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(54) Title: CO-FABRICATION OF PAPER ELECTRONICS AND MICROFLUIDICS

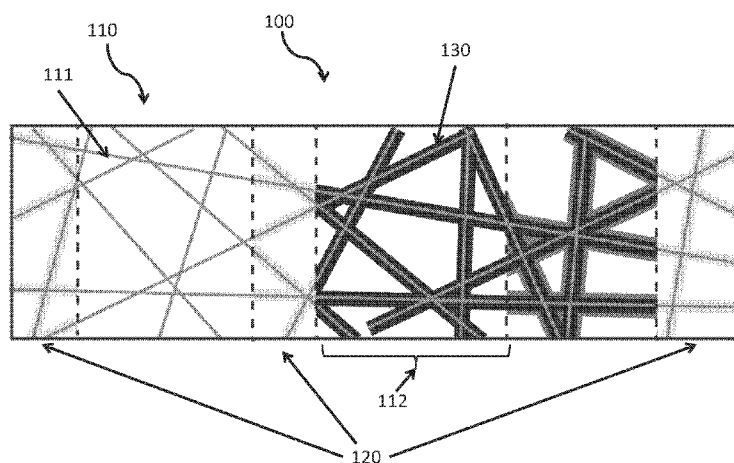


FIG. 1

(57) Abstract: In an aspect, a device includes a substrate including a cellulose matrix that provides an interconnected porous structure, a hydrophobic barrier disposed through the thickness of the substrate to define at least one porous channel within the volume of the cellulose matrix, and an electrically conducting material. The electrically conducting material is disposed within the volume of the porous channel to coat at least a portion of the cellulose matrix therein. A method of making and using actuators, electrochemical sensors, and batteries based on the device are also disclosed.





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CO-FABRICATION OF PAPER ELECTRONICS AND MICROFLUIDICS**CROSS-REFERENCE TO RELATED APPLICATIONS**

[0001] This application claims priority to U.S. Provisional Patent Application No. 62/213,297, filed September 2, 2015 and titled “Co-Fabrication of Paper Electronics and Microfluidics,” the entire contents of which are hereby incorporated by reference in their entirety.

STATEMENT OF GOVERNMENT RIGHTS

[0002] This invention was made with government support under Grant No.: HDTRA1-14-C-0037 awarded by the Defense Threat Reduction Agency. The government has certain rights in the invention.

BACKGROUND

[0003] Paper is an abundant, lightweight, and biodegradable material that has been used for centuries for printing, packaging, and absorbing liquids. It is composed of intertwined cellulose fibers that form a porous hydrophilic network that define the mechanical and fluidic properties of this material. In recent years, paper has become increasingly interesting as a material for new applications. For example, paper has been used for microfluidic devices, as 3-D scaffolds for cell growth, as a substrate for printed electronics, and in micro-electromechanical systems (MEMS).

[0004] However, paper fluidics and electronics have historically developed separately, and the techniques developed for their fabrication are incompatible in many respects. Many factors contribute to this incompatibility. First to note are the different objectives of the two applications. Second, the paper fluidics are related to transporting water, whereas the electronics are related to transport of charges, holes, and/or electrons. In electronics, the electrical conductors are printed on the surface of the paper, while paper fluidics use structures formed by hydrophobic barriers that penetrate the paper.

SUMMARY

[0005] In an embodiment, a device includes a substrate comprising a cellulose matrix that provides an interconnected porous structure, a hydrophobic barrier disposed through the thickness of the substrate to define at least one porous channel within the volume of the cellulose matrix, and an electrically conducting material. The electrically conducting material is disposed within the volume of the porous channel to coat at least a portion of the cellulose matrix therein.

[0006] In some embodiments, the hydrophobic barrier is made of a wax, a thermosetting resin, or a UV cured resin.

[0007] In any of the embodiments described herein, the electrically conducting material can be a nanoparticulate carbon, a conducting polymer, a metallic dust, or metallic nanoparticles. In some other embodiments, the electrically conducting material comprises carbon black or carbon nanotubes. In still other embodiments, the electrically conducting material is the polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid).

[0008] In any of the embodiments described herein, the cellulose matrix can have a first side and a second side, wherein one of the first side or the second side has a barrier layer. In some such embodiments, the barrier layer is a coating or a film.

[0009] In some embodiments, the device further includes a fold which forms a first region and a second region on the device.

[0010] In an aspect, an actuator including any of the devices described above further includes a controller configured to control a flow of electricity through the electrically conducting material as a function of a temperature and a relative humidity.

[0011] In some embodiments, the hygroscopic pick-up of moisture by the cellulose matrix in the channels causes the cellulose matrix to swell, and said swelling of the cellulose matrix can be configured to produce a change in a shortest distance along at least one dimension of the actuator. In some other embodiments, said swelling of the cellulose matrix results in the first region and the second region of the device to move towards or away from each other about the fold, and said moving towards and away from each other about the fold can change the shortest distance along at least one dimension of the actuator.

[0012] In some embodiments, the flow of electricity through the electrically conducting material results in an electrothermal heating of the cellulose matrix in the channels. The electrothermal heating of the cellulose matrix can cause a reduction in the moisture content which causes a shrinkage in the cellulose matrix. The shrinkage in the cellulose matrix can thereby restore the shortest distance along at least one dimension of the actuator to its original state.

[0013] In an aspect, an electrochemical sensor can include any of the devices set for the herein, and the device can further include a first region of channels in the cellulose matrix that are configured to form a working electrode; a second region of channels in the cellulose matrix that are configured to form a separator; and a third region of channels in the cellulose matrix that are configured to form a counter electrode. The first region, the second region and the third region can be in an electrochemical contact with each other.

[0014] In some embodiments, the electrochemical sensor further includes a reference electrode. In some embodiments, the reference electrode includes Ag/AgCl.

[0015] In an aspect, a battery can include any of the devices described herein, wherein the device further includes a first region of channels in the cellulose matrix that are configured to form a cathode; a second region of channels in the cellulose matrix that are configured to form a separator; a third region of channels in the cellulose matrix that are configured to form an anode; and an electrolyte disposed in the first region, the second region and the third region, wherein the first region, the second region and the third region are in an electrochemical contact with each other.

[0016] In some embodiments of the electrochemical sensor and the battery described above, the cellulose matrices in the channels in the first region, the second region and the third region are coated with similar or different electrically conducting materials.

[0017] In an aspect, the method of making a device includes providing a substrate including a cellulose matrix that provides an interconnected porous structure, providing a hydrophobic barrier disposed through the thickness of the substrate to define at least one porous channel within the volume of the cellulose substrate, and providing an electrically conducting material, wherein the electrically conducting material is disposed within the volume of the porous channel to coat at least a portion of the cellulose matrix therein.

[0018] In some embodiments, the hydrophobic barrier is made of a wax, a thermosetting resin, or a UV cured resin.

[0019] In any of the embodiments described herein, the electrically conducting material can comprise a nanoparticulate carbon, a conducting polymer, a metallic dust, and/or metallic nanoparticles. In some embodiments, the electrically conducting particle can include carbon black or carbon nanotubes. In some other embodiments, the electrically conducting particle is the polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid).

[0020] In any of the above embodiments, the cellulose matrix has a first side and a second side, and a barrier layer is disposed on one of the first side or the second side. In some other embodiments, the barrier layer is disposed on the cellulose matrix as a coating or a film.

[0021] In any of the above embodiments, the method can further include forming a fold in the device that forms a first region and a second region on the device.

[0022] In any of the above embodiments, the electrically conducting material can be introduced into the channels of the cellulose matrix as an ink. In some such embodiments, the ink is an aqueous solution or a solvent-based solution.

[0023] In an aspect, a method of making an electrochemical sensor includes providing any of the devices described above, wherein the device further includes a first region of the porous channel in the cellulose matrix that is configured to form a working electrode; a second region of the porous channels in the cellulose matrix that is configured to form a separator; a third region of the porous channel in the cellulose matrix that is configured to form a counter electrode; and a reference electrode, wherein the first region, the second region, the third region and the reference electrode are in an electrochemical contact.

[0024] In an aspect, a method of electrochemical analysis using any of the electrochemical sensors described above includes further providing a loading electrolyte that enters the porous channels of the first region, the second region and the third region to produce a first interaction with the electrically conducting material disposed therein. Said first interaction can produce a baseline electrochemical signal. The method can further include performing an electrochemical measurement to measure the baseline electrochemical signal, providing an analyte sample that enters the porous channels of the working electrode to produce a second electrochemical signal, and analyzing the second electrochemical signal

and comparing it with the baseline electrochemical signal to gather information regarding the analyte.

[0025] In some embodiments, measuring an electrochemical signal comprises an impedance measurement, a current measurement or the measurement of voltage.

[0026] In some embodiments, the electrochemical measurement is selected from the group consisting of: amperometry, biamperometry, stripping voltammetry, differential pulse voltammetry, cyclic voltammetry, coulometry, chronoamperometry, and potentiometry.

[0027] In some embodiments, the electrochemical measurement is chronoamperometry, and the analyte comprises glucose, cholesterol, uric acid, lactate, blood gases, DNA, hemoglobin, nitric oxide, and/or blood ketones.

[0028] In any of the embodiments described above, the measuring an electrochemical signal can comprise anodic stripping voltammetry.

[0029] In an aspect, a method of making an battery includes: (1) providing any of the devices described above, wherein the device further includes: a first region of channels in the cellulose matrix that are configured to form a cathode; a second region of channels in the cellulose matrix that are configured to form a separator; and a third region of channels in the cellulose matrix that are configured to form an anode, wherein the first region, the second region and the third region are in an electrochemical contact with each other; and (2) providing an electrolyte to be deposited in the channels formed within the cellulose matrix.

[0030] In some embodiments, the cathode and/or anode are formed by reacting the electrically conducting material with a chemical reagent to change its oxidative state. In some such embodiments, the electrically conductive material is PEDOT and the chemical reagent is polyenimine (PEI).

[0031] In any of the above embodiments, the electrolyte is a salt solution.

[0032] In any of the above embodiments, the electrochemical contact with each other is formed through folding the substrate at predetermined regions.

[0033] In an aspect, a printed circuit board includes the device in accordance with any of devices described above, and further includes a microprocessor or a microcontroller, wherein the microprocessor or the microcontroller controls a flow of electricity through the device.

[0034] In an aspect, a method of making a printed circuit board includes providing any of the devices described above, and further includes providing a microprocessor or a microcontroller, wherein the microprocessor or the microcontroller controls the flow of electricity through the device.

BRIEF DESCRIPTION OF THE DRAWINGS

[0035] **FIG. 1** shows a schematic of the device in accordance with this disclosure;

[0036] **FIG. 2A** shows a schematic representation of the fabrication of the “Hygroexpansive Electrothermal Paper Actuators” (HEPAs);

[0037] **FIG. 2B** shows an image of the wax patterned channel;

[0038] **FIG. 2C** shows an image of the patterned channel with conducting polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT);

[0039] **FIG. 2D** shows an image of the cross section showing PEDOT embedded in the paper channel;

[0040] **FIG. 2E** shows the schematic representation of the three HEPAs (straight, pre-curved, and creased), and of their motion of actuation;

[0041] **FIG. 3A** shows the infrared (IR) thermal images demonstrating uniform distribution of heat across the surface of the conducting path;

[0042] **FIG. 3B** shows the motion of actuation by operating a straight HEPA at RH = 30% and recording the radius of bending curvature;

[0043] **FIGS. 4A-4C** show time-lapse images of the same pre-curved HEPA operated at room temperature, 100 V, and 1 W at RH = 15% and using a 50 μ L of a solution of a blue dye;

[0044] **FIGS. 4D-4F** show time-lapse images of the same pre-curved HEPA operated at room temperature, 100 V, and 1 W at RH = 85% and using a 50 μ L of a solution of a red dye;

[0045] **FIG. 5A** Photograph of a HEPA optical shutter operated at room temperature, 100 V, 1 W, and RH = 30%;

[0046] **FIG. 5B** shows the number of on / off cycles vs. normalized light intensity calculated from the videos of actuation.

[0047] **FIG. 5C** shows the time lapse images of the HEPA optical shutter during operation with the device placed on a backlit table, and light visible only when the shutter is open (The dashed-lines highlight the shutter area);

[0048] **FIG. 6** shows the resistance measured as a function of the fold angle;

[0049] **FIG. 7A** shows the time-lapse images of a folded/creased-circular HEPA fabricated with tape on one side operated at 100 V at 1W, and RH of 30-40% (dashed lines highlight the attached passive paper);

[0050] **FIG. 7B** shows the time-lapsed images of a folded/creased-linear HEPA fabricated with the tape positioned on alternating sides operated at 100 V at 1W, and RH of 30-40% (dashed lines highlight the attached passive paper);

[0051] **FIG. 8A** is a schematic diagram of an embodiment of a fabrication procedure for making an electronic pattern;

[0052] **FIGS. 8B-8D** are images of the printed structures with top view (bottom) and cross sections (top);

[0053] **FIG. 8E** shows a schematic diagram, and images (top and side view) of a water droplet placed on a printed electronic pattern;

[0054] **FIG. 8F** shows a schematic of a 2 layer paper device showing 3D wicking in electrofluidic structures (top) and time-lapse photos of same electrofluidic 3D assemblies, showing transport of water through the top and bottom paper layers in carbon printed (middle), and conducting polymer (bottom) electrofluidics;

[0055] **FIG. 8G** shows the relative resistance measured across electronic structures on paper with a water drop on top (see the structure in figure **FIG. 8E**) for an electronic pattern with MWNT (Solid line) and PEDOT (dashed line);

- [0056] **FIGS. 9A and 9B** show a printed multi-layer paper circuit board;
- [0057] **FIG. 9C** shows an assembled printed multi-layer paper circuit board;
- [0058] **FIG. 10A** shows a schematic diagram for the assembly and operation of a printed, three-layer flow-through electrochemical analytical paper sensor;
- [0059] **FIG. 10B**, on the left, shows the image of the sensor before folding into the final structure, shown on the right, which is further connected to three copper clips;
- [0060] **FIG. 10C** shows the chronoamperometry for ferrocyanide in 1xPBS (error bars calculated based on measurement of 3 different devices); and the red line shows the theoretical value of the total amounts of charge per analyte;
- [0061] **FIG. 10D** shows the chronoamperometry for a glucose assay (error bars extracted from 3 devices) and the red line represents a linear fit;
- [0062] **FIG. 11** shows a capacitive discharge curve for a conducting polymer 2 electrode sensor, such as, PEDOT, (dashed line) and a carbon 2 electrode sensor, such as, MWNTs (solid line), results of the samples in cyclic voltammetry are shown in the inset (right, PEDOT and, left, MWNTs);
- [0063] **FIG. 12A** shows a schematics diagram of the assembly of a printed paper battery, using folding;
- [0064] **FIGS. 12B-12D** show images of a fully printed device, that contains six serial connected batteries, before folding, during folding, and folded, respectively;
- [0065] **FIG. 12 E** shows the equivalent circuit of the device shown in **FIG. 12D**;
- [0066] **FIG. 13** shows the constant current (5 μ A) discharge curve of for six serially connected batteries similar to the ones shown in **FIG. 12**;
- [0067] **FIG. 14A** shows a circuit diagram for a microcontrolled heating device;
- [0068] **FIG. 14B** shows images of a printed paper circuit being folded to form a final device having all the components on one side and a fluidic channel on the other/opposite side;

[0069] **FIG. 14C** is an image of the device shown in **FIG. 14A**, where all the wires are printed in paper, and the electrical components are mounted on one side using a conductive glue; and

[0070] **FIG. 14D** shows, on the left, images showing drops of water placed in the fluid reservoir with a pipette, which upon reaching the fluid detector, starts the heating cycle as shown on the right, through the IR images.

DETAILED DESCRIPTION

[0071] In an aspect, a device includes a substrate including a cellulose matrix that provides an interconnected porous structure, a hydrophobic barrier disposed through the thickness of the substrate to define at least one porous channel within the volume of the cellulose matrix, and an electrically conducting material, wherein the electrically conducting material is disposed within the volume of the porous channel to coat at least a portion of the cellulose matrix therein.

[0072] **FIG. 1** shows a schematic of the device **100** in accordance with this disclosure. **FIG. 1** shows a substrate **110** including a cellulose matrix **111** where a hydrophobic barrier **120** is disposed through thickness of the substrate. The hydrophobic barrier **120** defines at least one porous channel **112** within the volume of the cellulose matrix **111**. An electrically conducting material **130** is disposed within the volume of the porous channel to coat at least a portion of the cellulose matrix therein.

[0073] In some embodiments, the substrate **100** including a cellulose matrix is paper. Any variety of paper may be selected for the purpose of use as a substrate as long as one of the surfaces of the paper is uncoated, providing access to the interconnected porous structure inside the cellulose matrix. In some embodiments, it may be preferred to have one of the sides of the paper coated or filled with a barrier coating or film. In some embodiments, the paper can also include inorganic additives such as, talc, silica, calcium carbonate, titanium dioxide, kaolinite, bentonite, montmorillonite, clay, etc. In some other embodiments, the paper may also contain polymeric fibers to enhance the mechanical strength of the resulting device.

[0074] In some embodiments, the hydrophobic barrier **120** layer comprises wax, a thermosetting resin or a UV cured resin. Additional additives may be added to the wax to further tune the hydrophobicity of the hydrophobic barrier.

[0075] In some embodiments, the electrically conducting material **130** is made of nanoparticulate carbon, a conducting polymers, a metallic dust, or a metallic nanoparticles. In some other embodiments, the electrically conducting material **130** is carbon black, or carbon nanotubes. In some other embodiments, the electrically conducting particle is polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid).

[0076] In some embodiments, the device further includes a fold that forms a first region and a second region on the device.

[0077] It is envisaged that a person of ordinary skill in the art may use the devices in accordance with this disclosure in innumerable applications. Some non-limiting examples of such applications have been described below.

Cellulose-Matrix Actuators

[0078] Microfluidic using the cellulose matrix, for e.g., in paper, as 3-D scaffolds for cell growth, as a substrate for printed electronics, and in micro-electromechanical systems (MEMS) are known. However, a type of component for cellulose matrix-based devices that is still missing is an electrically controlled actuator that can be embedded within the cellulose matrix, can be fabricated by simple processes, such as, roll-coating, gravure coating or printing, and that is unaffected by creasing. Cellulose matrix based actuators that fulfill these requirements have the potential to allow control of liquid transport in paper-based microfluidic devices, to enable assembly of micro machines through self-folding, and to actuate MEMS and paper robots. Hence, this disclosure describes a new class of devices that have the ability to perform mechanical work with cellulose matrix based materials, such as, paper.

[0079] Although paper possesses such attractive properties, only three types of actuators are known. These are: (i) *Magnetic paper-based actuators*. These actuators are made by integrating magnetic particles in paper. The actuation in these systems is achieved by (and requires) an external magnetic field. This approach produces tunable composite materials, but requires large quantities of magnetic additives, and the application and control of a localized

external magnetic field: this control is difficult and/or inconvenient to accomplish. (ii) *Electrostatic zippers*. These consist of two sheets of paper that are coated with carbon nanotubes and are separated by a dielectric layer. They actuate using electrostatic fields. The paper zippers are simple in design, and low in cost, but have the disadvantage that they require several kilovolts to actuate, and achieve only small movement. (iii) *Electroactive papers*. These structures are fabricated by printing electrodes (usually made from gold) on both sides of paper or of cellulose films. They are lightweight and flexible, but have the drawback that they require a metallic electrode. This requirement adds to both their cost and complexity, their performance degrades over time, and they do not function when creased. Because paper is hydrophilic, most systems based on it are affected by the relative humidity (RH) of the environment; variations in the RH render their actuation difficult to control, and lower their reliability.

[0080] In some embodiments of the present disclosure, an actuator includes any of the above described devices and further includes a controller configured to control a flow of electricity through the electrically conducting material as a function of a temperature and a relative humidity. The electrically activated paper actuators exploit the hydrophilicity of paper, and operate based on its hygroexpansion, i.e., they expand or contract based on the moisture content of the cellulose matrix. These actuators have also been referred to as “Hygroexpansive Electrothermal Paper Actuators” (HEPAs) throughout this manuscript. These simple devices are lightweight, inexpensive, and resistant to bending and scratching.

[0081] In some embodiments, the hygroscopic pick-up of moisture by the cellulose matrix in the channels results in the cellulose matrix to swell. In some embodiments, due to expansion from the swelling of the cellulose matrix, the actuator is configured to produce a change in the shortest distance along at least one dimension. In some other embodiments, where a fold forms a first region and second region in the actuator, the hygroscopic pick-up of moisture by the cellulose matrix in the channels results in the cellulose matrix to swell; and the swelling of the cellulose matrix subsequently results in the first region and the second region of the device to move towards or away from each other about the fold. In some embodiments, where a fold is not present in the actuator, the change in the shortest distance along at least one dimension could mean an elongation in the shortest distance due to straightening of the actuator or reduction in the shortest distance because of curling of the actuator. In some embodiments, the change in the shortest distance along at least one

dimension could mean an elongation in the shortest distance due to opening of the actuator or reduction in the shortest distance because of closing of the actuator. Some non-limiting examples of the motions envisaged for the actuators, in accordance with this disclosure, are schematically shown in **FIG. 2E**. Additionally, the flow of electricity through the electrically conducting material results in an electrothermal heating of the cellulose matrix in the channels. The electrothermal heating of the cellulose matrix causes the reduction in the moisture content which causes a shrinkage in the cellulose matrix; that in turn restores the shortest distance along at least one dimension of the actuator to its original state.

Example 1

[0082] Referring to **FIG. 2A**, the steps for the constructions of HEPAs, according to some embodiments, are shown. First, using printing, a hydrophobic barrier is formed in a cellulose matrix, such as a paper. In some embodiments, wax printing is used to form a fluidic “U-shaped” channel in the cellulose matrix. In some embodiments, when paper is used as the cellulose matrix, the paper may be a Chromatography Paper Grade A. This type of paper is composed of pure cellulose, and has no inorganic additives. Its hygroexpansive properties are, therefore, defined entirely by the cellulose fibers, and the arrangement of the fibers in the paper sheet. Although, the illustrations of actuators included in this disclosure use a Chromatography Paper Grade A, other types of papers are also envisaged. The devices used as illustrative examples in this disclosure were fabricated by printing wax patterns with a Xerox ColorQube Wax printer on Whatman[®] Chromatography Paper Grade A. The wax was melted into the paper by placing the paper in an oven at 140°C for 2 minutes. A person skilled in the art would readily recognize that other routes for obtain the desired result may be equally implemented.

[0083] After printing the hydrophobic barrier and forming the channel, an electrically conducting material is deposited into the channel. In some embodiments this is done using a pipette. Other techniques such as index printing, gravure coating, mask coating, screen printing are equally conceived as process for this step. In some embodiments, the electrically conducting material is deposited as a suspension in water or a solvent. In the illustrations of the actuators demonstrated in this disclosure, using a pipette, the conducting polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT) suspended in water, was deposited on the paper. PEDOT solution 10% in water, Clevios[™] PH1000 was purchased from Heraeus. A 5 wt% dimethylsulfoxide (DMSO) was added to the solution of PEDOT,

and this solution was added with a pipette to the channels that were defined by the wax. The excess ink was removed with a tissue and it was allowed to air dry at room temperature (30 minutes). In some embodiments, the paper may be heated to expedite evaporation. To obtain higher conductivity, the solution was added twice to the channel. The PEDOT suspension in water wicked into the entire channel, which was defined by the hydrophobic barrier formed by the wax printing. Upon drying, the PEDOT coated the cellulose fiber, and importantly, it formed a conducting path that extended across the thickness of the sheet of paper rather than localizing on the surface of paper. These are shown in **FIGS. 2B, 2C and 2D**. It is noteworthy that without the patterned wax barrier (which also spans the width of the paper), the PEDOT would spread unevenly across the paper by capillary wicking, and would not form a well-defined conducting path. In these illustrations PEDOT was selected because it is highly conducting (>1000 S/cm), water dispersible, and stable in ambient conditions. It forms thin films that are resilient to bending and stretching. However, as noted elsewhere, it is equally possible to use other electrically conducting materials. Some examples include nanoparticulate carbon, conducting polymers, metallic dust, and metallic nanoparticles.

[0084] In a final step, the patterned actuators were cut, and a layer of Scotch® tape (40 μ m thick) was attached to obtain the HEPA. (**FIG. 2A**). This tape was unaffected by moisture and heat (at least up to 100°C), and acted as the strain-limiting layer to direct the movement.

[0085] To establish the parameters describing the operation of the HEPAs, three characteristics, and their influences were analyzed. These were as follows: (i) operating power and voltage, (ii) motion, and (iii) influence of relative humidity on the performance. **FIG. 3A** shows the infrared (IR) thermal images demonstrating uniform distribution of heat across the surface of the conducting path, and established that a power (P) of 800 mWcm⁻² was needed to reach a temperature of 100°C. Thermal images were acquired using a FLIR T600- Series infrared imaging camera. The temperature of 100°C was selected since it is slightly above the boiling point of water. Using a two-point probe, the sheet resistance (R) of PEDOT/paper (800 ± 200 Ω /sq) was measured. From these, the operating voltage (V) per area of the HEPA (28 ± 5 Vcm⁻²) was calculated, using $V = \sqrt{PR}$. The motion of actuation by operating a straight HEPA at RH = 30% and recording the radius of bending curvature is shown in **FIG. 3B**. When the actuator was turned on and the flow of electricity started, the actuator reaches its final curvature ($\kappa=0.16$ cm⁻¹) within 20 seconds, and recovered to its initial position within 30 seconds of turning the power off. The reversible actuation of the HEPA is due to the porosity

of the conducting path, which allows rapid diffusion of air (containing water vapor) in and out of the HEPA, and results in faster hygrothermal responses (dehydration and hydration occur at comparable speeds) than a non-porous conductor.

Mechanical Model

[0086] To understand the behavior of HEPAs, an analytical mechanical model is included. This model relates the curvature κ of the bi-layer actuator to the temperature-induced strain ϵ_h of the paper by Equation (1).

$$\kappa = \frac{6\epsilon_h E_1 E_2 t_1 t_2 (t_1 + t_2)}{(E_1 t_1^2 - E_2 t_2^2)^2 + 4E_1 E_2 t_1 t_2 (t_1 + t_2)^2} \quad (1)$$

[0087] Here, t is the thickness, and E is the Young's modulus, for the paper layer (t_1 , E_1), and the tape layer (t_2 , E_2). This result is analogous to a bi-layered beam under thermal expansion, but instead of a thermal strain, this model uses the hygroexpansive strain (ϵ_h) defined as the ratio between the changes in length to initial length as a function of moisture content (mc). In certain regions ϵ_h is a linear, and reversible, function of the moisture content described by Equation (2) where β is defined as the hygroexpansion coefficient, and Δmc is the change in the gravimetric moisture content.

$$\epsilon_h = \beta \Delta mc \quad (2)$$

[0088] A typical value of β for many types of paper is approximately 0.1. Using Equation (1), the calculated value of $\epsilon_h = 0.4\%$ for the straight HEPA. This value is in agreement with the reported values for the hygroexpansion of paper. Equation (1) can also be used to optimize the relation between t_1 , t_2 and E_2 , and achieve maximum bending for a given type of paper (with fixed thickness and elastic modulus).

[0089] To study the influence of RH on the motion of bending, and on the range of actuation, a pre-curved HEPA was used as shown in **FIGS. 4A-4F**. The HEPA was fabricated as described above and manually curled along one side of a straight actuator with a dull blade (similar to curling a ribbon). The HEPA was operated at $RH = 15\%$ and $RH = 85\%$. The experiment was started at low RH (15%). On applying power (1 W), moisture

evaporated from the paper layer, the HEPA moved down, and an extra paper section (attached to the end of the actuator) contacted and absorbed a droplet of a solution of a blue dye, as shown in **FIG. 4B**. When the power was turned off, the HEPA returned to its original position, as shown in **FIG. 4C**. Similarly, the experiment was repeated with an increased RH at 85%. The results of this experiment are shown in **FIGS. 4D-4F**. It is noteworthy that at the higher RH of 85%, the HEPA absorbed more ambient moisture, which resulted in an initial state (off-state) that had greater curvature (**FIG. 4D**). However, the final state (on-state), was not visibly affected by the increase in RH, and the actuator picked up a solution of a red dye (**FIG. 4E**). This experiment conclusively demonstrates that (i) the HEPAs can move weights (in the form of a water droplet), and (ii) actuate over a wide range of values of RH, because the electrothermal heating (to 100°C) releases the majority of the moisture absorbed in the paper irrespective of RH.

Example 2

[0090] **FIG. 5A** shows a pre-curved HEPA that acts as an optical shutter. The HEPA in this example was designed to have an almost semi-circular shape, with an extra paper section that forms a shutter. The HEPA with the shutter was mounted onto a backlit table, as shown in **FIG. 5A**. When the power was off, the shutter covered the hole and blocked the light. When the electricity flow was turned on, the shutter moved, uncovered the hole, and allowed the light to pass through, as illustrated in **FIG. 5C**. The shutter opened in 8 seconds, and closed in 16 seconds (at room temperature and RH = 30%). 260 open/close cycles were tested, during which period no degradation in actuation occurred, as shown in the plot of **FIG. 5B**. MATLAB® was used for calculating the light intensity from each frame of a video from the optical shutter. The intensity was calculated as the average gray-scale intensity of pixels corresponding to the circular optical window.

Example 3

[0091] To test the influence of creasing or making a fold on the HEPAs, a conducting path of 1 mm by 18 cm was fabricated and folded 11 times. The resistance was measured as a function of the fold angle, as shown in **FIG. 6**. The resistance changed less than 10 % between the unfolded and folded structures, even after 1000 open/close cycles (see **FIG. 6**). These experiments suggest that HEPAs work when folded/creased, unlike other paper actuators

(fabricated with conventional conductors on the surface of the paper) that break upon repeated creasing when subject to high strain on bending.

Example 4

[0092] Two types of creased/folded HEPAs were designed and fabricated. These were as follows: (i) circular, which was made with the tape on one side, and (ii) linear, which was made with the tape on alternate sides. Upon actuation, each crease changed its angle and provided an angular motion (see schematic representation in **FIG. 2E**). The total motion of the creased HEPAs is the sum of the change in angular motion of each individual crease. **FIG. 7A** shows time-lapse photographs of the creased circular HEPA that operated by closing and opening the half circular shape. This HEPA closed at a greater angle than the pre- curved variations, and could lift a weight (a piece of paper, $m = 46$ mg). **FIG. 7B** shows time-lapse photographs of the linear HEPA that was creased in an accordion-shape. The difference between these two designs was the position of the tape. When the tape is positioned on one side of the paper, the angular motion of each crease is in the same direction, which resulted in curving (**FIG. 7A**). When the tape was positioned on alternate sides, the cumulative angular motion resulted in linear actuation (**FIG. 7B**), which is an essential motion in many mechanical machines.

[0093] As described above, a central element of the HEPAs is the porous conducting polymer path (used to provide electrothermal heating) that is fabricated by printing, and is embedded within the paper. The properties of the conducting path give the HEPAs at least four advantages: (i) They are lightweight, inexpensive, and biodegradable. (ii) They are easy to fabricate using a commercial printer. (iii) They are resistant to bending and scratching, because the element that provides electromechanical work is embedded within the paper. These features offer the possibility of designing complex folded structures. (iv) They can actuate many times without showing signs of degradation of performance. HEPAs are similar to other paper-based actuators, in that they have the disadvantage that their initial state is influenced by the relative humidity of the environment. Unlike most other paper-based actuators, however, their final state is not affected by relative humidity.

[0094] The ability to fabricate small (sub mm-scale) porous wires of PEDOT that extend across the full thickness of a sheet of paper by using capillary wicking of an aqueous suspension of PEDOT into a channel defined by wax-printed walls (a procedure, described in

more detail in other papers), is a new fabrication procedure with the potential for wide application in paper-based devices and machines. These properties make the HEPAs potentially useful in applications benefitting from monolithic integration in paper-based printed microfluidic and electronic devices, paper MEMS, printable and foldable micro machines, and robots. HEPAs have the potential to be useful in large-scale manufacturing applications that require moving parts, where cost, speed, low packing volume and/or weight are an issue: Interactive printed media / books, green houses, or humidity sensors, are examples.

Electronic Patterns

[0095] **FIG. 8A** is a schematic diagram of an embodiment of a fabrication procedure for making an electronic pattern. **FIGS. 8B-8D** are images of the printed structures with top views (top) and cross sections (bottom). **FIG. 8B** shows the formation of fluidic channels from printing of a first hydrophobic barrier. The printing was performed using techniques similar to the one described above. In the embodiment shown in **FIG. 8B**, in accordance with this disclosure, a first hydrophobic barrier is formed using a yellow wax.

[0096] As a second step, a conducting liquid may be disposed in the channels formed above. **FIG. 8C** shows the embodiment where two different conducting inks, PEDOT (gray) and MWNT (black) have been patterned in different parts of the channels formed in the cellulose matrix.

[0097] In the embodiment shown in **FIGS. 8A-8F**, the PEDOT ink was prepared in a manner similar to the one described above. The carbon ink was prepared by mixing MWNT powder (5 g/L) with dissolved carboxymethylcellulose in de-ionized water (2.5 g/L). The mixture was ultra-sonicated with a tapered microtip for 15 minutes using a Branson sonifier 340 with an output power of 400W. The sonicated ink was purified by centrifuging at 4500 rpm for 30 minutes and then decanted. The carbon nanotubes used were MWNTs (>95% carbon), obtained from Sigma Aldrich (product of Southwest Nanotechnology).

Carboxymethyl cellulose, sodium salt (M.W. 250,000) was procured from Acros Organics.

[0098] After depositing, the ink was allowed to dry through evaporation at room temperature for about 30 minutes. Heating the paper to expedite evaporation is also envisaged. In some embodiments, the channels may be treated with a silane solution to improve the fluidic properties. In some embodiments, the fluidic property may be enhanced

by the spontaneous wicking of the conducting parts in the channels formed by the hydrophobic barrier in the cellulose matrix. In the sample illustrated in **FIG. 8B**, where the conducting polymer used was the PEDOT:PSS structures, we added a 2wt% solution of 3-glycidoxypropyl-trimethoxysilane in amounts that completely wicked the paper, and allowed the solution to dry. For the carbon structures, after the inks had dried, a 2wt% solution of 3-aminopropoyldimethylethoxysilane (in deionized water) was added in the same way as described above.

[0099] **FIG. 8C** shows that both of the conductors penetrate the full thickness of the paper. Due to the penetration of the full thickness of paper, the connection of points on opposite sides of the paper is facilitated, so that complex 3D circuits can be fabricated by stacking several sheets of paper, as shown in some embodiments described later in this disclosure.

[0100] Additionally, the electrical resistance of the dry PEDOT and MWNT conductors was measured on patterned lines with a width of 4mm, and with lengths from 1cm up to 15 cm. The resistance per square area of the PEDOT was $280 \Omega/\square$ ($\pm 11\%$), and MWNT printed lines $500 \Omega/\square$. These conductivity values are comparable to the values for the same inks printed on top of planar substrates, and show that we form continuous conducting films across the fibers in the paper.

[0101] In some embodiments, another layer of hydrophobic barrier can be printed on top of the areas of the cellulose matrix where the first hydrophobic barrier, such as a yellow wax, was deposited and/or over the areas where the electrically conducting material as deposited inside the channels formed by the deposition of the first hydrophobic barrier. This is shown as the green wax in **FIG. 8D**.

[0102] **FIG. 8E** shows a schematic diagram, and images (top and side view) of a water droplet placed on a printed electronic pattern shown in **FIG. 8D**. As seen in **FIG. 8E**, the contact angle of a 50 μ L water droplet on top of a PEDOT conductor that was fabricated with a second wax-printing step shows that the structure is hydrophobic after ($\theta_{\alpha}^{\text{H}_2\text{O}} > 90^\circ$). A 50 μ L water droplet was placed on top of electronic conductors for both PEDOT and MWNT. The resistance of PEDOT decreased slightly $\sim 4\%$, and the resistance for the carbon ink increased by $\sim 5\%$, 10 minutes after the drop was applied, as shown in **FIG. 8G**. **FIG. 8G** shows the relative resistance measured across electronic structures on paper with a water droplet on top (see the structure in figure **FIG. 8E**) for an electronic pattern with MWNT (solid line) and PEDOT

(dashed line). The relatively stable resistance and hydrophobic nature of the conductors indicate that these can indeed be used as water impermeable conducting elements in the paper devices.

[0103] **FIG. 8F** shows schematics of a 2 layer paper device showing 3D wicking in electrofluidic structures (top) and time-lapse photos of same electrofluidic 3D assemblies, showing transport of water through the top and bottom paper layers in carbon printed (middle), and conducting polymer (bottom) electrofluidics. Water based conducting inks, added to some of these wax-defined channels formed electronic conductors. These water-based inks move by spontaneous wicking, and cover the entire hydrophilic area of the paper within the region defined by the wax barriers. On drying the inks coat the cellulose fibers in the paper and form electrical conductors, but without filling the pores. The surface area of the conductors thus is closer to the surface area of the paper, rather than the projected, smaller, 2D area of a wire printed on a non-porous substrate.

[0104] More importantly, the surface of the inks are hydrophilic, so the combination of open pores and hydrophilicity implies that water can spontaneously wick the electrical conductors, thus forming both electronic and fluidic (“electrofluidic”) conductors. The electrofluidic conductors can also be stacked just like conventional paper microfluidic patterns. Stacking and spontaneous wicking was demonstrated in **FIG. 8F**. **FIG. 8F** shows a two-layer paper structure, with MWNT electrofluidic conductor. By placing a water droplet at the top of one of the circular shapes, spontaneous wicking allowed the fluid to move from the top layer through the conductor and down to the bottom layer, then continued across the conducting line to the other circular shape and moved upwards to the first layer again.

[0105] However, in many electrochemical device designs it is necessary to have conductors that do not conduct fluids but that can be connected seamlessly to electrofluidic conductors, for example to form connection points to instruments. To achieve this, as described above, a method to fabricate a conductor in the co-fabrication process includes a second step of wax printing. In the regions where the second wax intersects with the electrofluidic patterns, see **FIGS. 8D** and **8E**, the wax melted into and around the cellulose matrix covered by the conductors, upon which the surface of the conductors became hydrophobic turning the intersecting regions into purely electrical conductors.

Printed three-dimensional paper circuit boards

[0106] To demonstrate one of the many options that arise from the possibility to co-fabricate three-dimensional structures using stacked paper designs, a three-layer electronic paper circuit board (PCB) was fabricated.

[0107] **FIGS. 9A** and **9B** show a printed multi-layer paper circuit board. **FIG. 9A**, on the left, shows a schematic diagram of a circuit board assembled by folding and spontaneous wicking of conducting polymer ink. The completed folded structure is shown on the right in **FIG. 9A**. **FIG. 9B** shows an image of a printed device before folding, **FIG. 9C** shows top view photos of the circuit board with mounted LEDs. On the left side of **FIG. 9C**, the upper LED is powered through the two lines in the bottom layer connected to the top layer through vias and, in the right side of **FIG. 9C**, the righthand LED is powered through the two top lines.

[0108] The paper PCB was fabricated by wax printing the three-layer design on a single sheet of paper, and then folded and glued the three layers into a single multi-layer device. As shown in **FIG. 9A**, the folding procedure automatically aligned the structures for correct positioning of the vias. As an alternative method, the three folded sections could be printed separately on different sheets of paper and stacked on top of each other to attain a similar functioning structure. Variations in steps of manufacturing and sequence of operations are conceived and envisaged within the scope of this disclosure.

[0109] In one embodiment disclosed here, the design consisted of two parallel lines on the top layer, and two parallel lines in the third layer crossing the lines in the first. The middle and top layer contained quadratic shaped openings that were positioned to connect to the end of the lines in the third layer and thus acted as electronic vias. One of ordinary skill in the art will readily recognize that other more complicated designs are easily contemplated and are envisaged within the scope of this disclosure.

[0110] An electrically conductive material, such as PEDOT ink or a carbon ink, can then be added in the fluidic patterns and filled the paper structure by wicking all the three layers simultaneously. In the embodiment shown in **FIG. 9A**, PEDOT ink was used for this purpose. Here too, as discussed above, if the various folded sections were alternatively printed on different sheets of paper, they can be stacked. After drying of the ink, a continuous conducting assembly was formed both in-plane and through-plane (i.e., between the paper layers).

[0111] Finally, two light emitting diodes were mounted to the ends of the wires, and by applying potential between the two electrodes at the top layer, the LED could be powered as seen in **FIG. 9C**, on the left. More interestingly, the other LED could be contacted as well through the electrical vias, as shown in **FIG. 9C** on the right.

[0112] The foregoing demonstrates the possibility to co-fabricate 3D wires in stacked paper using only wax printing and, optionally, folding. The electrical connection points between the layers of paper are fabricated without making holes.

[0113] A more advanced device that included several off-the shelf electronic components mounted on a printed paper circuit board was fabricated. **FIG. 14A** shows the circuit diagram of the device, and **FIGS. 14B** and **14C** show photos of the paper device.

[0114] PEDOT ink was used to form the conducting wires in the circuit, as well as for making a resistive heating element and a “pull-up” resistor. Wax printing was used to define the hydrophobic barriers, wherein the resolution of the wax patterns, enable wires with a minimum feature size of around 1mm, which was small enough for the mounting of standard surface mounted (SMD) components such as the diode and the transistor. The low resistance of the wires allowed interconnection between the components in the circuit. The components can be mounted on the paper by using a conductive glue which connects the legs of the SMD component to the conducting part of the paper wire.

[0115] The device was folded in the middle to form a two-layer structure where the resistive heater and the fluidic channel were brought into contact (see **FIG. 14B**). The ability to fold the paper circuit is possible because of an insensitivity of the wires to folding.

[0116] **FIG. 14D** shows the paper device of **FIG. 14B** when it is powered. The microprocessor is programmed to detect the presence of a liquid inside a paper microfluidic channel. Once a liquid is detected, the microprocessor powers the resistive heater, which is in contact with the liquid, and executes a programmed sequence of heating cycles (80 C°, 60 C°, 40 C°, 20 C°). **FIG. 14D**, on the right, shows time-lapse infrared heat images of the resistive heater.

A flow-through paper electrochemical device

Device fabrication and basic electrochemical characterization

[0117] In an aspect, the method of making an electrochemical sensor includes providing any of the devices disclosed above, wherein the device further includes a first region of the porous channel in the cellulose matrix that is configured to form a working electrode; a second region of the porous channels in the cellulose matrix that is configured to form a separator; and a third region of the porous channel in the cellulose matrix that is configured to form a counter electrode. A reference electrode is also provided. Additionally, the first region, the second region, the third region and the reference electrode are in electrochemical contact with one another.

[0118] An electrochemical sensor that includes three layers of stacked paper, according to some embodiments, is shown in **FIG. 10A**. In some embodiments, a separator is placed between two circularly shaped electrofluidic electrodes (the 2D print area of the circle is 31 mm²). Other geometries and dimensions for the various electrodes as are envisaged and considered within the scope of this application. Each electrode is in turn connected to printed conductors that are contacted with metallic clips and connected to electrical measurement instrument, as shown in **FIG. 10B**. A reference electrode is also included. In some embodiments, as shown in **FIG. 10B**, a Ag/AgCl ink may be printed partly into the separator layer to act as a reference electrode.

[0119] When drops of liquid electrolyte are placed on top of the device, the liquid electrolyte passes through the top electrode, into the separator and down into the bottom electrode layer, to form a continuous column of ionic liquid between the electrodes.

[0120] To estimate the stability and electroactivity of the electrofluidic patterns of PEDOT and MWNTs, the capacitive discharge was measured by applying a DC step voltage of 0.5 V. The decay current was measured as a response. This is shown in **FIG. 11**. Evaluation of the stability and electroactivity of the electrofluidic patterns of PEDOT and MWNTs were also performed using cyclic voltammetry. These results are shown in **FIG. 11** (insets, PEDOT (right) and MWNTs (left)).

[0121] For carbon electrodes, the current discharge comes mainly from the formation of a double layer, and the capacitance of the device was calculated from the discharge curves to be

17 $\mu\text{F}/\text{mm}^2$. The calculations for the capacitance for the paper electrodes was done by numerical integration of the area of the discharge curve vs. time to obtain the total charge. The charge was divided by DC voltage (0.5 V) and the print area of the electrodes to get a capacitance/area value. A theoretical value of the maximum double layer capacitance was taken to be 0.2 $\mu\text{F}/\text{cm}^2$ from literature values assuming a mercury electrode at 0.5V in 0.1 M salt solution (close to 1x PBS). The electrical characterization was made using Keithley 2400, and data acquisition using GPBIB and MATLAB. The ratio between the ideal 2D capacitor and the measured capacitor of the MWNT electrofluidic structure was estimated to 85. This means that the electrical area of the porous electrodes is 85 times larger than its corresponding projected “footprint” area. This value is close to the actual ratio between the specific surface area of the bulk paper and its corresponding 2D area (between 90-100 for Whatman grade 1). These estimates therefore suggest that the conducting paper electrodes are indeed active and are covering the majority of the bulk surface area of the paper.

[0122] For the conducting polymer electrodes larger capacitance 56 $\mu\text{F}/\text{mm}^2$, was calculated since the discharge for the conducting polymer also comes from Faradaic redox reactions at each polymer site even for voltages under 0.5 V.

[0123] The estimated capacitance values suggest that the electrofluidic structures have electrochemically active surface area close to the surface area of the paper. It can be inferred from these observations that the electrofluidic structures consist of thin layers of the conductor surrounding the majority of paper fibers, and that the layer is electrically connected (through percolated networks) even when filled with a liquid.

[0124] The capacitance values of the device, and the symmetrical shape of the voltammograms, even at slow scan rates, also indicated that MWNT and PEDOT electrofluidic structures did not degrade considerably over time, when filled with a liquid, neither due to dissolution, nor structural changes.

Electrochemical Analysis

[0125] In an aspect, a method for electrochemical analysis using the above described electrochemical sensor includes further providing a loading electrolyte that enters the porous channels of the first region, the second region and the third region to produce a first interaction with the electrically conducting material disposed therein; wherein, said first

interaction produces a baseline electrochemical signal; performing an electrochemical measurement to measure the baseline electrochemical signal; providing an analyte sample that enters the porous channels of the working electrode to produce a second electrochemical signal; analyzing the second electrochemical signal and comparing it with the baseline electrochemical signal to gather information regarding the analyte.

[0126] In some embodiments, said measuring an electrochemical signal includes impedance measurement, current measurement or measurement of voltage.

[0127] In some embodiments, the electrochemical measurement is selected from the group consisting of amperometry, biamperometry, stripping voltammetry, differential pulse voltammetry, cyclic voltammetry, coulometry, chronoamperometry, and potentiometry.

[0128] In some embodiments, the electrochemical measurement is chronoamperometry and the analyte includes glucose, cholesterol, uric acid, lactate, blood gases, DNA, hemoglobin, nitric oxide, and blood ketones.

[0129] In some embodiments, measuring an electrochemical signal comprises anodic stripping voltammetry.

[0130] **FIG. 10C** shows the chronoamperometry for ferrocyanide in 1xPBS (error bars calculated based on measurement of 3 different devices); and the diagonal line shows the theoretical value of the total amounts of charge per analyte. **FIG. 10C** (inset) shows the redox reaction of potassium ferri/ferrocyanide measured by cyclic voltammetry (CV) using the paper electrochemical sensor with MWNT electrodes. The anodic peak potential was seen at around 0.3 V, which is in agreement with the values measures on planar carbon electrodes with a Ag/AgCl reference electrodes. Due to the high surface area, the CV curves were measured at lower scan rates (5 mV/s).

[0131] The combination of a vertical flow-through electrode (fluids have to move small distances only through a single sheet of paper, <200 μm) and the large surface area of the electrode, allows for measurements on small volumes (around $2\mu\text{L}/50\text{mm}^2$). To further demonstrate the usability of the device for electroanalysis, coulometric measurements on a potassium ferri/ferrocyanide redox system were performed.

[0132] In an embodiment, the measurement procedure can be as follows:

- 1) The vertical flow device was filled with 30 μL of a loading electrolyte (1M KCl buffer), whereupon the electrodes and the separator were filled and the reference electrode also connected to this electrolyte. This resulted in a relatively large double layer capacitive discharge current due to the large surface area of the electrodes.
- 2) A potentiostatic coulometry measurement was started with an applied DC voltage of 0.8V on the working electrode.
- 3) After the double layer discharge current approached a baseline, small amounts (2 μL) of a sample solution of ferrocyanide were added to the working electrode in a sequence with increasing concentrations.

[0133] The small amount of sample solutions easily wicked into the working electrode, which with its high surface area oxidized all the species within tens of seconds. Each sample addition therefore resulted in a peak oxidation current that decayed rapidly. The area under each peak corresponded to the total charge that is correlated with the concentration of ferrocyanide in the sample solution. **FIG. 10C** shows the measured charge as a function of the amount of ferrocyanide. The relationship is linear over 2 orders of magnitude and is sensitive below 1mM. The red line shows the theoretical value of the total charge as a function of the amount of ferrocyanide and follows the measured values. This indicates that all the electroactive ferrocyanide species are consumed in the potentiometric measurement, so the concentration can be directly estimated without calibration.

[0134] The ability to detect concentrations of a mediator was used for demonstrating a glucose sensor with a ferrocyanide mediator. The analysis of glucose was performed by adding a solution (250 U/mL glucose oxidase, 500mM potassium ferricyanide in 1 M KCl in PBS buffer pH 7.0) to the device. A DC potential of 0.8 V was then applied to the device, and after the discharge of the double layer, different concentrations of glucose were added in small amounts (2 μL). The added glucose was oxidized by the glucose oxidase to gluconic acid, which then reduced ferricyanide to ferrocyanide, and the total concentration of the produced ferrocyanide was measured as previously.

[0135] **FIG. 10D** shows the chronoamperometry for a glucose assay (error bars extracted from 3 devices) and the diagonal line represents a linear fit.

[0136] The procedure for performing the glucose assay included 250 U/ml Gox in pH 7.0 PBS buffer 1M KCl and 600 mM Ferricyanide was added in 30uL to the electrode. A DC potentiometric was applied and after 10 minutes of discharge and equilibration time, the glucose solutions were added on the top working electrode at 2uL per concentration. The measurements were made using an Autolab device. A constant potential of +0.8V (against the Ag/AgCl built into the paper device) was used and measurements were made using an Autolab device. **FIG. 10D** shows the measured total charge vs. the glucose concentration in a range of 2.7-11.1 mM (which is a relevant range for the glucose in human blood).

[0137] These results show that the printed electrofluidic paper structures do not interfere with the enzymatic reaction, and instead the microporous nature of the electrodes in the paper matrix is advantageous as they allow for a very fast conversion and detection. It can be inferred that when the glucose is added to the electrofluidic structure spontaneous wicking allows immediate mixing between glucose and the solution with the enzyme and ferricyanide, which are already present on the fibers in the paper, so the reaction is not diffusion limited. Furthermore, the small pore size of the paper, and the large surface area also lead to a faster conversion of all the ferrocyanide species within less than 1 minute.

Configurable, and foldable paper batteries

[0138] The electrochemical stability, high surface area and configurability of printed electrofluidic structures are also advantageous for energy storage devices. In order to demonstrate the energy storage, using cellulose matrix-based devices, paper batteries were fabricated in accordance with the procedure described above. Although here the example presented represents a structure where the entire battery was printed on a single sheet of paper one of ordinary skill in the art can easily modify the procedure for manufacturing the various elements of the battery on separate sheets and assembling them by stacking the different sheets in the correct sequence.

[0139] In an embodiment according the disclosure, the PEDOT anodes were made by adding a few drops of 50 mg/ml of branched polyenimine (PEI) to the FE paper, followed by drying. The branched polyethylenimine PEI (60 kDa) was procured from Sigma Aldrich. Electrical characterization was conducted using Keithley 2400.

[0140] **FIG. 12A** shows a schematic diagram of the assembly of a printed paper battery using folding, according to some embodiments. **FIGS. 12B-12D** show images of a fully printed

device that contains six serial connected batteries. **FIG. 12B** shows the structure before folding, **FIG. 12C** shows the structure during folding, and **FIG. 12D** shows the folded structure. The batteries are connected to an LED and a paper switch button, which can be in an off-state (left) or an on-state (right), as shown in **FIG. 12D**. **FIG. 12E** shows the equivalent circuit of the device shown in **FIG. 12D**.

[0141] The printed single sheet could be folded into a final battery structure according to the schematics shown in **FIG. 12A**. Alternatively, as discussed above, the structure may be assembled using stacks of appropriately printed papers and making the necessary connections. In this particular design, six batteries are integrated (although other quantities of batteries, such as 2, 4 or 8 are also contemplated), and are connected in series through the paper conductors to achieve higher voltages. Additional circuit designs may be developed by changing the stacking/folding arrangement accompanied by modifications in the design printed on the paper. The connection of electronic, fluidic and electrofluidic elements in both 2D and 3D are necessary for the realization of this design. In the embodiment shown in **FIG. 12A**, folding aligns the patterns in each layer. It is also noteworthy that the electrodes are insensitive to folding and the performance is not hampered in any way because of this. In contrast, conventional systems where the printed electrode is on the surface of the paper cannot be configured by simply folding and require serial connection of the batteries to work in the folded state.

[0142] Advantageously, PEDOT has different reduction states. Thus, it can act both as anode or cathode in a battery. In the embodiment shown here a battery which is charged in its initial dry state is shown. The charging was done by adding a cationic polymer PEI, to segments the conducting paper, where PEI reduced PEDOT to act as anode. The reduced PEDOT has a darker color as can be seen from photos in **FIG. 12B**.

[0143] Another significant advantage demonstrated by these paper batteries is the extended shelf life. These batteries could be activated on-demand by addition of the electrolyte to the device, and if no electrolyte was added the printed battery could be stored for months.

[0144] In order to demonstrate the operation of the six serial paper battery, it was connected to a red Light Emitting Diode LED component using silver paint on paper. For including a switch an electrical push button was created by folding the edge of the paper, as

shown in **FIG. 12D**, and corresponding equivalent circuit diagram shown in **FIG. 12E**. When the electrolyte, 1M NaCl, was added to the battery and the button was pressed the LED turned on, as shown in **FIG. 12D** right, and emitted light for approximately 15 seconds before the voltage dropped below the drive voltage of the LED. **FIG. 13** shows the constant current ($5\mu\text{A}$) discharge curve of the 6 serial connected batteries similar to the one shown in **FIG. 12**. The initial voltage was 2.5V corresponding to the additive voltage of each individual battery element (around 0.5 V). A full discharge curve of the battery setup at $5\mu\text{A}$ constant current showed a decreasing voltage from 2.5 V down to 0V over the course of around one hour, with a peak power of $12.5\mu\text{W}$ and an energy density of $\sim 6\mu\text{Wh}$.

[0145] Upon review of the description and embodiments provided herein, those skilled in the art will understand that modifications and equivalent substitutions may be performed in carrying out the invention without departing from the essence of the invention. Thus, the invention is not meant to be limited by the embodiments described explicitly above.

CLAIMS

What is claimed is:

1. A device, comprising:
 - a substrate comprising a cellulose matrix that provides an interconnected porous structure,
 - a hydrophobic barrier disposed through the thickness of the substrate to define at least one porous channel within the volume of the cellulose matrix; and
 - an electrically conducting material,
 - wherein the electrically conducting material is disposed within a volume of the porous channel to coat at least a portion of the cellulose matrix therein.
2. The device of claim 1, wherein the hydrophobic barrier is made of a wax, a thermosetting resin, or a UV cured resin.
3. The device of any one of claims 1 or 2, wherein the electrically conducting material is a nanoparticulate carbon, a conducting polymer, a metallic dust, or a metallic nanoparticle.
4. The device of claim 3, wherein the electrically conducting material is carbon black or carbon nanotubes.
5. The device of claim 3, wherein the electrically conducting material is polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid).
6. The device of any of claims 1 through 5, wherein:
 - the cellulose matrix has a first side and a second side; and
 - one of the first side or the second side has a barrier layer.
7. The device of claim 6, wherein, the barrier layer is a coating or a film.

8. The device of any one of claims 1 through 7, further comprising a fold which forms a first region and a second region on the device.
9. An actuator comprising the device of any of claims 1 through 8, further comprising a controller configured to control a flow of electricity through the electrically conducting material as a function of a temperature and a relative humidity.
10. The actuator of claim 9, wherein:
 - the hygroscopic pick-up of moisture by the cellulose matrix in the channels results in the cellulose matrix to swell; and
 - wherein, said swelling of the cellulose matrix is configured to produce a change in the shortest distance along at least one dimension of the actuator.
11. The actuator of claim 10, wherein:
 - said swelling of the cellulose matrix results in the first region and the second region of the device to move towards or away from each other about the fold; and
 - wherein, said moving towards and away from each other about the fold changes the shortest distance along at least one dimension of the actuator.
12. The actuator of claim 10 or 11, wherein:
 - the flow of electricity through the electrically conducting material results in an electrothermal heating of the cellulose matrix in the channels;
 - wherein the electrothermal heating of the cellulose matrix causes the reduction in the moisture content which causes a shrinkage in the cellulose matrix; and
 - wherein the shrinkage in the cellulose matrix restores the shortest distance along at least one dimension of the actuator to its original state.
13. An electrochemical sensor comprising the device in any of claims 1 through 8, wherein:
 - the device further comprises;

a first region of channels in the cellulose matrix that are configured to form a working electrode;

a second region of channels in the cellulose matrix that are configured to form a separator; and

a third region of channels in the cellulose matrix that are configured to form a counter electrode;

wherein the first region, the second region and the third region are in an electrochemical contact with each other.

14. The electrochemical sensor of claim 13, further comprising a reference electrode.

15. The electrochemical sensor of claim 14, wherein the reference electrode comprises Ag/AgCl.

16. A battery comprising the device in any of claims 1 through 8, wherein the device further comprises:

a first region of channels in the cellulose matrix that are configured to form a cathode;

a second region of channels in the cellulose matrix that are configured to form a separator;

a third region of channels in the cellulose matrix that are configured to form an anode; and

an electrolyte disposed in the first region, the second region and the third region,

the first region, the second region and the third region being in an electrochemical contact with each other.

17. The device of claim 13 or 16, wherein the cellulose matrix in the channels in the first region, the second region and the third region are coated with similar or different electrically conducting materials.

18. A method of making a device, the method comprising:

providing a substrate comprising a cellulose matrix that provides an interconnected porous structure;

providing a hydrophobic barrier disposed through the thickness of the substrate to define at least one porous channel within the volume of the cellulose substrate; and

providing an electrically conducting material,

wherein the electrically conducting material is disposed within the volume of the porous channel to coat at least a portion of the cellulose matrix therein.

19. The method of claim 18, wherein the hydrophobic barrier is made of a wax, a thermosetting resin, or a UV cured resin.
20. The method of any one of claims 18 or 19, wherein the electrically conducting material comprises a nanoparticulate carbon, a conducting polymer, a metallic dust, or a metallic nanoparticle.
21. The method of claim 20, wherein the electrically conducting particle comprises carbon black or carbon nanotubes.
22. The method of claim 20, wherein the electrically conducting particle is polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid).
23. The method of any of claims 18 through 22, wherein:
 - the cellulose matrix has a first side and a second side; and
 - a barrier layer is disposed on any one of the first side or the second sides.
24. The method of claim 23, wherein the barrier layer is disposed on the cellulose matrix as a coating on or a film.
25. The method of any one of claims 18 through 24, further comprising forming a fold in the device that forms a first region and a second region on the device.

26. The method of any one of claims 18 through 24, wherein the electrically conducting material is introduced into the channels in the cellulose matrix as an ink.
27. The method of claim 26, wherein the ink is an aqueous solution or a solvent-based solution.
28. A method of making an electrochemical sensor, the method comprising:
providing the device in any of claims 18 through 27, wherein,
the device further comprises;
a first region of the porous channel in the cellulose matrix that is configured to form a working electrode;
a second region of the porous channels in the cellulose matrix that is configured to form a separator; and
a third region of the porous channel in the cellulose matrix that is configured to form a counter electrode;
a reference electrode;
wherein the first region, the second region; the third region and the reference electrode are in an electrochemical contact.
29. A method of electrochemical analysis using the electrochemical sensor of claim 27, the method comprising:
further providing a loading electrolyte that enters the porous channels of the first region, the second region and the third region to produce a first interaction with the electrically conducting material disposed therein;
wherein said first interaction produces a baseline electrochemical signal;
performing an electrochemical measurement to measure the baseline electrochemical signal;
providing an analyte sample that enters the porous channels of the working electrode to produce a second electrochemical signal; and
analyzing the second electrochemical signal and comparing it with the baseline electrochemical signal to gather information regarding the analyte.

30. The method of claim 29, wherein said measuring an electrochemical signal comprises impedance measurement, current measurement or measurement of voltage.
31. The method of claim 29, wherein the electrochemical measurement is selected from the group consisting of: amperometry, biamperometry, stripping voltammetry, differential pulse voltammetry, cyclic voltammetry, coulometry, chronoamperometry, and potentiometry
32. The method of claim 31, wherein the electrochemical measurement is chronoamperometry and the analyte comprises glucose, cholesterol, uric acid, lactate, blood gases, DNA, hemoglobin, nitric oxide, and blood ketones.
33. The method of claim 29 through 32, wherein measuring an electrochemical signal comprises anodic stripping voltammetry.
34. A method of making a battery, the method comprising:
providing the device in any of claims 18 through 27, wherein:
the device further comprises;
a first region of channels in the cellulose matrix that are configured to form a cathode;
a second region of channels in the cellulose matrix that are configured to form a separator; and
a third region of channels in the cellulose matrix that are configured to form an anode;
wherein the first region, the second region and the third region are in an electrochemical contact with each other; and
providing an electrolyte to be deposited in the channels formed within the cellulose matrix.
35. The method of claim 34, wherein the cathode or anode is formed by reacting the electrically conducting material with a chemical reagent to change its oxidative state.

36. The method of claim 35, wherein the electrically conductive material is PEDOT and the chemical reagent is polyenimine (PEI).
37. The method of any one of claims 34 through 36, wherein the electrolyte is a salt solution.
38. The method of any of claims 34 through 37, wherein the electrochemical contact with each other is formed through folding the substrate at predetermined regions.
39. A printed circuit board comprising the device in accordance with any of claims 18 through 27, further comprising a microprocessor or a microcontroller, wherein the microprocessor or the microcontroller control the flow of electricity through the device.
40. A method of making a printed circuit board, the method comprising providing a device in accordance with any of the claims 18 through 27, and further providing a microprocessor or a microcontroller, wherein the microprocessor or the microcontroller control the flow of electricity through the device.

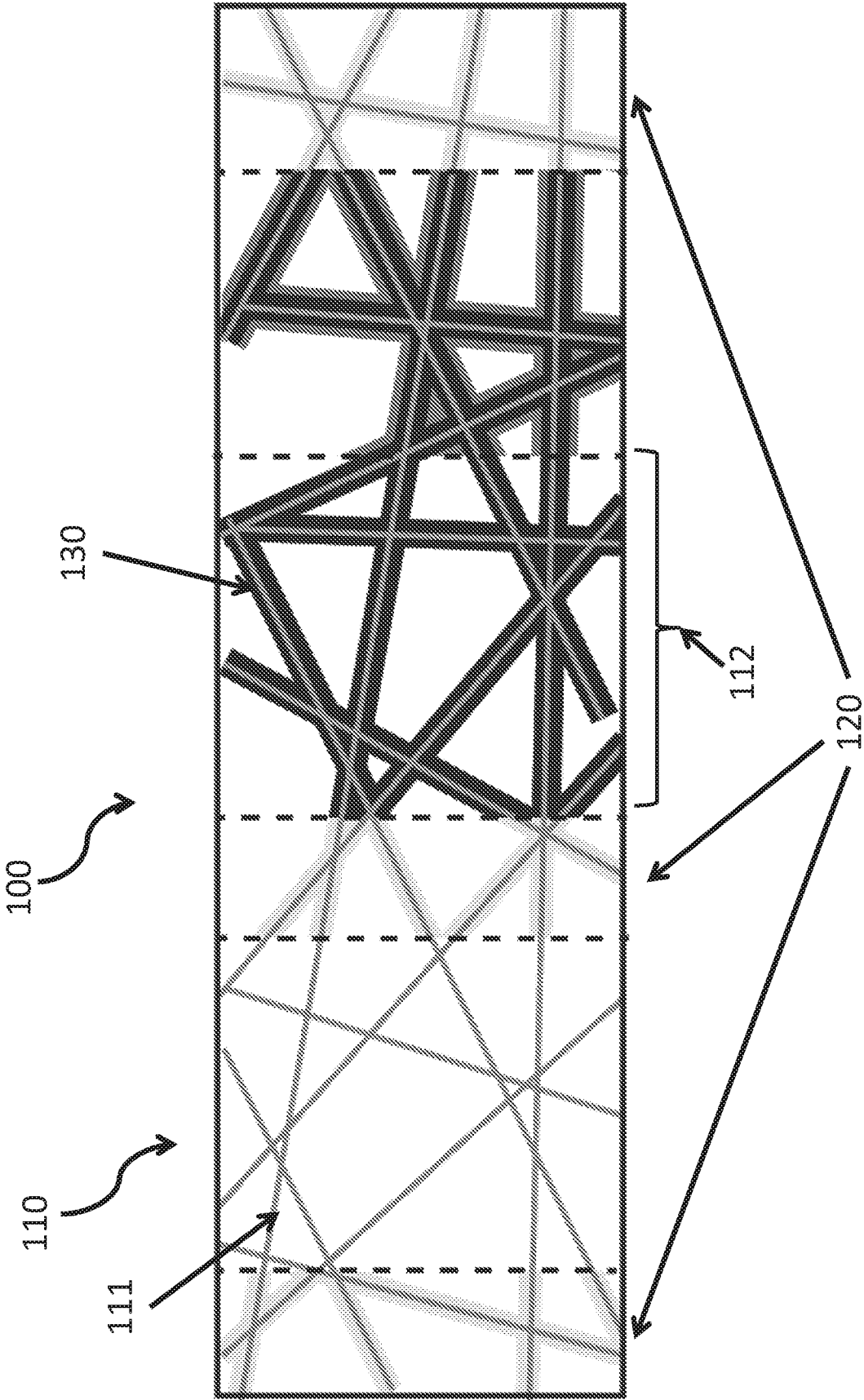
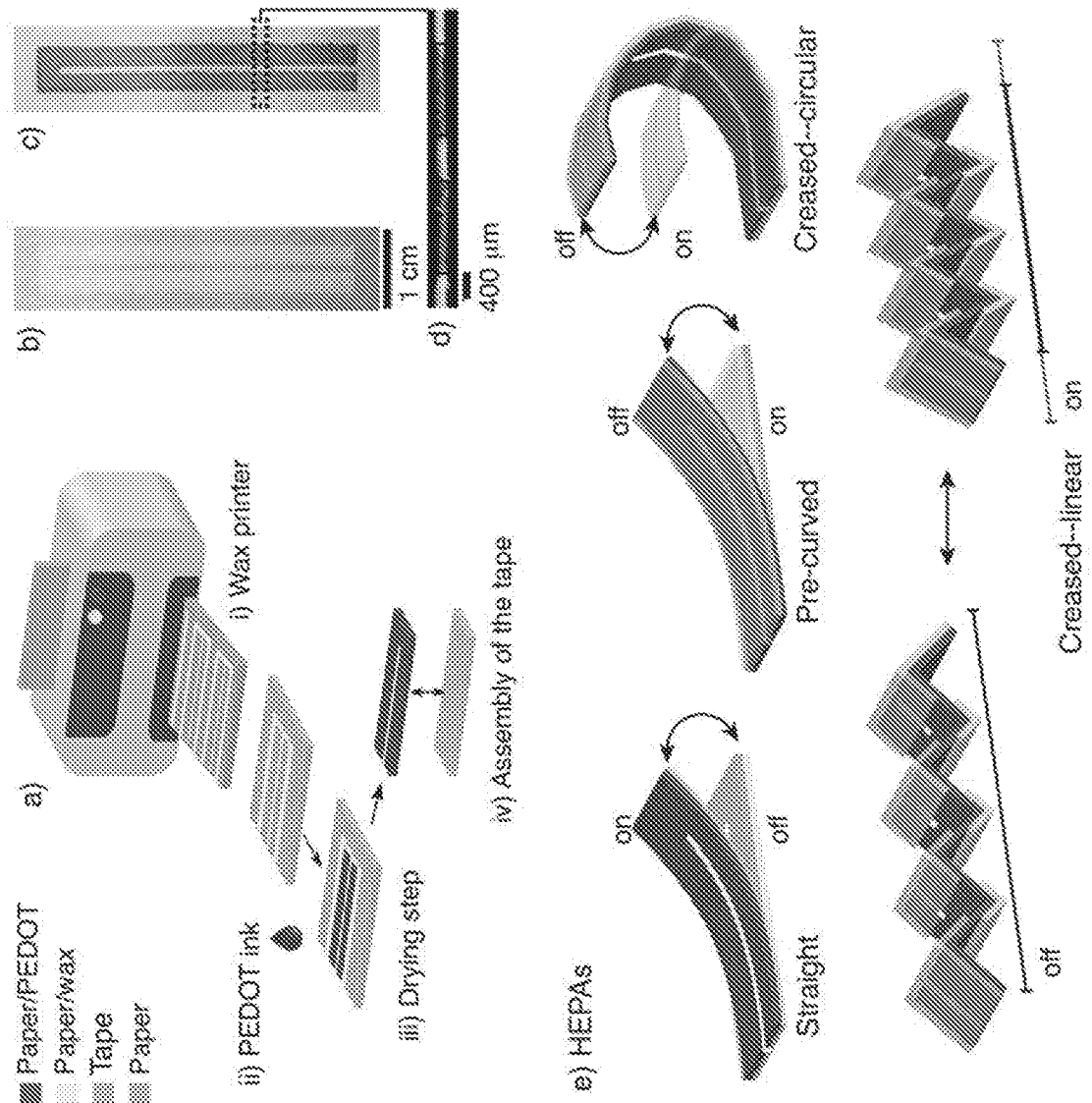


FIG. 1



FIGS. 2A-2E

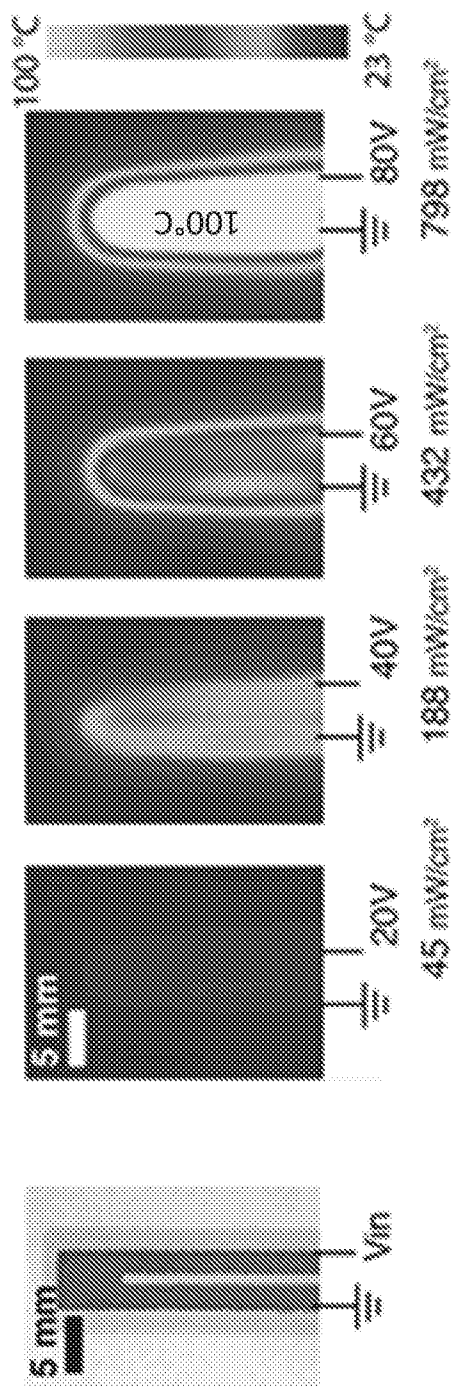


FIG. 3A

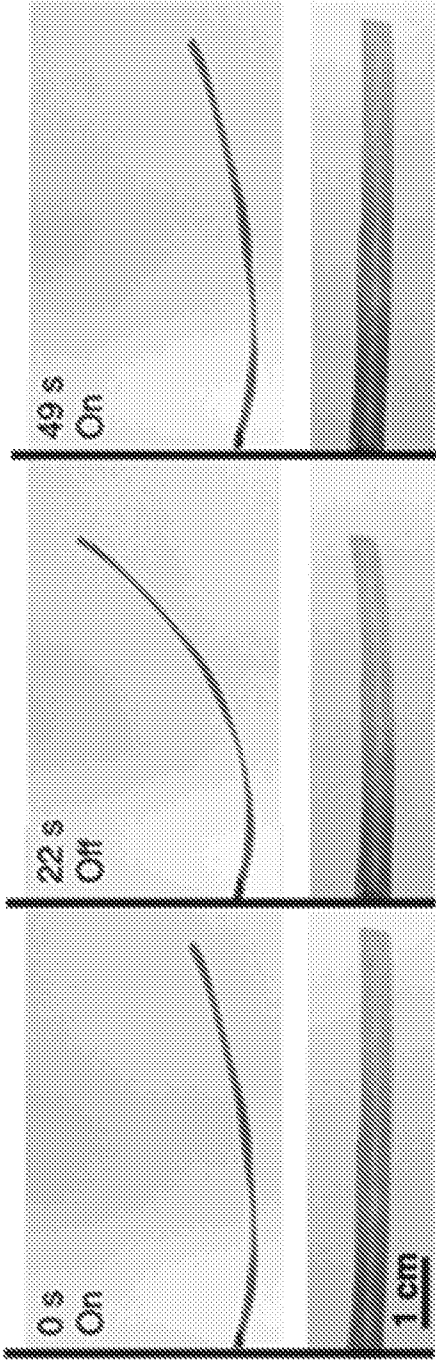
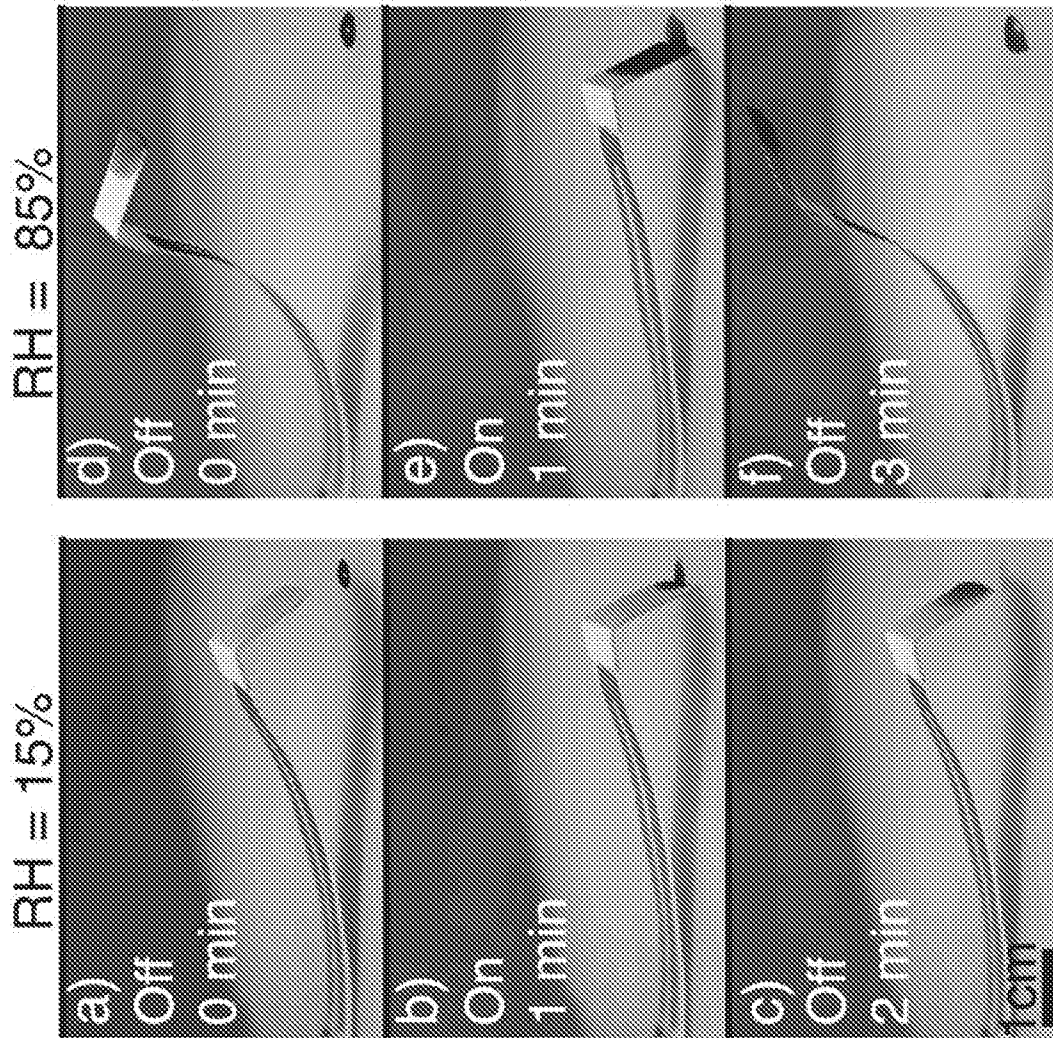
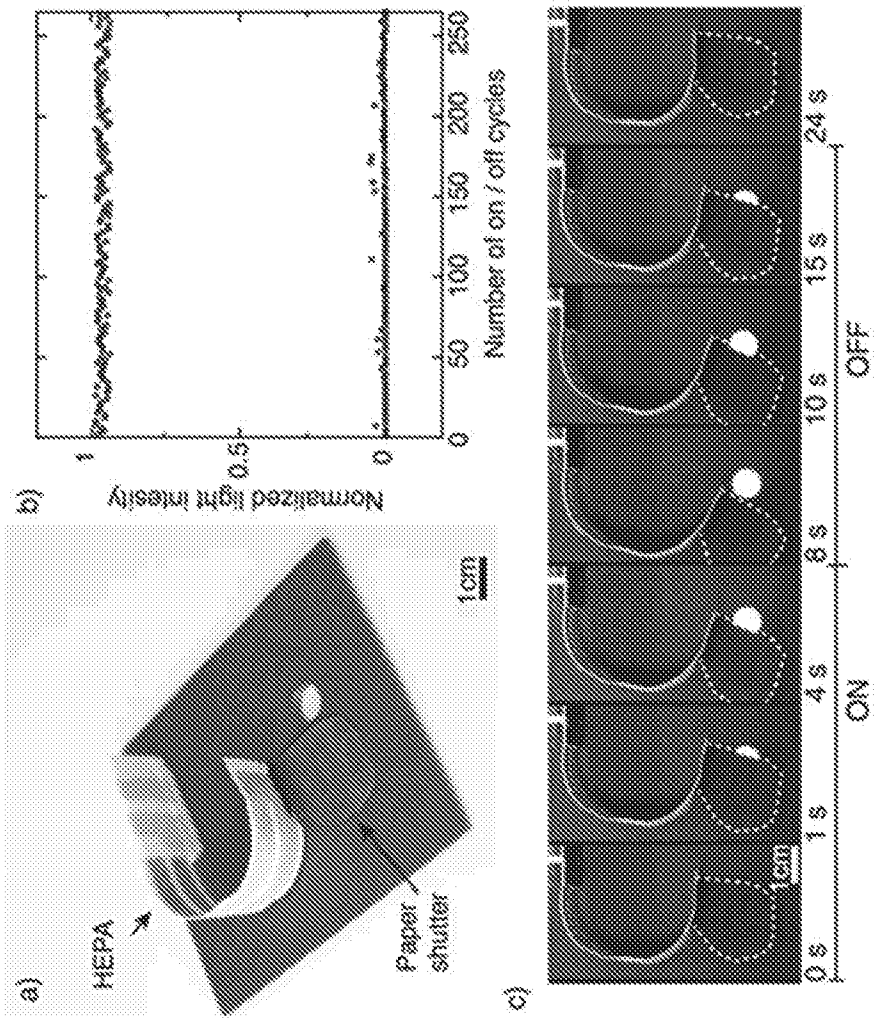


FIG. 3B



FIGS. 4A-4F



FIGS. 5A-5C

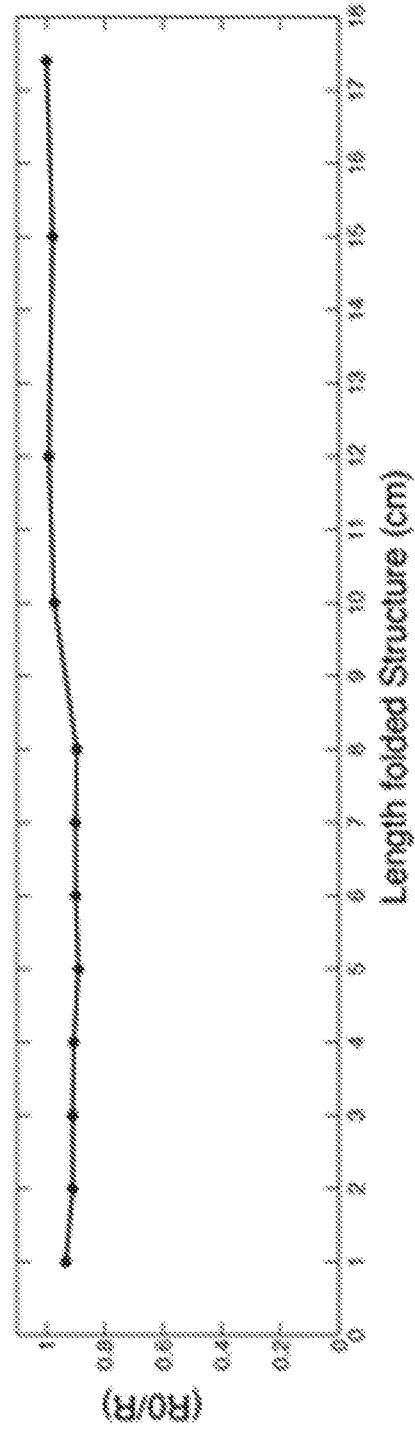
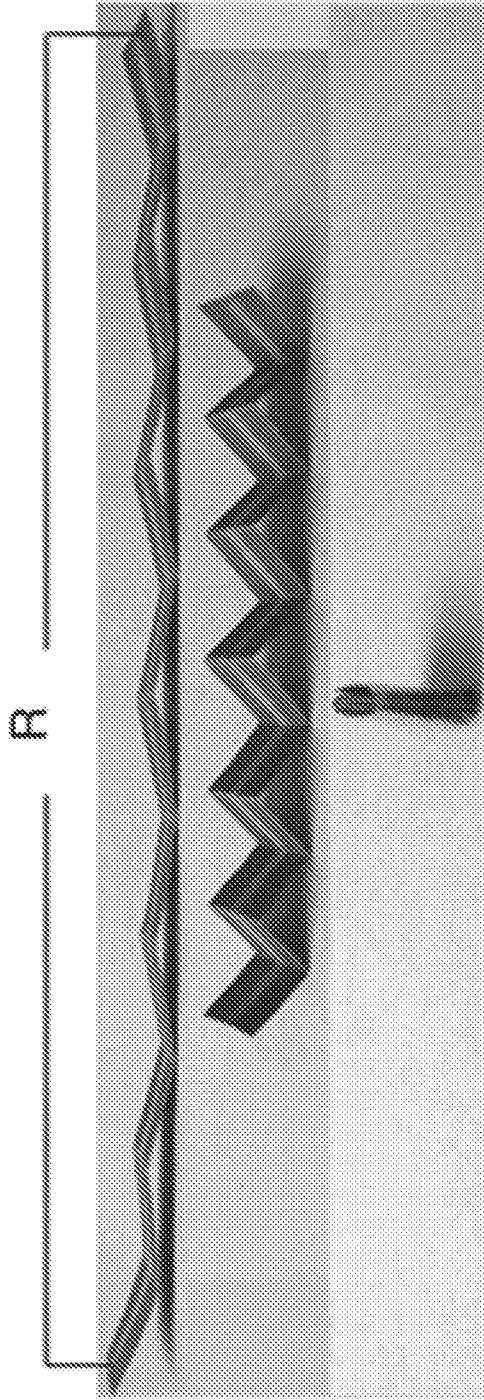
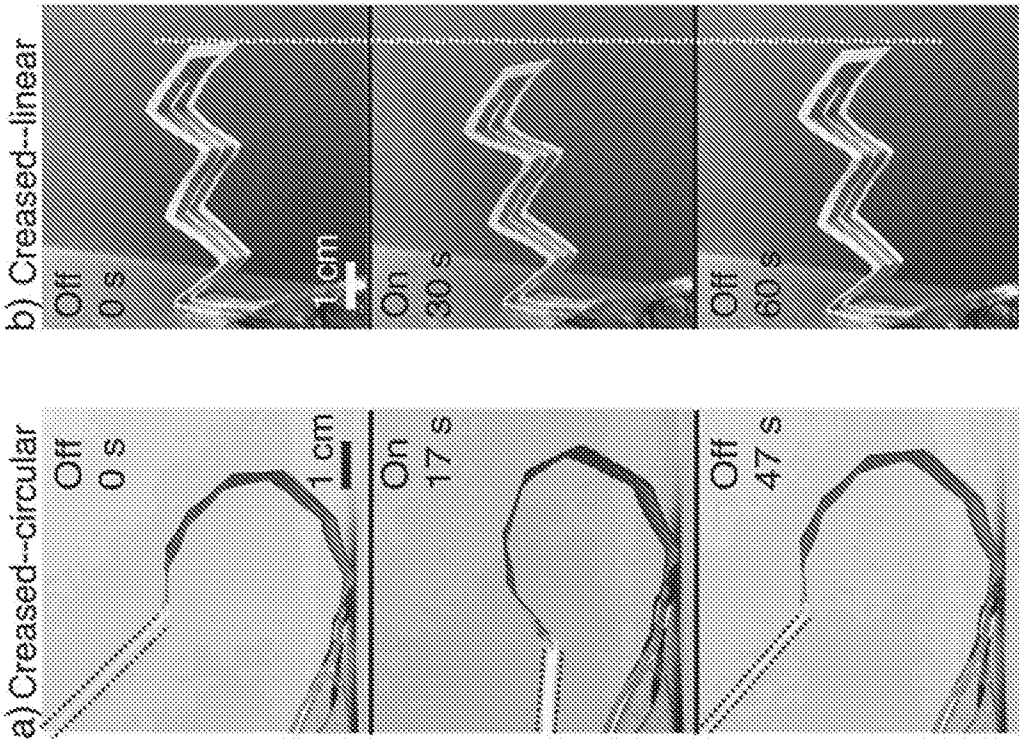
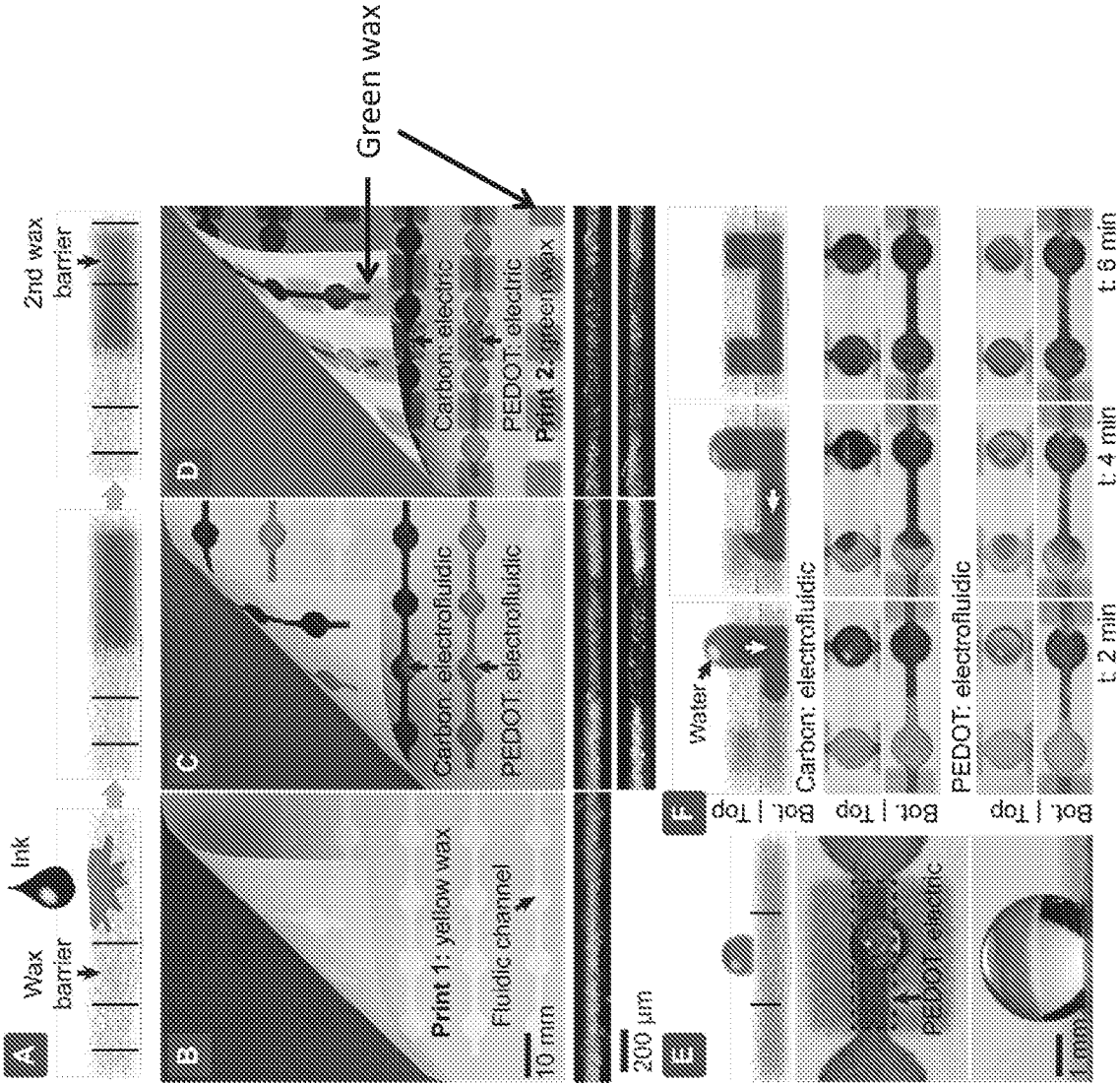


FIG. 6



FIGS. 7A-7B



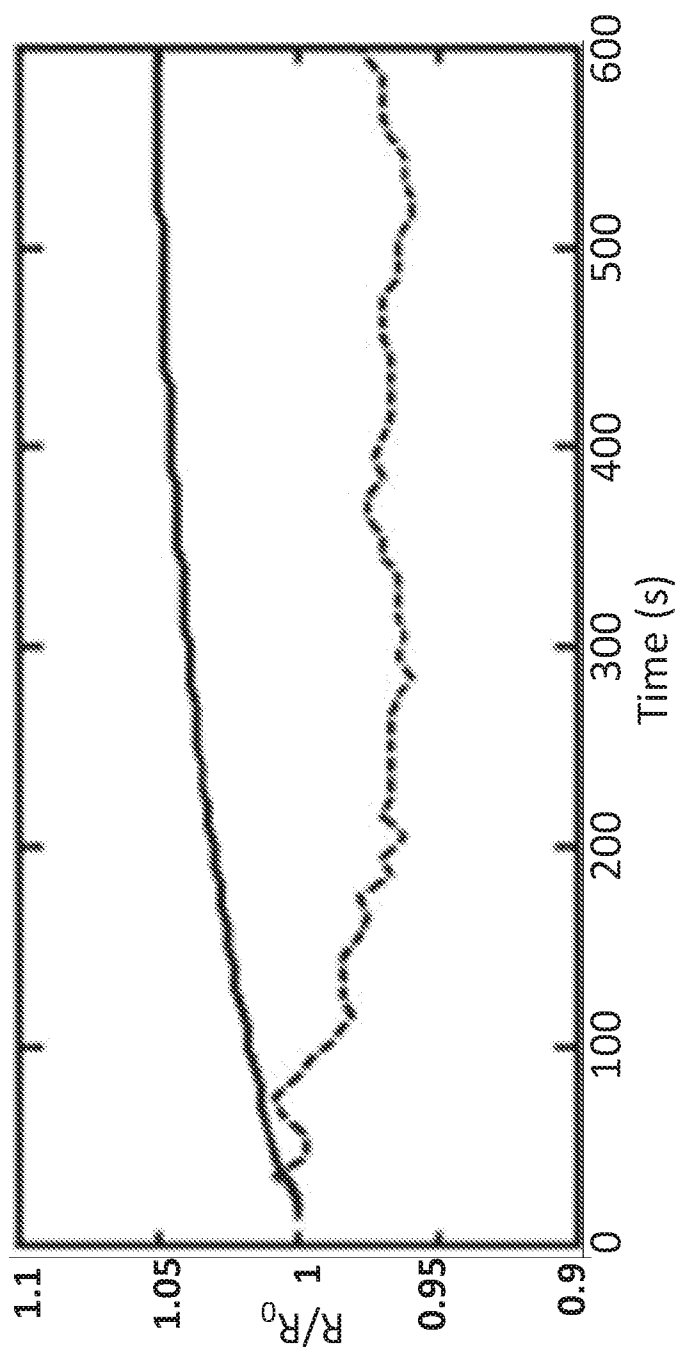


FIG. 8G

FIG. 9A

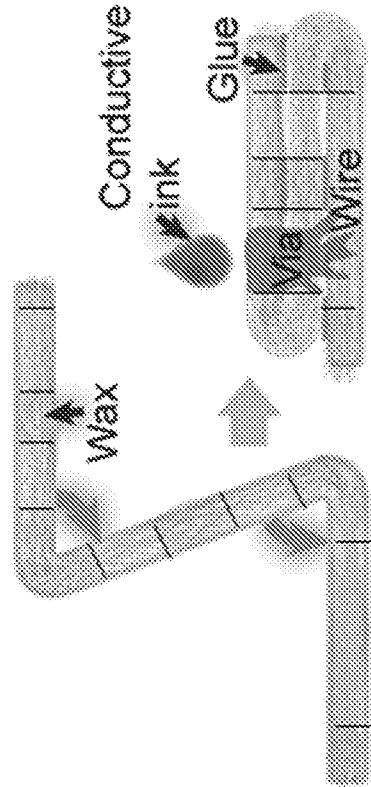


FIG. 9B

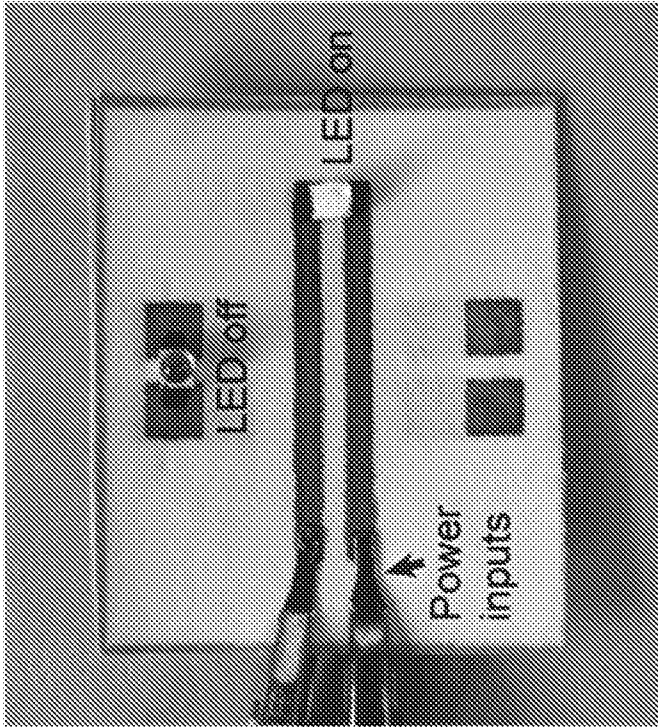
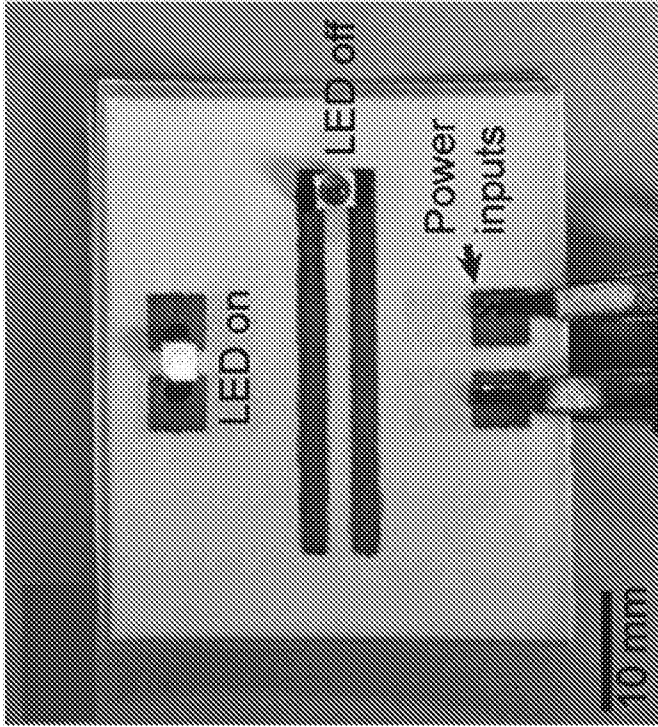
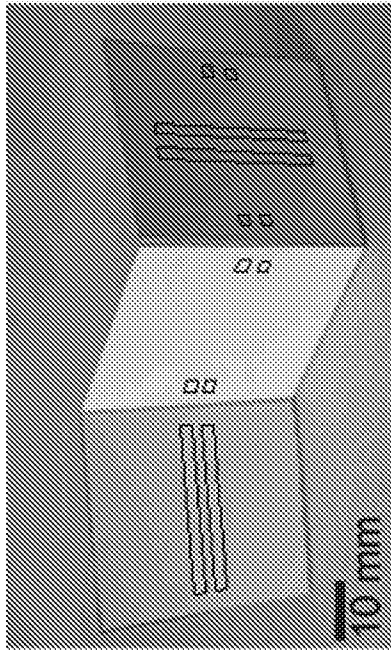
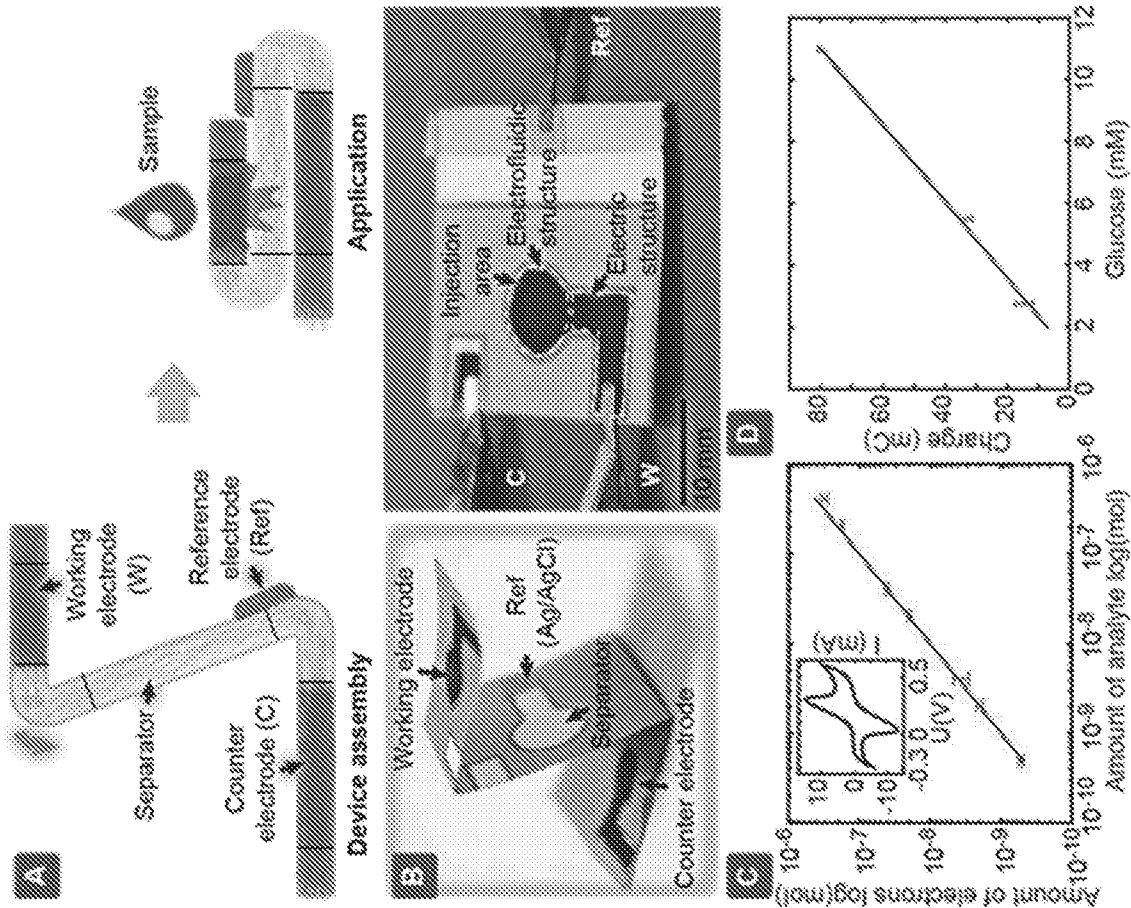


FIG. 9C



FIGS. 10A-10D

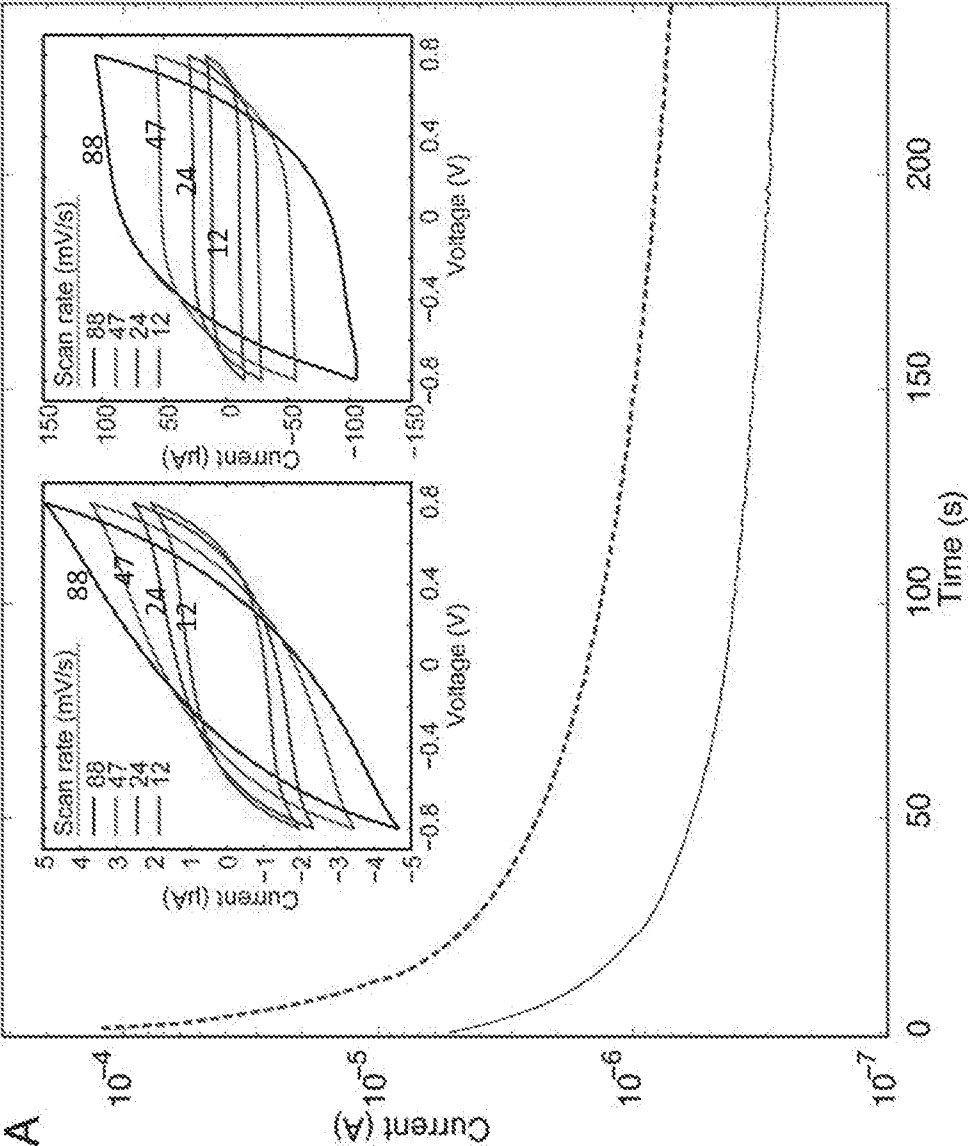
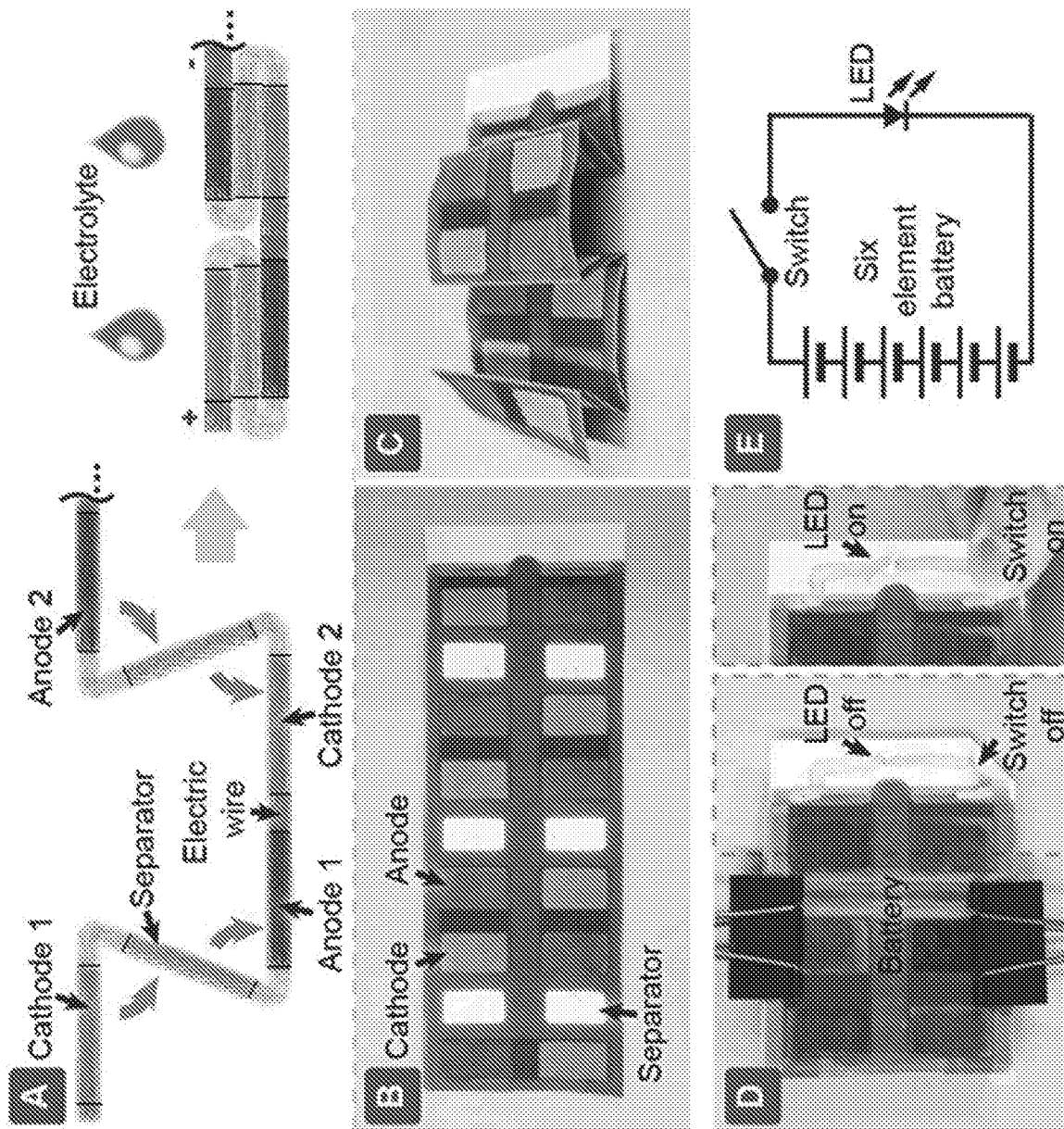


FIG. 11



FIGS. 12A-12E

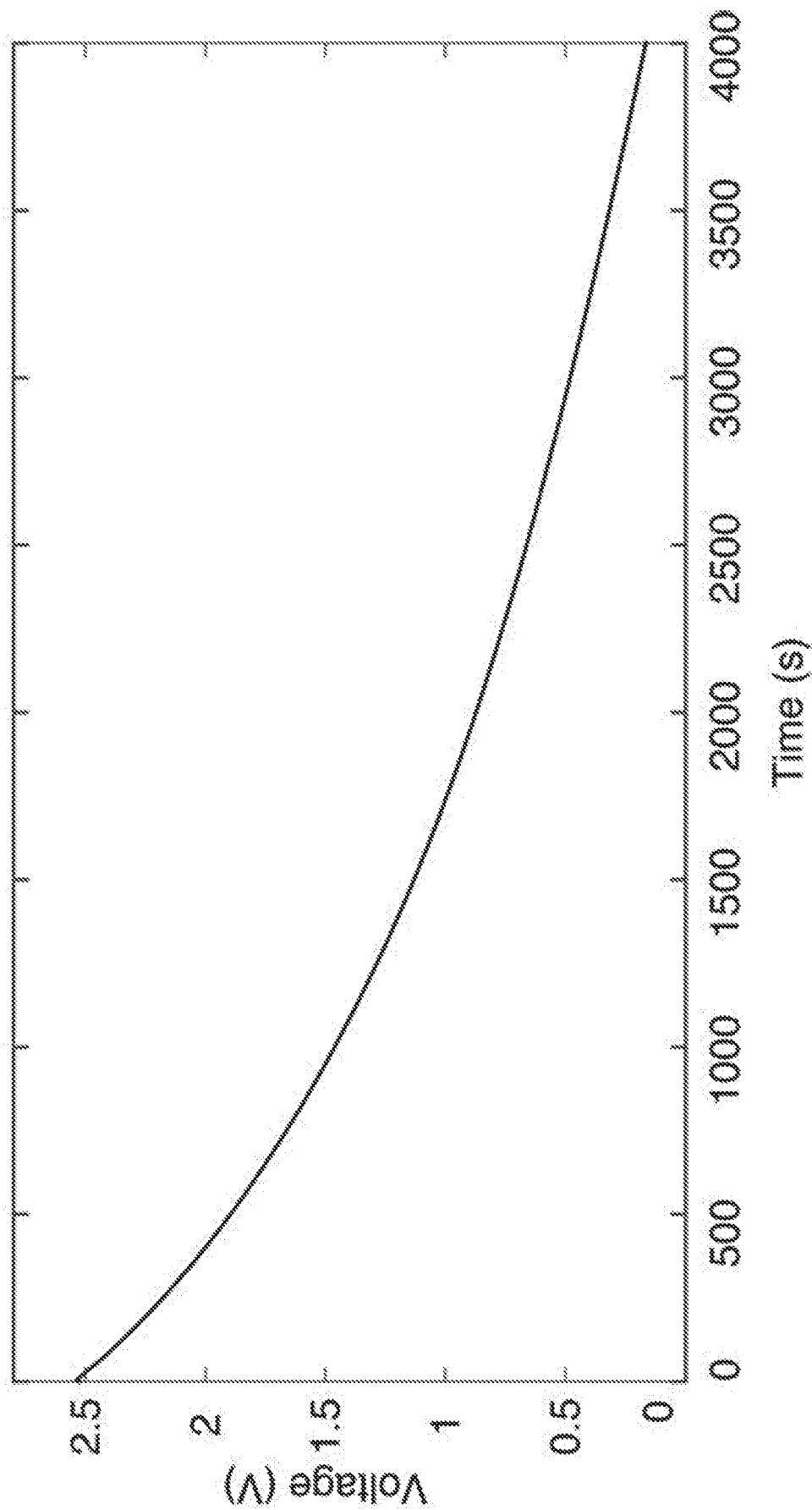
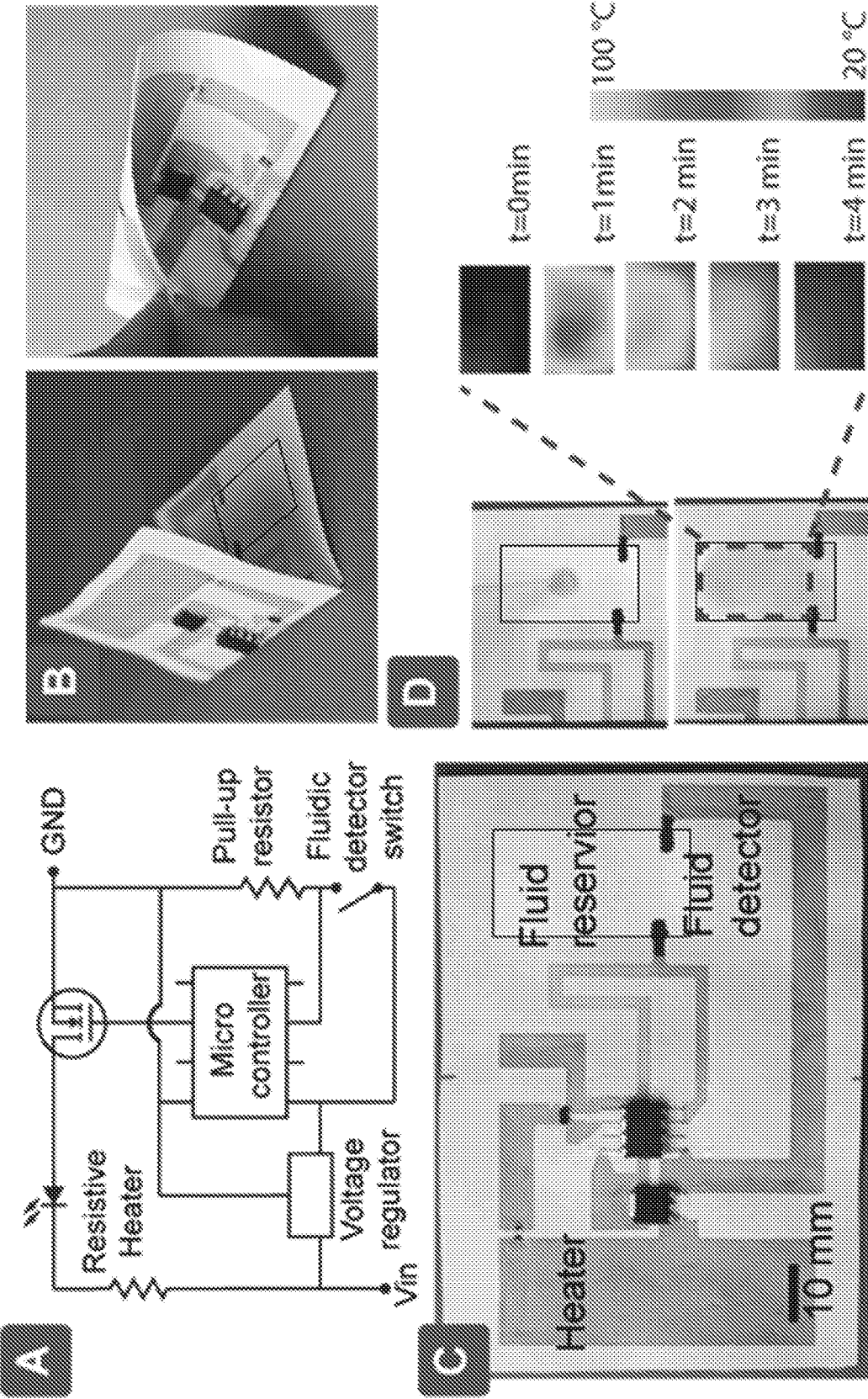


FIG. 13



FIGS. 14A-14D

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 16/50133

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B32B 3/00 (2016.01)

CPC - B32B 27/00; B44C 5/0469; B44C 1/24

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)

IPC(8): B32B 3/00 (2016.01)

CPC: B32B 27/00; B44C 5/0469; B44C 1/24

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC: 428/165,191Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatBase, Google Scholar, Google Patents, cellulose matrix, interconnected porous structure, hydrophobic barrier, thickness, electrically conducting material, carbon black, wax, carbon nanotubes, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid), paper

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2005/0079386 A1 (Brown et al.) 14 April 2005 (14.04.2005); Abstract, para [0010], [0012], [0020], [0062], [0091], [0198]	1, 3-5, 18, 20-22 ----- 2, 19
Y	US 2014/0147346 A1 (Chitnis et al.) 29 May 2014 (29.05.2014); para [0033]	2, 19
A	Yetisan et al., 'Paper-based microfluidic point-of-care diagnostic devices', Lab on a Chip, 08 May 2013, (08.05.2013) Issue 12, Abstract	1, 18

☐ Further documents are listed in the continuation of Box C.

* 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

24 October 2016

Date of mailing of the international search report

29 NOV 2016

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Lee W. Young

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 16/50133

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.: 6-17, 23-40
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.