100 nm to about 1 micron). In an example, a method comprises forming (*e.g.*, drawing) a two-dimensional geometry on the collector with the
30 material.

[0088] The positioning and/or biasing may include using a continuously phased oscillation to accelerate (*e.g.*, centripetally and/or linearly) a jet of the material with respect to an x-y plane in a sequential manner.

[0089] Additional non-limiting examples of articles include non-transitory computer readable media storing a program configured to instruct a processor to perform the positioning and/or biasing and the like.

[0090] In an aspect, the present disclosure provides articles of manufacture. An article
5 may be produced using a system and/or method of the present disclosure.

[0091] An article may have various shapes. Non-limiting examples of shapes include circle, polygons, and the like. In an example, an article has a non-linear shape. An article may be flexible. In various examples, an article has a two-dimensional geometry. In various examples, an article comprises a plurality of layers forming a three-dimensional shape, where each layer is
10 a particular shape, which may be the same shape or a different shape than one or more of the other layers, formed by a plurality of electrospun fibers (*e.g.*, electrospun nanofibers). The article may be formed of a material comprising an aqueous polymer solution. In some examples, the material comprises a polymer solution involving exotic or encapsulated particles, *e.g.*, conductive, magnetic materials, DNA, etc.

[0092] The fibers of an article of manufacture or an individual layer or layers of an article of manufacture may be substantially aligned (*e.g.*, aligned). In various examples, the fibers or a portion thereof of an article of manufacture or an individual layer or layers are conducting (*e.g.*, formed from a conducting polymer). In an example, the fibers or a portion thereof of an article of manufacture or an individual layer or layers are not randomly distributed.
15

[0093] Non-limiting examples of articles of manufacture include sensors (*e.g.*, bio-sensors, chemical sensors, electronic sensors, and combinations thereof, and the like), fuel cells or components thereof, tissue scaffolding, optical components (*e.g.*, optical polarizers and the like), electrical components (*e.g.*, conductors, resistors, capacitors, and the like), filtration devices, drug-delivery systems, and component(s) thereof.
20

[0094] An article of manufacture may be integrated in another article of manufacture. As an illustrative example, an article of manufacture (*e.g.*, a sensor) is integrated into an article of clothing or the like. Such articles of manufacture may be referred to as a wearable electronics.
25

[0095] The following Statements describe various examples of systems, methods, and articles of the present disclosure:

Statement 1. A method of electrospinning, comprising:
30 dispensing a solidifiable fluid from a nozzle, wherein the solidifiable fluid is biased at a first DC voltage;
drawing a fiber stream from the solidifiable fluid along a direct stream path using a collector, wherein the collector is biased at a second DC voltage selected to attract the solidifiable fluid;

applying a midstream voltage to at least one electrode of a plurality of inter-electrodes located between the nozzle and the collector, to cause the fiber stream to move in a direction which is orthogonal to the direct stream path; and
collecting the fiber stream on the collector.

5 Statement 2. A method according to Statement 1, wherein the plurality of inter-electrodes is arranged in a first plane, the first plane being orthogonal to the direct stream path.

Statement 3. A method according to any of Statements 1–2, further comprising moving the collector relative to the nozzle.

10 Statement 4. A method according to any of Statements 1–3, wherein the collector is rotated about an axis parallel to the direct stream path.

Statement 5. A method according to any of Statements 1–4, wherein the collector is translated in a direction orthogonal to and/or parallel to the direct stream path.

Statement 6. A method according to any of Statements 1–5, further comprising moving one or more electrodes of the plurality of electrodes relative to the nozzle and/or the collector.

15 Statement 7. A method according to any of Statements 1–6, wherein the midstream voltage varies over time.

Statement 8. A method according to any of Statements 1–7, wherein the midstream voltage is an oscillating voltage, and the oscillating voltage is set to various amplitudes, phases, frequencies, and/or duty cycles, as applied to each inter-electrode or combinations of inter-electrodes.

20 Statement 9. A method according to any of Statements 1–8, where the midstream voltage is configured to accelerate the fiber stream centripetally with respect to the direct stream path.

Statement 10. A method according to any of Statements 1–9, wherein the midstream voltage is configured to accelerate the fiber stream radially with respect to the direct stream path.

25 Statement 11. A method according to any of Statements 1–10, wherein the solidifiable fluid comprises a polymer solution.

Statement 12. A method according to any of Statements 1–11, wherein the polymer solution comprises Polyethylene Oxide (PEO) or polyethylene glycol (PEG).

Statement 13. An electrospinning system, comprising:

30 a nozzle configured to dispense a solidifiable fluid as a fiber stream biased to a first DC voltage;
a collector spaced apart from the nozzle, wherein the collector is biased to a second DC voltage, and the second DC voltage is selected to attract the fiber stream in a flow direction;
a plurality of inter-electrodes arranged on a first plane orthogonal to the flow direction, wherein the first plane is located between the nozzle and the collector; and

a voltage generator in electrical communication with the plurality of inter-electrodes, wherein the voltage generator is configured to apply a midstream voltage to the inter-electrodes.

Statement 14. A system according to Statement 13, further comprising a plurality of actuators configured to move the plurality of inter-electrodes relative to the nozzle and/or the collector.

5 Statement 15. A system according to any of Statements 13–14, wherein the actuators are linear driving mechanisms and/or stepper motors.

Statement 16. A system according to any of Statements 13–15, further comprising a stage actuator for rotating the collector about an axis substantially parallel to the direct stream path and/or moving the collector relative to the nozzle.

10 Statement 17. A system according to any of Statements 13–16, further comprising a nozzle actuator for moving the nozzle relative to the collector.

Statement 18. A system according to any of Statements 13–17, wherein the voltage generator is configured to apply an oscillating voltage to the plurality of inter-electrodes.

Statement 19. A system according to any of Statements 13–18, wherein the oscillating voltage
15 applied to each inter-electrode of the plurality of inter-electrodes is phase-shifted relative to the oscillating voltage applied to one or more other inter-electrodes.

Statement 20. A system according to any of Statements 13–19, further comprising a controller in operable communication with the voltage generator, wherein the controller is programmed to instruct the voltage generator to generate the time-dependent voltage.

20 Statement 21. A system according to any of Statements 13–20, further comprising a plurality of actuators in operable communication with the controller, the plurality of actuators configured to move the plurality of inter-electrodes relative to the nozzle and/or the collector.

Statement 22. An article produced using the method of one of Statements 1–12 and/or the system of one of Statements 13–21.

25 Statement 23. The article of Statement 22, wherein the article has a two-dimensional geometry.

[0096] The steps of the method described in the various embodiments and examples disclosed herein are sufficient to carry out the methods of the present disclosure. Thus, in an embodiment, a method consists essentially of a combination of the steps of the methods disclosed herein. In another embodiment, a method consists of such steps.

30 [0097] The following examples are presented to illustrate the present disclosure. They are not intended to limiting in any matter.

EXAMPLE 1

[0098] The following example provides examples of methods and systems of the present application.

[0099] Path control for an electrospun jet was developed for the fabrication of controlled nanofibrous geometries with aligned morphologies. The designs described herein electrically manipulate the jet and prints multi-dimensional nanofibrous structures and incorporates various methods in linear particle acceleration, ion optics, mechanical motion, AC electronics, DC

5 lensing and real-time electrode actuation, to accelerate a charged polymer solution continuously in the x-y plane, during its trajectory in the z-direction. This is done by continuously oscillating the intermediate electric field over several interchangeable electrodes using a novel electro-mechanical system. A time varying high voltage signal is employed using custom electronics alongside specific switching protocols, which manipulate the electric field at a specific

10 frequency, amplitude, relative phase difference or a combination thereof to control various deposition patterns. By inducing x-y accelerations (*e.g.*, linear and/or centripetal x-y accelerations) along the jet path to promote planar velocities comparable to the jet's axial velocity, (at fast enough frequencies) macro/microscopic nanofiber (straight and curved) alignment is permitted. Likewise, large-scale production of such structures may be collected

15 using a rotating substrate to collect each structure more efficiently.

[0100] Experimental. The current system is shown in Figure 2(a) with a closer view of the injection chamber in Figure 2(b). To account for gravity, the jet path is oriented vertically with the injection point positioned at the base of the system, and the collector above it ($\frac{1}{2}$ " thick, 8" diameter 6061 Aluminum plate). In between, are six interchangeable electrodes, placed

20 intermediate to the jet path (inter-electrodes) that are $\frac{1}{2}$ " in length and $\frac{1}{8}$ " in diameter, made of 'super conductive' copper 101. Each of these are oriented 60° from one another in a segmented, but symmetrical, electric lens formation. Eight stepper-motors (0.9° steps at 400 steps per revolution) drive a rotary-linear actuation mechanism to drive each conductive element within the chamber, *i.e.*, the syringe needle, the collector and each inter-electrode. The metrics of

25 actuation with are achieved with respect to a central origin (Figure 3). Since high voltage is necessarily applied to each conductive element, a blend of Acetal, Delrin, Teflon and high-density polyethylene (HDPE) is utilized, as they are good electrical insulators and are easily machined. $\frac{5}{16}$ "-18 threaded rod is also used to achieve displacement accuracies of less than 0.1". For real-time electrode positioning and automation (during the electrospinning process), a

30 remote control, as well as an algorithm preprogrammed into a microcontroller is used.

[0101] A Harvard Apparatus infusion pump, rated with an accuracy of $\pm 0.25\%$, feeds a (blunt 23 gauge, stainless steel) needle at a rate of 0.5 ml/hr. The polymer solution used in this experiment is a 10% mixture of deionized water and Polyethylene Oxide (PEO), with a molecular weight of 600,000 (*Sigma Aldrich*). A Gamma High Voltage Research, DC power

supply rated at 0–30 kV at 0–200 μ A, is connected to the syringe needle (with little to no current requirement), and a Spellman *SL300*, (negative) DC power supply rated from 0–(–40kV), 0–7.5mA is connected to the collector. Six, high-voltage amplifiers are designed using *6BK4B* vacuum triodes in a common-cathode configuration, which are driven by a Spellman *SL150* power supply, rated from 0–15 kV at 0–10 mA. The components of the amplifier are chosen with the *SL150* current rating in mind. A bypass cathode resistor of 4.4k and a load resistance of 10M are chosen to obtain a Q-point of .39 mA with a grid voltage of 1.7 V, which can be sufficiently handled with a *Tektronix AFG2021* function generator (one for each of the six amplifiers). A BK Precision 9122A DC power supply is used to drive the filament of the vacuum tube (6.3 V requirements at less than 2A) for thermionic emission. From this, –5V is maintained at the grid of each vacuum tube to suppress the current (keeping the plate voltage high) for DC lensing. Likewise, +5 V pulses are sent to the grid, which short-circuits the anode to cathode. This essentially grounds the plate of the tube (as well as the connected inter-electrode), on command. During the electrospinning process, if the planar-inter-electrode array is placed perpendicular to the jet path (Figure 3), a grounded electrode will attract the positively charged jet off axis as it moves in the z-direction. By adjusting the collector to sufficient negative voltages, substrate deposition is maintained by tuning the following parameters: the distance between the needle and the origin, the distance between the collector and the origin, the distance between each inter-electrode and the origin, needle and collector voltages, inter-electrode pk-pk voltages, frequency, duty cycle, and the relative phases of each pulse.

[0102] Mathematically, to reposition a focused jet, the electric field is manipulated near each inter-electrode by sending a positive pulse (+5 V) to each respective grid, *i.e.*, with various amplitudes, frequencies, duty cycles, and relative phases, using the following equation:

$$\phi_n = \frac{D_N (n-1)}{f \cdot 100}, \quad (1)$$

where, ϕ_n , is the relative phase, f is the frequency, D_N is the duty cycle for a total of N electrodes, and n corresponds to one of the n function generators, and subsequently to the n th inter-electrode. This sequentially grounds each inter-electrode with respect to ϕ_n . Here, the duty cycle is defined as:

$$D_N = \frac{1}{N} (100). \quad (2)$$

[0103] In the case of six electrodes, *i.e.*, $N = 6$, the duty cycle, D_N is 16.6% (useful for centripetal motion). From this, it is possible to fluctuate each of the six inter-electrode potentials between ground and the *SL150* output (although there are maximum limitations on the amplifier).

[0104] For this application, timing is important. Therefore, to keep the pulses continuously oscillating in a controlled manner, a 10MHz external clock reference is utilized for each generator. Likewise, burst mode is invoked and the burst count is set to infinite while allowing the generator outputs to be triggered externally. Adjusting the lead phase for each generator according to equation (1) allows a continuous high voltage oscillation to be preprogrammed along each inter-electrode. Depending on the desired deposition geometry, the charged jet will then be attracted (and repelled) in a predetermined manner (Figure 4).

[0105] Results

[0106] Without pulsing the amplifier, the inter-electrodes will default to the *SL150*

output. This creates a DC electric lens with six pointed electrodes. From this, a single spot is obtained on the order of mm, which is shown along the z-axis of the collector in Figure 5(A). Furthermore, it is possible to arbitrarily change the x-y coordinates of the collected spot at the substrate by changing the DC voltage on one of the electrodes (acting as an auxiliary electrode) using a sustained pulse. It is also possible to draw a one-dimensional fibrous pathway between two spots. However, it is possible to draw continuous two-dimensional geometries. To do this, a continuously phased oscillation to accelerate (centripetally or linearly) the jet with respect to the x-y plane in a sequential manner is required. This can be done using the proposed AC system using at least three steering electrodes, *i.e.*, N is greater than 2.

[0107] In an example, the *SL150* output is set to 5 kV , the syringe needle to 13 kV and the collector to -7.3 kV . Since the inter-electrodes reach a minimum of 0 V , a negative voltage on the collector is required to keep the jet from depositing directly onto the inter-electrodes (if interception occurs, a dielectric buildup will diminish the electric field at each point). The collector and the syringe needle are positioned from the origin at $1.25''$ and $2.5''$, respectively. A $2''$ diameter gap is obtained between the inter-electrodes, *i.e.*, each electrode at $1''$ from the origin. Choosing a frequency, $f = 10\text{ Hz}$, the relative phase output is calculated for each electrode in the pulsing sequence, *e.g.*, to create a triangle (Figure 5(B)), it is possible to pulse electrode 1 then 3 then 5 and repeat. This requires three electrodes, $N=3$. Therefore, from Eq. 1 and Eq. 2, for $f=10\text{ Hz}$, and $N=3$, then a 33.3% duty cycle will require a relative phase of $\phi_n = 33.3(n - 1)\text{ ms}$. This can be adjusted for a preferred morphology by drawing the fiber faster along the geometric perimeter (using higher pulsing frequencies), *i.e.*, to achieve more or less aligned nanofibers.

[0108] To obtain the star in Figure 5(A), a superposed image of two triangles is obtained by oscillating the electrodes between 2 then 4 then 6, then 1, 3 and 5 etc. Using this logic, and by adjusting the pulse permutation over specific inter-electrodes, the spot can be drawn from point

to point along predetermined two-dimensional pathways as seen in Figure 5, *e.g.*, a hexagon, square, etc.

[0109] In a similar fashion, it is also possible to centripetally accelerate the spot around the z-axis (Figure 6). To see how this works, one may start at slow speeds, *i.e.*, with a low frequency, $f=1\text{Hz}$, and utilize all six of the electrodes so that $N=6$ in Eq. 1, which gives a relative phase difference of $\phi_n = (n-1)166\text{ ms}$. This will deposit random nanofibers at each spot for 166 ms before switching to the next x-y position on the collector. Although this is very slow, it is evident that with a high enough frequency, it is possible to obscure the spot indefinitely by centripetally accelerating the jet toward neighboring electrodes.

[0110] To begin obscuring the spot toward a more continuous deposition patterns, an increase in the centripetal acceleration of the jet is required. To do this, it is possible to adjust the pulsing frequency, or increase the radius of deposition, to obtain higher tangential velocities along the perimeter of deposition. These tangential velocities are defined by the following equation:

$$v_t = 2\pi r f \quad (3)$$

Where r is the displacement from the central axis and f is the frequency at which the pulses are administered. While this will not resolve the drawing-line width, *i.e.*, the spot diameter ($\sim 1\text{ mm}$), it will increase the rate at which it is drawn around the perimeter. To see how this works, one may start by increasing the frequency from 1 Hz to 15 Hz. From Figure 6(B) and Figure 7, the transition from a discrete pattern to a smooth circle can be seen. From this continuous deposition pattern, a more continuous morphology can be expected. Here, the syringe needle is set to 13 kV, the collector to -2.6 kV and set the inter-electrodes to oscillate between 0 V and 4.78 kV. If the number of inter-electrodes is $N=6$, then by equation (1), the relative phase shift between each pulse will be 11.1 ms. Here, the syringe needle and the collector are both set at 3" from the origin. Likewise, the inter-electrode lensing diameter is set at 1.5" from the origin.

[0111] It is also possible to change the deposition radius of the circle. This can be accomplished in two different ways: by changing the relative distances of each electrode or by changing the frequency. To change the radius by electrode displacement, one can use the same voltage on the syringe needle and inter-electrodes, but change the syringe needle and the collector from 3" to 4.5" from the origin. It is then possible to change the collector voltage from -2.6 kV to -9.2 kV . From this, the deposition radius of the circle will decrease by a factor of two (Figure 8).

[0112] On the other hand, one can change the deposition radius by changing the frequency (Figure 9). To do this, the following parameters are maintained: 13 kV at the needle,

−7 kV at the collector, and change the needle and collector displacements from the origin at 3'' and 2.25'', respectively. Likewise, one can also change the inter-electrode spacing diameter to 2''. Using a 30 Hz pulse and a 45 Hz pulse, diameters of 1 cm and 0.75 mm are obtained, respectively.

5 [0113] To transition toward more aligned morphologies, one may need to accelerate the jet centripetally toward higher tangential velocities. This can be achieved by, a) maintaining a single deposition radius while increasing the frequency of the pulse, or b) maintaining a single frequency while increasing the radius. This should increase the tangential (x-y planar) velocity of the jet, and will subsequently align the fibers as they approach those comparable to the z-axis velocity, *i.e.*, 0 – 5 m/s.

10 [0114] As seen previously (Figure 8), it is possible to maintain a fixed frequency while drawing two circles with different radii by altering the displacements of each electrode. Here, a frequency of $f = 45 \text{ Hz}$ chosen, the voltage at the needle is set to 13 kV, and the inter-electrode oscillation pk-pk voltage will be 6.5 kV. For a 45 Hz circle with a diameter of 1 cm, and a displacement of the inter-electrodes from the origin by 1.5''. Likewise the collector and needle are spaced at 4'' from the origin and the collector voltage is set to −6.2 kV. Similarly, for a 45 Hz circle with a diameter of 2 cm, inter-electrodes can be displaced from the origin by .75'', and space the collector and needle from the origin by 1.25''. From Figure 10, one can see a more aligned fiber from increasing the centripetal acceleration of the jet.

20 [0115] Large Scale Production. Using this system, large-scale production of printed nanofibrous geometries is also possible with the addition of a pivoting collector. In this example, each structure may be printed sequentially, *i.e.*, one after the other. For applications involving chemical sensors, which require two-dimensional resistor networks, this printing scheme would allow polymers with dispersions of conductive particles to be generated consistently with high efficiency. This type of setup can be seen in Figure 11.

25 [0116] Improvements. If the charge on the collector is not sufficiently negative, the polymer jet may be intercepted midway by one of the grounded electrodes (Figure 12). This may cause an accumulation of polymer residue on the tip of the inter-electrodes, forming a dielectric build up on its surface. In an example, it provides the option to print structured nanofibrous material directly onto the electrodes to be collected separately. However, the fibers printed here may possess some alignment permutations that aren't typically available using DC voltages. Nevertheless, when attempting to deposit the jet onto the actual collector, such dielectric build up will minimize the electric field in its vicinity so each electrode should be cleaned when necessary.

EXAMPLE 2

[0117] The following example provides examples of methods and systems of the present application.

[0118] The following discusses features in the design and construction of the disclosed system. This includes the electrical and mechanical systems needed to accelerate the charged jet continuously to collect controlled 2D nanofibrous geometries/morphologies. Regarding the materials used for construction: since high voltage is necessarily applied to each conductive element, a blend of Acetal, Delrin, Teflon and HDPE is utilized, as they are good electrical insulators and are easily machined using a mill or lathe etc. This allows a user (or automated system) to continually adjust the distances of each electrode while the high-voltage amplification process ensues. Figure 13 shows a list of major components used to construct the invention. A more extensive list of components is available at the end of this document.

[0119] Design and Construction. To oscillate the electric field rapidly and continuously, custom high-voltage amplifiers are utilized. Here, a total of six common-cathode, high-voltage amplifiers were designed and driven using two different power supplies (1. and 22.) as seen from Figure 14. Various pulses are then delivered to each amplifier (7.) using algorithms preprogrammed into each function generator (8.). The syringe pump (4.) holding the syringe (6.) contains a solution of polymer fibers (and sometimes other mixtures), which are pushed at various volumes per unit time down a tube to the tip of the syringe needle (5.). The tip of the needle is connected to a positive high-voltage power supply (1.) and the collector plate (17.) is connected to a negative power supply (2.) as seen in Figure 14. The copper electrodes, in between the needle and the electrodes are pulsed by the amplifiers (7.) and driven at various duty cycles, frequencies, amplitudes and relative phases to manipulate the electric field along the jet path continuously. This electric field is used to manipulate the charged polymer solution into making the patterns seen in Figure 19.

[0120] Electronics and Switching Algorithms. Figure 16 shows a circuit diagram of the high-voltage amplifier used for the invention. This was designed using a 6BK4B vacuum triode (9.) in a common-cathode configuration with a bypass cathode resistor, $R_k = 4.4k$ (13.). A Tektronix P6015A high-voltage probe (44.) was utilized to measure the voltage at the plate of the triode, (V_p), while a high-voltage power supply (2.), V_{supply} , was varied. A multi-meter was connected at the cathode of the triode (V_k) to measure the bias value, and thus the quiescent operation.

[0121] The grid was driven with a Tektronix2021 function generator (15.). The components were chosen with the current rating in mind. Choosing a cathode resistance, $R_k =$

4.4K, and a load resistance, $R_L = 10M$, gives the load lines drawn (blue and red) in Figure 15. The Q-point shows an expected .39 mA at a grid voltage of $V_k = 1.7$ V. This is experimentally verified below as the V_P ranges between 5.8 kV and 6.2 kV (Figure 17). This is taken directly from a Tektronix TDS2024C 4-channel oscilloscope, which specifies a specific pk-pk voltage as well as frequency applied at the grid.

[0122] Electrode Actuation and Movement. Figure 23 shows an exploded view of the driving mechanism used to move the electrodes, collector plate, and syringe needle with respect to each other. To electrically insulate the system/user from the high-voltage being pulsed on the copper electrodes (11.), HDPE, Teflon and Delrin is used. As each copper electrode is threaded into the Teflon spacer (10.), the high-voltage wiring (3.), which is connected to the amplifier (7.), is fed through the slotted cylinder (15.) and connected to the bottom of the electrode. The Teflon spacer is then threaded into the Delrin cylinder, which is inserted into a Delrin sleeve (16.). The threaded rod (14.) is threaded on one end into the Delrin cylinder (15); on the other end, it is fastened to the stepper motor (21.). To keep the Cylinder from turning with the threaded rod, which is powered by the motor, an oval set screw is inserted (18.) into the side of the Delrin sleeve (16.), which is also fed into the side of the Delrin cylinder (15.). The entire length of the cylinder is then notched for longer linear displacements (15.). This driving mechanism provides a means to translate the rotational momentum of the stepper motors into linear motion. Since the electric field is dependent on the distance of each electrode in the system, this provides a way to change the electric field in real-time using an algorithm or a remote control. The syringe needle and collector operate in the exact same way.

[0123] A remote control is connected to a microcontroller, which processes the buttons being pressed to drive cylinder displacements. The stepper motors are controlled via pulse width modulation that is also processed by another microcontroller. This allows for real-time control of the electric field without changing the amplitude settings of the amplifier. Moving the electrodes, collector, and syringe needle at various distances, while changing their voltages and other settings, allows for the ability print various geometries. An algorithm programmed into the microcontroller can also be used to automate the process.

[0124] This invention can be used to print 2D geometries composed of various polymers for applications in tissue engineering, sol-gel precursors, nano-wiring, filtration, energy production/fuel cells, chemical sensors, and drug delivery systems (to name a few).

[0125] Additional Details For Selected Materials Used:

[0126] 1 – SL15P300 power supply:

Voltage Minimum	−40 kV
Voltage Maximum	0 V

Current Range	0–7.5 mA
Type	DC

[0127] 1 - Spellman SL40P150 power supply:

Voltage Minimum	0 V
Voltage Maximum	15 kV
Current Range	0–10 mA
Type	DC

[0128] 1 – Gamma High Voltage Research power supply:

Voltage Minimum	0 V
Voltage Maximum	30 kV
Current Range	0–200 μ A
Type	DC

[0129] 1 - Harvard Apparatus syringe pump:

Specifications	70-300S
Accuracy	$\pm 0.25\%$
Classification	Class I
Dimensions LxDxH in cm	12.0 x 8.5 x 7.25 (30.48 x 21.59 x 18.42)
Display	4.3" WQVGA TFT Color Display with Touchpad
Drive Motor	0.9° Stepper Motor
Environmental Humidity	20% to 80% RH, non condensing
Environmental Operating Temperature English	40°F to 104°F
Environmental Operating Temperature Metric	4°C to 40°C
Environmental Storage Temperature English	14°F to 158°F
Environmental Storage Temperature Metric	–10°C to 70°C
Flow Rate Maximum	216 ml/min using 140 ml syringe
Flow Rate Minimum	1.5 pl/min using 0.5 μ l syringe
I/O & TTL Connectors	15 pin D-Sub Connector
Input Power	50 W, 0.5 A fuse
Installation Category	II
Max Linear Force	75 lbs @ 100% Force Selection
Mode of Operation	Continuous
Motor Drive Control	Microprocessor with 1/16 micro-stepping
Net Weight English	10 lb
Net Weight Metric	4.5 kg
No of Syringes	2
Non Volatile Memory	Storage of all settings
Number of Micro-steps per one rev of Lead Screw	12,800
Pollution Degree	1
Pump Configuration	Standard
Pump Function	Infusion Only
Pusher Travel Rate Maximum	190.8 mm/min
Pusher Travel Rate Minimum	0.18 μ m/min
Regulatory Certifications	CE, UL, CSA, CB Scheme, EU RoHS
Reproducibility	$\pm 0.05\%$
Step Rate Maximum	26 μ sec/ μ step
Step Rate Minimum	27.5 sec/ μ step
Syringe Rack Type	Standard Rack
Syringe Size Maximum	140 ml
Syringe Size Minimum	0.5 μ l
USB Connectors	Type B
Voltage Range	100–240 VAC, 50/60 Hz

RS-232Connectors	9-pin D-Sub Connector
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[0130] 23 Gauge syringe needles:

Gauge	23
Inner Diameter	0.01325"
Outer Diameter	0.02525"
Length	1.5"
Material	Stainless steel

[0131] 8 - Stepper Motors:

Type	Hybrid
Coil Type	Bipolar
Voltage - Rated	3 VDC
Current Rating	1.7 A
Steps per Revolution	400
Step Angle	0.9°
Accuracy	- NA
Torque - Holding (oz-in / mNm)	67.97 / 480
Size / Dimension	Square - 1.665" x 1.665" (42.30 mm x 42.30 mm)
NEMA Frame Size	17
Diameter - Shaft	0.197" (5.00 mm)
Length - Shaft and Bearing	0.945" (24.00 mm)
Mounting Hole Spacing	1.220" (31.00 mm)
Termination Style	Wire Leads
Operating Temperature	- NA
Coil Resistance	1.8 Ohms
Features	Round Shaft

[0132] 8 – Stepper motor drivers:

Type	Board
Motor Type	Stepper
Control / Drive Type	Stepper, Bipolar
Number of Motors	1
Voltage - Load	35 V
Current - Output	2 A
Wattage - Load	- NA
Voltage - Supply	5 VDC
Interface	Step / Direction
Mounting Type	Chassis Mount
Operating Temperature	-20°C ~ 85°C

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EXAMPLE 3

[0133] The following example provides examples of methods and systems of the present application.

[0134] A novel jet deflection protocol was developed for the electrospinning process to generate nanofibrous materials with pre-determined geometries. This is achieved by continuously oscillating the intermediate electric field at various frequencies by supplying a time-varying, high-voltage signal to several intermediate electrodes using a series of custom high-voltage amplifiers alongside various switching protocols. Each time-varying high-voltage signal is pulsed at a specific frequency, duty cycle, amplitude, and relative phase, to create different

10

oscillation sequences for the charged jet to follow. The positively charged polymer jet is then deflected in a predetermined manner to produce different geometries of nanofibrous material. By rapidly alternating high-voltages along the electrodes in this way, it is possible to induce linear and/or centripetal accelerations orthogonally along the jet path to promote x-y planar velocities comparable to those in the z-direction (Figure 30 shows the x-y-z orientation), providing better control for fiber alignment.

[0135] The system is illustrated in Figure 30. It consists of one injection nozzle, a collector electrode, and six intermediate electrodes (inter-electrodes) that are evenly spaced in the horizontal (x-y) plane, intermediary to the injection nozzle and the collector. The number of inter-electrodes and their positions can vary depending on different applications. For gravitational symmetry, the flight path of the polymer jet is oriented vertically with the injection point (nozzle) positioned at the base of the system, and the collector above it. Each inter-electrode is connected to an electrically insulated linear driving mechanism so that the distance between the tip of the inter-electrode and the origin (defined in Figure 30), can be individually varied electronically. Likewise, the nozzle and collector are also connected to a linear electro-mechanical driving mechanism so as to vary their respective distances from the origin when necessary. A detailed description of the experimental setup can be found in the supplementary information (shown in Figure 44).

[0136] The output of a sequentially oscillating, high-voltage source is connected to each inter-electrode to create the necessary electric field needed to manipulate the jet trajectory. Each pulse is generated using a custom high-voltage vacuum tube amplifier, the principle of which is illustrated in Figure 31. Low voltage oscillations from several function generators are connected to the grid of each vacuum tube to suppress the current therein, or short circuit the anode to cathode to produce the desired oscillating high-voltage signal at the plate of each tube. Each pulse is triggered to continuously deflect the jet for two dimensional control over the plane of deposition. To demonstrate, Figure 32 shows a low-voltage input oscillation at the grid of the vacuum tube and a corresponding high-voltage output at the plate. These signals correspond with the before-and-after images of the deflected polymer jet shown in Figure 33.

[0137] During the deflection process, a positively charged electrode will repel the positive jet, while a grounded electrode will attract it from its lensed trajectory (see Figure 30). However, if the collector is not sufficiently charged to a negative voltage, or the electrodes are too close to the origin, the positive jet could be intercepted by a grounded inter-electrode (see Figure 43). To avoid this, we maintain substrate deposition by tuning the following parameters: 1) the distance between the needle and the origin, 2) the distance between the collector and the

origin, 3) the distance between each inter-electrode and the origin, 4) the needle and collector voltages, 5) the inter-electrode pk-pk voltages, and 6) the amplitude, frequency, duty cycle, as well as the relative phases of each pulse.

[0138] To sequentially and continuously deflect the jet from one inter-electrode to another, we manipulate the electric field near each inter-electrode by sending a positive, out of phase, low-voltage pulse to each high-voltage AC amplifier using the following switching protocol:

$$\phi_n = \frac{D_N (n-1)}{f \cdot 100}, \quad (1)$$

where ϕ_n is the relative phase in seconds, f is the frequency in Hz, and D_N is the % duty cycle for a total of N electrodes; while n corresponds to one of the six function generators (and subsequently to the n th inter-electrode). This grounds each electrode sequentially with respect to ϕ_n . Here, the duty cycle is defined as:

$$D_N = \frac{1}{N}. \quad (2)$$

[0139] For the case of six electrodes, *i.e.*, when $N = 6$, the duty cycle would be $D_N = 16.6\%$. From this, we can fluctuate each of the six inter-electrode potentials sequentially between ground and high-voltage, which would pulse the six electrodes one-by-one in a circular pattern. In this case, each neighboring n th electrode would be out of phase by equation (1), where $\phi_N = \frac{16.6 (n-1)}{f \cdot 100}$ seconds. The deflection of polymer jet can be better understood by visualizing the changing electric field, which was simulated in Comsol 5.3 (see Figures 49–50).

[0140] We use a typical polymer solution containing a 10% (w/w) concentration of Polyethylene Oxide (PEO) in deionized (DI) water. The molecular weight of the polymer is $M_w = 600,000$ (Sigma Aldrich) with a relative density of 1.21 g/cm^3 . The rheological properties of the polymer solution are also measured and listed in Table 1.

[0141] Table 1: Physical properties of the polymer solution.

Measured Parameters for PEO 10%		
Variable	Definition	Value
μ	Viscosity	4–42 Pa·s
α	Surface Tension	30.95 mN/m
G	Elastic Modulus	190–1020 Pa
ρ	Mass Density	1.02 g/cm ³

[0142] Without pulsing the amplifier, the inter-electrodes will default to high-voltage. This creates a DC electric lens similar to that previously demonstrated except that we are using six pointed electrodes along one cross-sectional plane instead of several concentric rings along

the trajectory (z-axis). In this setting, we can obtain a single spot of polymer with a diameter on the order of millimeters, as shown on the collector in Figure 34 (Left). We can arbitrarily change the x-y coordinates of the collected spot by changing the DC voltage on one of the inter-electrodes using a sustained pulse. We can also draw a one-dimensional fibrous path between

5 two spots by switching the high-voltage supply between two inter-electrodes, while holding the other four inter-electrodes at high voltage.

[0143] Predetermined Nanofibrous Geometries

[0144] With this experimental setup, it is possible to fabricate nanofibrous materials with predetermined 2D geometries. To see how this works, we connect a high-voltage power supply

10 (at 5 kV) to a load resistor (RL) as seen in Figure 31, which is then connected to the inter-electrodes. We set the syringe needle to 13 kV and the collector to -7.3 kV. Since the inter-electrodes oscillate between a minimum of 0 V and roughly 5 kV (due to quiescent conditions), we required a negative voltage on the collector to keep the jet from depositing directly onto the inter-electrodes as seen in Figure 43. If interception does occur, a dielectric buildup will

15 diminish the electric field at each point, which will effect the deposition symmetry about the z-axis. We position the collector and the syringe needle from the origin to 31.75 mm and -63.5 mm, respectively. We also provide a 25.4 mm radius between the inter-electrodes and the z-axis. Choosing $f = 10$ Hz, we may calculate a relative phase output for each electrode in the pulsing sequence, *e.g.*, if we want to create a triangle (Figure 35), we pulse electrode 1 then 3 then 5 and

20 repeat. This requires three electrodes, $N = 3$. Therefore, from Eq. 1 and Eq. 2, if $f = 10$ Hz, and $N = 3$, then $D_n = 33.3\%$, which will require a relative phase of $\phi_n = 33.3(n - 1)$ ms. This can be adjusted for a preferred morphology. Likewise, to obtain the star in Figure 36 (Left), we may superpose two triangles by oscillating the electrodes between 2 then 4 then 6, then 1, 3 and 5 etc. Using this logic, and by adjusting the pulse permutation over the desired inter-electrodes, the

25 spot can be drawn from point to point along predetermined two-dimensional pathways as seen in Figure 36 (Right), *e.g.*, a hexagon.

[0145] To transition toward more aligned nanofibers and/or a more continuous deposition geometry, *e.g.*, from the six points of the hexagon shown in the right image of Figure 36 to the circle shown in the left image of Figure 38, we can accelerate the jet centripetally toward higher

30 tangential velocities, $v_t = 2\pi r f$, spending less time ($\phi_n = 11.1$ ms) accumulating nanofibers at each point. This can be achieved by: 1) maintaining a single deposition radius while increasing the frequency of the sequential pulses, or 2) maintaining a single frequency while increasing the deposition diameter D_{Dep} . This will increase the tangential (x-y planar) velocity, and will

subsequently pull the fibers orthogonally as we achieve speeds comparable to those along the z-axis, *i.e.*, rotating the jet orthogonally faster than its z-velocity of 0 – 5 m/s.

[0146] If the number of inter-electrodes is $N = 6$, then by Equation 1, the relative phase shift between each pulse can be calculated to achieve more continuous geometries. In an

5 example, we began by increasing the frequency from 1 Hz, moving the spot from point to point every $\phi_n = 166$ ms, to 15 Hz, moving the spot every $\phi_n = 11.1$ ms. This transition can be seen in Figure 37, as we transitioned from a discrete deposition of points to a smooth circle. In the latter case, we set the syringe needle to 13 kV, the collector to -2.6 kV and set the inter-electrodes to oscillate between 0 V and 4.78 kV. Here, the syringe needle and the collector were both set at
10 -76.2 mm and 76.2 mm from the origin, respectively. Likewise, the inter-electrode lensing radius was set at 19.1 mm from the z-axis.

[0147] Without changing the pulsing frequency or amplitude, it possible to change the deposition radius of each circle by changing the nozzle and collector voltages as well as their relative distances to the origin, *i.e.*, by changing the ratio, $\frac{\Delta V}{\Delta Z}$ (see Figure 38). To change the
15 nozzle and collector displacements from the origin, we utilized the mechanical driving system with the remote control. Here, we kept the pulsing frequency at 15 Hz, the inter-electrode distance at 19.1 mm, and the oscillation amplitudes of 4.78 kV constant, while changing the distance between the nozzle and the origin from -76.2 mm to -114.3 mm. Similarly, we adjusted the distance between the collector and the origin from -76.2 mm to 114.3 mm. We then changed
20 the collector voltage from -2.6 kV to -9.2 kV. From this, the deposition radius of the circle decreased by a factor of $2/3$ (for more details, see Table 2).

[0148] Table 2: Deposition diameters, D_{Dep} , by changing the electrode distances and voltages (with fixed frequencies).

PEO 10%	$\frac{\Delta V}{\Delta Z}$	Dependency
Frequency (f)	15 Hz	15 Hz
Nozzle Position from Origin (Z_N)	-76.2 mm	-114.3 mm
Collector Position from Origin (Z_c)	76.2 mm	114.3 mm
Nozzle Voltage (V_N)	13 kV	13 kV
Collector Voltage (V_c)	-2.6 kV	-9.2 kV
Intermediary-electrode Position from Z-axis	19.1 mm	19.1 mm
Deposition Diameter (D_{Dep})	~ 30 mm	~ 20 mm

[0149] On the other hand, we may change the deposition diameter by changing the frequency (Figure 39). To do this, we maintained the following parameters: 13 kV at the nozzle, −7 kV at the collector, and position the nozzle and collector displacements from the origin to −76.2 mm and 57.15 mm, respectively. Likewise, we held each inter-electrode spacing radius at 25.4 mm from the origin. Next, we imposed a 30 Hz and 45 Hz pulse in two different experiments, which resulted in deposition diameters of 1 cm and .75 mm, respectively. Table 3 lists the experimental results of deposition diameter with respect to frequency, while maintaining all other parameters.

[0150] Table 3: Deposition diameters, D_{Dep} , due to changing the frequency (with fixed electrode distances and voltages).

PEO 10%	f Dependency	
Frequency (f)	30 Hz	45 Hz
Nozzle Position from Origin (Z_N)	−114.3 mm	−114.3 mm
Collector Position from Origin (Z_c)	57.5 mm	57.2 mm
Nozzle Voltage (V_N)	13 kV	13 kV
Collector Voltage (V_c)	−7 kV	−7 kV
Intermediary-electrode Position from Z-axis	12.7 mm	12.7 mm
Deposition Diameter (D_{Dep})	~ 10 mm	~ 7.3 mm

[0151] To demonstrate the effects of deposition radius on fiber alignment, we maintained a fixed frequency while drawing two different circles, each with different radii. Here, we chose $f = 45$ Hz, the voltage at the nozzle at 13 kV, and the inter-electrode oscillation pk-pk voltage at 6.5 kV. To print a circle with a diameter of 10 mm using a 45 Hz pulse, we displaced the inter-electrodes from the origin by 38.1 mm and space the collector and nozzle at 101.6 mm from the origin. Likewise, we set the collector voltage to −6.2 kV. Similarly, for a 45 Hz circle with a diameter of 2 cm, we displaced the inter-electrodes from the origin by 19.1 mm, and space the collector and needle from the origin by 31.75 mm. We then adjusted the collector voltage to −1.8 kV and keep the nozzle voltage at 13 kV. From this, we could increase the deposition diameter by a factor of two, while maintaining the same pulsing frequency of 45 Hz on the inter-electrodes, providing tangential velocities on the order of $\sim v_t = 2\pi r f = .14 \text{ m}\cdot\text{s}^{-1}$ for a circle with a deposition diameter of $D_{Dep} = 1 \text{ cm}$, and a tangential velocity of $\sim v_t = 2\pi r f = .28 \text{ m}\cdot\text{s}^{-1}$ for a circle with a diameter of $D_{Dep} = 2 \text{ cm}$, where $r = \frac{D_{Dep}}{2}$. Figure 40 shows an SEM comparison of the fiber orientation from both experiments.

[0152] Fiber alignment can also be achieved by cross-deposition using a set of symmetrically opposing electrodes driven 90° out of phase with a square wave pulse between 10 Hz and 45 Hz. By placing the nozzle, inter-electrodes and collector at 11 cm, 4 cm and 3 cm from the origin, respectively, and by inducing pulses between 0 V and 5.03 kV on the opposing
5 set of inter-electrodes (keeping all other inter-electrodes set to 5.03 kV), setting a constant voltage of -2.7 kV on the collector, and a constant voltage of 12 kV on the nozzle, aligned fiber structures can be achieved as seen in Figures 41 and 42.

[0153] Since the emitted jet is positively charged, it accelerated toward the inter-electrodes and onward to the collector. If the collector is not sufficiently negative, the polymer jet
10 may be intercepted midway by one of the grounded electrodes (Figure 43). This may cause an accumulation of polymer residue on the tip of the inter-electrodes, forming a dielectric build up on the surface of the conductor. This is not ideal, and may transmit unwanted current between grounded and high voltage inter-electrodes (loading the circuit and potentially damaging the final material) but it could provide the option to print structured nanofibrous material directly onto the
15 electrodes to be collected separately. However, when attempting to deposit the jet onto the actual collector, such dielectric build up will minimize the electric field in its vicinity so it should be cleaned when necessary.

[0154] Conclusion. A new electrospinning procedure was developed to continuously accelerate a charged polymer jet (linearly and/or centripetally) in two dimensions to print aligned
20 nanofibers with predetermined geometries. This is achieved by oscillating an electric field in the x-y plane during its trajectory in the z-direction using custom high-voltage amplifiers connected to several electrodes placed intermediary along the flight path. Novel switching protocols are utilized to produce sequential low-voltage pulses at the amplifiers, each with various duty cycles, amplitudes, frequencies and relative phases, to deflect the jet in a controlled manner. While this
25 example focuses on the ability to print pre-determined nanofibrous geometries in two dimensions, it demonstrates the potential for further developments in stacking controlled nanofibrous geometries in three dimensions using jet deflection technology.

[0155] Experimental Setup

[0156] The actual experimental setup is shown in Figure 44 with a closer view of the
30 injection chamber in Figure 46. For gravitational symmetry, the flight path is oriented vertically with the injection point (nozzle) positioned at the base of the system, and the collector above it (12.7 mm thick, 203.2 mm diameter 6061 Aluminum plate), each connected to an insulated mechanical driving mechanism. In between, are six-interchangeable conductors (inter-electrodes), positioned in between the nozzle and the collector, each with an orthogonal point-

like architecture. While the inter-electrodes could be designed in various shapes, *e.g.*, with a much larger $\frac{L_z}{D}$ ratio, where L_z is the length of each inter-electrode in the z-direction and D is the diameter between opposing inter-electrodes in the x-y plane, point-like geometries are chosen for two reasons: 1) they facilitate in demonstrating the electrospun pathway for point-like deposition (see Figure 35), and 2) they are relatively easy to maintain and clean (see Figure 43). Each inter-electrode is 12.7 mm in length, 3.175 mm in diameter, made of super-conductive-copper 101, and attached to an insulated mechanical driving mechanism. For the inter-electrodes, each driver is machined to be oriented 60° from adjacent inter-electrodes in a segmented, but symmetrical, electric lens formation. Eight stepper-motors (0.9° steps at 400 steps per revolution) provide linear actuation to move each conductor in the system, *i.e.*, the nozzle, collector and inter-electrodes, forward or backward with respect to a central origin, which is chosen to be at the center of the inter-electrodes.

[0157] Since high voltage is necessarily applied to each conductive element, we use a blend of Acetal, Delrin, Teflon and HDPE, as they are good electrical insulators and are easily machined. For real-time electrode positioning and automation during the electrospinning process, we use both a remote control, as well as an algorithm preprogrammed into a microcontroller.

[0158] A Harvard Apparatus infusion pump, rated with an accuracy of $\pm 0.25\%$, feeds a blunt 23 gauge, stainless steel needle (nozzle) at a rate of 0.5 mL/hr. The polymer solution is a 10% (w/w) mixture of deionized (DI) water and Polyethylene Oxide (PEO), with a molecular weight of $M_w = 600,000$ (Sigma Aldrich) with a relative density of 1.21 g/cm³. A Gamma High Voltage Research, DC power supply rated at 0 – 30 kV, 0 – 200 μ A is connected to the syringe needle (with little to no current requirement), and a Spellman SL300, (negative) DC power supply, rated at 0 – (–40 kV), 0 – 7.5 mA, is connected to the collector.

[0159] High-voltage amplifiers are built using 6BK4B vacuum triodes in a common-cathode configuration, each driven by a Spellman SL150 power supply, rated at 0 – 15 kV from 0 – 10 mA. The components of the amplifier are chosen with the SL150 current rating in mind. To operate within the required tolerances, *i.e.*, between 5 – 10 kV with the given current limitations (and using six amplifiers), the required load lines for a single 6Bk4B amplifier are drawn in Figure 45. The required bypass cathode resistor of 4.4k and a load resistance of 10 M is used to obtain a Q-point of .39 mA with a grid voltage of 1.7 V. This is sufficiently handled with a Tektronix AFG2021 function generator (one for each of the six amplifiers).

[0160] A BK Precision 9122A (positive) DC power supply is used to drive the filament of the vacuum tube at 6.3 V, requiring less than a total of 2 A for thermionic emission (at

quiescent conditions for each tube). From this, we are able to maintain -5 V or -10 V at the grid of each vacuum tube to suppress the current therein to produce high voltage at the plate.

Similarly, by maintaining $+5\text{ V}$ or $+10\text{ V}$ at the grid, we can essentially short circuit the anode to cathode, causing current to flow, which sends the plate to ground. In this manner, while

maintaining a high voltage at the plate with a high voltage load resistor, and by oscillating the voltage on the grid of the vacuum tube between -10 V and $+10\text{ V}$, we are able to produce a time varying high voltage signal along the connected electrodes.

[0161] To keep the pulses continuously oscillating (without drifting from each other) in a synchronized manner, we utilize a 10 MHz external reference clock for each function generator.

We then invoke burst mode and set the burst count to infinite, while allowing the output to be triggered externally. Adjusting the leading phase for each generator according to Eq. 1 allows a continuous high voltage oscillation to be preprogrammed along each inter-electrode. Depending on the desired deposition geometry, the charged jet will then be attracted (and deflected) in a predetermined manner.

[0162] Measurement of the Material Properties of the Polymer Solution

[0163] Viscosity Measurements

[0164] The viscosity of a 10% (w/w) mixture of deionized (DI) water and Polyethylene Oxide (PEO), with a molecular weight of $M_w = 600,000$, is measured using an Advanced Rheometer AR2000 using a 20 mm , 4° , steel-cone attachment (New Lab SN987409). The sample is tested at room temperature, *i.e.*, 20°C , over a 4 minute interval and subjected to shear rates ranging between $(0 - 180)\text{ s}^{-1}$. As is evident from Figure 47, this polymer solution is non-Newtonian.

[0165] Surface Tension Measurements

[0166] The surface tension of the same solution is measured to be $30.95\text{ (m}\cdot\text{N)/m}$ at room temperature, *i.e.*, at 21°C , using a KSV Sigma 701 and a T107 Wilhelmy probe with a cross sectional width of 19.6 mm , a $.1\text{ mm}$ thickness, and a wetted length of 39.4 mm . The vessel is 46 mm in diameter with a 40 mL max volume. This method used a light phase (air) wetting depth with an upward and downward velocity of 6 mm and 20 mm/min , respectively.

[0167] Elastic Modulus Measurements

[0168] Similar to the viscosity measurement above, we used the same Advanced Rheometer AR2000 with a 20 mm , 4° , steel-cone attachment to measure the loss modulus G'' and the storage modulus G' for the solution. Here, we used a frequency sweep from 1 to 10 Hz , with 20 sample points, at 25°C using a strain percentage of $.6\%$ (see Figure 48).

[0169] Simulations

[0170] Visualizing the Electric Field Deflection

[0171] To visualize the electric field, which promotes jet deflection similar to that seen in Figure 33, we will need to utilize the specific boundary conditions, electrode architecture and relative distances used in our experiment. To do this, a scaled three-dimensional CAD depiction of the experimental setup (without dielectrics) is developed in Autodesk Inventor (see Figure 51) and imported into Comsol 5.3. Comsol is a simulation environment incorporating a finite element method (FEM) and boundary element method (BEM) capability, which can easily handle electrostatics. To obtain a solution, the origin is specified at the center of the inter-electrodes with each inter-electrode spaced 19.1 mm from the z-axis. Likewise, the nozzle and collector are set at -76.2 mm and 76.2 mm from the origin along the z-axis, respectively. Based on each boundary condition (excluding the jet), a cross-sectional snapshot of the voltage profile is obtained (see Figure 30 and Figure 49) while the electric field lines can be seen in Figure 50. In these simulations, the collector is set at -2.6 kV, the nozzle set to 13 kV, and each of the five inter-electrodes are set to 4.78 kV, while one is set at 0 V, which are the parameters used to obtain the experimental results shown in Figure 38 (Left). Note, that while only two inter-electrodes are shown in the cross section of Figures 49 – 50, the electric field lines and profiles are calculated with respect to the entire three-dimensional system as seen in Figure 51 (Left).

We claim:

1. A method of electrospinning, comprising:
dispensing a solidifiable fluid from a nozzle, wherein the solidifiable fluid is biased at a first
5 DC voltage;
drawing a fiber stream from the solidifiable fluid along a direct stream path using a collector,
wherein the collector is biased at a second DC voltage selected to attract the solidifiable
fluid;
applying a midstream voltage to at least one electrode of a plurality of inter-electrodes
10 located between the nozzle and the collector, to cause the fiber stream to move in a
direction which is orthogonal to the direct stream path; and
collecting the fiber stream on the collector.
2. The method of claim 1, wherein the plurality of inter-electrodes is arranged in a first plane,
15 the first plane being orthogonal to the direct stream path.
3. The method of claim 1, further comprising moving the collector relative to the nozzle.
4. The method of claim 3, wherein the collector is rotated about an axis parallel to the direct
20 stream path.
5. The method of either of claims 3 or 4, wherein the collector is translated in a direction
orthogonal to and/or parallel to the direct stream path.
- 25 6. The method of claims 1, further comprising moving one or more electrodes of the plurality of
electrodes relative to the nozzle and/or the collector.
7. The method of claim 1, wherein the midstream voltage varies over time.
- 30 8. The method of claim 1, wherein the midstream voltage is an oscillating voltage, and the
oscillating voltage is set to various amplitudes, phases, frequencies, and/or duty cycles, as
applied to each inter-electrode or combinations of inter-electrodes.

9. The method of claim 1, where the midstream voltage is configured to accelerate the fiber stream centripetally with respect to the direct stream path.

10. The method of claim 1, wherein the midstream voltage is configured to accelerate the fiber stream radially with respect to the direct stream path.

11. The method of claim 1, wherein the solidifiable fluid comprises a polymer solution.

12. The method of claim 11, wherein the polymer solution comprises Polyethylene Oxide (PEO) or polyethylene glycol (PEG).

13. An electrospinning system, comprising:

a nozzle configured to dispense a solidifiable fluid as a fiber stream biased to a first DC voltage;

a collector spaced apart from the nozzle, wherein the collector is biased to a second DC voltage, and the second DC voltage is selected to attract the fiber stream in a flow direction;

a plurality of inter-electrodes arranged on a first plane orthogonal to the flow direction, wherein the first plane is located between the nozzle and the collector; and

a voltage generator in electrical communication with the plurality of inter-electrodes, wherein the voltage generator is configured to apply a midstream voltage to the inter-electrodes.

14. The system of claim 13, further comprising a plurality of actuators configured to move the plurality of inter-electrodes relative to the nozzle and/or the collector.

15. The system of claim 14, wherein the actuators are linear driving mechanisms and/or stepper motors.

16. The system of claim 13, further comprising a stage actuator for rotating the collector about an axis substantially parallel to the direct stream path and/or moving the collector relative to the nozzle.

17. The system of claim 13, further comprising a nozzle actuator for moving the nozzle relative to the collector.

18. The system of claim 13, wherein the voltage generator is configured to apply an oscillating voltage to the plurality of inter-electrodes.

19. The system of claim 18, wherein the oscillating voltage applied to each inter-electrode of the plurality of inter-electrodes is phase-shifted relative to the oscillating voltage applied to one or more other inter-electrodes.

20. The system of claim 13, further comprising a controller in operable communication with the voltage generator, wherein the controller is programmed to instruct the voltage generator to generate the time-dependent voltage.

21. The system of claim 16, further comprising a plurality of actuators in operable communication with the controller, the plurality of actuators configured to move the plurality of inter-electrodes relative to the nozzle and/or the collector.

22. An article produced using the method of one of claims 1–12 and/or the system of one of claims 13–21.

23. The article of claim 22, wherein the article has a two-dimensional geometry.

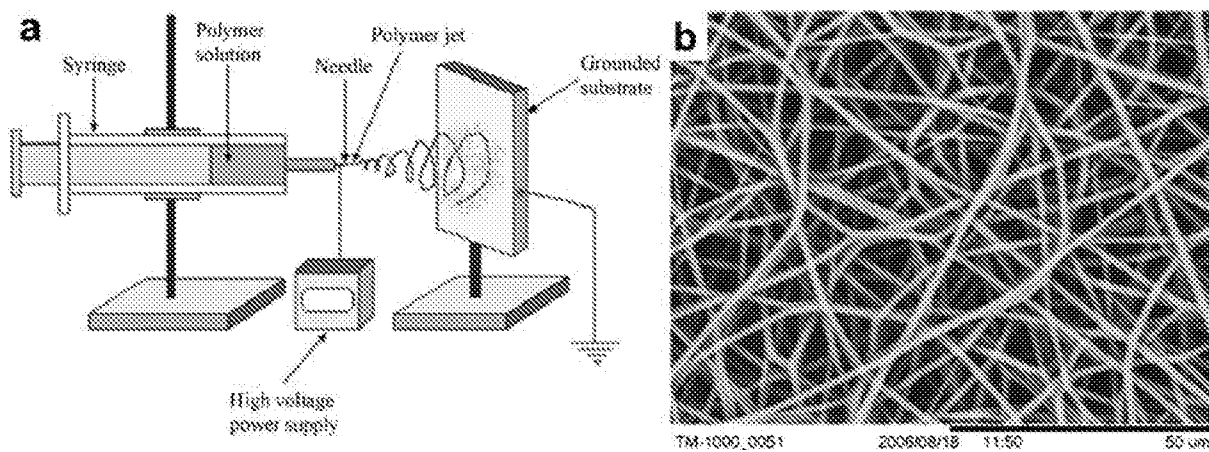
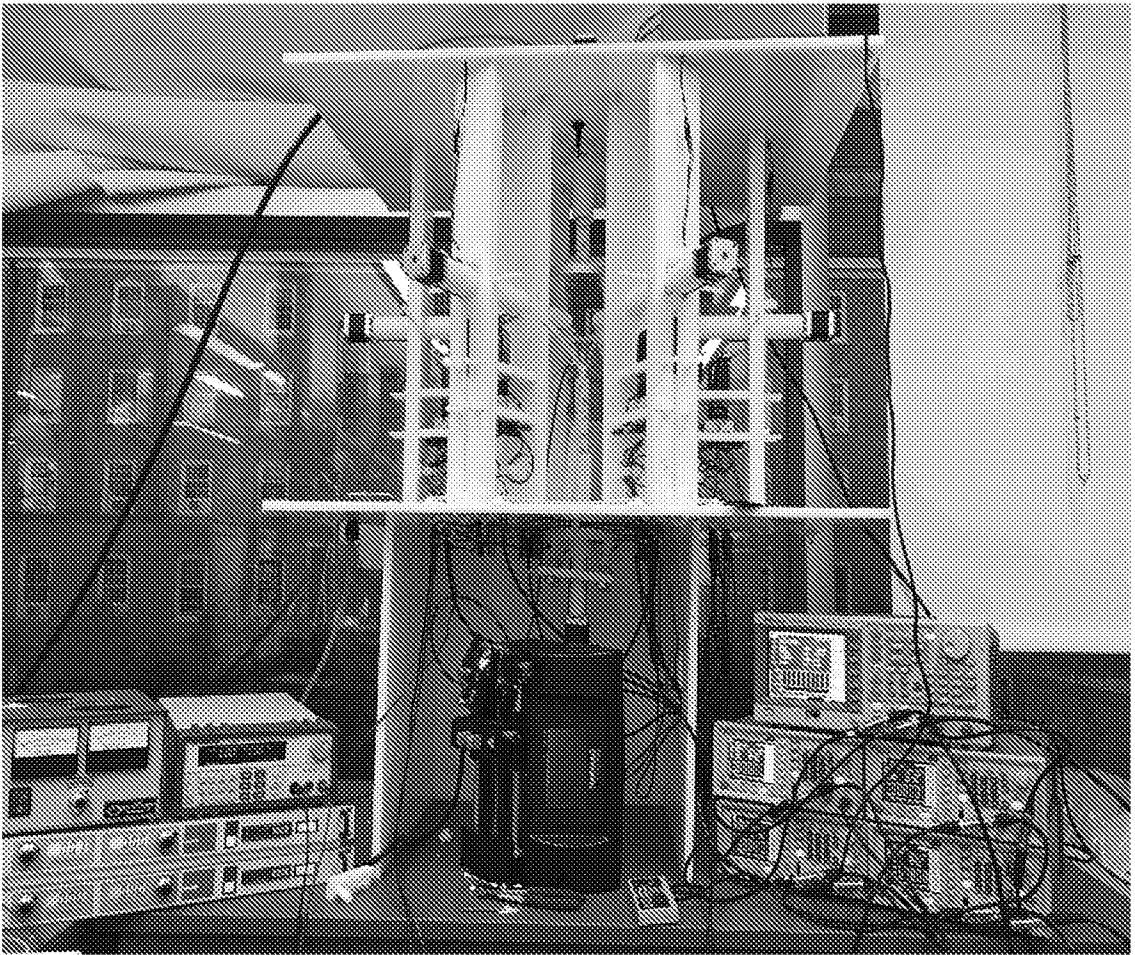


Figure 1
PRIOR ART

A



B

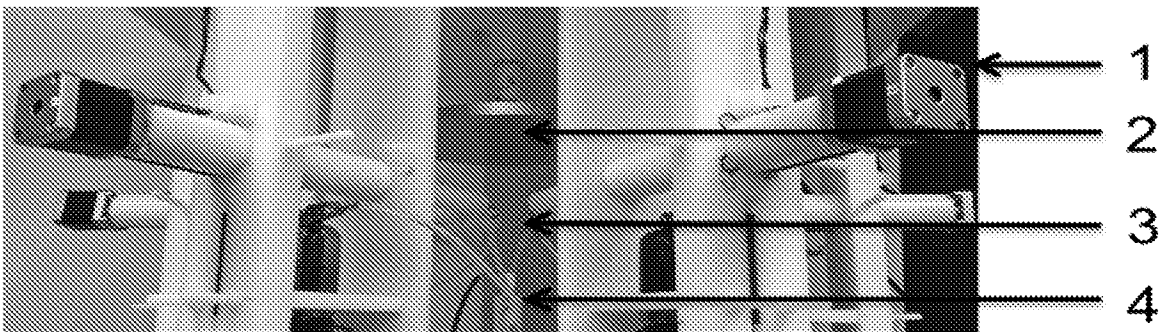


Figure 2

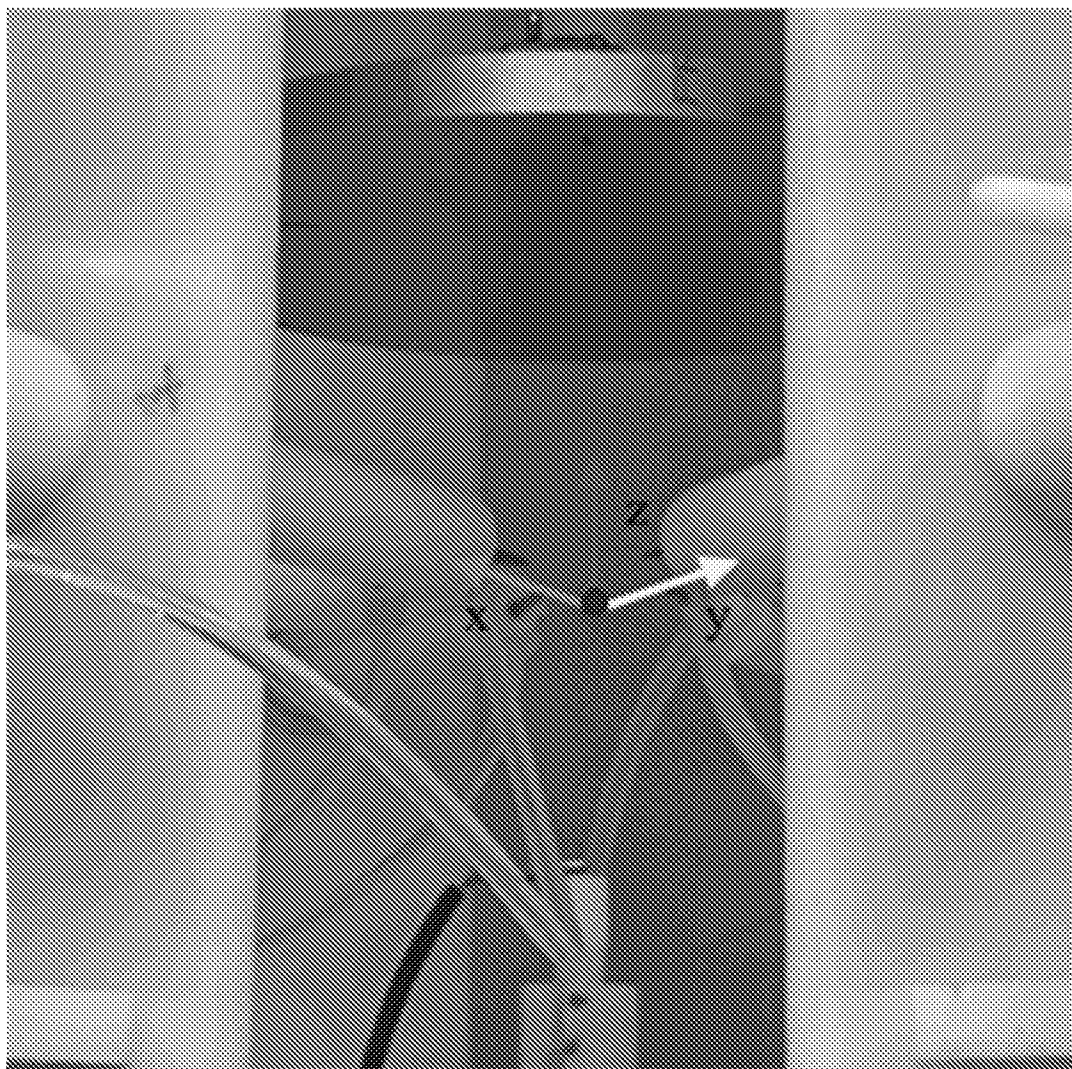
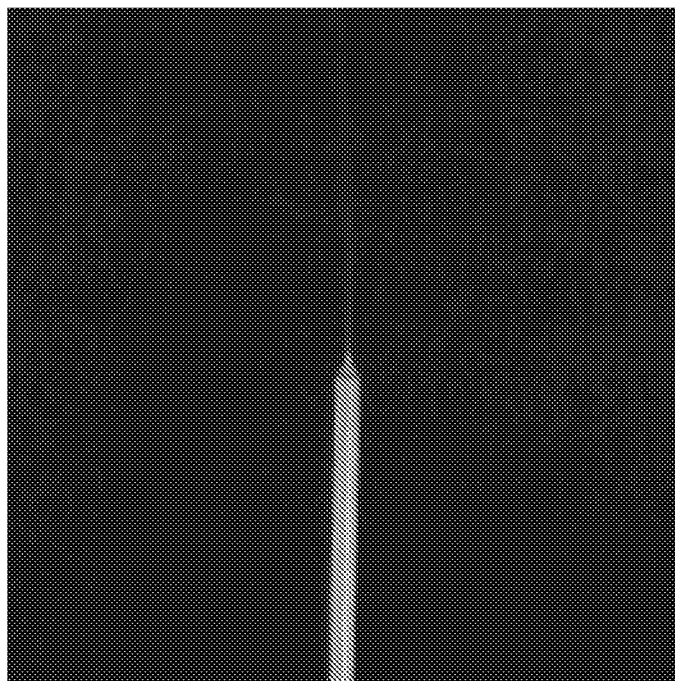


Figure 3

A



B

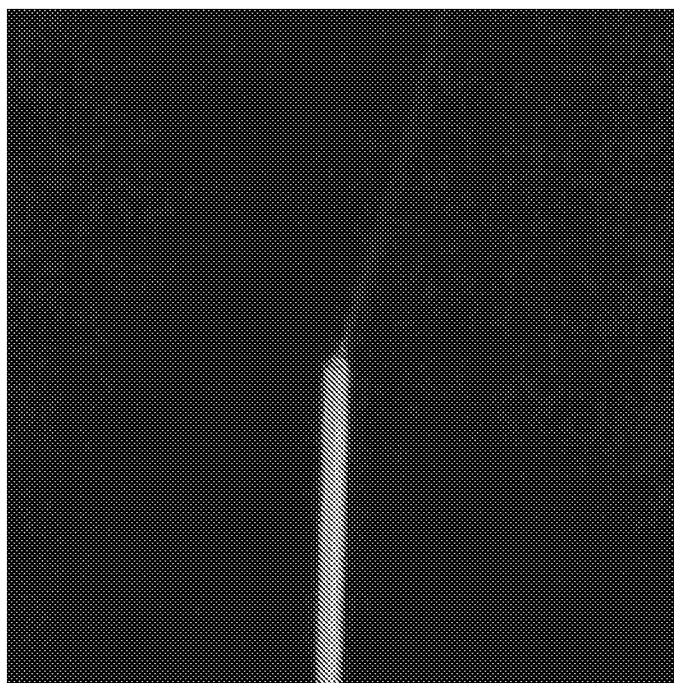


Figure 4

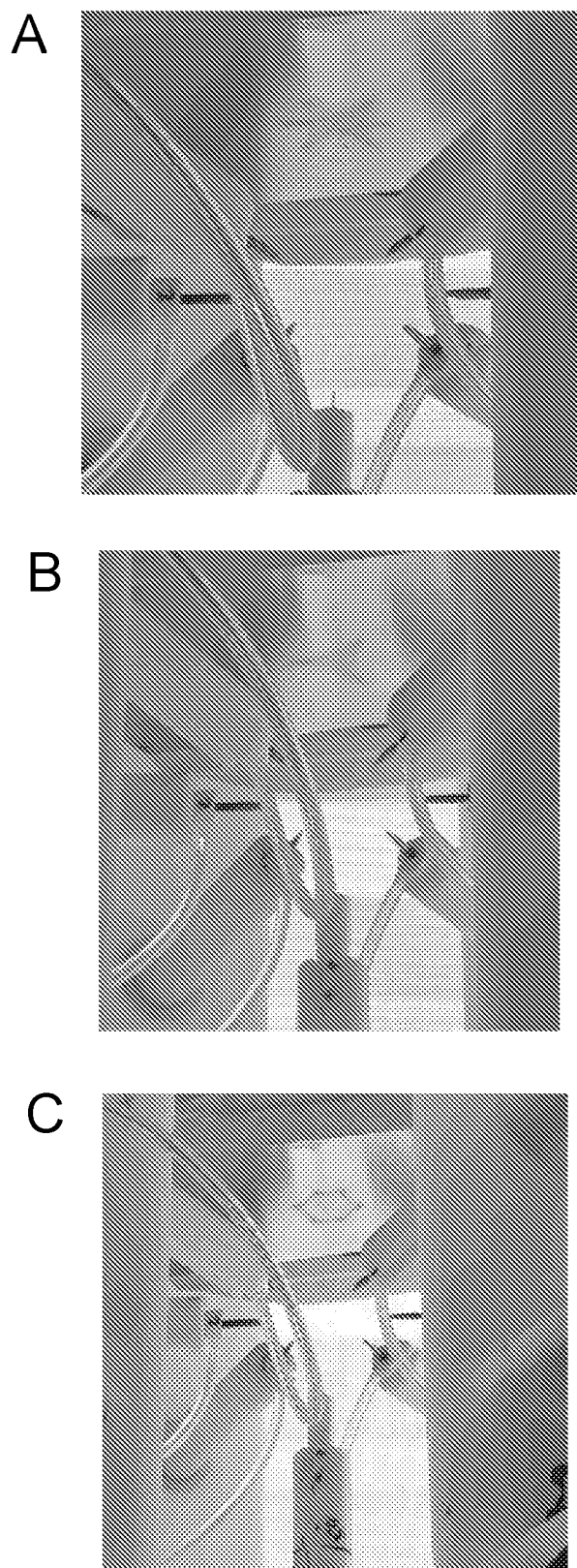
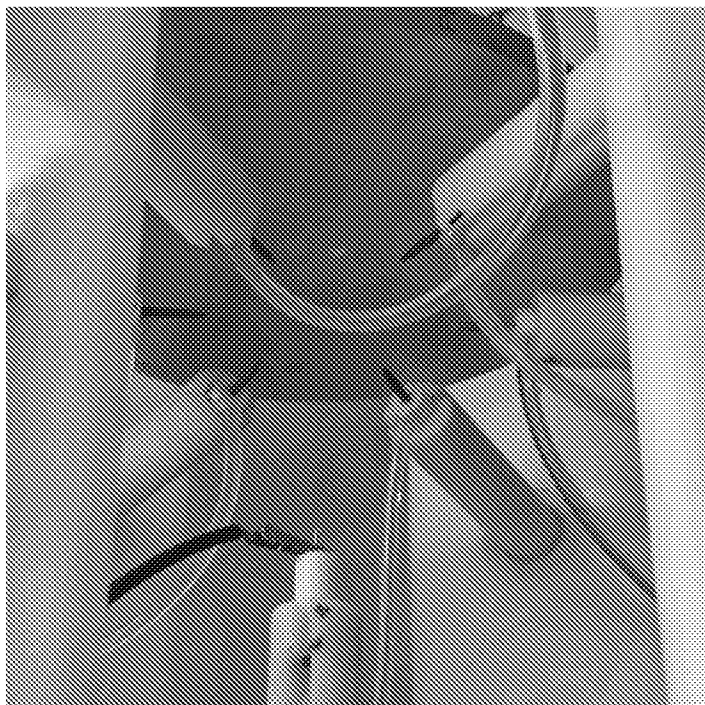


Figure 5

A



B

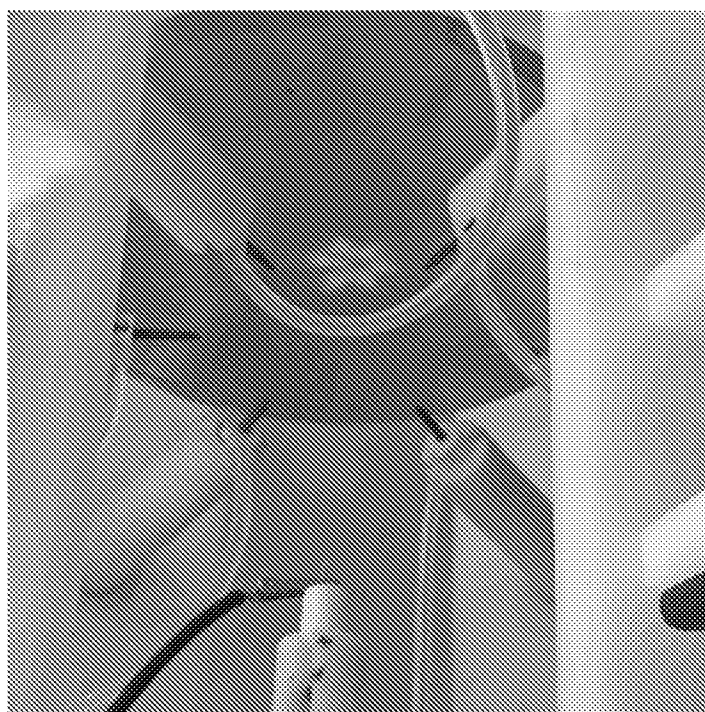


Figure 6

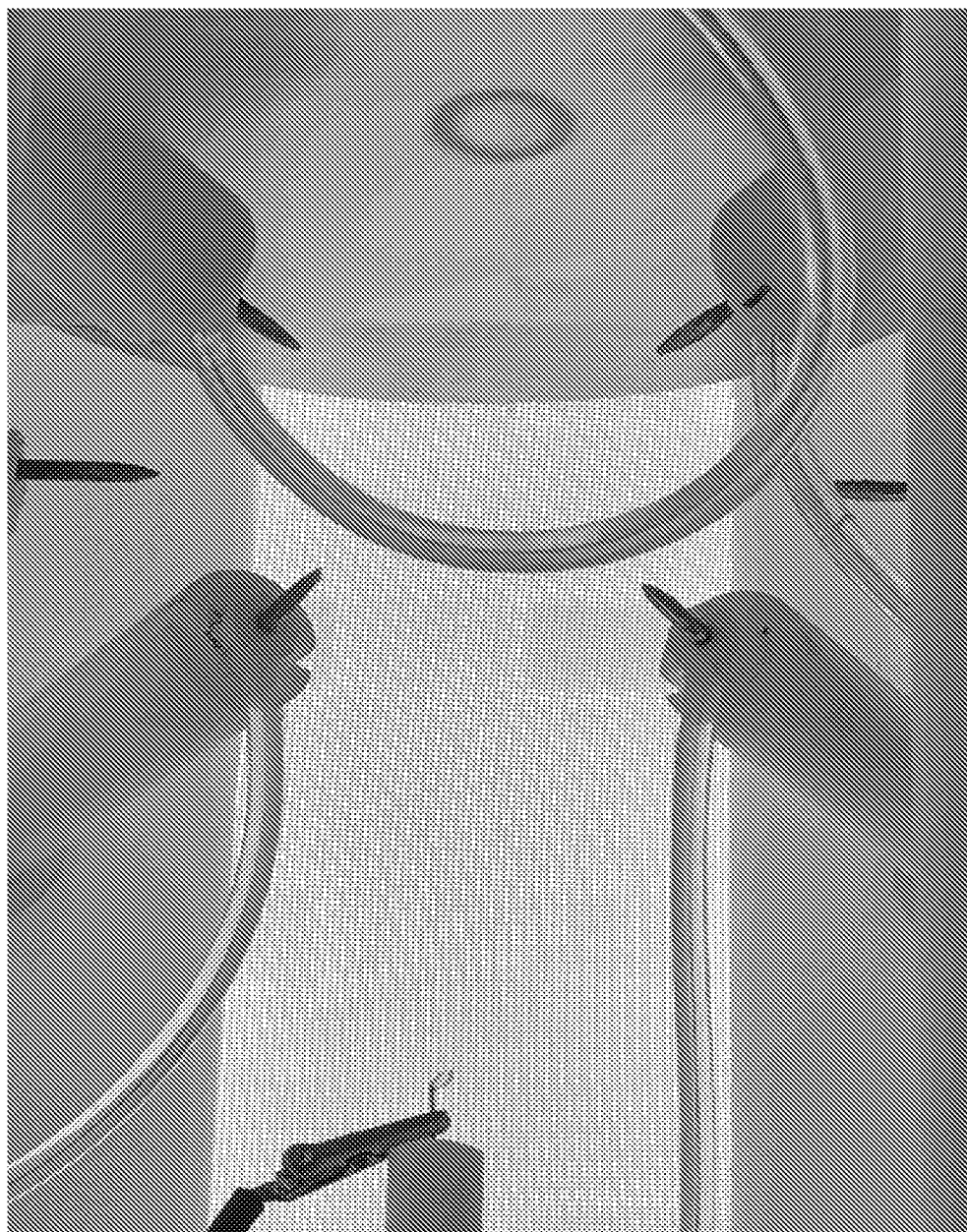
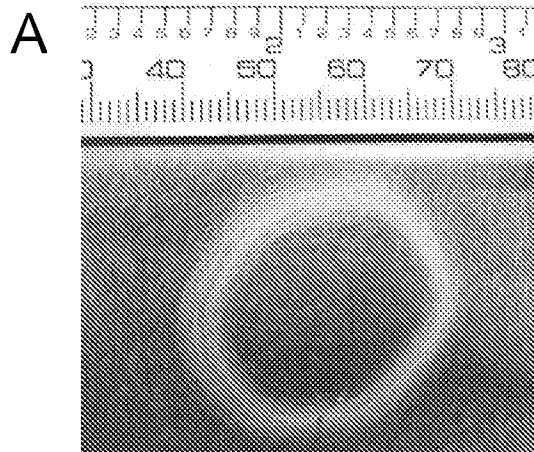
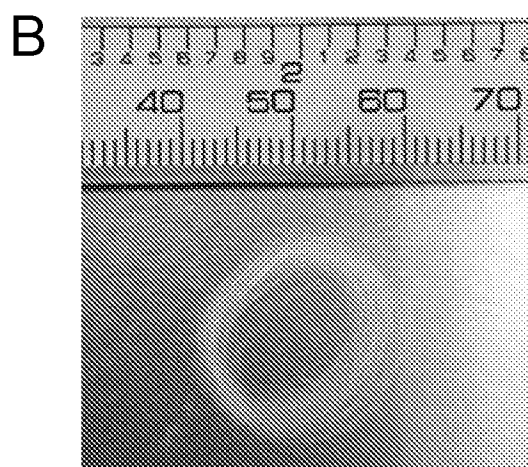


Figure 7

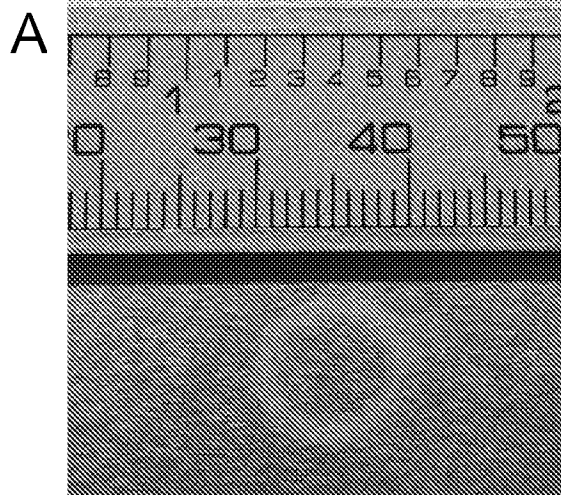


Frequency = 15Hz
Deposition Radius = ~1.5cm
Needle Distance = 3"
Collector Distance = 3"
Collector Voltage = -2.6kV
Inter-Electrode Diameter 3"

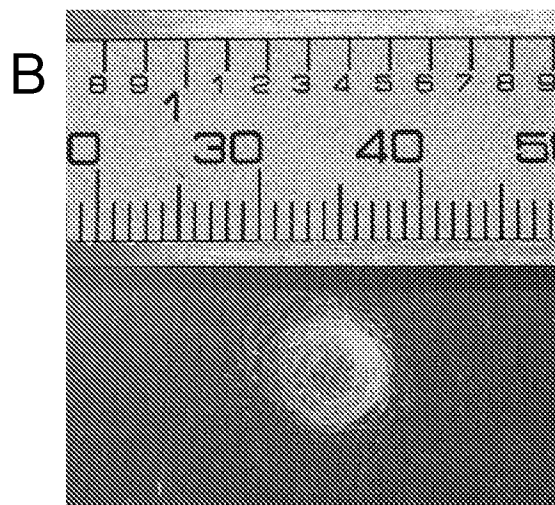


Frequency = 15Hz
Deposition Radius = ~1cm
Needle Distance = 4.5"
Collector Distance = 4.5"
Collector Voltage = -9.2kV
Inter-Electrode Diameter 3"

Figure 8

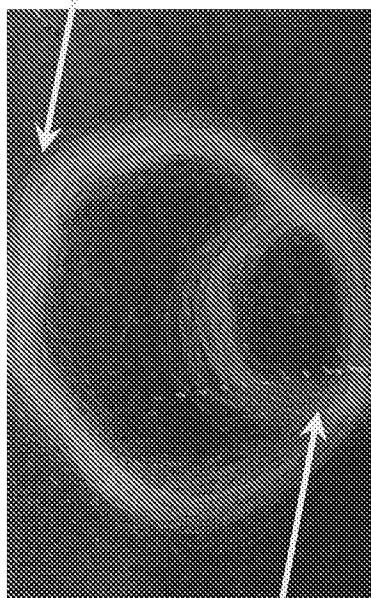


Frequency = 30Hz
Deposition Radius = $\sim .5$ cm
Needle Distance = 3"
Collector Distance = 2.25"
Collector Voltage = -7kV
Inter-Electrode Diameter 2"



Frequency = 45Hz
Deposition Radius = $\sim .375$ cm
Needle Distance = 3"
Collector Distance = 2.25"
Collector Voltage = -7kV
Inter-Electrode Diameter 2"

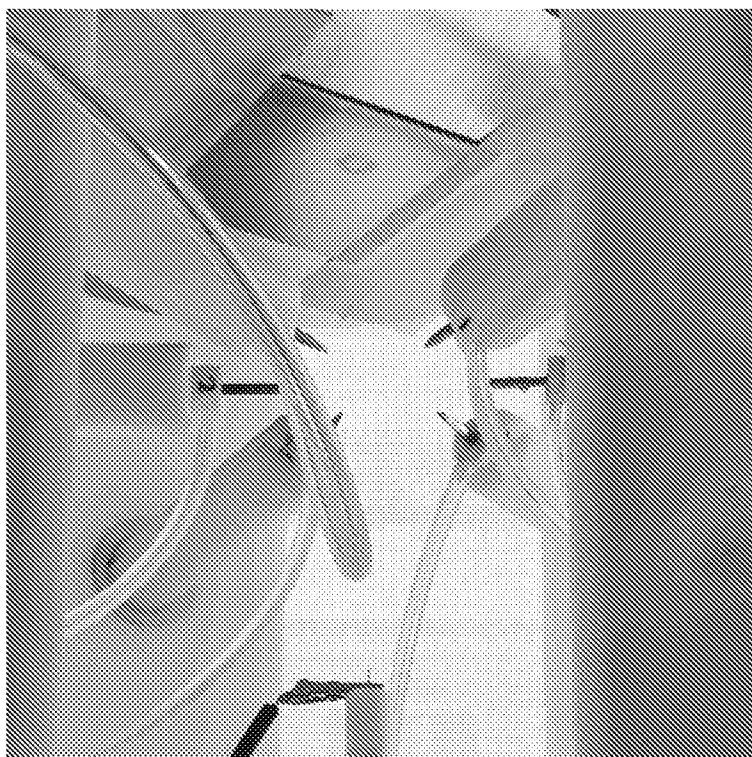
Figure 9



Frequency = 45Hz
Diameter = 1cm
 $v_t = .283m/s$

Figure 10

A



B

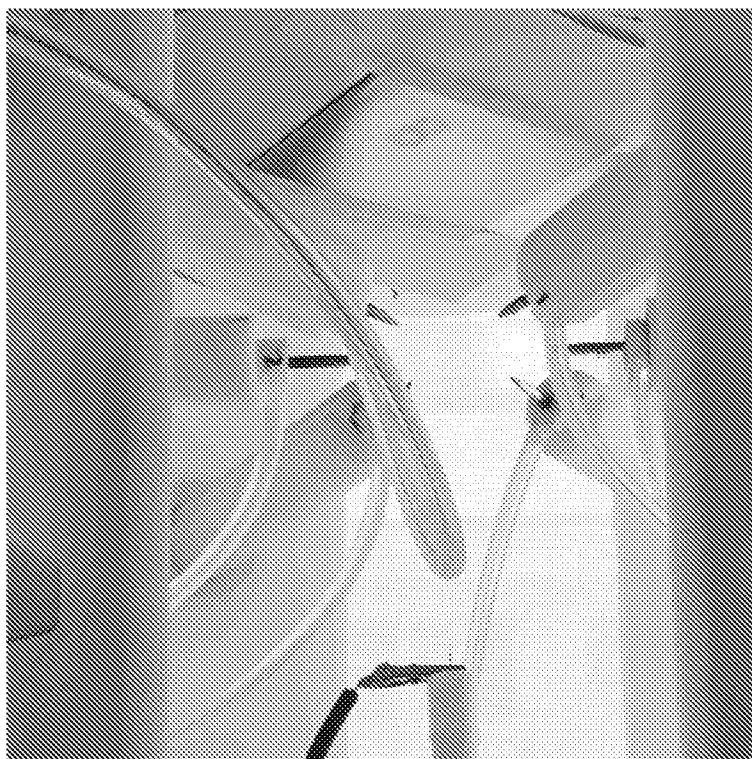


Figure 11

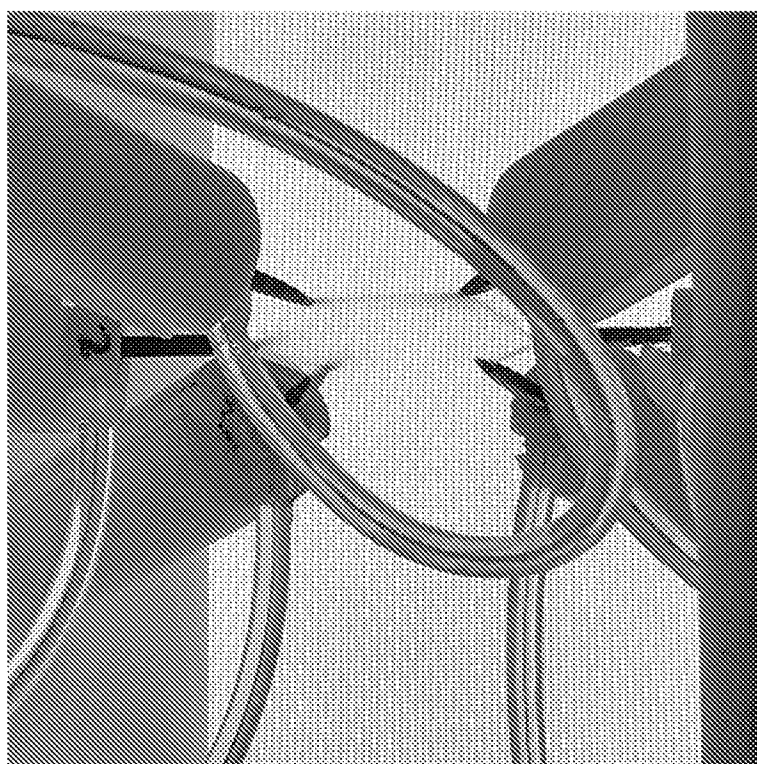


Figure 12

Item Number	Amount	Item
1.	2	Positive high-voltage power supply
2.	1	Negative high-voltage power supply
3.	25ft	High voltage wiring
4.	1	Syringe pump
5.	1	Syringe needle
6.	6	High voltage amplifiers
7.	6	Function generators
8.	1	10MHz external reference clock
9.	2ft	Teflon PTFE rod
10.	2ft	1/8" diameter Copper 101 rod
11.	2ft	1/8" diameter Copper 101 rod
12.	2 - 4 x 48	1/2" thick, white HDPE sheet
13.	2 - 4 x 48	1" thick, white HDPE sheet
14.	2 - 4 x 48	Delrin Acetal 5/16" - 18 threaded rod
15.	2 - 4 x 48	Delrin Acetal 1" diameter solid rod
16.	2 - 4 x 48	Delrin Acetal hollow tube 1 1/2" OD x 1" ID
17.	1	1/2" thick, 6061 8" diameter Aluminum plate
18.	8	10-32 oval set screws
19.	8	Nylon threaded rod
20.	32	Nylon hex nuts
21.	8	Stepper motors
22.	1	Precision DC power supply

Figure 13

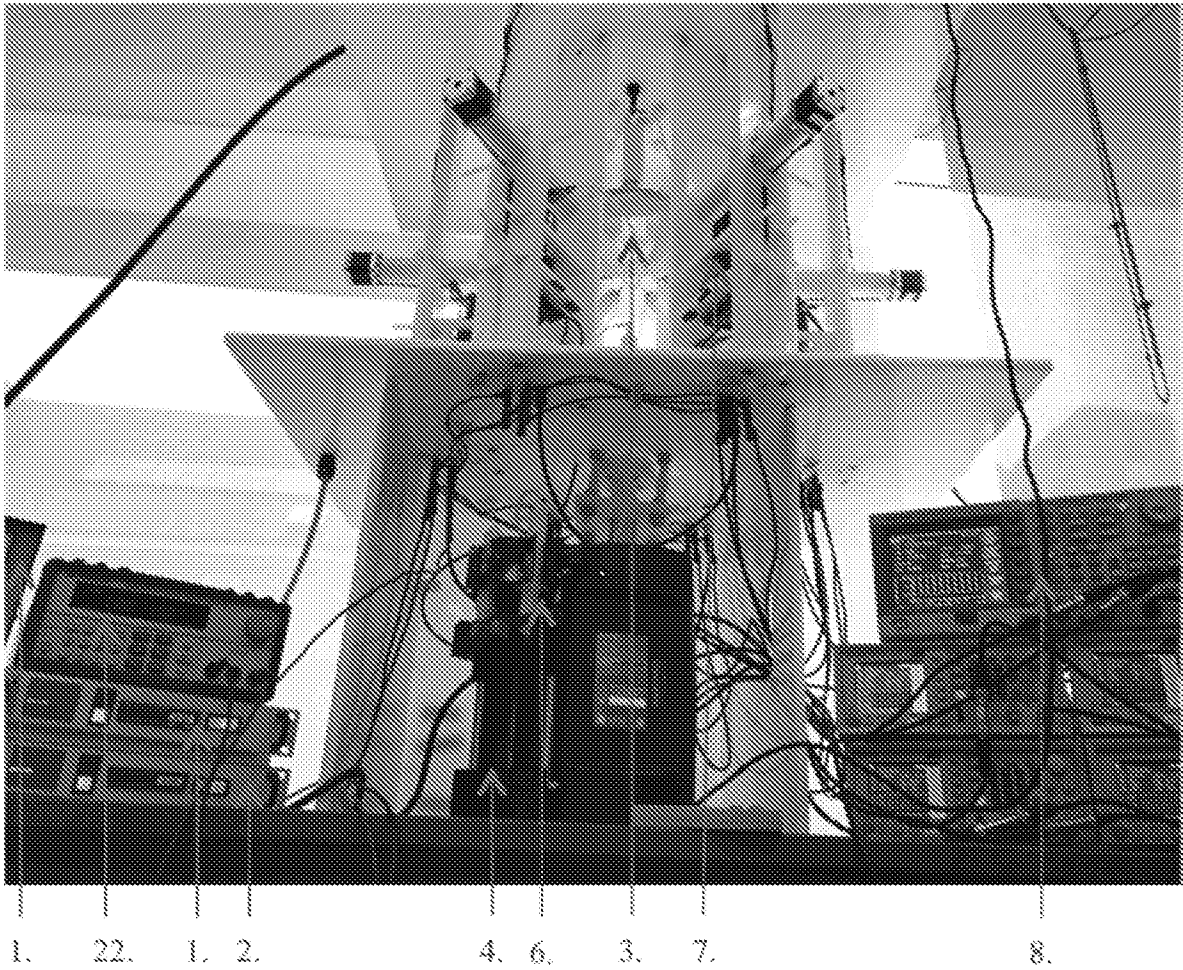


Figure 14

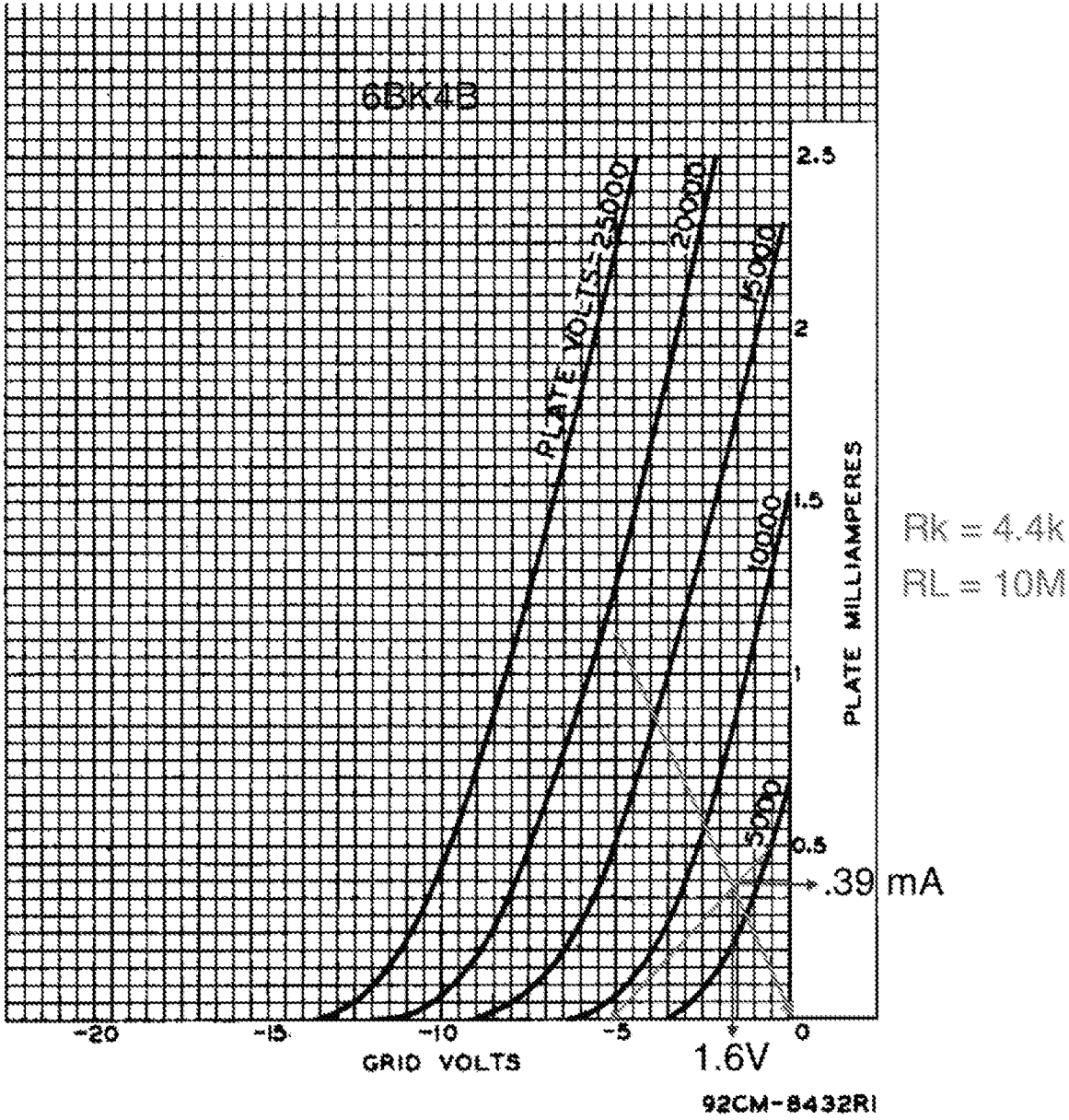


Figure 15

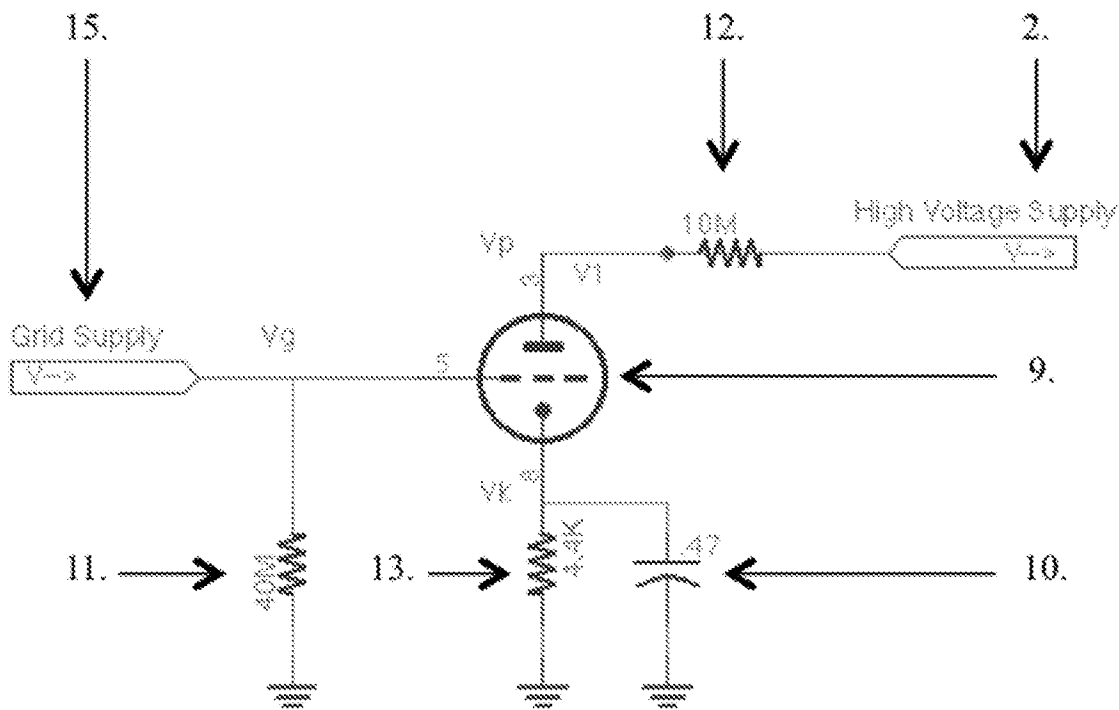


Figure 16

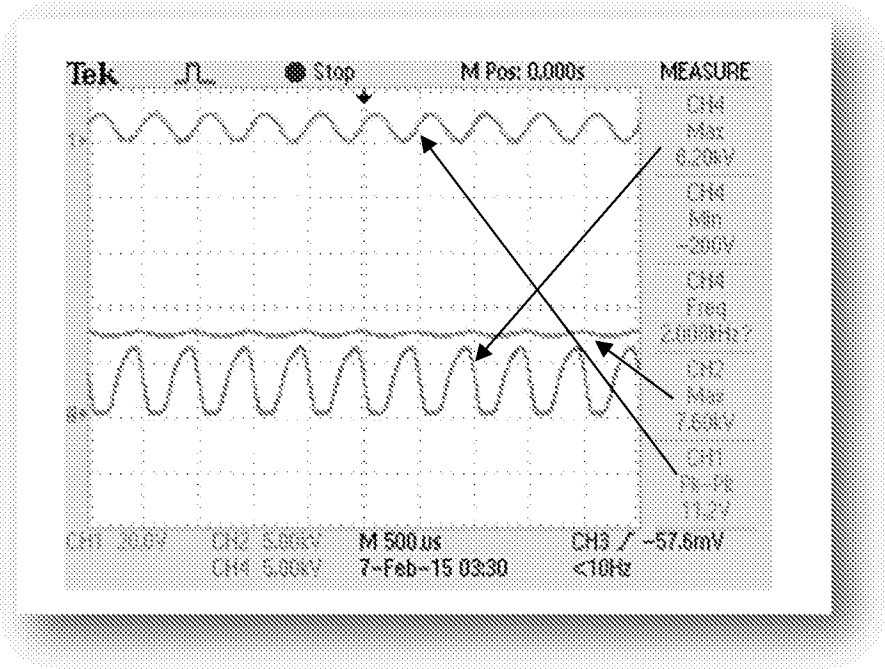
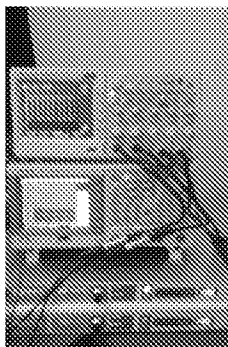


Figure 17

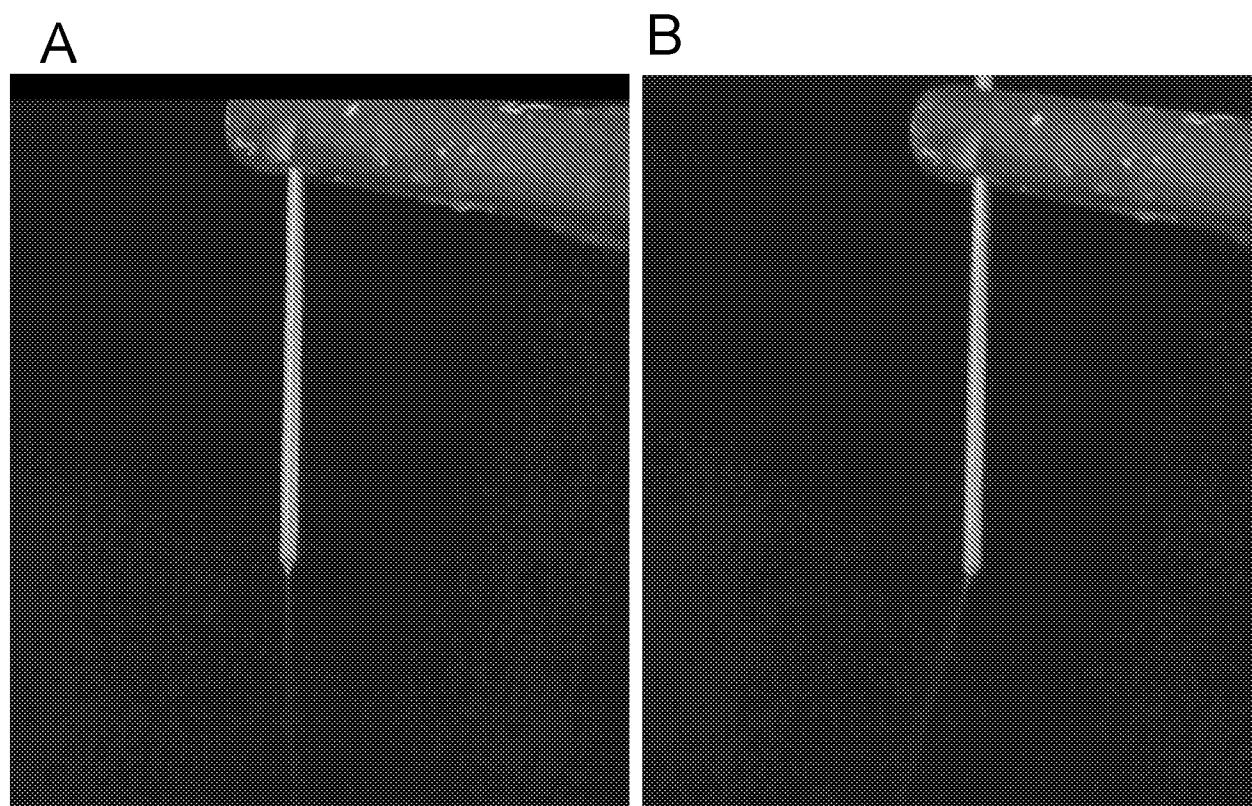


Figure 18

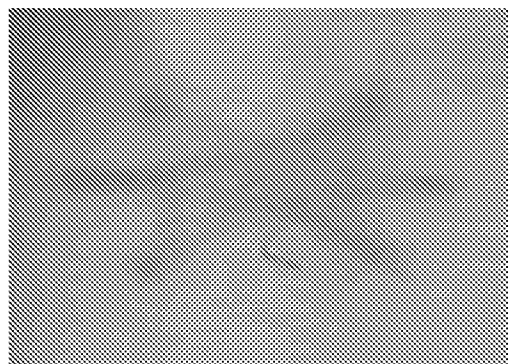
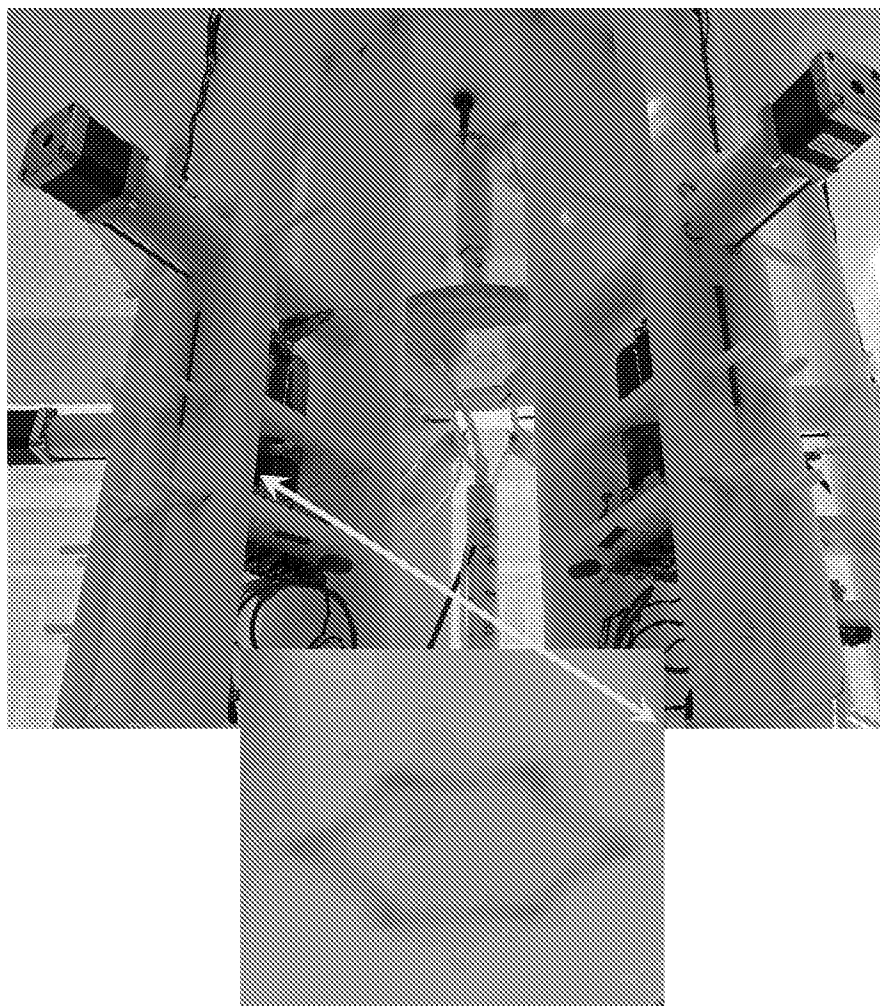


Figure 19

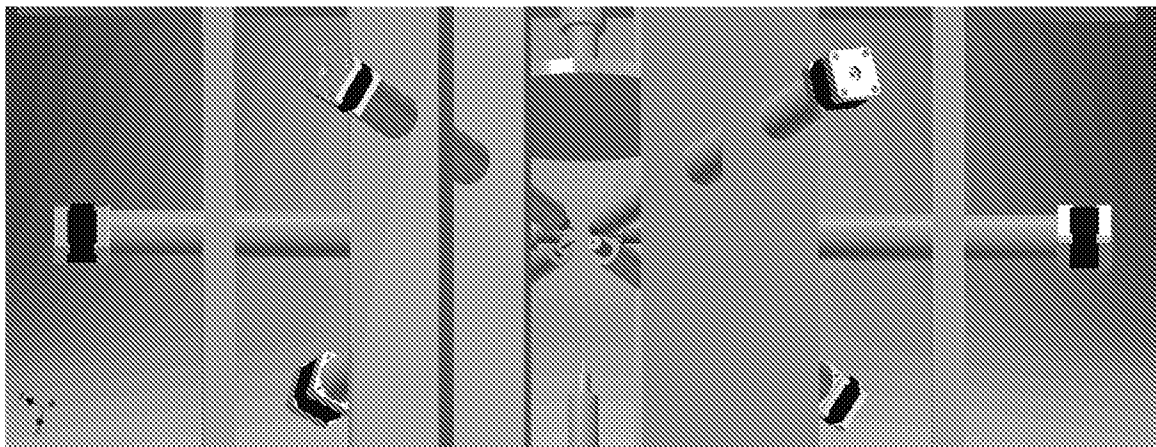


Figure 20

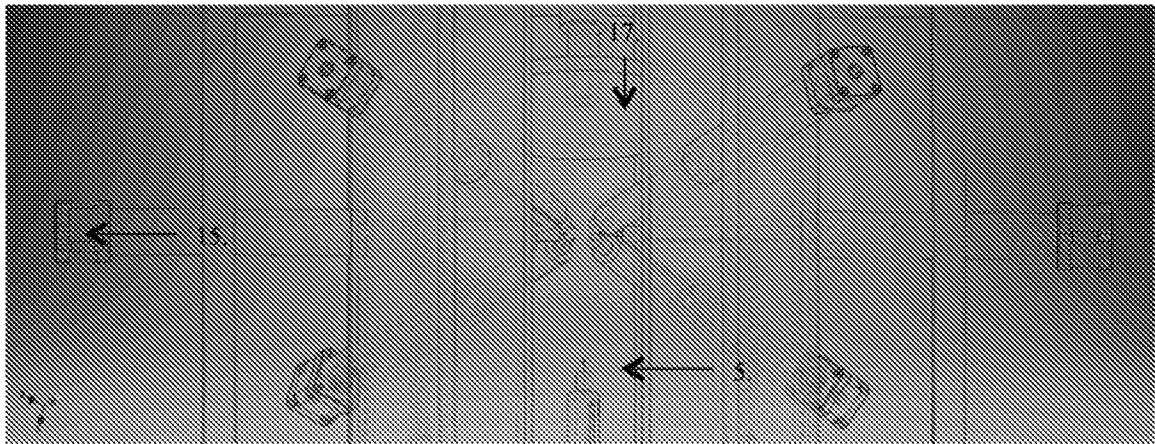


Figure 21

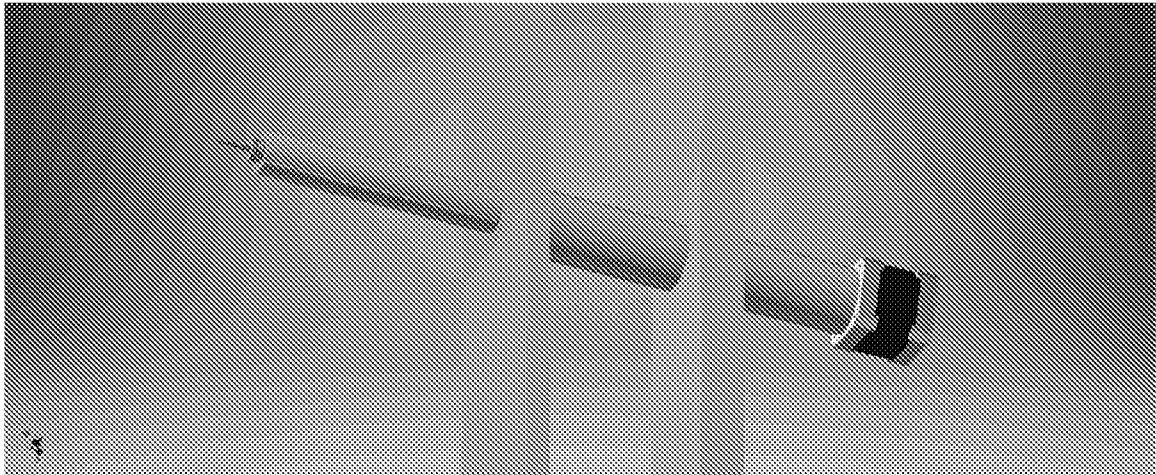


Figure 22

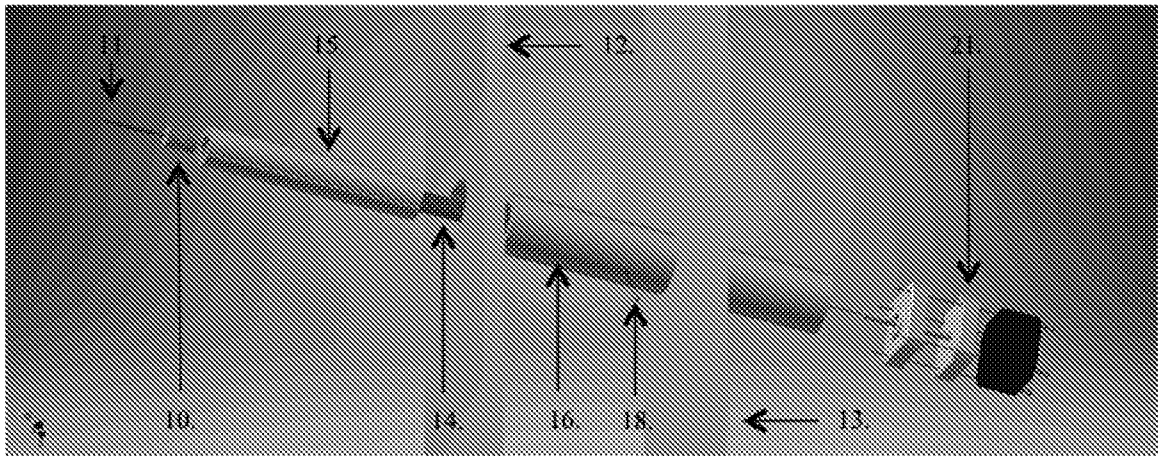


Figure 23

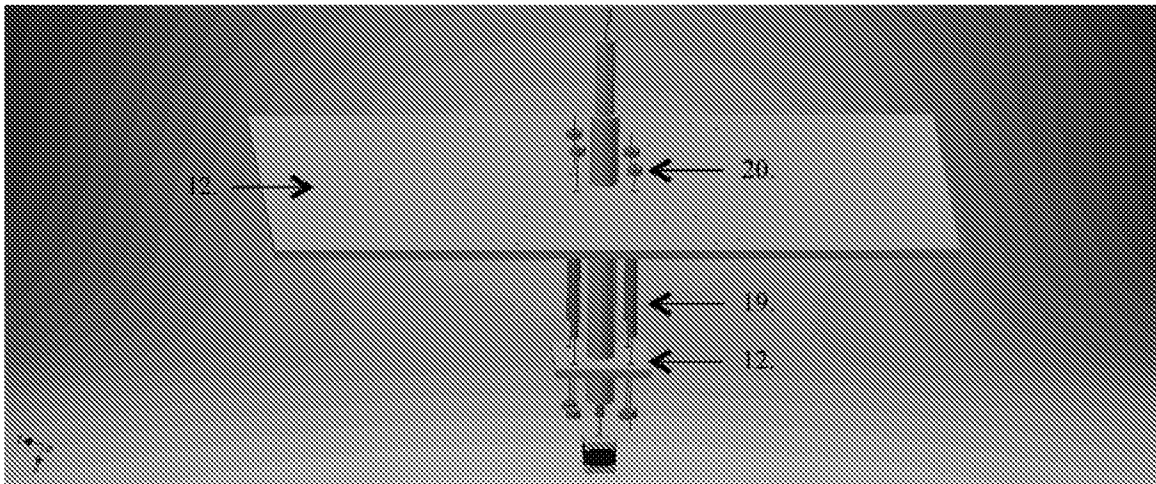


Figure 24

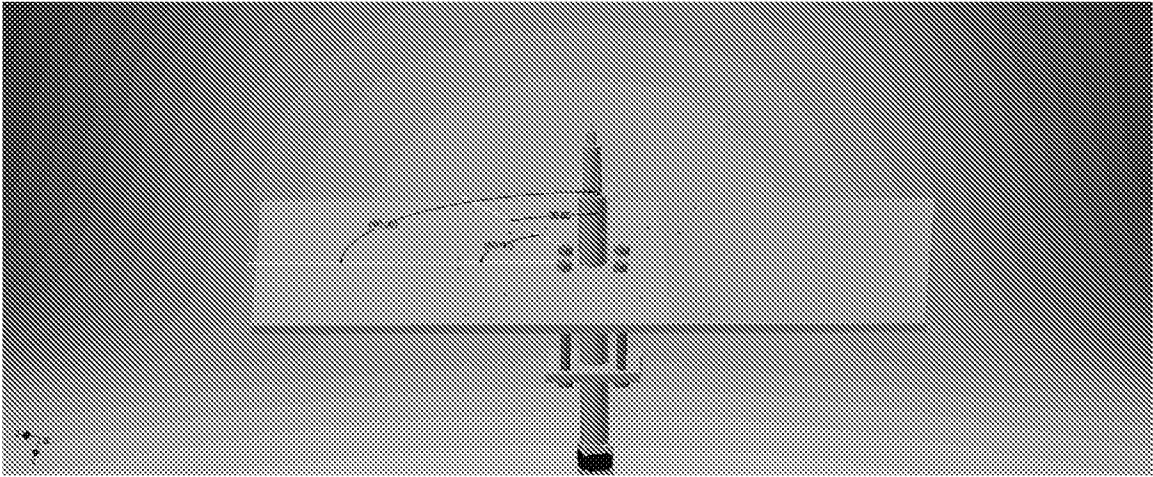


Figure 25

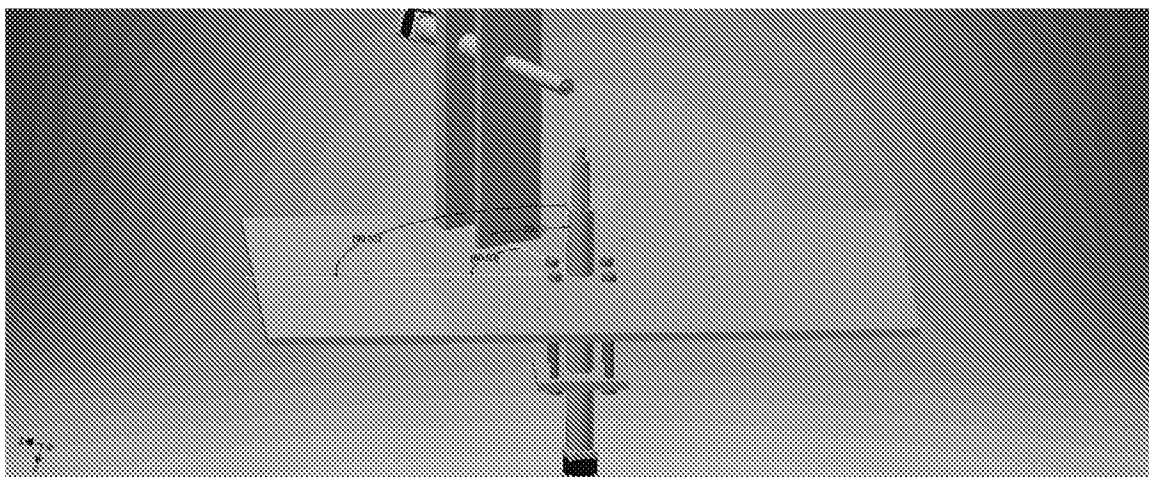


Figure 26

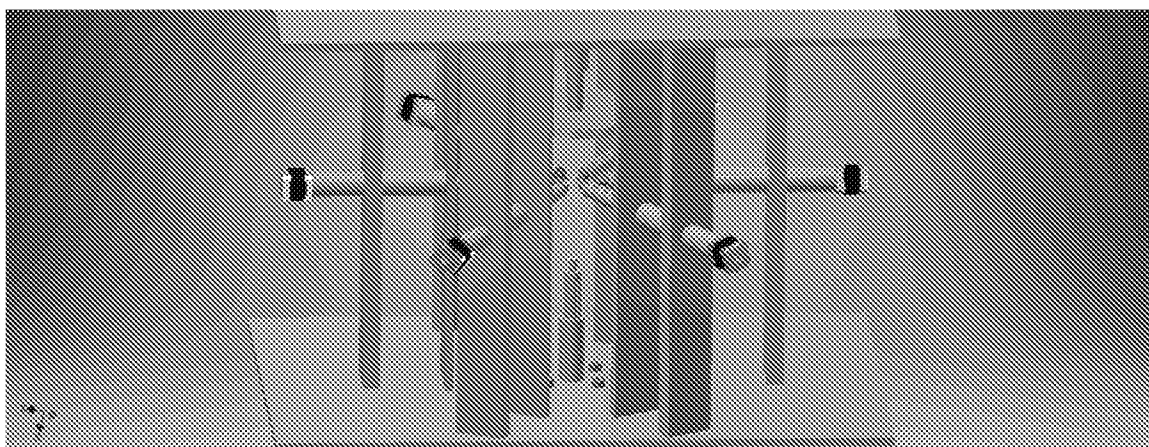


Figure 27

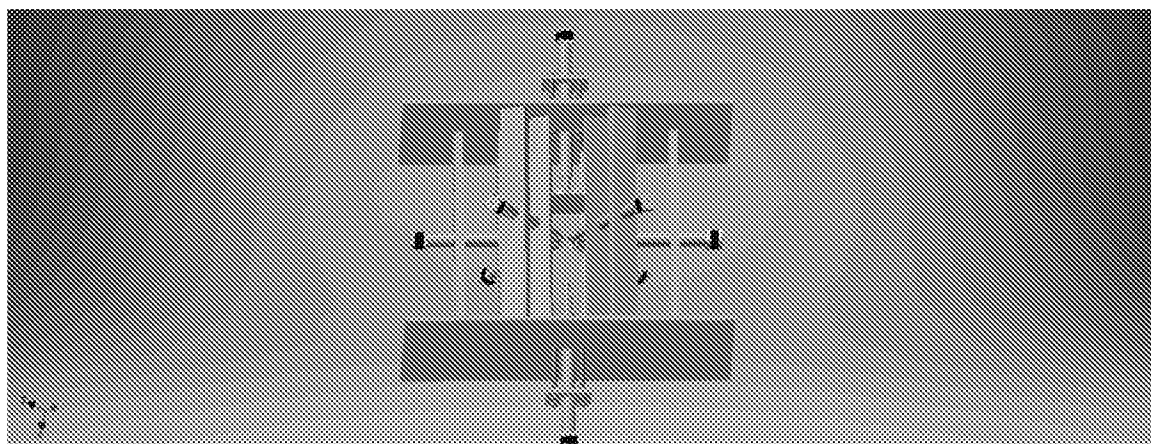


Figure 28

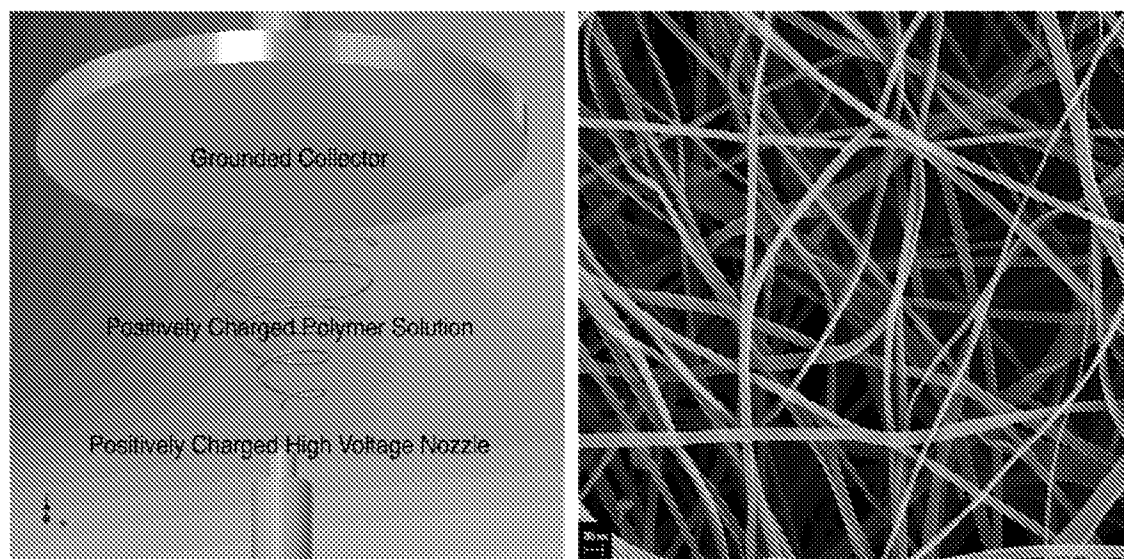


Figure 29
PRIOR ART

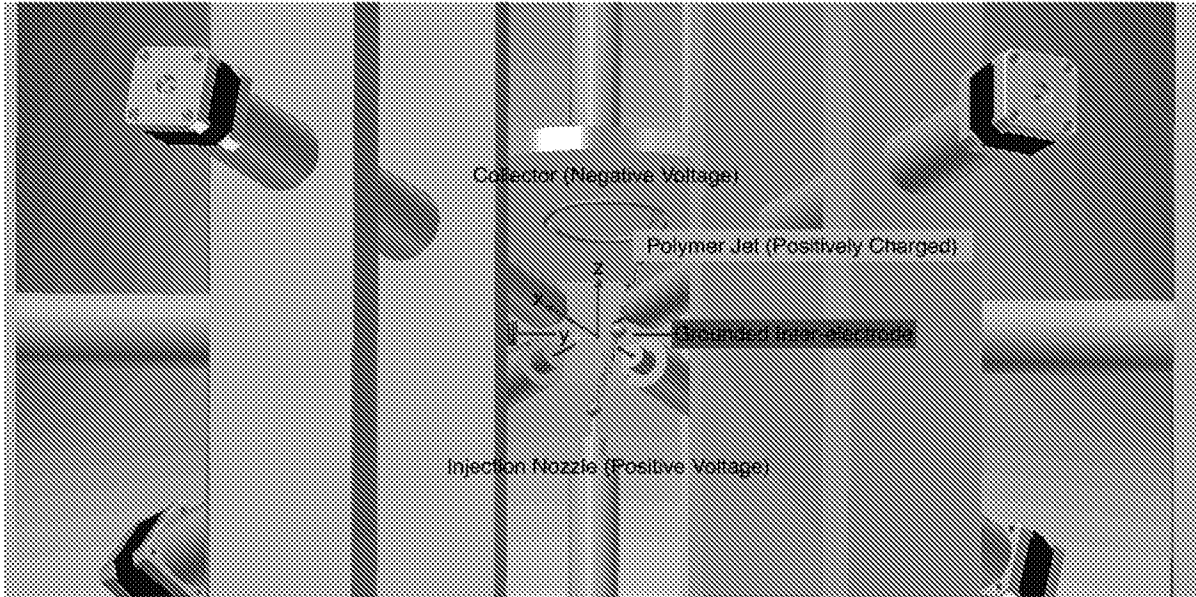


Figure 30

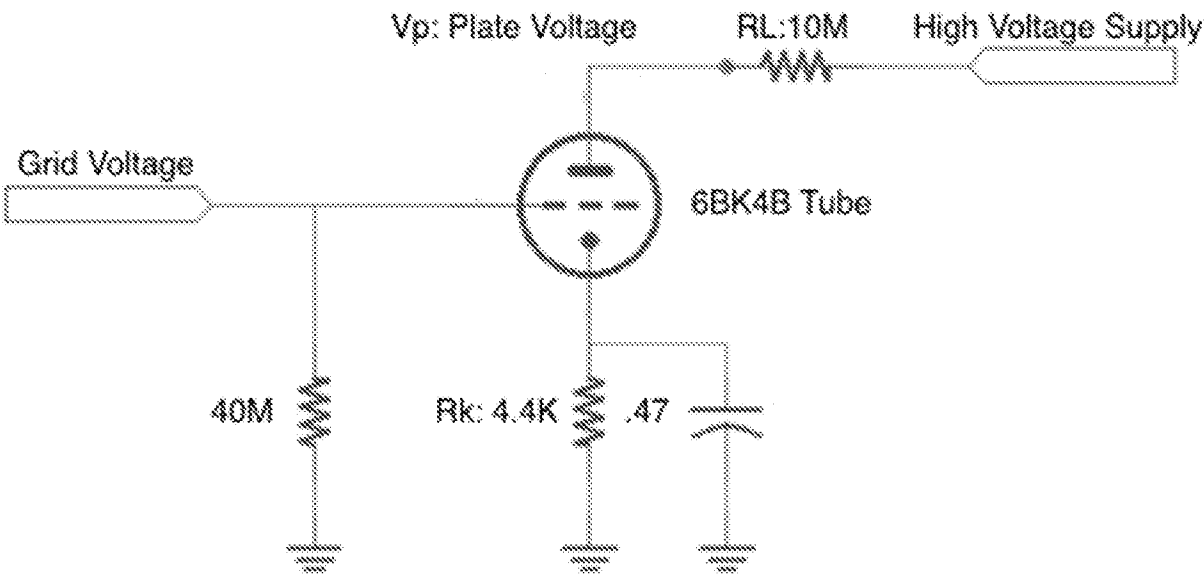


Figure 31

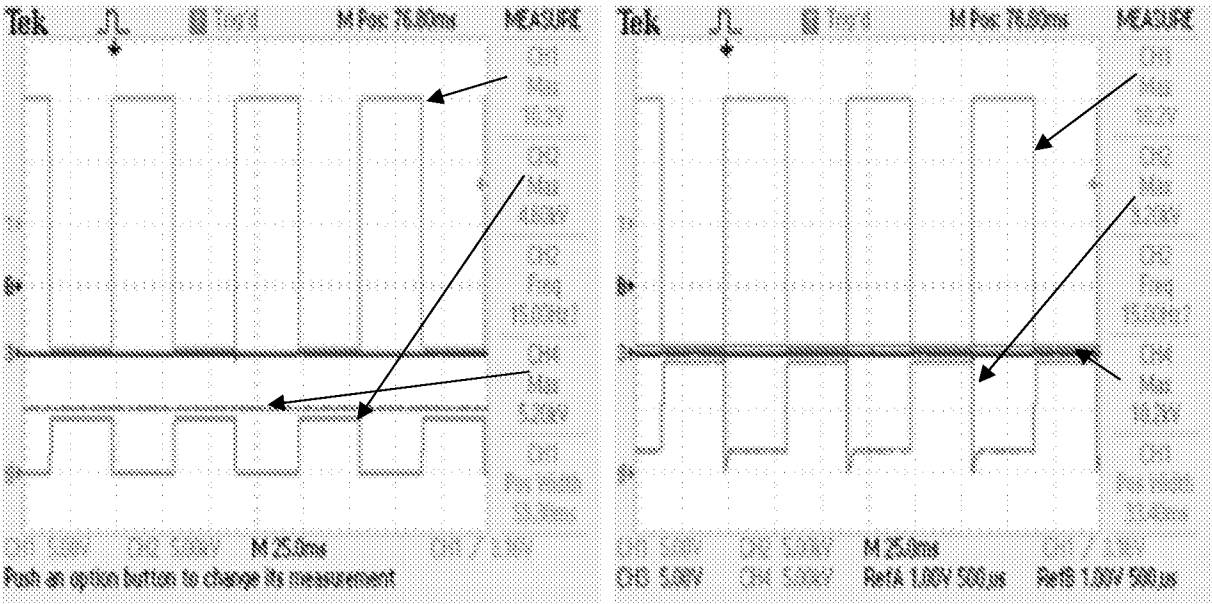


Figure 32

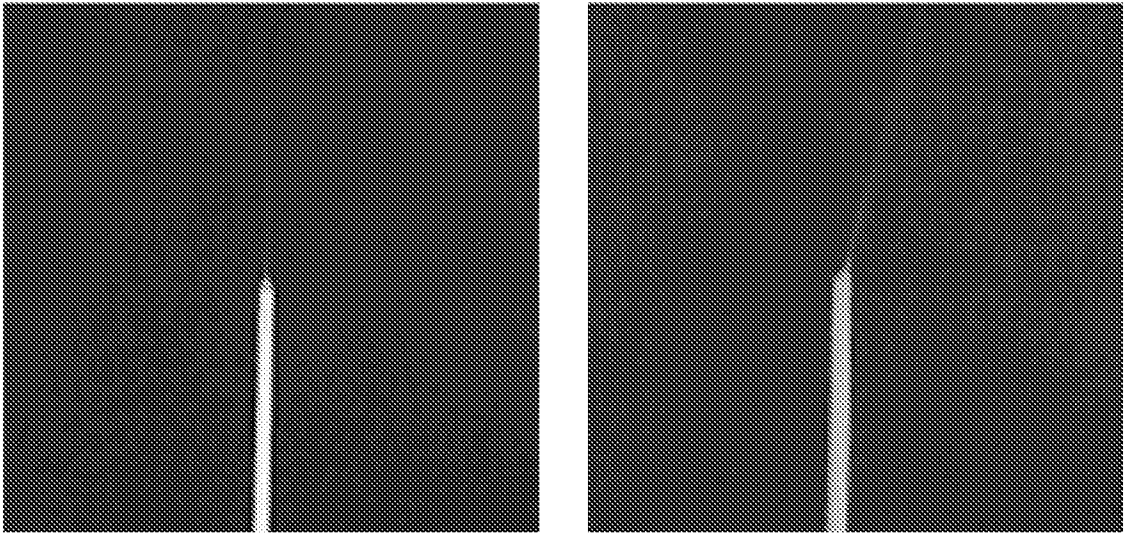


Figure 33

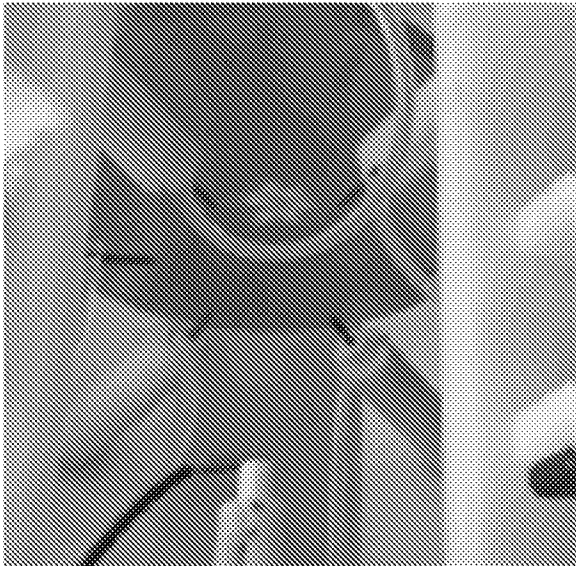
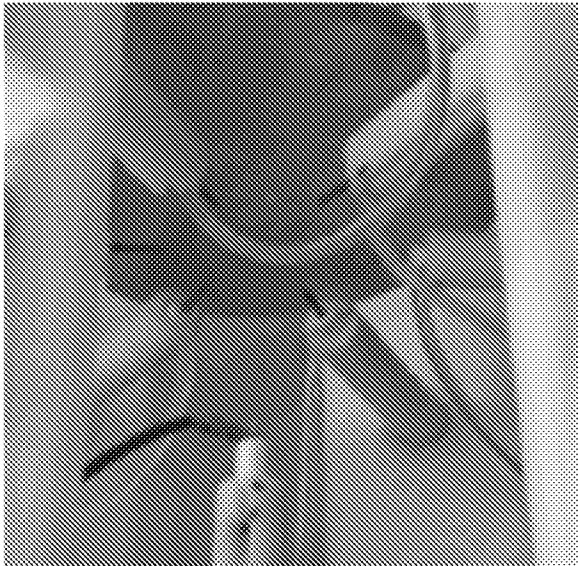


Figure 34

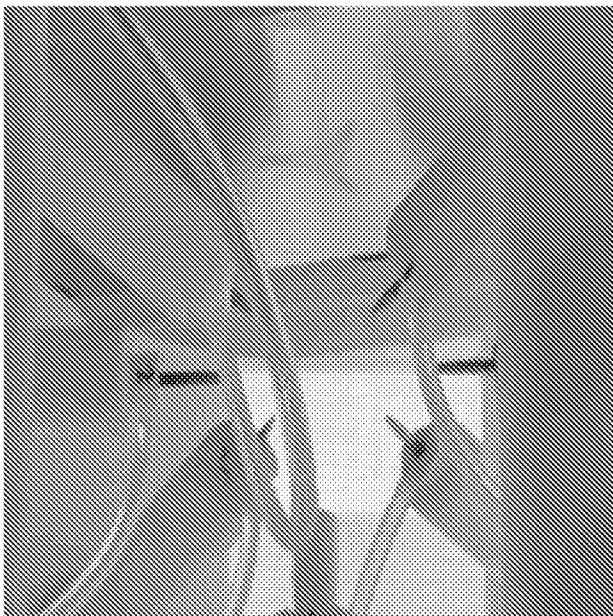
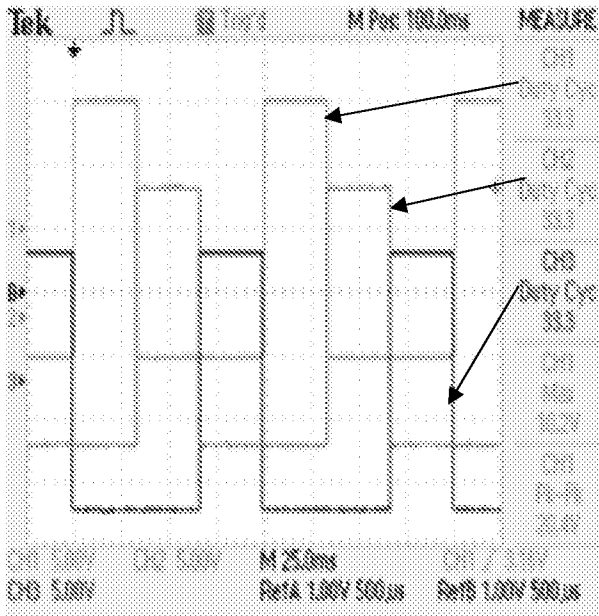


Figure 35

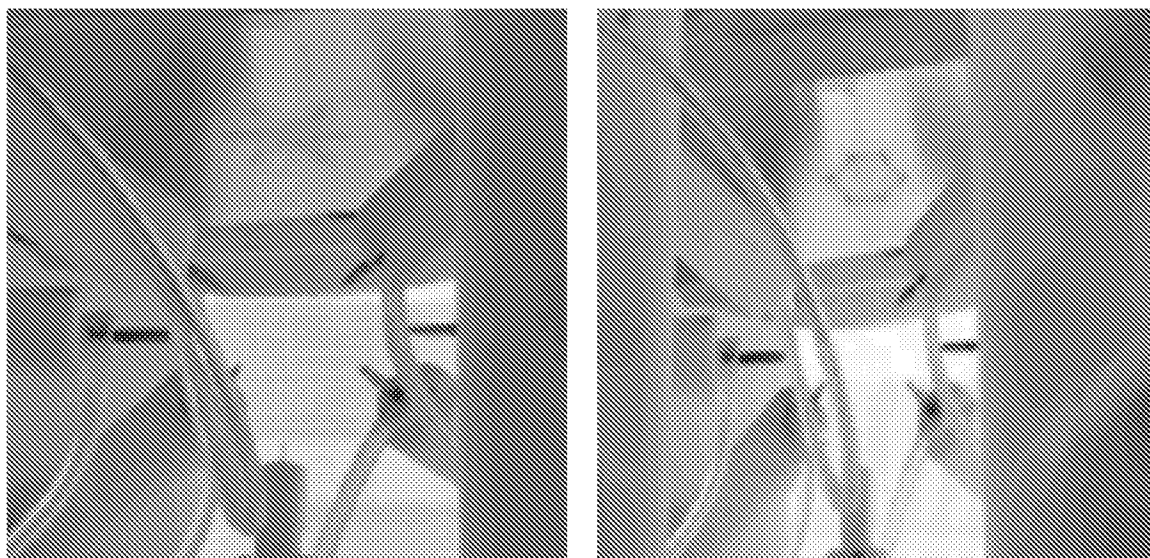


Figure 36

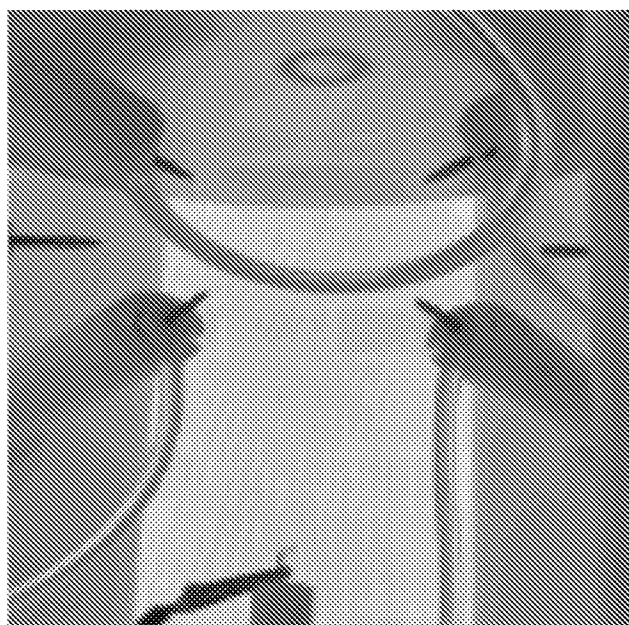


Figure 37

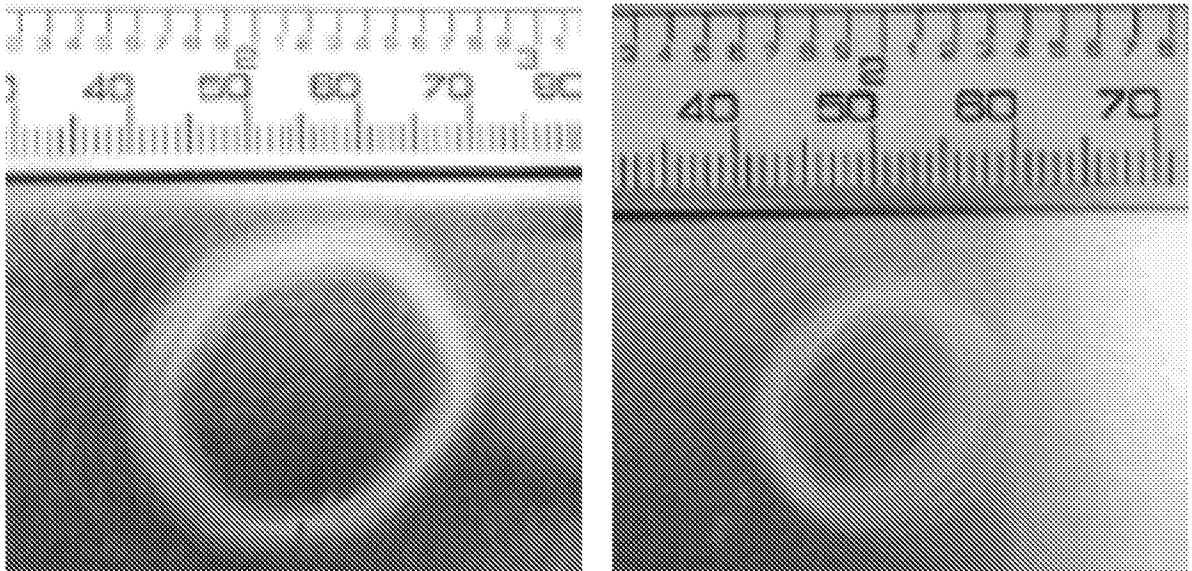


Figure 38

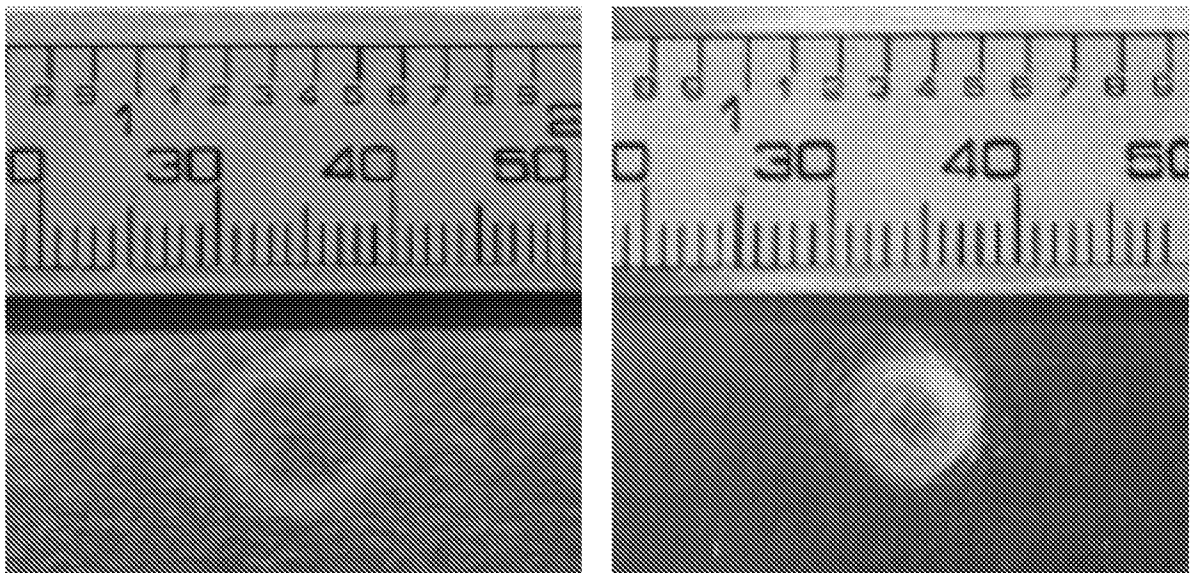


Figure 39

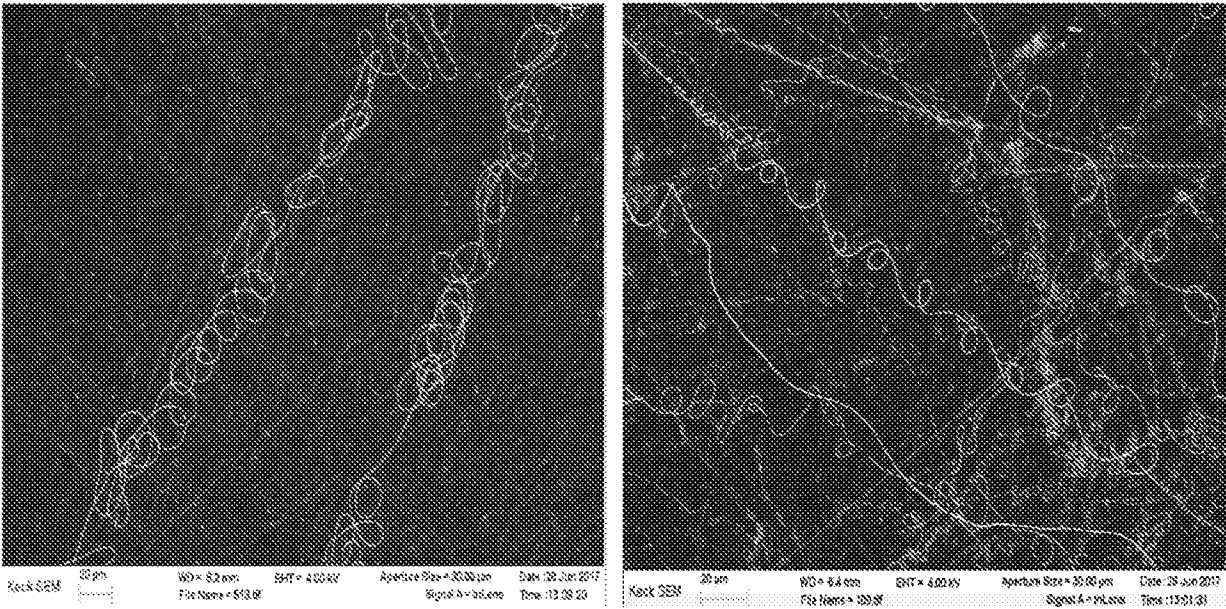


Figure 40

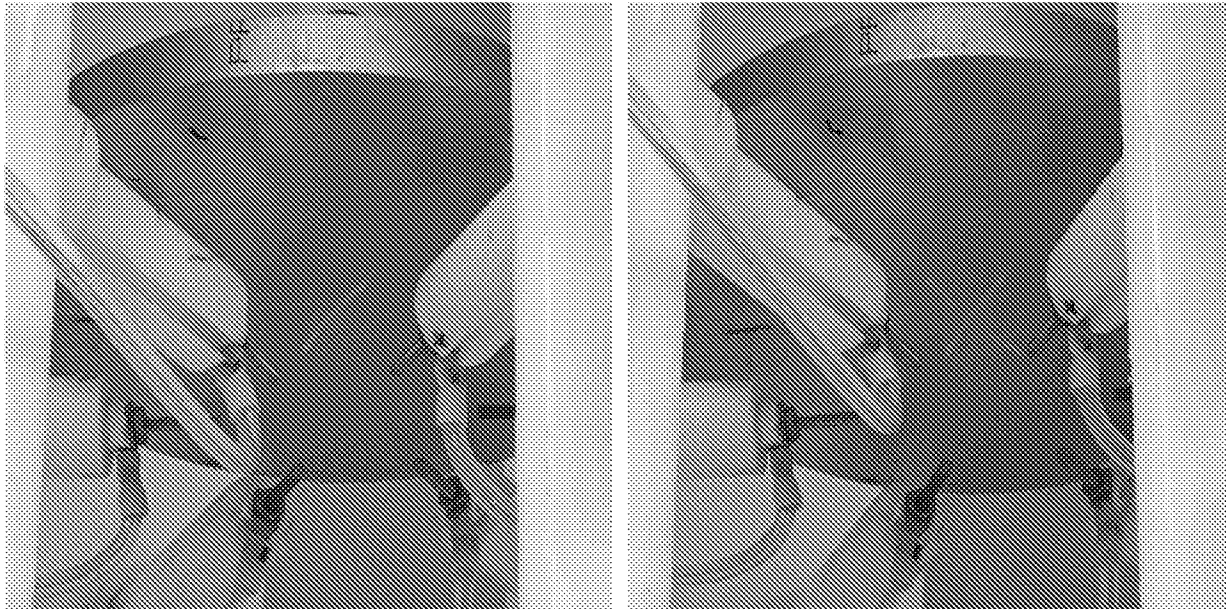


Figure 41

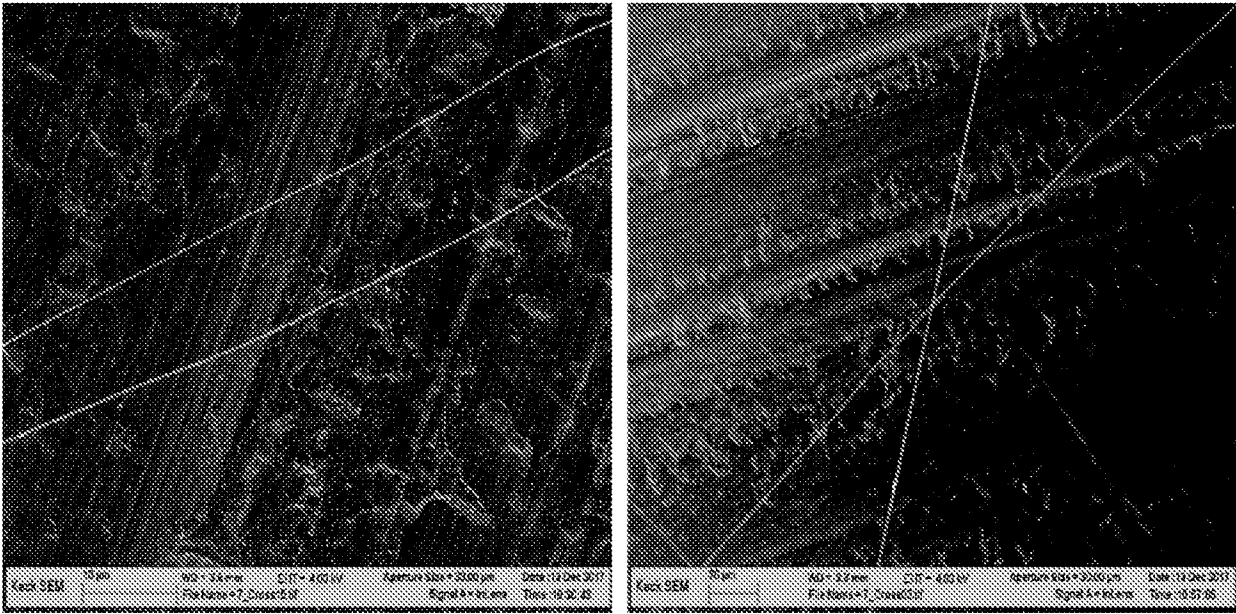


Figure 42

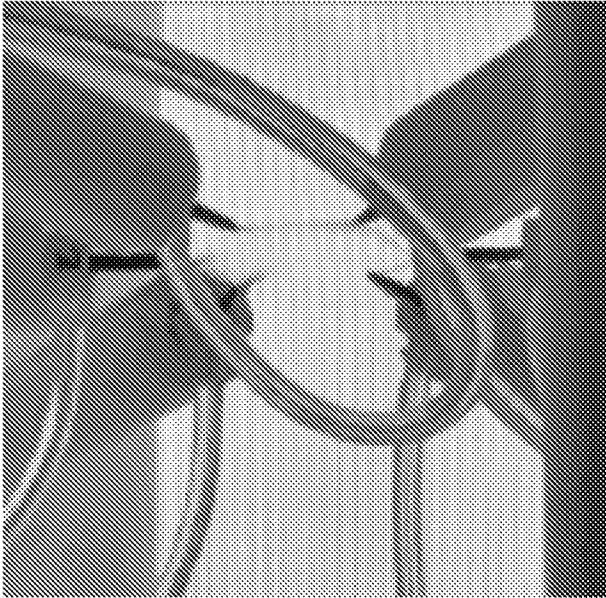


Figure 43

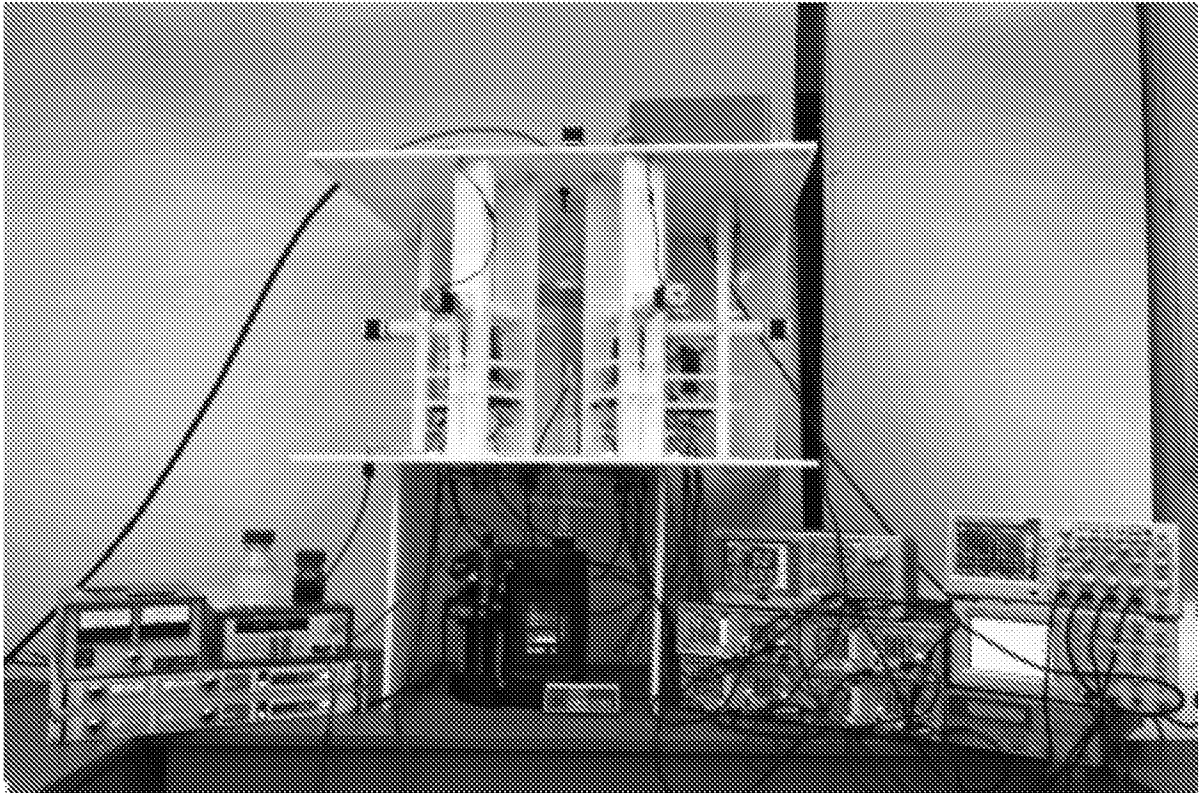


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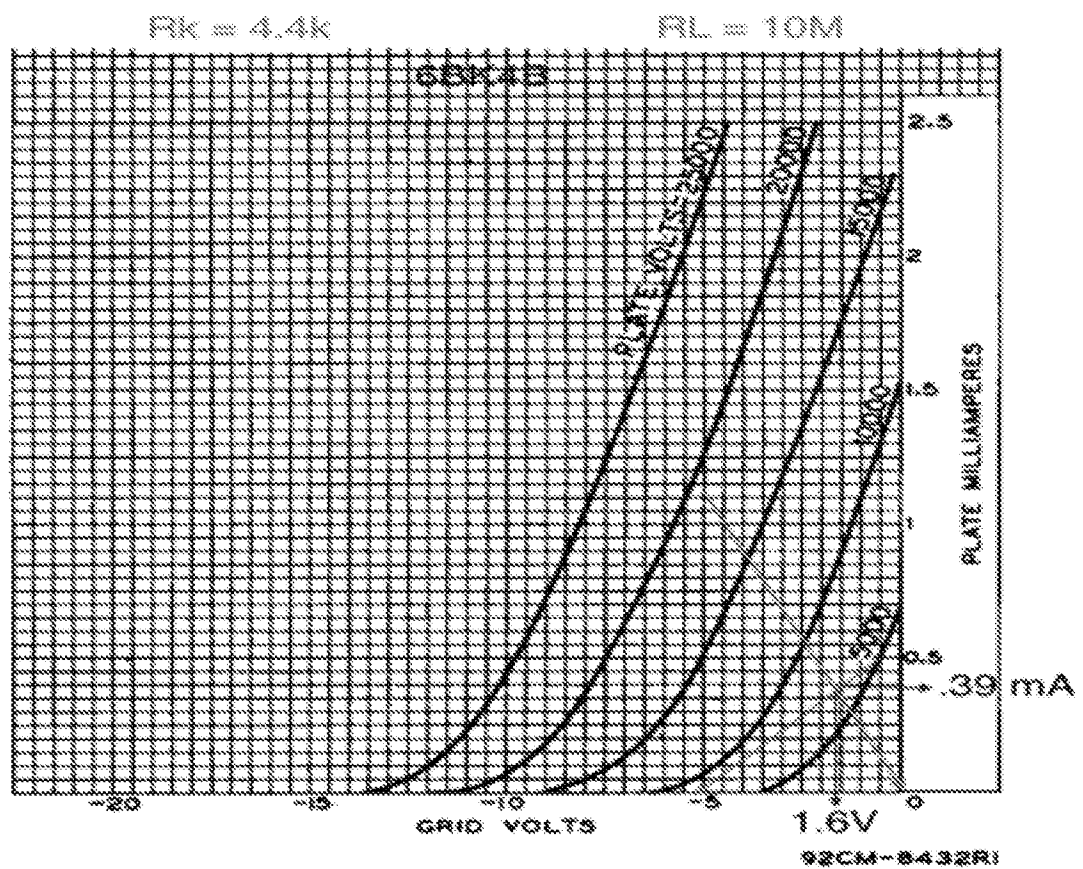


Figure 45

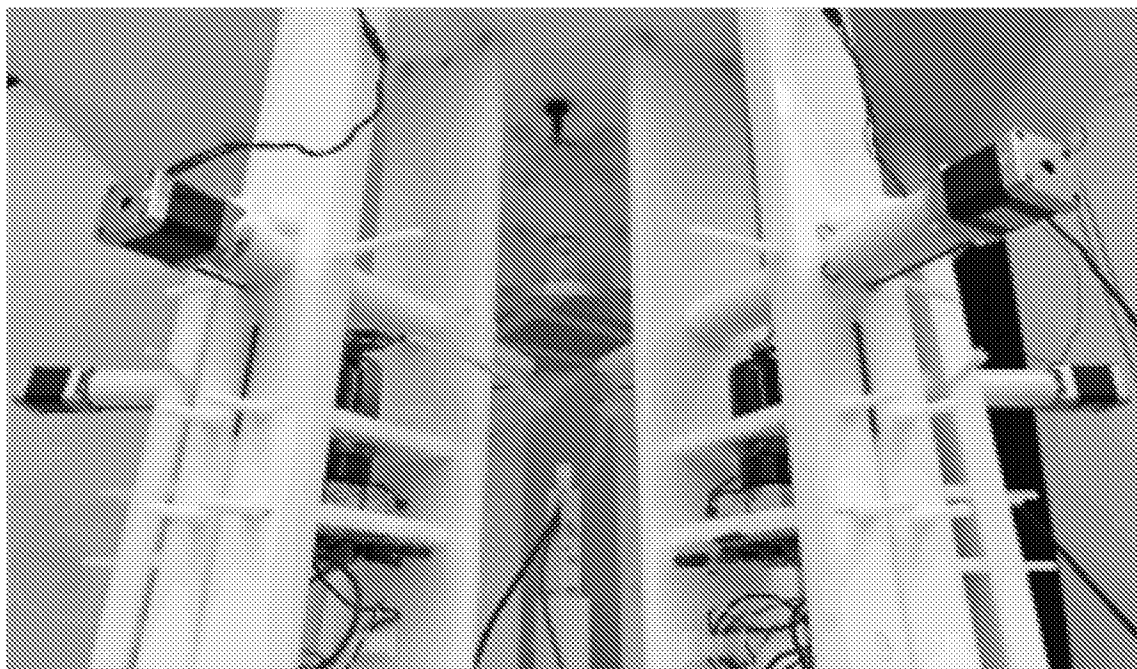


Figure 46

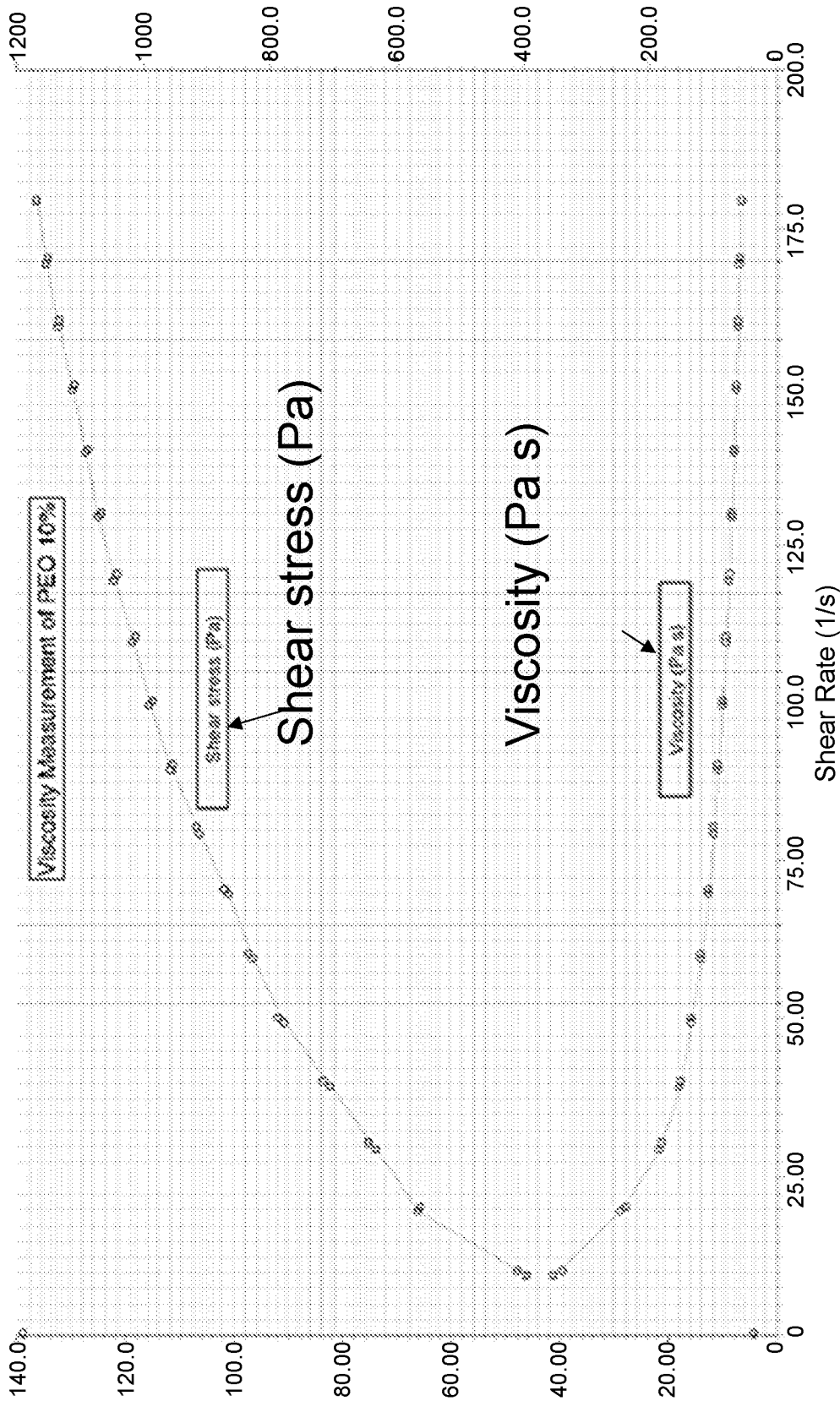


Figure 47

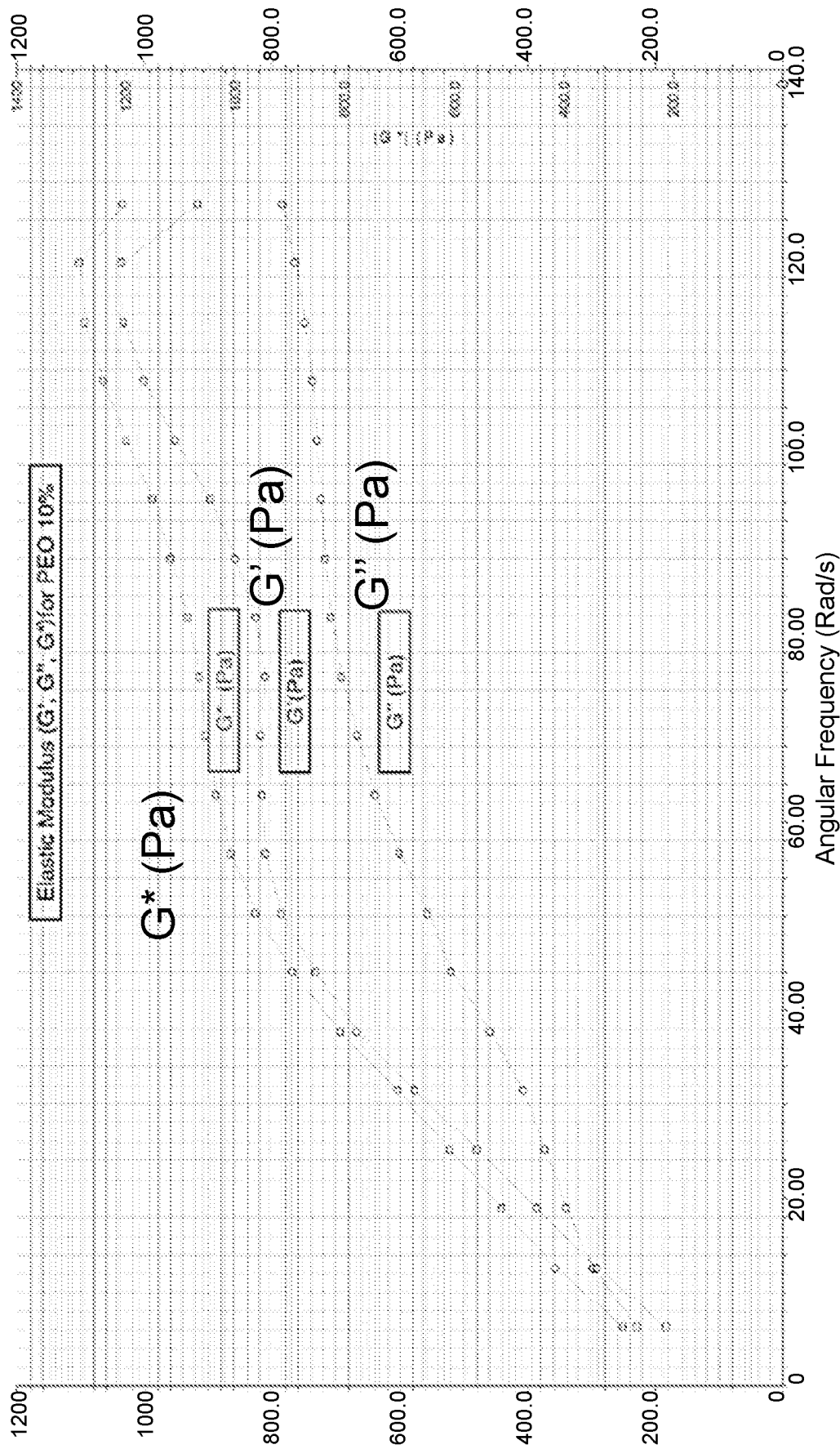


Figure 48

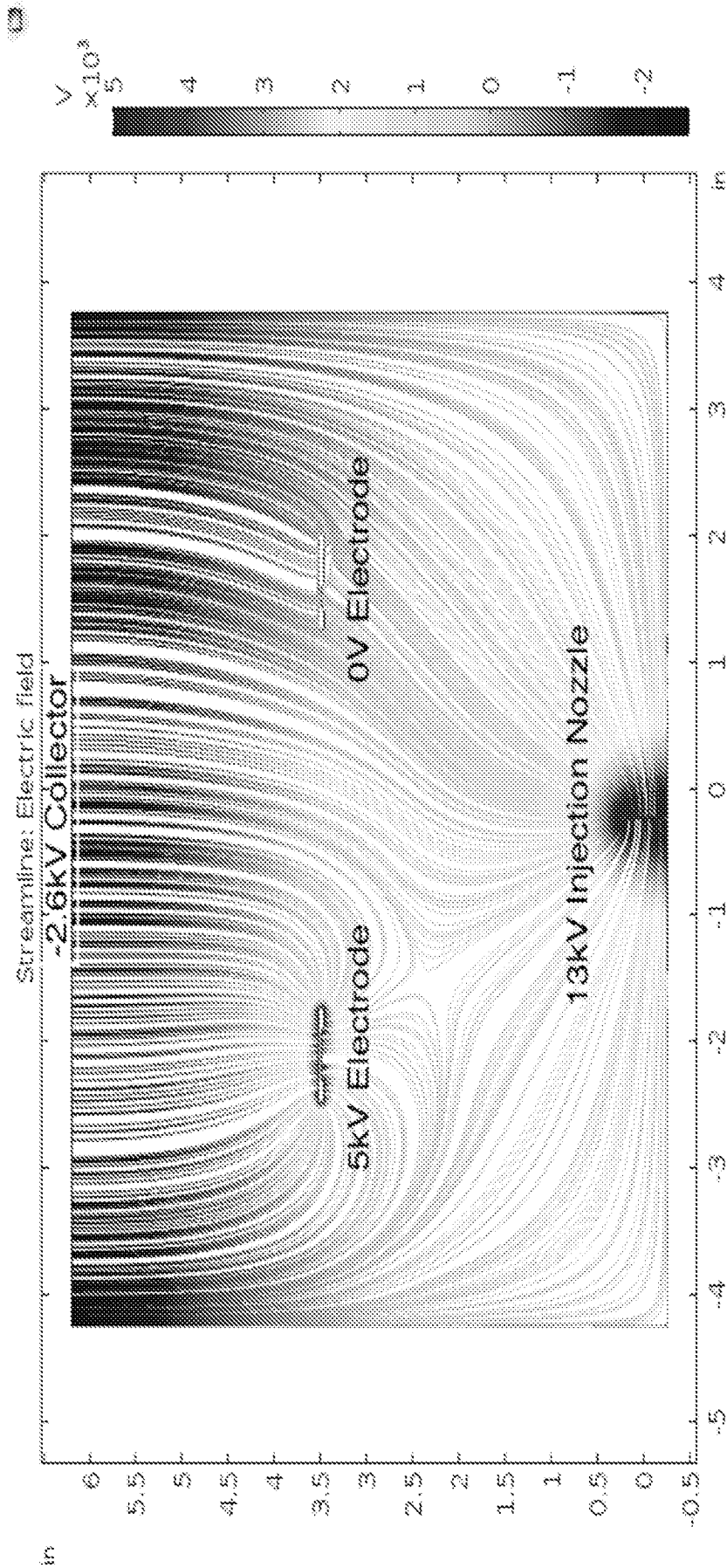


Figure 49

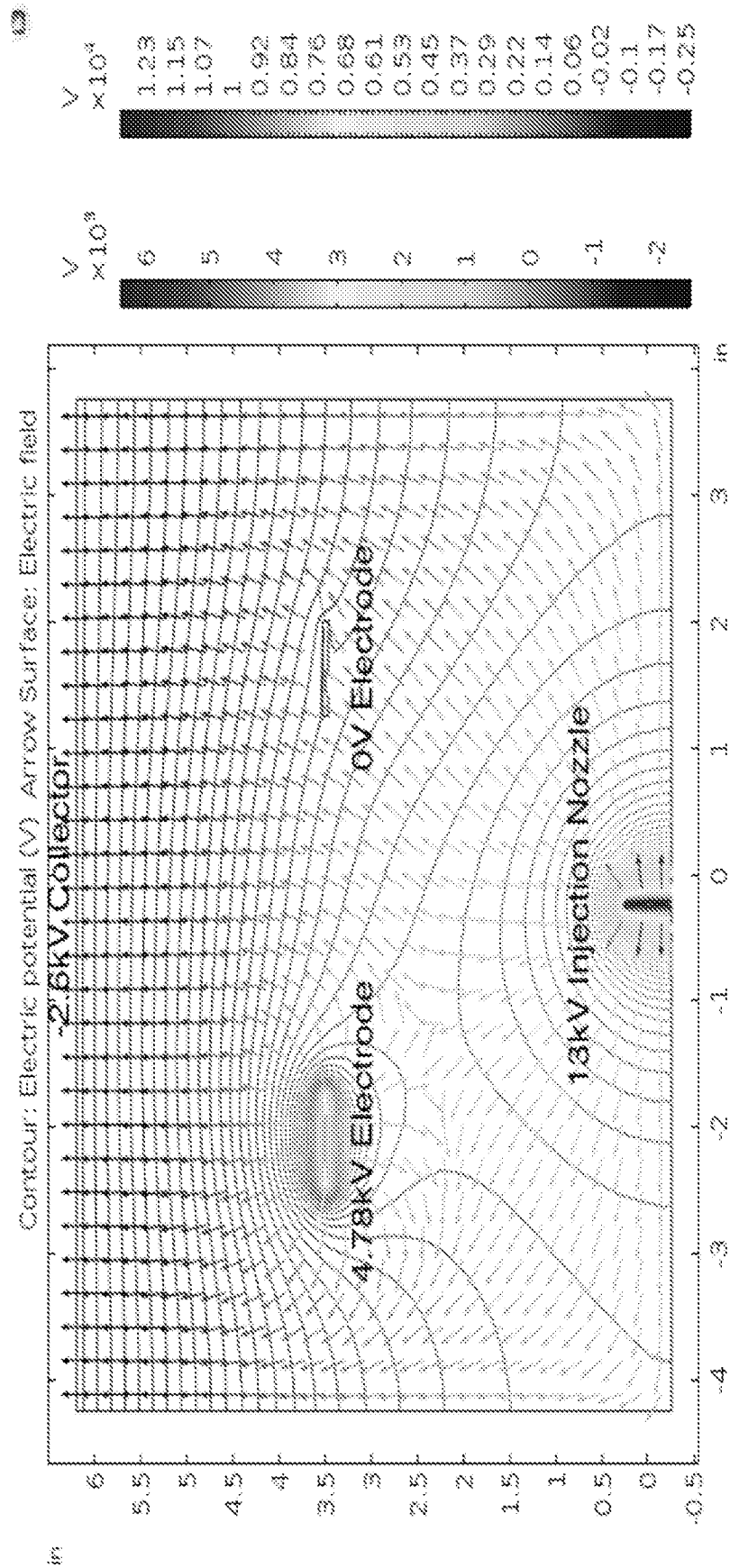


Figure 50

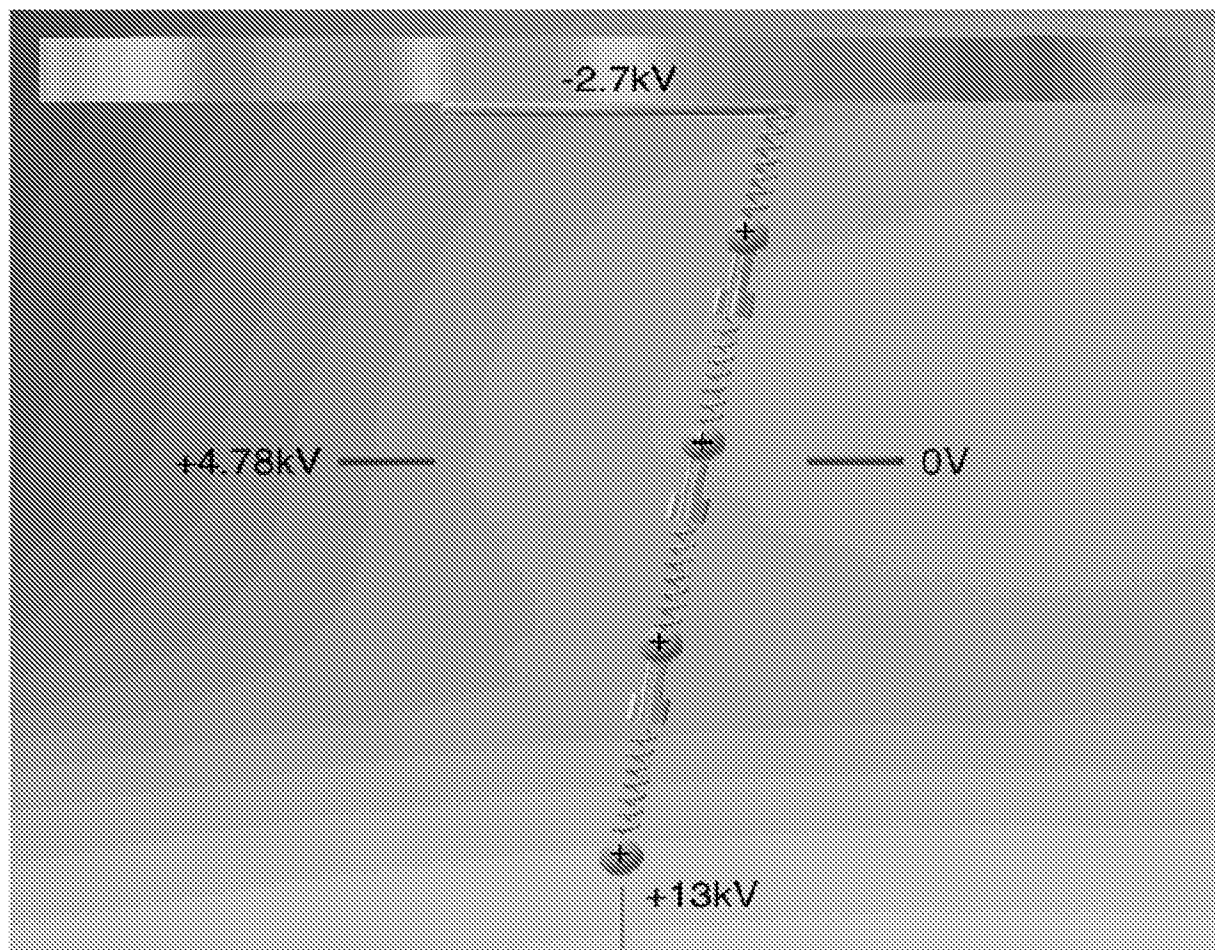


Figure 51

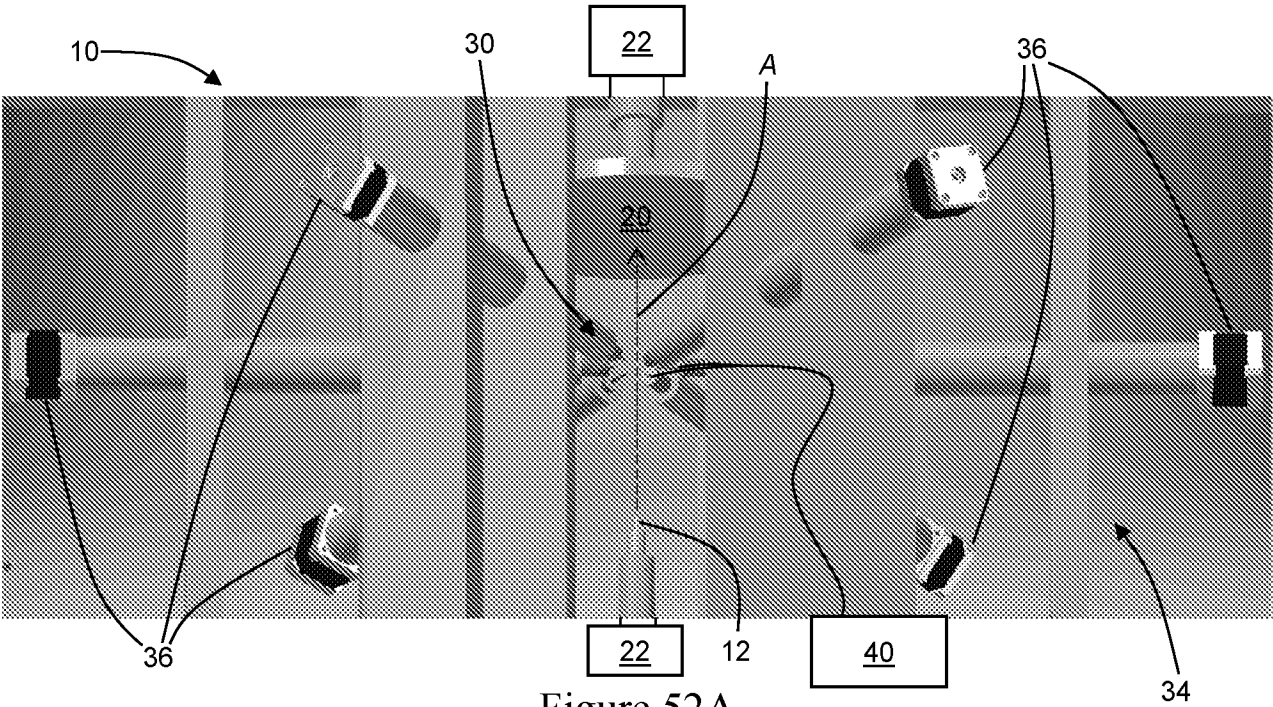


Figure 52A

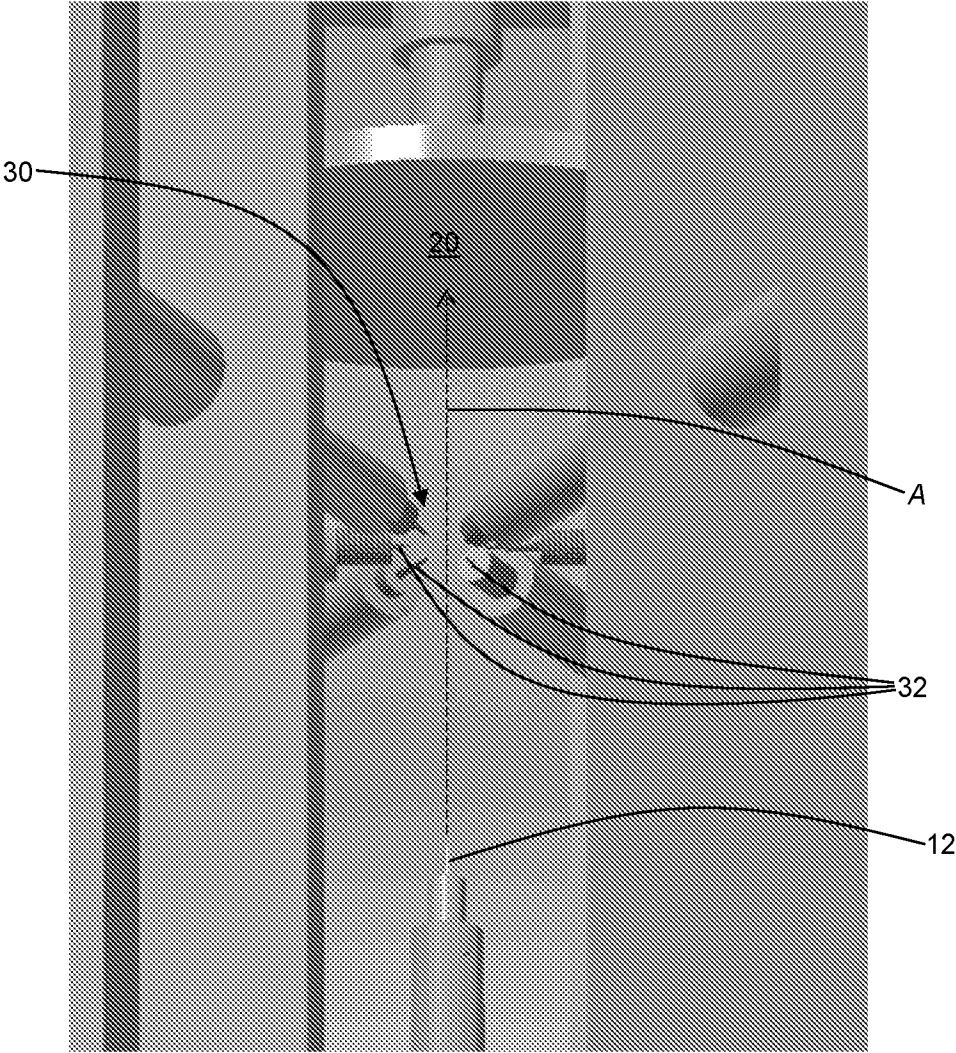


Figure 52B

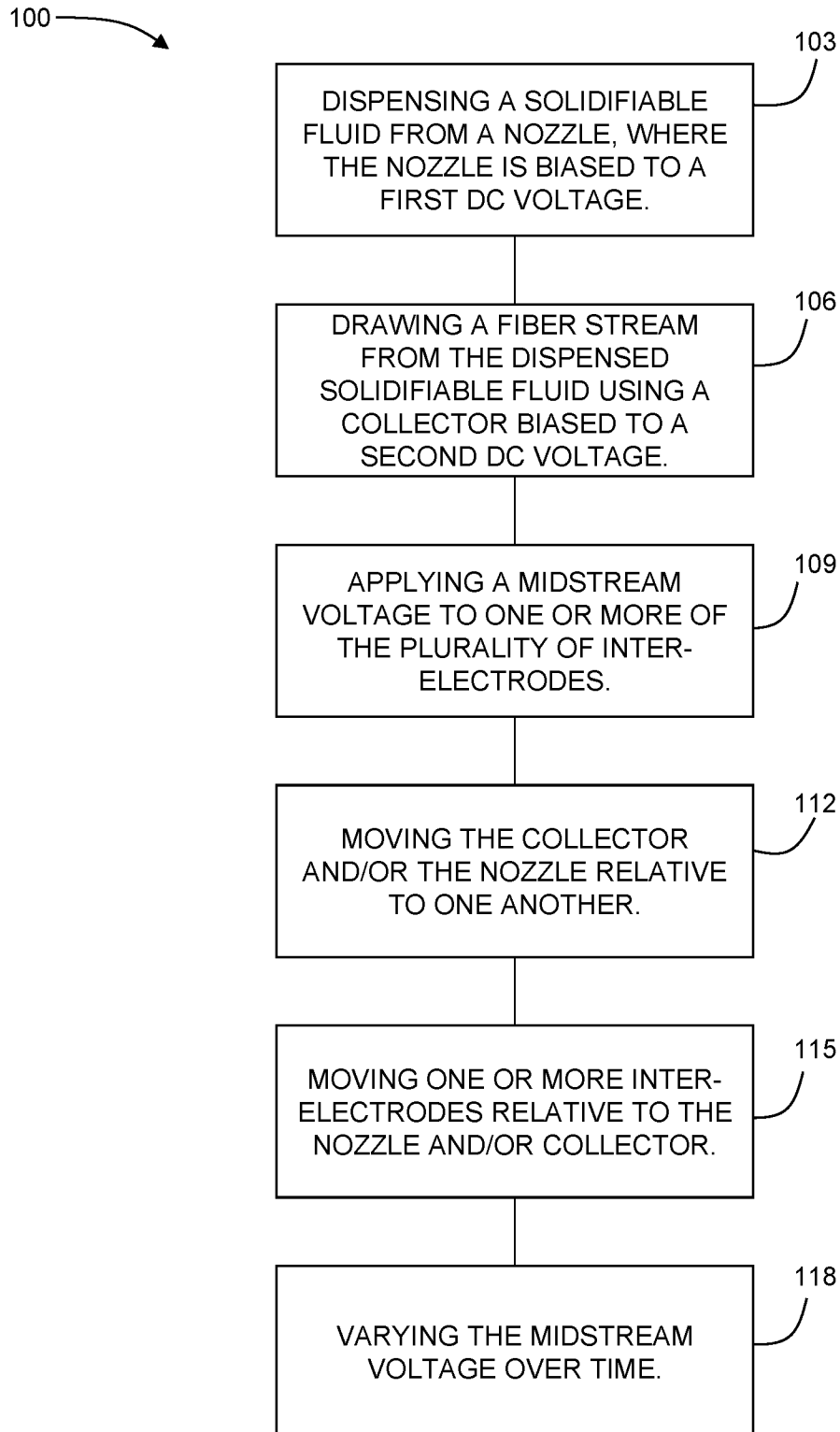


Figure 53

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2018/042354

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B29C 47/36; B29C 47/80; B29C 47/86; H05H 1/48 (2018.01)

CPC - B29C 47/36; B29C 47/802; B29C 47/862; H05H 1/48 (2018.08)

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)

See Search History document

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)

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 8,241,537 B2 (CHANG et al) 14 August 2012 (14.08.2012) entire document	1-21
A	US 8,308,075 B2 (EASTIN et al) 13 November 2012 (13.11.2012) entire document	1-21
A	US 2012/0107900 A1 (GREINER et al) 03 May 2012 (03.05.2012) entire document	1-21
A	US 2004/0013819 A1 (HOU et al) 22 January 2004 (22.01.2004) entire document	1-21
A	US 2009/0091065 A1 (KATTI et al) 09 April 2009 (09.04.2009) entire document	1-21



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

28 August 2018

Date of mailing of the international search report

14 SEP 2018

Name and mailing address of the ISA/US

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P.O. Box 1450, Alexandria, VA 22313-1450

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Authorized officer

Blaine R. Copenheaver

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2018/042354

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 22, 23
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.