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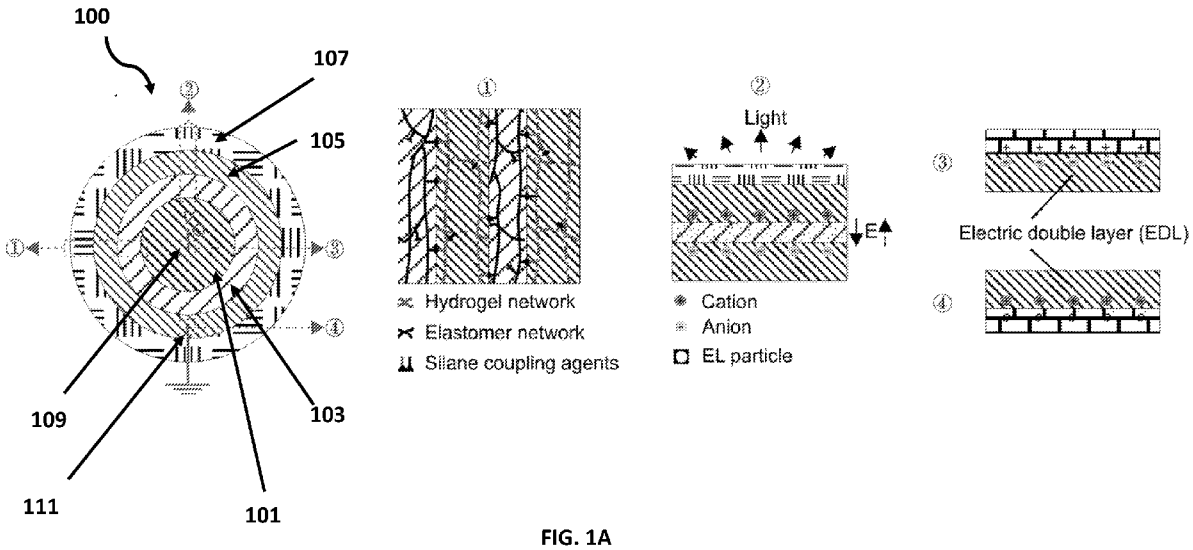

FIG. 1A

(57) Abstract: A luminescent device is described, including: a fiber-shaped core including a first hydrogel including a first hydrogel polymer, wherein the fiber-shaped core has an elongated body and a side-wall surface along the elongated body; a luminescent layer including a first elastomeric polymer and a luminescent material, coaxially disposed with the fiber-shaped core, and surrounding the fiber-shaped core's side-wall surface; a hydrophilic layer including a second hydrogel comprising a second hydrogel polymer, coaxially disposed with the fiber-shaped core, and surrounding the luminescent layer; and an elastomeric layer including a second elastomeric polymer, coaxially disposed with the fiber-shaped core, and surrounding the hydrophilic layer. Methods of fabricating the luminescent device and using the luminescent device are also described.

[Continued on next page]

WO 2019/217199 A1

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LUMINESCENT DEVICES

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit and priority of U.S. Provisional Patent Application No. 62/668,992, filed on May 9, 2018, the contents of which are hereby incorporated by reference in their entirety.

INCORPORATION BY REFERENCE

[0002] All patents, patent applications and publications cited herein are hereby incorporated by reference in their entirety in order to more fully describe the state of the art as known to those skilled therein as of the date of the invention described herein.

FIELD OF THE INVENTION

[0003] The invention relates generally to the field of luminescence. More particularly, the invention relates to electroluminescent device.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0004] This invention was made with government support from NSF MRSEC (DMR-1420570). The U.S. Government has certain rights in the invention.

SUMMARY

[0005] Described herein are luminescent devices including hydrogel material(s), elastomeric material(s), and luminescent material(s). In certain embodiments, the luminescent devices are soft and stretchable. In certain embodiments, the hydrogel material and elastomeric material are adhered together, which allows the luminescent device to be stretched while maintaining its functions. The adhesion of hydrogel material and elastomeric material may also allow the luminescent devices to have a curved design or shape, *e.g.*, a tubular shape. In certain embodiments, the hydrogel material and elastomeric material are transparent to allow the emitted light to come through.

[0006] In one aspect, a luminescent device is described, including a fiber-shaped core, a luminescent layer comprising a first elastomeric polymer and a luminescent material, a

hydrophilic layer, and an elastomeric layer, wherein the fiber-shaped core, the luminescent layer, the hydrophilic layer, and the elastomeric layer are disposed coaxially with each other. In certain embodiments, one or more of the fiber-shaped hydrogel core, the hydrogel layer, and the elastomeric layer are transparent. In certain embodiments, the fiber-shaped core is a hydrogel core. In certain embodiments, the hydrophilic layer is a hydrogel layer. In certain embodiments, one or more of the fiber-shaped hydrogel core, the hydrogel layer, and the elastomeric layer are transparent. In certain embodiments, the hydrogel layer and the elastomeric layer are transparent, allowing easy viewing of the luminescence emitted. In certain embodiments, the luminescent device is soft and/or stretchable. For instance, the luminescent device may be stretched to 1.5, 2, 3, 4, or 5 times its original length under a force, and may return to its origin length when the force is removed. A non-limiting example of the luminescent device described herein is a hydrogel ionotronic luminescent fiber ("HILF").

[0007] In one aspect, a luminescent device is described, including:

a fiber-shaped core including a first hydrogel including a first hydrogel polymer, wherein the fiber-shaped core has an elongated body and a side-wall surface along the elongated body;

a luminescent layer including a first elastomeric polymer and a luminescent material, coaxially disposed with the fiber-shaped core, and surrounding the fiber-shaped core's side-wall surface;

a hydrophilic layer including a second hydrogel including a second hydrogel polymer, coaxially disposed with the fiber-shaped core, and surrounding the luminescent layer; and

an elastomeric layer including a second elastomeric polymer, coaxially disposed with the fiber-shaped core, and surrounding the hydrophilic layer.

[0008] In any one or more of the embodiments described herein, the hydrophilic layer is a hydrogel layer.

[0009] In any one or more of the embodiments described herein, the first and/or second hydrogels further include a salt.

[0010] In any one or more of the embodiments described herein, the salt is selected from the group consisting of LiCl, NaCl, KCl, $MgCl_2$, $NaNO_3$, KNO_3, CH_3COOK, Na_2SO_4, K_2SO_4, $Na_2B_4O_7$, and a combination thereof.

[0011] In any one or more of the embodiments described herein, the first and second hydrogel polymers are each independently selected from the group consisting poly(hydroxyethylmethacrylate) (PHEMA), poly(acrylamide) (PAAm), poly(dimethylacrylamide) (PDMA), poly(N-isopropylacrylamide) (PNIPAM), sodium polyacrylate (NaPAA), [2-(Acryloyloxy)ethyl] trimethylammonium chloride (PDMAEA), alginate, chitosan, cellulose, polyvinyl alcohol (PVA), poly(lactic acid) (PLA), hyaluronic acid, poly (ethylene glycol) (PEG), and a combination thereof.

[0012] In any one or more of the embodiments described herein, the first and second hydrogel polymers are both poly(acrylamide) (PAAm).

[0013] In any one or more of the embodiments described herein, the fiber-shaped core has two end surfaces and a cross-section surface each independently having a shape selected from the group consisting of circle, oval, square, triangle, rectangle, diamond, trapezoidal, pentagon, hexagon, heptagon, and octagon.

[0014] In any one or more of the embodiments described herein, the first and second elastomeric polymers are each independently selected from the group consisting of polydimethylsiloxane (PDMS), Ecoflex, polyurethane (PU), poly (isoprene), and poly (butadiene).

[0015] In any one or more of the embodiments described herein, the first and second elastomeric polymers are each polydimethylsiloxane (PDMS).

[0016] In any one or more of the embodiments described herein, the luminescent material is selected from the group consisting of ZnS doped with copper (Cu), aluminum (Al), chloride (Cl), bromine (Br), iodine (I), or manganese (Mn), ZnSe doped with Cu or Cl, ZnCdS doped with Cu, Cl, Mn, or silver (Ag), ZnSSe doped with Cu or Cl, and a combination thereof.

[0017] In any one or more of the embodiments described herein, the luminescent layer adheres to the fiber-shaped core.

[0018] In any one or more of the embodiments described herein, the first hydrogel polymer comprises a first coupling agent, the first elastomeric polymer comprises a second coupling agent, and covalent bonds formed by reacting the first and second coupling agents adhere together the luminescent layer and the fiber-shaped core.

[0019] In any one or more of the embodiments described herein, the covalent bond is a siloxy bond (Si-O-Si) and the first and second coupling agents each comprises a molecular moiety comprising a silicon atom linked to a functional group selected from a group consisting of OH, Cl, Br, I, OPh, ester, and sulfonate ester.

[0020] In any one or more of the embodiments described herein, the first hydrogel polymer and/or the first elastomeric polymer are cross-linked.

[0021] In any one or more of the embodiments described herein, the hydrophilic layer adheres to the luminescent layer.

[0022] In any one or more of the embodiments described herein, the second hydrogel polymer comprises a third coupling agent, the first elastomeric polymer comprises a fourth coupling agent, and covalent bonds formed by reacting the third and fourth coupling agents adhere together the hydrophilic layer and the luminescent layer.

[0023] In any one or more of the embodiments described herein, the covalent bond is a siloxy bond (Si-O-Si) and the third and fourth coupling agents each comprises a molecular moiety comprising a silicon atom linked to a functional group selected from a group consisting of OH, Cl, Br, I, OPh, ester, and sulfonate ester.

[0024] In any one or more of the embodiments described herein, the luminescent device further includes a first adhesion polymeric network comprising a plurality of first adhesion polymer chains joined together by a bonding force and interwoven with the second hydrogel polymer to adhere together the luminescent layer and the hydrophilic layer; wherein the first adhesion polymeric network is covalently bonded to the first elastomeric polymer while topologically bonded to the second hydrogel polymer.

[0025] In any one or more of the embodiments described herein, each of the first adhesion polymer chains is independently selected from the group consisting of poly(4-aminestyrene), chitosan, alginate, cellulose, poly(N-isopropylacrylamide), polymers

containing silane groups and/or catechol groups, a copolymer thereof, a terpolymer thereof, and a block copolymer thereof.

[0026] In any one or more of the embodiments described herein, the second hydrogel polymer and/or the first elastomeric polymer are cross-linked.

[0027] In any one or more of the embodiments described herein, the elastomeric layer adheres to the hydrophilic layer.

[0028] In any one or more of the embodiments described herein, the second hydrogel polymer comprises a fifth coupling agent, the second elastomeric polymer comprises a sixth coupling agent, and covalent bonds formed by reacting the fifth and sixth coupling agents adhere together the hydrophilic layer and the elastomeric layer.

[0029] In any one or more of the embodiments described herein, the covalent bond is a siloxy bond (Si-O-Si) and the fifth and sixth coupling agents each comprises a molecular moiety comprising a silicon atom linked to a functional group selected from a group consisting of OH, Cl, Br, I, OPh, ester, and sulfonate ester.

[0030] In any one or more of the embodiments described herein, the silicon atom is linked to OH.

[0031] In any one or more of the embodiments described herein, the silicon atom is linked to Cl.

[0032] In any one or more of the embodiments described herein, the bonding force results from a bond or interaction selected from the group consisting of hydrogen bond, ionic bond, van der Waals interaction, covalent bond, π–π stacking, cation-π interaction, host-guest interaction, and a combination thereof.

[0033] In any one or more of the embodiments described herein, the luminescent layer further comprises a hydrophilic polymer covalently bonded to the first elastomeric polymer.

[0034] In any one or more of the embodiments described herein, the hydrophilic polymer comprises a seventh coupling agent, the first elastomeric polymer comprises an eighth coupling agent, and the covalent bonds are formed by reacting the seventh and the eighth coupling agents.

[0035] In any one or more of the embodiments described herein, the hydrophilic polymer is the second hydrogel polymer.

[0036] In any one or more of the embodiments described herein, the covalent bond is a siloxy bond (Si-O-Si) and the seventh and eighth coupling agents each comprises a molecular moiety comprising a silicon atom linked to a functional group selected from a group consisting of OH, Cl, Br, I, OPh, ester, and sulfonate ester.

[0037] In any one or more of the embodiments described herein, the fiber-shaped core further comprises a first electrode and the hydrophilic layer further comprises a second electrode.

[0038] In any one or more of the embodiments described herein, the first and/or second electrodes are made from carbon or an inert metal.

[0039] In any one or more of the embodiments described herein, the first elastomeric polymer and the luminescent material have a weight ratio of about 1:1.

[0040] In any one or more of the embodiments described herein, one or more of the fiber-shaped core, the hydrophilic layer, and the elastomeric layer are transparent.

[0041] In any one or more of the embodiments described herein, the luminescent device is soft and/or stretchable.

[0042] In any one or more of the embodiments described herein, the luminescent device is stretchable to 1.5, 2, 3, 4 or 5 times of its original length.

[0043] In any one or more of the embodiments described herein, the fiber-shaped core is a hydrogel core.

[0044] In another aspect, a method of providing luminescence is described, including:

providing a luminescent device of any one of the embodiments described herein;

applying a voltage between the fiber-shaped core and the hydrophilic layer; and

activating the luminescent material to emit luminescence.

[0045] In any one or more of the embodiments described herein, the fiber-shaped core further comprises a first electrode and the hydrophilic layer further comprises a second electrode, and the voltage is applied to the first and second electrodes.

[0046] In any one or more of the embodiments described herein, the voltage is an alternating voltage.

[0047] In any one or more of the embodiments described herein, the voltage ranges from 100 volts to 1 kilovolt.

[0048] In yet another aspect, a method of fabricating the luminescent device of any one of the embodiments described herein is disclosed, including:

providing the fiber-shaped core comprising the first hydrogel comprising the first hydrogel polymer;

disposing the luminescent layer comprising the first elastomeric polymer coaxially with the fiber-shaped core and surrounding the fiber-shaped core's side-wall surface;

disposing the hydrophilic layer comprising the second hydrogel polymer coaxially with the fiber-shaped core and surrounding the luminescent layer; and

disposing the elastomeric layer coaxially with the fiber-shaped core and surrounding the hydrophilic layer.

[0049] In any one or more of the embodiments described herein, step (3) further comprises coating the luminescent layer with a coating comprises a hydrophilic polymer. In any one or more of the embodiments described herein, the hydrophilic layer is disposed onto and surrounding the coating comprising the hydrophilic polymer.

[0050] In any one or more of the embodiments described herein, the hydrophilic polymer comprises a ninth coupling agent, the first elastomeric polymer comprises a tenth coupling agent, and the method comprises forming covalent bonds by reacting the ninth and tenth coupling agents.

[0051] In any one or more of the embodiments described herein, the ninth and tenth coupling agents each comprises a molecular moiety comprising a silicon atom linked to a functional group selected from a group consisting of OH, Cl, Br, I, OPh, ester, and sulfonate ester. In any one or more of the embodiments described herein, the hydrophilic polymer

forms covalent bonds with the second hydrogel polymer, topologically entangled with the second hydrogel polymer, or both.

[0052] In any one or more of the embodiments described herein, the hydrophilic polymer is the second hydrogel polymer.

[0053] In any one or more of the embodiments described herein, the method further includes providing a first electrode into the fiber-shaped core and providing a second electrode into the hydrophilic layer.

[0054] In yet another aspect, a method of increasing hydrophilicity of a hydrophobic polymer's surface is described, including:

providing a hydrophobic polymer comprising an eleventh coupling agent;

providing a hydrophilic polymer comprising a twelfth coupling agent; and

reacting the eleventh coupling agent and the twelfth coupling agent to form covalent bonds.

[0055] In any one or more of the embodiments described herein, the covalent bond is a siloxy bond (Si-O-Si) and the eleventh and twelfth coupling agents each comprises a molecular moiety comprising a silicon atom linked to a functional group selected from a group consisting of OH, Cl, Br, I, OPh, ester, and sulfonate ester.

[0056] In any one or more of the embodiments described herein, the hydrophobic polymer is selected from the group consisting of polydimethylsiloxane (PDMS), Ecoflex, polyurethane (PU), poly (isoprene), and poly (butadiene).

[0057] In any one or more of the embodiments described herein, the hydrophilic polymer is selected from the group consisting poly(hydroxyethylmethacrylate) (PHEMA), poly(acrylamide) (PAAm), poly(dimethylacrylamide) (PDMA), poly(N-isopropylacrylamide) (PNIPAM), sodium polyacrylate (NaPAA), [2-(Acryloyloxy)ethyl] trimethylammonium chloride (PDMAEA), alginate, chitosan, cellulose, polyvinyl alcohol (PVA), poly(lactic acid) (PLA), hyaluronic acid, poly (ethylene glycol) (PEG), and a combination thereof.

[0058] In yet another aspect, a luminescent device is described, including:

one or more first composite fibers each comprising:

a first fiber-shaped core comprising a first hydrogel comprising a first hydrogel polymer, wherein the first fiber-shaped core has an elongated body and a side-wall surface along the elongated body; and

a luminescent layer comprising a first elastomeric polymer and a luminescent material, coaxially disposed with the first fiber-shaped core, and surrounding the first fiber-shaped core's side-wall surface; and

one or more second composite fibers each comprising:

a second fiber-shaped core comprising a second hydrogel comprising a second hydrogel polymer, wherein the second fiber-shaped core has an elongated body and a side-wall surface along the elongated body; and

an elastomeric layer comprising a second elastomeric polymer, coaxially disposed with the second fiber-shaped core, and surrounding the second fiber-shaped core's side-wall surface;

wherein at least one of the first composite fibers and at least one of the second composite fibers are disposed at an angle such that the first and second composite fibers at least partially overlap.

[0059] In any one or more of the embodiments described herein, the angle is less than 180 degrees and more than 0 degree.

[0060] In any one or more of the embodiments described herein, the first and/or second hydrogels further comprise a salt.

[0061] In any one or more of the embodiments described herein, the first and second hydrogel polymers are each independently selected from the group consisting poly(hydroxyethylmethacrylate) (PHEMA), poly(acrylamide) (PAAm), poly(dimethylacrylamide) (PDMA), poly(N-isopropylacrylamide) (PNIPAM), sodium polyacrylate (NaPAA), [2-(Acryloyloxy)ethyl] trimethylammonium chloride (PDMAEA), alginate, chitosan, cellulose, polyvinyl alcohol (PVA), poly(lactic acid) (PLA), hyaluronic acid, poly (ethylene glycol) (PEG), and a combination thereof.

[0062] In any one or more of the embodiments described herein, the first and/or second fiber-shaped cores each have two end surfaces and a cross-section surface each having a

shape independently selected from the group consisting of circle, oval, square, triangle, rectangle, diamond, trapezoidal, pentagon, hexagon, heptagon, and octagon.

[0063] In any one or more of the embodiments described herein, the first and second elastomeric polymers are each independently selected from the group consisting of polydimethylsiloxane (PDMS), Ecoflex, polyurethane (PU), poly (isoprene), and poly (butadiene).

[0064] In any one or more of the embodiments described herein, the luminescent material is selected from the group consisting of ZnS doped with copper (Cu), aluminum (Al), chloride (Cl), bromine (Br), iodine (I), or manganese (Mn), ZnSe doped with Cu or Cl, ZnCdS doped with Cu, Cl, Mn, or silver (Ag), and ZnSSe doped with Cu or Cl.

[0065] In any one or more of the embodiments described herein, the luminescent layer adheres to the first fiber-shaped core.

[0066] In any one or more of the embodiments described herein, the elastomeric layer adheres to the second fiber-shaped core.

[0067] In any one or more of the embodiments described herein, the first fiber-shaped core further comprises a first electrode and the second fiber-shaped core further comprises a second electrode.

[0068] In any one or more of the embodiments described herein, the luminescent device is soft and/or stretchable.

[0069] In any one or more of the embodiments described herein, the luminescent device comprises a plurality of the first composite fibers parallel to each other, a plurality of the second composite fibers parallel to each other; and wherein the first and second composite fibers form a grid.

[0070] In any one or more of the embodiments described herein, the angle is less than 180 degrees and more than 0 degree.

[0071] In yet another aspect, a method of providing luminescence is described, including:

providing a luminescent device of any one of the embodiments described herein;

applying a voltage between the first and second fiber-shaped cores; and

activating the luminescent material to emit luminescence at the area wherein the first and second composite fibers partially overlap.

[0072] In any one or more of the embodiments described herein, the first fiber-shaped core further comprises a first electrode and the second fiber-shaped core further comprises a second electrode, and the voltage is applied to the first and second electrodes.

[0073] In any one or more of the embodiments described herein, the voltage is an alternating voltage.

[0074] In any one or more of the embodiments described herein, the voltage ranges from 100 volts to 1 kilovolt.

[0075] Any aspect or embodiment disclosed herein may be combined with another aspect or embodiment disclosed herein. The combination of one or more embodiments described herein with other one or more embodiments described herein is expressly contemplated.

[0076] As used herein, the term "polymer" includes, but is not limited to, the homopolymer, copolymer, terpolymer, and block copolymer, and random copolymers and terpolymers of that polymer. As used herein, copolymer refers to a polymer derived from two monomeric species; similarly, a terpolymer refers to a polymer derived from three monomeric species. Block copolymers include, but are not limited to, block, graft, dendrimer, and star polymers. The polymer also includes various morphologies, including, but not limited to, linear polymer, branched polymer, crosslinked polymer, and dendrimer systems. As an example, polyacrylamide polymer refers to any polymer including polyacrylamide, *e.g.*, a homopolymer, copolymer, terpolymer, block copolymer, or terpolymer of polyacrylamide. Polyacrylamide can be a linear polymer, branched polymer, crosslinked polymer, or a dendrimer of polyacrylamide. As used herein, a "hydrogel polymer" refers to the polymer contained in a hydrogel.

[0077] As used herein, the term "polymer chain" refers to a molecular chain formed by multiple repeat units that are covalently linked to one another, where a portion of the polymer chain (*e.g.*, less than about 10%, 5%, 3%, or 1% of the monomer repeating units in the polymer chain) may optionally be branched or crosslinked. As used herein, "polymeric network" refers to a plurality of polymer chains optionally branched or crosslinked at a

certain monomer repeating unit (*e.g.*, about or less than about 10%, 5%, 3%, or 1% of the monomer repeating units in the polymer chain). As used herein, the "adhesion polymeric chain" refers to a polymer which is capable of interweaving into the first and second polymeric networks of the first and second materials, respectively, but optionally does not form any covalent bond with the first and second polymeric networks or the first and second materials. As used herein, the "adhesion polymeric network" refers to a polymeric network formed by joining a plurality of the adhesion polymer chains together by a bonding force, where the adhesion polymeric network is interwoven with the first and second polymeric networks to adhere the first and second materials together. In some condiments, the adhesion polymeric network is stable, stretchable and/or flexible. As used herein, the term "interweave" or "interwoven" refers to the phenomena where two or more polymer chains or polymeric networks, or a polymer chain and a polymeric network, weave or become woven together.

[0078] Unless otherwise defined, used, or characterized herein, terms that are used herein (including technical and scientific terms) are to be interpreted as having a meaning that is consistent with their accepted meaning in the context of the relevant art and are not to be interpreted in an idealized or overly formal sense unless expressly so defined herein.

[0079] Although the terms, first, second, third, etc., may be used herein to describe various elements, these elements are not to be limited by these terms. These terms are simply used to distinguish one element from another. Thus, a first element, discussed below, could be termed a second element without departing from the teachings of the exemplary embodiments. Spatially relative terms, such as "above," "below," "left," "right," "in front," "behind," and the like, may be used herein for ease of description to describe the relationship of one element to another element, as illustrated in the figures. It will be understood that the spatially relative terms, as well as the illustrated configurations, are intended to encompass different orientations of the apparatus in use or operation in addition to the orientations described herein and depicted in the figures. For example, if the apparatus in the figures is turned over, elements described as "below" or "beneath" other elements or features would then be oriented "above" the other elements or features. Thus, the exemplary term, "above," may encompass both an orientation of above and below. The apparatus may be otherwise oriented (*e.g.*, rotated 90 degrees or at other orientations) and the spatially relative descriptors used herein interpreted accordingly. Further still, in this disclosure, when an element is

referred to as being "linked to," "on," "connected to," "coupled to," "in contact with," etc., another element, it may be directly linked to, on, connected to, coupled to, or in contact with the other element or intervening elements may be present unless otherwise specified.

[0080] The terminology used herein is for the purpose of describing particular embodiments and is not intended to be limiting of exemplary embodiments. As used herein, singular forms, such as "a" and "an," are intended to include the plural forms as well, unless the context indicates otherwise. Additionally, the terms, "includes," "including," "comprises," and "comprising" specify the presence of the stated elements or steps but do not preclude the presence or addition of one or more other elements or steps.

DESCRIPTION OF THE DRAWINGS

[0081] The invention is described with reference to the following figures, which are presented for the purpose of illustration only and are not intended to be limiting. In the Drawings:

[0082] FIGS. 1A-1F demonstrate the principle, fabrication, and structure of a luminescent device (also referred to as a hydrogel ionotronic luminescent fiber (HILF) in certain embodiments), according to one or more embodiments described herein. FIG. 1A illustrates an HILF including a hydrogel core, an EL layer, a hydrogel, and an elastomer coating. FIG. 1B shows the schematic of the fabrication process of a HILF. FIG. 1C shows the cross-sectional view of a HILF. The hydrogels are polyacrylamide (PAAm) hydrogels containing 8.0 M lithium chloride, the EL layer is ZnS particles dispersed PDMS with weight ratio of 1:1. The elastomer coating is PDMS. The thickness of EL layer is ~150 μm. FIG. 1D shows the SEM image of ZnS particles dispersed PDMS. The size of ZnS particle ranges from ~10 μm to ~50 μm. FIG. 1E shows a photograph of a HILF at bent state. The applied electric field is ~3 V μm^{-1} with frequency 1 kHz. FIG. 1F shows a luminescent device described herein and its cross-sectional view.

[0083] FIGS. 2A-2G show wetting behaviors and microscopic characterizations of the luminescent device, according to one or more embodiments described herein. Photographs showing various wetting behaviors and schematics showing various wetting mechanism of DI water on the surface of untreated PDMS in FIG. 2A, PDMS precursor on the surface of PAAm hydrogel in FIG. 2B, and DI water on the surface of PAAm hydrogel resin treated PDMS in FIG. 2C. FIG. 2D shows the contact angle evolutions of various cases (n=3). The

evolution of PDMS on PAAm hydrogel obeys a power law with a power index of -0.33. FIG. 2E shows the SEM images of the surface of untreated PDMS, showing homogeneous surface. FIG. 2F shows SEM image of the surface of PAAm hydrogel resin-treated PDMS, showing cracked surface. FIG. 2G shows an XPS survey of the surfaces of untreated PDMS and PAAm hydrogel resin treated PDMS. Four elements (C1s, N1s, O1s, Si2s, and Si2p) are tracked. PAAm hydrogel resin-treated PDMS surface shows obvious N1s absorption while untreated PDMS surface does not.

[0084] FIGS. 3A-3F shows the performances of a luminescent device (also referred to as a hydrogel ionotronic luminescent fiber (HILF) in certain embodiments), according to one or more embodiments described herein. FIG. 3A shows the luminance-time curve and voltage-time curve. The HILF responds accordingly to the applied electric field of ~5 V μm^{-1} and 1 kHz. FIG. 3B shows luminance as a function of electric field intensity. Insets: Images of a HILF subject to various electric fields as indicated. FIG. 3C shows luminance as a function of frequency with fixed electric field of ~6 V μm^{-1}. FIG. 3D shows photographs of a HILF at various stretched states at ~5 V μm^{-1}. FIG. 3E shows stress-stretch curves of PDMS, EL layer, PAAm hydrogel, and the HILF. The inset zooms in the curves at small stress range. FIG. 3F shows fatigue behaviors of a HILF regarding electro-optical performance and mechanical performance (n=3) along with images of a HILF at undeformed state at different stretch cycles.

[0085] FIGS. 4A-4H shows hydrogel ionotronic luminescent devices of various kinds, an embodiment of the luminescent device described herein. FIG. 4A shows a fabric display including two types of fibers assembled in rows and columns. FIG. 4B shows that each junction of the fabric display forms a pixel. When a voltage is applied, only the junctions light up while the remaining parts do not. FIG. 4C shows that the pixels are movable. The movable pixels can display more information by changing arrangement of the fibers. FIG. 4D shows an EL closed ring containing PAAm hydrogel core (421) and three closed cylindrical shells: EL layer shell (423), PAAm hydrogel shell (425), and PDMS shell (427). FIG. 4E shows an EL handbag having a cage structure and is viewed from different angles. FIG. 4F shows multi-color luminescent device described herein (the colors are labeled in the Figure) (also referred to as "HILF" in certain embodiments). FIG. 4G shows an EL heart made of one orange luminescent device and one blue luminescent device (the colors are labeled in the Figure) (the luminescent device may be referred to as "HILF" in certain

embodiments). FIG. 4H shows an "EL" pattern made of multi-color luminescent device described herein (the colors are labeled in the Figure) (also referred to as "HILF" in certain embodiments).

[0086] FIG. 5A demonstrates that in a silane coupling agent, a silicon atom links three hydrolyzable groups such as hydroxy, acetoxy, or Cl, and an organofunctional group, according to one or more embodiments described herein. In the presence of water, the hydrolyzable groups hydrolyze into silanol groups. The silanol groups undergo condensation to form a siloxane bond. FIG. 5B shows that during the formation of a polymer network, the organofunctional group covalently incorporates the silane coupling agent into the network. In hydrogel, the hydrolyzable groups are readily hydrolyzed into silanol groups, while in elastomer, the hydrolyzable groups do no hydrolyze due to the low water content within the elastomer matrix. When elastomer contacts with hydrogel, hydrolyzable groups on the surface of elastomer meet water and hydrolyze into silanol groups. After condensation, hydrogel network and elastomer network are bonded covalently.

[0087] FIG. 6A shows digital images of spin-coated EL films with different ZnS particle content on Perspex substrates, and corresponding images at EL state under a sinusoidal voltage of amplitude 500 V and frequency 1000 Hz. The spin coating speed and time are 450 rpm and 60 seconds, respectively. FIG. 6B shows luminance as a function of voltage with various contents of ZnS particles. The EL intensity increases with the increasing amount of ZnS particles, but the blend becomes a slurry, thereby not being possible for dip-coating when too many ZnS particles are added. To balance the EL intensity and the feasibility of dip-coating, weight ratio of ZnS particles to PDMS is fixed at 1:1.

[0088] FIG. 7A shows digital and microscopic images of EL layer coated hydrogel fibers with different coating times. FIG. 7B illustrates the thickness of the EL layer varies with coating time. n=5. A higher voltage is required for electroluminescence due to the thicker EL layer when the coating times are more (e.g. 3 or 4 times), while the EL particle density becomes too low to fully cover the fiber surface when the coating times are less (e.g. 1 time). As a result, the dip-coating time of EL layer is fixed at 2. As used herein, n=5 means that 5 parallel samples are tested and averaged. Similarly, n=3 means that 3 parallel samples are tested and averaged.

[0089] FIGS. 8A-8B demonstrate peeling tests of PAAm hydrogel on pure PDMS substrate and ZnS particles dispersed PDMS (weight ratio 1:1) substrate, respectively, according to one or more embodiments described herein. FIG. 8A shows that during the tests, fracture of PAAm hydrogel happens and hydrogel residue on the substrate is observed in both cases. FIG. 8B shows the force-displacement curves. PAAm hydrogel on pure PDMS substrate gives an adhesion energy of ~46.4 J m^{-2}, and PAAm hydrogel on ZnS particles dispersed PDMS substrate gives an adhesion energy of ~50.7 J m^{-2}. Embedding ZnS particles into PDMS matrix does not affect the adhesion. n=3.

[0090] FIG. 9A shows the cut-away view of a luminescent device with the hydrogel core connected to a voltage source and the hydrogel grounded. The radius of hydrogel core is *a*, the external radius of EL layer is *b*, the external radius of hydrogel is *c*, and the length of the luminescent device is *l*. FIG. 9B shows the equivalent circuit of the luminescent device under a voltage.

[0091] FIG. 10 shows the peeling tests of casting PDMS precursor on preformed PAAm hydrogel and casting PAAm precursor on preformed PDMS. Casting PDMS on PAAm hydrogel gives an adhesion energy of ~51.4 J m^{-2}, and casting PAAm hydrogel on PDMS gives an adhesion energy of ~54.4 J m^{-2}. After peeling tests, PAAm hydrogel residues are observed in both cases, indicating that fracture occurs in the hydrogel instead of the interface. The fabrication sequence does not affect the adhesion (n=3).

[0092] FIG. 11A shows that water does not wet the untreated surface of EL layer. Dip-coating of untreated fiber results in an inhomogeneous hydrogel layer. FIG. 11B shows that water wets the PAAm hydrogel resin-treated surface of EL layer. Dip-coating of treated surface results in a homogeneous hydrogel layer.

[0093] FIG. 12 shows complete wetting of a PDMS droplet on the surface of a PAAm hydrogel after 24 hours. The dash lines indicate the edges of PDMS.

[0094] FIG. 13 shows normalized luminance of a luminescent device versus applied voltage.

[0095] FIG. 14 shows the dependence of luminance on view angle of the luminescent device. The luminescent device possesses a one-dimensional structure and luminance in all directions, so that the brightness of the luminescent device is independent of view angle. n=3.

[0096] FIG. 15A shows the resistance of PAAm hydrogel fiber under cyclic loading and unloading. FIG. 15B shows R/R_0 as a function of stretch λ. R: resistance of hydrogel fiber at deformed state. R_0: resistance of hydrogel fiber at undeformed state.

[0097] FIG. 16A shows the stretchabilities of PDMS, EL layer, HILF, and PAAm hydrogel. FIG. 16B shows the moduli of PDMS, EL layer, HILF, and PAAm hydrogel. From the cross-sectional view of the HILF, the area fractions of three components are estimated as: PDMS ~15.1%, EL layer ~10.2%, and hydrogel 74.7%. The modulus of HILF can be estimated as $E_{PDMS}\times 0.151+E_{EL\ layer}\times 0.102+E_{hydrogel}\times 0.747$, and E_{HILF} ~268.0 kPa is obtained, which agrees with the value calculated from experimental measurement, ~246.9 kPa. n=5.

[0098] FIG. 17 shows fatigue test of the luminescent device. Cyclic loading and unloading is conducted with a maximum stretch of 2 up to 10000 cycles. The peak stress in each cycle only drops slightly from ~32.0 kPa to ~31 kPa, and the hysteresis already stabilizes after 10 cycles. n=3.

[0099] FIGS. 18A-18D shows passive matrix addressing circuit for fabric display. FIG. 18A shows the pattern of row and column of a fabric display with $N \times n$ pixels. The dash lines represent EL layer coated PAAm hydrogel fibers and the solid lines represent PDMS coated PAAm hydrogel fibers. FIG. 18B shows the typical sequential scanning pulses for row addressing in a passive matrix with frame period, T_{frame}, and pulse width, T_{on}. FIG. 18C shows schematic showing the structure of one fabric display pixel. Diameter of the hydrogel fiber is D, and thickness of the coating is d. FIG. 18D shows the equivalent circuit of one fabric display pixel.

[0100] FIGS. 19A-19B show a luminescent device, *e.g.*, a hydrogel ionotronic luminescent device, fabricated by direct assembling, accordingly one or more embodiments described herein. FIG. 19A shows the schematic of the multi-layer assembling and top-view image of the device at EL state. FIG. 19B shows the adhesion between hydrogel and EL layer allows the device to operate at upside-down and bent state without delamination.

[0101] FIG. 20 shows luminescent devices, *e.g.*, hydrogel ionotronic luminescent devices, of various colors, accordingly one or more embodiments described herein. Blue (B), orange (O), and green (G) particles are used solely, or mixed in certain weight ratios as indicated. In

all devices, the EL layers are made via spin-coating at a fixed speed of 450 rpm for 60 seconds. The resulting EL layer thickness is ~300 μm. The applied voltage is sinusoidal with amplitude 300 V and frequency 1 kHz.

[0102] FIG. 21A shows the emission spectra of various luminescent devices, *e.g.*, hydrogel ionotronic luminescent devices, accordingly one or more embodiments described herein. FIG. 21B shows the CIE chromaticity diagram of various EL devices. The chromaticity coordinates are: Blue (0.2674, 0.2609), Orange (0.3411, 0.3377), Green (0.2782, 0.3535), O:B=7:3 (0.3231,0.3437), O:B=8:2 (0.3315, 0.3528), and O:G=9:1 (0.337, 0.3432).

[0103] FIG. 22 shows rheology tests of various contents of chain transfer agent (10% v/v MPTMS in THF). 1 μl chain transfer agent results in hydrogel resin that is too viscous, while 5 μl and 10 μl chain transfer agents result in hydrogel resins that are too dilute for dip-coating. 10 μl chain transfer agent is used for hydrogel resin treatment and 2.5 μl chain transfer agent is used for dip-coating. Here the volume of chain transfer agent is relative to 1 ml of 2 M acrylamide solution.

[0104] FIG. 23 shows the schematic of a contact angle measuring set-up. A backlight is fed through from one end of an opaque tube, projecting on the target liquid drop on the other end of the tube. A digital camera is set up to focus on the liquid drop. The images are taken in darkroom conditions.

DETAILED DESCRIPTION

[0105] Protection and aesthetics are the two common attributes of textiles as clothing. But nowadays, the functions of textiles have gone far beyond these attributes. "Intelligent" textiles are becoming increasingly important to meet the fast-growing demands for mobile and wearable applications. Smart textile components may include new functionalities, such as body temperature modulation, communication, energy harvesting and energy storage, sensing, and lighting. Some exemplary light-emitting textiles include lighting vests for public safety and decorative clothes for entertainment, produced via direct integration of light-emitting diodes or attachment of light-emitting materials onto planar textiles via layer-by-layer lamination. However, it remains a challenge to make stretchable light-emitting textiles due to the simultaneous requirement of high stretchability and high transparency for the conductors.

[0106] Hydrogels are highly stretchable and transparent ionic conductors. Hydrogels can host ions of multiple moles per liter concentration in order to gain a resistivity of ~10^{-1} Ω m. Even though this resistivity is much higher than that of conventional electronic conductors (*e.g.*, ~ 10^{-8} Ω m for copper), a millimeter-thick hydrogel can achieve a surface resistance of 100 Ω sq^{-1}, and still retain an optical transparency of 99.9%. Hydrogels can sustain large deformation, recover elastically over a large number of cycles, and maintain conductivity even under a large stretch. Hydrogels can be as tough as natural rubber and retain water in low-humidity environment.

[0107] A hydrogel network is hydrophilic. An elastomer network, on the other hand, is hydrophobic. Consequently, the adhesion energy between a hydrogel and an elastomer is inherently weak, *e.g.*, < 1 J m^{-2}. Such weak adhesion easily causes delamination between the hydrogel and elastomer under deformation. In addition, the weak adhesion restricts the design of devices including hydrogels and elastomers, since hydrogels easily detach from elastomers in surfaces with curved or sharp convex configurations. Indeed, hydrogels are in contact with elastomers without forming strong adhesion, and only planar architectures can be used in previous devices.

Luminescent device including a fiber-shaped core, a luminescent layer, a hydrophilic layer, and an elastomeric layer

[0108] In one aspect, a luminescent device is described, including:

a fiber-shaped core including a first hydrogel comprising a first hydrogel polymer, wherein the fiber-shaped core has an elongated body and a side-wall surface along the elongated body;

a luminescent layer including a first elastomeric polymer and a luminescent material, coaxially disposed with the fiber-shaped core, and surrounding the fiber-shaped core's side-wall surface;

a hydrophilic layer including a second hydrogel comprising a second hydrogel polymer, coaxially disposed with the fiber-shaped core, and surrounding the luminescent layer; and

an elastomeric layer including a second elastomeric polymer, coaxially disposed with the fiber-shaped core, and surrounding the hydrophilic layer.

[0109] In some embodiments, the luminescent device includes:

a fiber-shaped core including a first hydrogel comprising a first hydrogel polymer, wherein the fiber-shaped hydrogel core has an elongated body and a side-wall surface along the elongated body;

a luminescent layer including a first elastomeric polymer and a luminescent material, coaxially disposed with the fiber-shaped core, and surrounding the fiber-shaped core's side-wall surface;

a hydrogel layer including a second hydrogel comprising a second hydrogel polymer, coaxially disposed with the fiber-shaped core, and surrounding the luminescent layer; and

an elastomeric layer including a second elastomeric polymer, coaxially disposed with the fiber-shaped core, and surrounding the hydrogel layer.

[0110] The luminescent device is described in more detail with reference to FIGS. 1A and 1F, which provide non-limiting examples of the aspects and/or embodiments of the luminescent device disclosed herein. FIG. 1F shows a luminescent device 100 which has an overall tubular fiber shape. As shown in the cross-section view of the luminescent device 100 in FIGS. 1A and 1F, the luminescent device 100 includes a fiber-shaped core (*e.g.*, a hydrogel core) 101 including a first hydrogel including a first hydrogel polymer, where the fiber-shaped core has an elongated body and a side-wall surface along the elongated body. The luminescent device 100 also includes a luminescent layer 103 including a first elastomeric polymer and a luminescent material, coaxially disposed with the fiber-shaped hydrogel core 101, and surrounding the fiber-shaped core's side-wall surface. The luminescent device 100 further includes a hydrophilic layer (e.g., a hydrogel) 105 including a second hydrogel comprising a second hydrogel polymer, coaxially disposed with the fiber-shaped hydrogel core 101, and surrounding the luminescent layer 103. The luminescent device 100 further includes an elastomeric layer 107 including a second elastomeric polymer, coaxially disposed with the fiber-shaped core 101, and surrounding the hydrogel layer 105.

[0111] In some embodiments, the Applicants have shown that there is a surface energy mismatch between the luminescent layer 103 (hydrophobic) and the hydrogel layer 105 (hydrophilic). In these embodiments, Applicants have surprisingly discovered that an efficient adhesion between the luminescent layer 103 and the hydrogel layer 105 can be achieved by first coating the luminescent layer 103 with a coating comprising a hydrophilic

polymer, which is adhered to the luminescent layer 103. In these embodiments, the hydrogel layer 105 can then be deposited onto and surrounding the coating comprising the hydrophilic polymer and adhere to the coating. In some embodiments, the coating of the hydrophilic polymer is a thin layer and the further coating of the hydrogel layer 105 is a much thicker layer. Without wishing to be bound by any particular theory, it is believed that the coating comprising the thin hydrophilic polymer effectively changes the surface energy of the luminescent layer 103 and allows the hydrogel layer 105 to be coated effectively. In some embodiments, the hydrophilic polymer and the first elastomeric polymer in layer 103 each include a coupling agent and form covalent bonds with each other to achieve good adhesion. In some embodiments, the hydrophilic polymer and the second hydrogel polymer in layer 105 also each include a coupling agent and form covalent bonds to achieve good adhesion. Non-limiting examples of the coupling agents include a molecular moiety including a silicon atom linked to a functional group selected from a group consisting of OH, Cl, Br, I, OPh, ester, and sulfonate ester. In further embodiments, the hydrophilic polymer in the coating and the second hydrogel polymer in layer 105 are interwoven together, or topologically entangled to achieve good adhesion. In some embodiments, the hydrophilic polymer and the second hydrogel polymer can be the same or different hydrophilic polymers.

[0112] Thus, as shown in FIGS. 1A and 1F, in certain embodiments, the fiber-shaped hydrogel core 101, the luminescent layer 103, the hydrogel layer 105, and the elastomeric layer 107 are all coaxially disposed with respect to each other. In certain embodiments, the fiber-shaped hydrogel core 101 has two end surfaces each independently selected from the group consisting of circle, oval, square, triangle, rectangle, diamond, trapezoidal, pentagon, hexagon, heptagon, and octagon. In certain embodiments, the cross-section surface of the fiber-shaped hydrogel core 101 has a shape selected from the group consisting of circle, oval, square, triangle, rectangle, diamond, trapezoidal, pentagon, hexagon, heptagon, and octagon. In certain embodiments, as shown in FIGS. 1A and 1F, the fiber-shaped hydrogel core 101 has two end surfaces each being circle and the fiber-shaped core is tubular. In certain embodiments, the luminescent device 100 is also fiber-shaped overall and has two end surfaces each independently selected from the group consisting of circle, oval, square, triangle, rectangle, diamond, trapezoidal, pentagon, hexagon, heptagon, and octagon. In certain embodiments, the cross-section surface of the overall luminescent device 100 has a shape selected from the group consisting of circle, oval, square, triangle, rectangle, diamond, trapezoidal, pentagon, hexagon, heptagon, and octagon. As used herein, the phrase "side-

wall surface" refers to all the surface(s) of the fiber-shaped core other than the two end-surfaces. Thus, the side-wall surface can be one continuous surface (in the case of a cylindrical fiber-shaped core), or can be a combination of multiple surfaces (*e.g.*, 4 surfaces in the case of a rectangular prism).

[0113] In certain embodiments, the first and/or second hydrogels further include a salt. Non-limiting examples of salts include LiCl, NaCl, KCl, $MgCl_2$, $NaNO_3$, KNO_3, CH_3COOK, Na_2SO_4, K_2SO_4, $Na_2B_4O_7$, and a combination thereof. The inclusion of salt allows the hydrogel to be conductive.

[0114] In certain embodiments, the first and second hydrogel polymers are each independently selected from the group consisting poly(hydroxyethylmethacrylate) (PHEMA), poly(acrylamide) (PAAm), poly(dimethylacrylamide) (PDMA), poly(N-isopropylacrylamide) (PNIPAM), sodium polyacrylate (NaPAA), [2-(Acryloyloxy)ethyl] trimethylammonium chloride (PDMAEA), alginate, chitosan, cellulose, polyvinyl alcohol (PVA), poly(lactic acid) (PLA), hyaluronic acid, poly (ethylene glycol) (PEG), and a combination thereof. In some specific embodiments, the first and second hydrogel polymers are both poly(acrylamide) (PAAm).

[0115] In certain embodiments, the first and second elastomeric polymers are each independently selected from the group consisting of polydimethylsiloxane (PDMS), Ecoflex, polyurethane (PU), poly (isoprene), and poly (butadiene). In some specific embodiments, the first and second elastomeric polymers are each polydimethylsiloxane (PDMS).

[0116] Any luminescent material known in the art can be used in the luminescent layer. The luminescent material may be electroluminescent, *i.e.*, capable of emitting light when subjected to an electric field. In certain embodiments, the luminescent material is selected from the group consisting of ZnS doped with copper (Cu), aluminum (Al), chloride (Cl), bromine (Br), iodine (I), or manganese (Mn), ZnSe doped with Cu or Cl, ZnCdS doped with Cu, Cl, Mn, or silver (Ag), ZnSSe doped with Cu or Cl, and a combination thereof. In some specific embodiments, the luminescent material is ZnS doped with Cu. In certain embodiments, the first elastomeric polymer and the luminescent material have a weight ratio of about 0.5:1, 1:1, 1:1.5, and 1:2. In certain embodiments, the first elastomeric polymer and the luminescent material have a weight ratio of about 1:1.

[0117] In certain embodiments, a first electrode 109 is disposed in the fiber-shaped core 101 and a second electrode 111 is disposed in the hydrogel layer 105. In certain embodiments, both the fiber-shaped core 101 and the hydrogel layer 105 are hydrophilic and conductive, and a voltage may be applied between the fiber-shaped core 101 and the hydrogel layer 105, *e.g.*, through the first and second electrodes. In certain embodiments, the first and/or second electrodes are carbon or a metal. Non-limiting examples of metals include Cu, Fe, Ni, Ag, Au, Pt, other noble metals, and alloys thereof. In these embodiments, the luminescent material in the luminescent layer 103 is subjected to an alternating electric field as a result of the voltage, thus emitting luminescence.

[0118] In certain embodiments, the adjacent two layers of the luminescent device 100 and/or the luminescent layer 103 and the fiber-shaped core 101 are adhered together. In certain embodiments, the adhesion is a result of covalent bonding of the polymers within the two adjacent layers and/or the polymers within the luminescent layer and the fiber-shaped core. In certain embodiments, the polymers within the two adjacent layers and/or the polymers within the luminescent layer and the fiber-shaped core each include a same or different coupling agent covalently bonded to the polymers. In certain embodiments, the coupling agent is a silane-based coupling agent. Covalent bonds may be formed by reacting these coupling agents. Non-limiting examples of the coupling agents include molecular moieties including a silicon atom linked to a functional group selected from a group consisting of OH, Cl, Br, I, OPh, ester, and sulfonate ester. Additional examples of coupling agents and methods of forming covalent bonds between polymers using the coupling agents are described in WO 2019/023212, filed on July 24, 2018, entitled "Bonding Dissimilar Polymer Networks In Various Manufacturing Processes," U.S. Provisional Patent Application No. 62/536,708, filed on July 25, 2017, entitled "Wearable and Washable Conductors for Active Textiles," and U.S. Patent Application No. 62/536,711, filed on July 25, 2017, entitled "A General Approach to Bond Dissimilar Polymer Networks," the entire contents of which are incorporated by reference.

[0119] In some specific embodiments, the luminescent layer adheres to the fiber-shaped core. In certain embodiments, the first hydrogel polymer includes a first coupling agent, the first elastomeric polymer includes a second coupling agent, and covalent bonds formed by reacting the first and second coupling agents adhere together the luminescent layer and the

fiber-shaped core. In certain embodiments, the first hydrogel polymer and/or the first elastomeric polymer are cross-linked.

[0120] In some specific embodiments, the hydrophilic layer (*e.g.*, hydrogel) adheres to the luminescent layer. In some embodiments, the hydrogel layer may bond to the luminescent layer via two ways: a third network (due to hydrogel resin treatment) covalently bonds to EL layer network while topologically bond to the hydrogel layer network; or the third network simply covalently bonds to both networks. In some specific embodiments, the second hydrogel polymer includes a third coupling agent, the first elastomeric polymer includes a fourth coupling agent, and covalent bonds formed by reacting the third and fourth coupling agents adhere together the hydrogel layer and the luminescent layer. In other embodiments, the luminescent device further includes a first adhesion polymeric network including a plurality of first adhesion polymer chains joined together by a bonding force and interwoven with the second hydrogel polymer to adhere together the luminescent layer and the hydrogel layer, where the first adhesion polymeric network is covalently bonded to the first elastomeric polymer while topologically bonded to the second hydrogel polymer. In certain embodiments, the second hydrogel polymer and/or the first elastomeric polymer are cross-linked.

[0121] In some specific embodiments, the elastomeric layer adheres to the hydrophilic layer (*e.g.*, the hydrogel). In some specific embodiments, the second hydrogel polymer includes a fifth coupling agent, the second elastomeric polymer includes a sixth coupling agent, and covalent bonds formed by reacting the fifth and sixth coupling agents adhere together the hydrophilic layer and the elastomeric layer. In certain embodiments, the second hydrogel polymer and/or the second elastomeric polymers are cross-linked.

[0122] In certain embodiments, the first, second, third, fourth, fifth, and sixth coupling agents are each a silane-based agent. In certain embodiments, the covalent bond is a siloxy bond (Si-O-Si) and the first, second, third, fourth, fifth, and sixth coupling agents each independently includes a molecular moiety including a silicon atom linked to a functional group selected from a group consisting of OH, Cl, Br, I, OPh, ester, and sulfonate ester.

[0123] In certain embodiments, the covalent bond is a siloxy bond (Si-O-Si) and the first, second, third, fourth, fifth, and sixth coupling agents each independently includes a molecular moiety including a silicon atom linked to OH or Cl.

[0124] In certain embodiments, each of the bonding forces described herein joining the adhesion polymer chains results from a bond or interaction each independently selected from the group consisting of hydrogen bond, ionic bond, van der Waals interaction, covalent bond, π–π stacking, cation-π interaction, host-guest interaction, and a combination thereof.

[0125] In certain embodiments, the first elastomeric polymer in the luminescent layer is bonded to one or more hydrophilic moieties, *e.g.*, functional groups, molecules, or polymers, to increase the hydrophilicity of the surface of the luminescent layer. In some embodiments, the luminescent layer further includes a hydrophilic polymer covalently bonded to the first elastomeric polymer. In some embodiments, the hydrophilic polymer includes a seventh coupling agent, the first elastomeric polymer includes an eighth coupling agent, and the covalent bonds are formed by reacting the seventh and the eighth coupling agents. In certain embodiments, the seventh and eighth coupling agents are each a silane-based agents. In certain embodiments, the covalent bond is a siloxy bond (Si-O-Si) and the seventh and eighth coupling agents each independently include a molecular moiety including a silicon atom linked to a functional group selected from a group consisting of OH, Cl, Br, I, OPh, ester, and sulfonate ester. In some embodiments, the hydrophilic polymer is the second hydrogel polymer.

[0126] In certain embodiments, one or more of the fiber-shaped hydrogel core, the hydrogel layer, and the elastomeric layer are transparent. In certain embodiments, all of the fiber-shaped hydrogel core, the hydrophilic layer, and the elastomeric layer are transparent. As a result, the luminescence may be observed through one or more of the fiber-shaped hydrogel core, the hydrogel layer, and the elastomeric layer.

[0127] In certain embodiments, the luminescent device is soft. In certain embodiments, the luminescent device is stretchable. In certain embodiments, the luminescent device is stretchable to 1.5, 2, 3, 4, or 5 times of its original length and still maintains its functions. In certain embodiments, the luminescent device returns to its original length when the stretching force is removed.

[0128] In another aspect, a method of providing luminescence is described, including: providing a luminescent device of any one of the embodiments described herein; applying a voltage between the fiber-shaped core (e.g., a fiber-shaped hydrogel core) and the hydrophilic

layer (e.g., a hydrogel layer); and allowing/activating the luminescent material to emit luminescence.

[0129] In certain embodiments, the fiber-shaped core further includes a first electrode and the hydrophilic layer (*e.g.*, a hydrogel layer) further includes a second electrode, and the voltage is applied to the first and second electrodes. In certain embodiments, the voltage is an alternating voltage. In certain embodiments, the voltage ranges from 100 volts to 1 kilovolt.

[0130] In yet another aspect, a method of fabricating the luminescent device of any one of the embodiments described herein is disclosed, including:

(1) providing the fiber-shaped core including the first hydrogel including the first hydrogel polymer;

(2) disposing the luminescent layer including the first elastomeric polymer coaxially with the fiber-shaped core and surrounding the fiber-shaped core's side-wall surface;

(3) disposing the hydrophilic layer (*e.g.*, a hydrogel layer) including the second hydrogel polymer coaxially with the fiber-shaped core and surrounding the luminescent layer; and

(4) disposing the elastomeric layer coaxially with the fiber-shaped core and surrounding the hydrophilic layer (*e.g.*, the hydrogel layer).

[0131] In certain embodiments, the method further includes providing a first electrode into the fiber-shaped core and providing a second electrode into the hydrophilic layer (*e.g.*, the hydrogel layer). In certain embodiments, step (3) further includes covalently bonding a hydrophilic polymer to the first elastomeric polymer. In certain embodiments, step (3) comprises coating the luminescent layer with a coating comprising the hydrophilic polymer and depositing the hydrophilic layer surrounding the coating. In certain embodiments, the hydrophilic polymer includes a ninth coupling agent, the first elastomeric polymer includes a tenth coupling agent, and the method includes forming covalent bonds by reacting the ninth and tenth coupling agents. In certain embodiments, the ninth and tenth coupling agents are each a silane-based agent. In certain embodiments, the covalent bond is a siloxy bond (Si-O-Si) and the ninth and tenth coupling agents each independently includes a molecular moiety including a silicon atom linked to a functional group selected from a group consisting of OH, Cl, Br, I, OPh, ester, and sulfonate ester. In certain embodiments, the hydrophilic polymer

forms covalent bonds with the second hydrogel polymer and/or topologically entangled (*i.e.*, interwoven) with the second hydrogel polymer to achieve good adhesion. In certain embodiments, the hydrophilic polymer is the second hydrogel polymer.

[0132] A non-limiting example of the method disclosed herein is described with reference to FIG. 1B. As shown in FIG. 1B, the fiber-shaped core (*e.g.*, hydrogel core) was dip-coated with a luminescent layer (*e.g.*, an electroluminescent coating). The electroluminescent coating was first treated to bond with a hydrophilic polymer (*e.g.*, hydrogel resin) to increase its surface hydrophilicity before being dip-coated with the hydrogel layer. Thus, in certain embodiments, a separate, thin coating is formed, having components identical to that of subsequent hydrogel layer except that one or more chain transfer agents are added to make the polymer chain length very short, such that the thin hydrophilic layer is formed. Another dip-coating was applied to apply the elastomeric layer (*e.g.*, the elastomer coating). Two electrodes were then added to the two hydrogel layers to fabricate the luminescent device.

Increasing hydrophilicity of a hydrophobic polymer's surface

[0133] In yet another aspect, a method of increasing hydrophilicity of a hydrophobic polymer's surface is described, including:

providing a hydrophobic polymer including an eleventh coupling agent;
providing a hydrophilic polymer including a twelfth coupling agent; and
reacting the eleventh coupling agent and the twelfth coupling agent to form covalent bonds.

[0134] In certain embodiments, the eleventh and twelfth coupling agents are each silane-based coupling agents each including a silicon atom linked to a functional group selected from a group consisting of OH, Cl, Br, I, OPh, ester, and sulfonate ester. In certain embodiments, the covalent bond is a siloxy bond (Si-O-Si). In certain embodiments, the hydrophobic polymer is selected from the group consisting of polydimethylsiloxane (PDMS), Ecoflex, polyurethane (PU), poly (isoprene), and poly (butadiene). In certain embodiments, the hydrophilic polymer is selected from the group consisting of poly(hydroxyethylmethacrylate) (PHEMA), poly(acrylamide) (PAAm), poly(dimethylacrylamide) (PDMA), poly(N-isopropylacrylamide) (PNIPAM), sodium polyacrylate (NaPAA), [2-(Acryloyloxy)ethyl] trimethylammonium chloride (PDMAEA),

alginate, chitosan, cellulose, polyvinyl alcohol (PVA), poly(lactic acid) (PLA), hyaluronic acid, poly (ethylene glycol) (PEG), and a combination thereof.

Luminescent devices including composite fibers

[0135] In yet another aspect, a luminescent device is described, including:

one or more first composite fibers each including:

a first fiber-shaped core including a first hydrogel comprising a first hydrogel polymer, wherein the first fiber-shaped core has an elongated body and a side-wall surface along the elongated body; and

a luminescent layer including a first elastomeric polymer and a luminescent material, coaxially disposed with the first fiber-shaped core, and surrounding the first fiber-shaped core's side-wall surface; and

one or more second composite fibers each including:

a second fiber-shaped core including a second hydrogel including a second hydrogel polymer, wherein the second fiber-shaped core has an elongated body and a side-wall surface along the elongated body; and

an elastomeric layer including a second elastomeric polymer, coaxially disposed with the second fiber-shaped core, and surrounding the second fiber-shaped core's side-wall surface;

where at least one of the first composite fibers and at least one of the second composite fibers are disposed at an angle such that the first and second composite fibers at least partially overlap.

[0136] A non-limiting example of the luminescent device is shown in FIG. 4A. As illustrated in FIG. 4A, the luminescent device 400 has a plurality of first composite fibers 401 and a plurality of second composite fibers 403. The first composite fibers 401 each have a first fiber-shaped core 409 including a first hydrogel comprising a first hydrogel polymer, where the first fiber-shaped core has an elongated body and a side-wall surface along the elongated body. The first composite fibers 401 also each have a luminescent layer 411 including a first elastomeric polymer and a luminescent material, coaxially disposed with the first fiber-shaped core 409, and surrounding the first fiber-shaped core 409's side-wall surface. The second composite fibers 403 each have a second fiber-shaped core 405 including a second hydrogel comprising a second hydrogel polymer, where the second fiber-shaped core 405 has an elongated body and a side-wall surface along the elongated body.

The second composite fibers 403 also each have an elastomeric layer 407 including a second elastomeric polymer, coaxially disposed with the second fiber-shaped core 405, and surrounding the second fiber-shaped core 405's side-wall surface.

[0137] In certain embodiments, the at least one of the first composite fibers 401 and at least one of the second composite fibers 403 are disposed at an angle θ (FIG. 4A). In certain embodiments, the angle is less than 180 degrees and more than 0 degree. In certain embodiments, the angle is about 15, 30, 45, 60, 75, 90, 115, 130, 145, 160, or 175 degrees. In certain embodiments, the angle is about 90 degrees. In certain embodiments, the luminescent device 400 includes a plurality of the first composite fibers 401 parallel to each other and a plurality of the second composite fibers 403 parallel to each other. In these embodiments, the first and second composite fibers are disposed at an angle to form a grid (FIG. 4A). Thus, when the first and second fiber-shaped cores are subject to a voltage, the luminescent material in the luminescent layer 411 at where the first and second composite fibers overlap (labeled in FIG. 4A as area 413) emits luminescence.

[0138] In certain embodiments, the first and/or second hydrogels further comprise a salt. Non-limiting examples of the salt include LiCl. In certain embodiments, the first and second hydrogel polymers are each independently selected from the group consisting of poly(hydroxyethylmethacrylate) (PHEMA), poly(acrylamide) (PAAm), poly(dimethylacrylamide) (PDMA), poly(N-isopropylacrylamide) (PNIPAM), sodium polyacrylate (NaPAA), [2-(Acryloyloxy)ethyl] trimethylammonium chloride (PDMAEA), alginate, chitosan, cellulose, polyvinyl alcohol (PVA), poly(lactic acid) (PLA), hyaluronic acid, poly (ethylene glycol) (PEG), and a combination thereof.

[0139] In certain embodiments, the first and/or second fiber-shaped cores each have two end surfaces each independently selected from the group consisting of circle, oval, square, triangle, rectangle, diamond, trapezoidal, pentagon, hexagon, heptagon, and octagon. In certain embodiments, the first and/or second fiber-shaped cores each have a cross-section surface having a shape each independently selected from the group consisting of circle, oval, square, triangle, rectangle, diamond, trapezoidal, pentagon, hexagon, heptagon, and octagon.

[0140] In certain embodiments, the first and second elastomeric polymers are each independently selected from the group consisting of polydimethylsiloxane (PDMS), Ecoflex, polyurethane (PU), poly (isoprene), and poly (butadiene).

[0141] In certain embodiments, the luminescent material is selected from the group consisting of ZnS doped with copper (Cu), aluminum (Al), chloride (Cl), bromine (Br), iodine (I), or manganese (Mn), ZnSe doped with Cu or Cl, ZnCdS doped with Cu, Cl, Mn, or silver (Ag), ZnSSe doped with Cu or Cl, and a combination thereof.

[0142] In certain embodiments, the luminescent layer adheres to the first fiber-shaped core. In certain embodiments, the elastomeric layer adheres to the second fiber-shaped core. As described above, in certain embodiments, the adhesion can be achieved by covalent bonds formed by coupling agents included in the polymers in the luminescent layer and the first fiber-shaped core; and/or by covalent bonds formed by coupling agents included in the polymers in the elastomeric layer and the second fiber-shaped core. Additional examples of coupling agents and methods of forming covalent bonds between polymers using the coupling agents are described in U.S. Provisional Patent Application No. 62/536,708, filed on July 25, 2017, entitled "Wearable and Washable Conductors for Active Textiles," and U.S. Patent Application No. 62/536,711, filed on July 25, 2017, entitled "A General Approach to Bond Dissimilar Polymer Networks," the entire contents of which are incorporated by reference.

[0143] In certain embodiments, the first fiber-shaped core further comprises a first electrode and the second fiber-shaped core further comprises a second electrode. In certain embodiments, the luminescent device is soft. In certain embodiments, the luminescent device is stretchable. In certain embodiments, the luminescent device is stretchable to 1.5, 2, 3, 4, or 5 times of its original length and still maintains its functions. In certain embodiments, the luminescent device returns to its original length when the stretching force is removed.

[0144] In yet another aspect, a method of providing luminescence is described, including:

providing a luminescent device of any one of the embodiments disclosed herein including the first and second composite fibers;

applying a voltage between the first and second fiber-shaped cores; and

activating the luminescent material to emit luminescence at the surface of the first composite fiber in contact with the second composite fiber.

[0145] In certain embodiments, the first fiber-shaped core further includes a first electrode and the second fiber-shaped core further includes a second electrode, and the voltage is applied to the first and second electrodes. In certain embodiments, the voltage is

an alternating voltage. In certain embodiments, the voltage ranges from 100 volts to 1 kilovolt.

EXAMPLES

[0146] In some embodiments, a coupling method is described, by incorporating silane coupling agents into both hydrogel precursor and elastomer precursor to form hydrogel network and elastomer network with strong adhesion. In this method, both networks can be synthesized through dip-coating, allowing devices of complex shapes. Herein, this method is adopted to fabricate hydrogel ionotronic luminescent devices of high stretchability and complex geometries.

[0147] In some embodiments, as a non-limiting representative example, a luminescent device, as referred to as a hydrogel ionotronic luminescent fiber (HILF), is described in FIGS. 1A-1F. The HILF has a coaxial structure consisting of alternative curved layers of hydrogel and elastomer (FIG. 1A). The EL layer is sandwiched between the two hydrogels. Outside the active area, the hydrogels connect to an external power source through metallic wires. Electric double layers (EDLs) form at the interfaces between hydrogel and metal. When an alternating voltage is applied, ions of opposite polarities accumulate at the interfaces between hydrogel and elastomer, generating an electric field over the EL layer and light it up. Hydrogel and elastomer are transparent, allowing the light to come through. Both hydrogel network and elastomer network are modified with silane coupling agents. After the device fabrication, silanes condense to form covalent bonds between the networks. The EL layer is made of phosphors dispersed elastomer. The hydrogels connect to an external power source through metallic wires. Ions in the hydrogel and electrons in the metal meet at the hydrogel/metal interfaces to form electric double layers (EDLs). Both hydrogel network and elastomer network are modified with silane coupling agents. After silane condensation, covalent bonds are formed between the two networks and strong adhesion is generated (FIGS. 5A-5B). In hydrogel, the hydrolyzable groups are readily hydrolyzing into silanol groups. While in elastomer, the hydrolyzable groups do not hydrolyze due to the low water content within the elastomer matrix. When elastomer contacts with hydrogel, hydrolyzable groups on the surface of elastomer meet water and hydrolyze into silanol groups. After condensation, hydrogel network and elastomer network are bonded covalently. When an alternating voltage is applied, ions of opposite polarities periodically accumulate at the hydrogel/elastomer interfaces, producing an electric field over the EL layer and lighting it up.

With suitable area ratio of EDL over EL layer, the voltage across EDL is within ±1 volt, so that the EDL can remain stable and behave like a capacitor. Both the hydrogel and the elastomer are transparent to allow the light produced by the EL layer to come through.

[0148] In some embodiments, the HILF is fabricated via a multi-step dip-coating process (FIG. 1B). Details are elucidated in the Experimental Section below. Briefly, a hydrogel fiber core is made by the extrusion of hydrogel resin, followed by dip-coating with an EL layer. Subsequently, a hydrogel resin treatment is conducted to make the surface of EL layer hydrophilic such that the fiber can be dip-coated with a hydrogel layer. After that, an elastomer coating is dip-coated to seal the overall device. Finally, two metallic wires are connected to the hydrogel core and the hydrogel layer respectively. When an alternating voltage is applied, the HILF illuminates.

[0149] In some embodiments, polyacrylamide (PAAm) hydrogels containing 8.0 M lithium chloride were used as the hydrogels, zinc sulfide (ZnS) particles were used as the phosphors, polydimethylsiloxane (PDMS, 10:1) was used as the elastomer, and tin-coated copper wires are used for the electrical connection. Hydrogels dissolved with lithium chloride can retain water under humidity of 10%, and a layer of PDMS coating further enhances the water retention capability. ZnS can luminesce under the application of voltage instead of direct injection of electrons, and has been used as EL phosphor for displays and solid-state lighting for many decades. Commercially available ZnS particles were mixed with PDMS to make the precursor for EL layer (FIGS. 6A-6B), and dip-coating is conducted twice (FIGS. 7A-7B). The EL intensity increases with the increasing amount of ZnS particles, but the blend becomes a slurry, which is not possible for dip-coating when too many ZnS particles are added. To balance the EL intensity and the feasibility of dip-coating, weight ratio of ZnS particles to PDMS is fixed at 1:1.

[0150] In some embodiments, the small ZnS particles are embedded within the PDMS matrix, and their effect on the adhesion between PAAm hydrogel and PDMS is negligible (FIGS. 8A-8B). The PAAm hydrogel on pure PDMS substrate gives an adhesion energy of ~46.4 J m^{-2}, and PAAm hydrogel on ZnS particles dispersed PDMS substrate gives an adhesion energy of ~50.7 J m^{-2}. Embedding ZnS particles into PDMS matrix does not affect the adhesion. n=3. The cross-sectional view of an as-prepared HILF shows a clear coaxial structure with an EL layer of thickness of ~150 μm (FIG. 1C). Scanning electron microscope

(SEM) shows the fine-dispersed ZnS particles (FIG. 1D). The sizes of ZnS particles range from several microns to tens of microns. If smaller particles are required, nanoscale ZnS particles can be synthesized via chemical precipitation method. When an electric field of ~3 V μm^{-1} and frequency 1 kHz is applied, the HILF iluminates (FIG. 1E). The HILF operates stably without electrolyzing the hydrogels (FIGS. 9A-9B).

[0151] In some embodiments, the fabrication process of the HILF involves making a PDMS coating on the surface of PAAm hydrogel and making a PAAm hydrogel layer on the surface of PDMS. The two inverse processes lead to comparable adhesion (FIG. 10). However, the kinetics of these two processes are very different: PDMS precursor wets the surface of PAAm hydrogel readily, but PAAm hydrogel precursor does not wet the surface of PDMS. This difference is due to the surface energy mismatch and understood as follows. The surface energy of water is ~72 mN m^{-1}, PDMS is ~20 mN m^{-1}, and the surface energy between water and PDMS is ~40 mN m^{-1}. These three surface energies define a spreading coefficient, $S = \gamma_{SG} - (\gamma_{LG} + \gamma_{SL})$, where subscript S, G, and L represent solid, gas, and liquid, respectively. When $S > 0$, the liquid wets the solid surface completely, when $S < 0$, partial wetting occurs and a contact angle forms. For a water droplet on the surface of PDMS, the spreading coefficient is negative. The water droplet does not wet the surface of PDMS and beads up, forming a large contact angle of ~107.1° (FIG. 2A). Direct dip-coating of PAAm hydrogel on the surface of PDMS is not possible. By contrast, for a PDMS droplet on the surface of PAAm hydrogel, the spreading coefficient is positive. The PDMS droplet wets the surface of PAAm hydrogel and spreads automatically (FIG. 2B). Dip-coating of PDMS on the surface of PAAm hydrogel is facile. The wetting behavior of PDMS on the surface of PAAm hydrogel is similar to the spontaneous spreading of an oil droplet on the surface of water.

[0152] In some embodiments, the surface of PDMS is modified to be hydrophilic to match its surface energy with that of PAAm hydrogel to enable dip-coating. Commonly used hydrophilic treatments for PDMS include plasma treatment and UV/ozone treatment. The treated surfaces degrade in the open air, and only form physical interactions with hydrogels. Polymer brushes can be covalently anchored onto the surface of PDMS through surface-initiated polymerization, but the fabrication processes, such as vapor deposition, are not compatible with hydrogels and an oxygen-free environment is required. In some embodiments, an oxygen-tolerant hydrogel resin is used for the hydrophilic treatment by

soaking silane-modified PDMS into a silane-modified PAAm hydrogel resin. During the soaking process, silane coupling agents condense to form covalent bonds between the two networks. As a result, PAAm hydrogels covalently bond to PDMS, making the surface of PDMS hydrophilic (FIG. 2C) and allowing the dip-coating of PAAm hydrogel resin to form a homogeneous hydrogel layer (FIG. 11B). In contrast, as shown in FIG. 11A, water does not wet the untreated surface of EL layer. Dip-coating of untreated fiber results in a heterogeneous hydrogel layer. Furthermore, the treated surface contains a thin layer of PAAm hydrogel crosslinked by silanes. The subsequent hydrogel layer can adhere to the treated surface through two possible ways: forming covalent bonds via silane condensation and forming topological adhesion. The resulting adhesion is strong, such that no debonding happens even when the fiber is stretched to rupture. One might also match the surface energy of PAAm hydrogel with that of PDMS by adding surfactants such as sodium dodecyl sulfate (SDS), as long as the surfactants do not significantly degrade the bulk properties of hydrogels and the adhesion.

[0153] In some embodiments, the contact angle evolutions of various cases (FIG. 2D) were compared. When a water droplet drops on the surface of an untreated PDMS, a large contact angle (~107.1°) forms and remains stable over time. When a water droplet drops on the surface of a treated PDMS, a small contact angle (~26.6°) forms and gradually decreases with time. The wetting of water on the surface of PDMS reaches steady state within 1 minute, so that the evaporation of water is negligible. When a PDMS droplet drops on the surface of a PAAm hydrogel, a large contact angle (96.5°) forms, subsequently decreases rapidly, and reaches a steady state afterward, approximately obeying a power law. A total wetting of PDMS on the surface of the PAAm hydrogel after 24 hours is observed (FIG. 12).

[0154] In some embodiments, two surface analyses were carried out to confirm the forming of PAAm hydrogel on the surface of treated PDMS. The SEM image of untreated PDMS surface exhibits a smooth and clear view (FIG. 2E), while the SEM image of hydrogel resin-treated PDMS surface exhibits a rough and cracked view (FIG. 2F). The cracks are due to the fracture of dried PAAm network. The PAAm network does not show porous structure, since the hydrogel layer is very thin and undergoes air drying in the ambient environment. Such air-drying process is known to cause collapse of hydrogel network and results in a compact network. PDMS does not contain nitrogen while PAAm hydrogel does. The X-ray photoelectron spectroscopy (XPS) analysis shows that untreated PDMS surface does not

show absorption for N1s while hydrogel resin-treated PDMS surface does (FIG. 2G). Indeed, a layer of PAAm hydrogel is coated on the surface of PDMS after the hydrogel resin treatment.

[0155] In some embodiments, it is further noted that the difference between making an elastomer coating on the surface of hydrogel and making a hydrogel layer on the surface of elastomer is generic, independent of specific devices. The hydrogel resin treatment provides a new way that is oxygen tolerant and free of mold and specific instrument requirements for hydrophilic treatment of elastomers, enabling fabrication of hydrogel ionotronic devices under extreme conditions, such as coating on curved surfaces, concave surfaces, sharp tips, and inner surfaces of shelled structures via dip-coating.

[0156] In some embodiments, the electro-optical and mechanical properties of HILF was studied (FIGS. 3A-3F). Subject to a pulsed electric field of ~5 V μm^{-1} and frequency 1 kHz, the HILF responds accordingly (FIG. 3A). When the frequency is fixed at 1 kHz, HILF starts to luminesce at a threshold of ~1 V μm^{-1}, and increases its EL intensity with the electric field (FIG. 3B). For an EL device, the measured luminance can be expressed as a function of amplitude of the applied voltage as $I = \alpha \exp(-\beta V^{-1/2})$, where I is the luminance, V is the voltage, and α and β are fitting parameters. The experimental results agree with the theoretical prediction (FIG. 13). The data points are measured from three samples at a constant frequency of 1000 Hz. Thus, the normalized luminance can be expressed as $\frac{I}{I_0} = \exp\left(\beta\left(V_0^{-1/2} - V^{-1/2}\right)\right)$, where I_0 and V_0 are the onset luminance and applied voltage, respectively. Based on the experimental set-up, the onset luminance was measured to be ~0.4 cd/m^2 under a voltage of amplitude 120 V. The solid line represents the theoretical prediction calculated using the above equation with a fitting parameter 70.5 via a least squares fit. The average of R^2 is 0.989. When the electric field is fixed at ~6 V μm^{-1}, luminance increases with frequency due to the higher input power at higher frequency (FIG. 3C). This tendency is consistent with other EL devices using ZnS particles dispersed PDMS as the EL layer. Since the HILF possesses a one-dimensional structure and luminance in all directions, its brightness is independent of view angle (FIG. 14).

[0157] In some embodiments, the luminescent device or HILF is stretchable and maintains its luminescing performance under stretching (FIG. 3D), which is attributed to the

unique combination of optical, electrical, and mechanical properties of the hydrogel (*e.g.*, PAAm hydrogel) and the elastomer (*e.g.*, PDMS) (FIG. 3E, FIGS. 15A-15B, 16A-16B), as well as the strong adhesion. The HILF is mechanically durable and only decreases its peak stress slightly after 10000 cycles of loading and unloading (FIG. 3F, FIG. 17). The ZnS particles are embedded in PDMS and thus insulated from the water in hydrogel and the ambient moisture, both of which are known to cause EL performance deterioration of ZnS particles. Dissolving of lithium chloride and a coating of PDMS contribute to the long-term maintenance of electrical properties of PAAm hydrogel. Consequently, the HILF is electro-optically durable and can still be light up without degrading its luminance intensity after the cyclic loading and unloading (FIG. 3F).

[0158] In some embodiments, the softness and stretchability of hydrogels, the strong adhesion between hydrogel and elastomer based on silane coupling chemistry, as well as the broad applicability of dip-coating based on hydrogel resin, together enable hydrogel ionotronic luminescent devices of complex geometries and new functionalities. A new concept of device - fabric display - is proposed, by assembling two types of fibers into rows and columns (FIG. 4A). One type of fiber is EL layer-coated hydrogel fiber, and the other is pure PDMS-coated hydrogel fiber. Each junction of the fabric display forms a pixel. When a voltage is applied, the junctions illuminate while the rest does not (FIG. 4B). Unlike conventional pixels where the functional parts are fixedly built in and the positions of two electrodes are fixed and rigid, the pixels in the fabric display are movable and soft. The movable pixels can display more information than the fixed pixels by changing the arrangement of the fibers. For example, the fabric display can show an "N" pattern by leaning the second vertical fiber (FIG. 4C). Circuit analysis indicates that the fabric display can be driven by passive matrix addressing with resolution up to 320×240, the upper limit of the passive matrix (FIGS. 18A-18D). Both *RC* delay and response speed of ZnS particles do not limit the device performance. The *RC* delay is independent of the hydrogel fiber diameter, allowing miniaturization of the fabric display. This new concept display provides new possibilities for EL devices, for example, for wearable display and smart clothes.

[0159] In some embodiments, to demonstrate EL devices of complex geometries, an EL closed ring was fabricated, containing closed cylindrical shells of EL layer, PAAm hydrogel and PDMS (FIG. 4D) and an EL handbag having a cage structure that cannot be molded (FIG. 4E). Both device configurations, with strong bonding between hydrogel and elastomer, are

not possible to achieve using other methods. The coupling agent method enables fabrication of planar hydrogel ionotronic luminescent devices via direct attachment without any surface treatment (FIGS. 19A-19B).

[0160] In some embodiments, a multi-color luminescent device or HILF was fabricated by using different ZnS particles for the EL layer (FIG. 4F). Three types of ZnS particles were selected and mixed by certain weight ratios to achieve six colors (FIGS. 20, 21A-21B). As a proof-of-concept, it was demonstrated that an EL heart using an orange HILF and a blue HILF (FIG. 4G), and an "EL" pattern using multi-color HILFs, can potentially be woven into textiles (FIG. 4H).

[0161] In summary, hydrogel ionotronic luminescent devices of high stretchability and complex geometries are described. Strong adhesion between hydrogel network and elastomer network is achieved by incorporating silane coupling agents into both networks. It has been shown that making an elastomer coating on the surface of hydrogel and making a hydrogel layer on the surface of elastomer is different due to the mismatch in surface energy. Based on a hydrogel resin strategy, the surface energy of elastomer was matched with that of hydrogel and synthesized a homogeneous hydrogel layer on the surface of elastomer. Several new concepts of EL devices have been demonstrated. It is believed that the hydrogel ionotronic luminescent devices will open up new applications of EL devices for smart textiles.

Experimental Section

[0162] *Materials*: Acrylamide (AAm, A8887), lithium chloride (LiCl, 310468), N,N'-methylenebisacrylamide (MBAA, M7279), α-ketoglutaric acid (75890), acetic acid (CH_3COOH, A6283), 3-(trimethoxysilyl) propyl methacrylate (TMSPMA, 440159), 2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959, 410896), triethoxy(vinyl)silane (TEOVS, 175560), (3-mercaptopropyl)trimethoxysilane (MPTMS, 175617), tetrahydrofuran (THF, 360589), pure ethyl alcohol (CH_3CH_2OH, 459844), sodium bicarbonate ($NaHCO_3$, S5761), and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (Pt-catalyst, 479519) are purchased from Sigma-Aldrich. Tin-coated copper wire (8871K48) and Perspex sheet are purchased from McMaster-Carr. Polydimethylsiloxane (PDMS, Sylgard 184) is purchased from Dow Corning. Zinc sulfide particles are purchased from Shanghai Keyan Co., China. Distilled water is purchased from

Poland Spring. Unless otherwise specified, all materials are used as received and DI water represents distilled water.

[0163] *HILF fabrication*: (1) PAAm hydrogel core. Acrylamide and lithium chloride are dissolved in distilled water with concentrations of 2 M and 8 M, respectively. For every 1 ml of the solution, 10 μl of 0.1 M acetic acid and 1.9 μl of TMSPMA are added. Then, 1 μl of 0.1 M photoinitiator Irgacure 2959 in ethanol is added. The solution is drawn into a syringe (10 ml, VWR) and exposed to UV (15 W, 365 nm, UVP XX-15L) for 30 minutes for curing. Finally, the syringe is compressed with an Instron (Instron 5966) machine with a 500 N load cell at fixed speed of 10 mm min^{-1}. The extruded PAAm hydrogel fibers are collected. The radius of as-prepared hydrogel fiber is ~1 mm. (2) EL layer. The EL precursor is made by first mixing the base and the curing agent of PDMS (Sylgard 184) at 10:1 weight ratio, followed by adding ZnS particles at 1:1 weight ratio. 2% v/w of TEOVS is then mixed into the precursor. The resulting mixture is stirred for 1 minute and defoamed for 30 seconds, both at 2000 rpm, using a mixture (Thinky, ARE 250). Then, the collected PAAm hydrogel fibers are dipped into the EL precursor, taken out, sealed in a beaker, and hung for 10 minutes. This process allows the EL precursor to flow on the surface of the PAAm hydrogel fiber, forming a thin and homogeneous coating. After that, the fiber is put into an oven at 65 °C for 30 minutes. The dip-coating process of EL layer is repeated one more time to get an adequate ZnS particle density. After the second dip-coating, the fiber is kept inside the oven overnight for complete curing of the EL layer. The thickness of as-prepared EL layer ranges from ~100 μm to ~150 μm. (3) PAAm hydrogel layer. A hydrogel resin was first prepared for hydrophilic treatment. The recipe is the same as previously described for the hydrogel fiber core except that 10 μl 10% v/v of MPTMS in THF is added for every 1 ml AAm solution. After curing under UV for 30 minutes, the obtained MPTMS-modified PAAm hydrogel resin is dilute, allowing the soaking of the fiber. The fiber is kept inside the dilute resin at 65 °C for 12 h. Then, a hydrogel resin was made for dip-coating. The rheology of the hydrogel resin was tuned by reducing the amount of MPTMS to 2.5 μl for every 1 ml AAm solution (FIG. 22). The hydrogel resin using 2.5 μl MPTMS is viscous but still allows for dip-coating. The hydrogel resin-treated fiber was carefully dipped into the viscous solution, the fiber pulled out, the fiber hung for 10 minutes, and the fiber placed into the oven at 65 °C for 30 minutes. The dip-coating process of hydrogel layer is repeated several times to get a relatively thick hydrogel layer. For example, 3 times of dip-coating results in hydrogel layer thickness of ~500 μm. (4) External PDMS coating. PDMS (Sylgard 184,

10:1) precursor is prepared with 2% v/w of TEOVS. The dip-coating process of external PDMS layer is identical to that of EL layer coating. The process is repeated twice. The final radius of as-prepared HILF is ~2 mm.

[0164] *EL measurement*: HILF is connected to a sinusoidal voltage and illuminated in a darkroom environment. The voltage is generated from a wave generator (KEYSIGHT, 33500B), amplified by a high voltage amplifier (Trek, Model 30/20A), and monitored by an oscilloscope (KEYSIGHT, DSO1004A). A luminance meter (TES-137, TES Electrical Electronic Corp.) is placed in front of the HILF at a distance of 1 cm. For EL membrane measurement, the luminance meter is placed on top of the membrane at a distance of 5 mm.

[0165] *Mechanical characterizations*: (1) Tensile tests. Pure PDMS samples and EL samples are prepared into rectangular shape with gauge length 3 cm, thickness 1 mm, and width 1 cm. The samples are loaded on a mechanical testing machine (Instron 5966) and elongated with a 500 N load cell. PAAm hydrogel samples are prepared with gauge length 3 cm, thickness 1.5 mm, and width 1 cm. The samples are stretched with a 10 N load cell. HILFs are prepared with gauge length 1 cm and outer diameter ~4 mm. The samples are stretched with a 10 N load cell. The loading speed is fixed at 0.3 mm s^{-1}. (2) Fatigue test. Fatigue test of HILF is conducted using a mechanical testing machine (Instron 5966) with a 10 N load cell. The HILF of diameter ~4 mm is fastened on the clamps with a gauge length 1 cm. The fiber is loaded to a maximum stretch of 2 and unloaded to its original length cyclically. (3) 90° peeling tests of laminating preformed PAAm hydrogel on preformed PDMS. Recipe of PAAm hydrogel is identical to that for hydrogel core except that for every 1 ml AAm solution, 4 µl 0.1 M MBAA and 20 µl 0.1 M α-ketoglutaric acid instead of 1 µl 0.1 M I2959 are added, and no acetic acid is required. Samples of the PAAm hydrogel are prepared with the sizes of 90 × 20 × 3 mm^3. Recipe of PDMS is identical to that for HILF coating. Samples of the PDMS elastomer are prepared on a glass substrate (length: 70 cm, width 55 cm, thickness 1 mm, VWR) via spin-coating at 450 rpm for 60 s, followed with curing in an oven at 65 °C for 12 hours. The resulting thickness of PDMS is ~300 µm, measured by a digital caliper. The prepared PAAm hydrogel is laminated on the elastomer, sealed, and stored for 24 hours. After that, the bilayer is taken out and the hydrogel side is glued to a thin stiff backing layer of polyester film (50.8 µm, McMaster-Carr) using a cyanoacrylate glue. Since the hydrogel is acidic, the surface of PAAm hydrogel is treated with 0.1 M $NaHCO_3$ solution before applying the cyanoacrylate glue. The sample is then

loaded to a mechanical testing machine (Instron 5966) with a 10 N load cell using the 90-degree peeling fixture with a peeling rate of 10 mm min^{-1}. (4) 90° peeling tests of laminating preformed PAAm hydrogel on preformed EL layer. All the recipes and procedures are identical to number (3) except that ZnS particles are mixed with PDMS precursor at 1:1 weight ratio for the EL layer preparation. (5) 90° peeling tests of casting PAAm hydrogel precursor on preformed PDMS. PDMS is spin-coated on a glass substrate as previously described. PAAm hydrogel precursor is prepared and poured into an acrylic mold. The PDMS-coated glass is then used as the sealing cover. After curing under UV illumination for 30 minutes, the sample is carefully released from the mold, sealed in a petri dish for one day, and manipulated for test. (6) 90° peeling tests of casting PDMS precursor on preformed PAAm hydrogel. PAAm hydrogel is prepared in an acrylic mold first. After removing the sealing cover, another mold is stacked and PDMS precursor is poured into the mold. Here, PDMS is cured with additional Pt-catalyst of 1 μl g^{-1} at room temperature for 12 hours to avoid bubbles. After curing of PDMS, the sample is carefully released from the mold, sealed in a petri dish for one day, and manipulated for test.

[0166] *Rheology test*: Rheology of PAAm hydrogel resin is tested using a rheometer (DHR-3, TA Instruments) with a cone indenter of diameter 40 mm and cone angle 1° at room temperature. All hydrogel resin samples are prepared using 5 ml syringes. For each test, 1 ml hydrogel resin is extruded onto the rheometer under the indenter. After loading the indenter, the gap between the indenter and the testing plate is set to be 26 μm. The exceeded hydrogel resin is carefully removed. Then acetone is applied along the sample edge to prevent water from drying out. Storage modulus and loss modulus are measured against angular velocity. Each test is repeated at least three times.

[0167] *Contact angle* measurement: Contact angles are measured using a home-made set-up at ambient temperature (FIG. 23). A strong backlight is provided through a 15 cm long tube. A horizontal platform is built up at front of the tube. PAAm hydrogels or PDMS membranes are placed on the horizontal platform as the substrates. A digital camera (Canon, EOS 70D) is set up, focusing on the target region. The liquid drops (3 μl for water and ~5 μl for PDMS) are carefully dropped onto the substrates. Images and videos are taken and imported into a common processing software, ImageJ. Contact angles are calculated by using a contact angle plugin. The average value of at least three measurements performed at different positions on the same substrate is adopted as the contact angle.

[0168] *Preparation of EL fabric*: EL layer-coated PAAm hydrogel fiber and pure PDMS-coated PAAm hydrogel fiber are prepared via dip-coating. The two kinds of fibers are assembled into rows and columns. The hydrogels in the rows are connected to the external power source and the hydrogels in the columns are grounded.

[0169] *Preparation of EL closed ring*: The EL closed ring is prepared by first making a PAAm hydrogel fiber. The two ends of the hydrogel fiber are glued together by applying a small amount of glue (Krazy glue, VWR) to form a closed hydrogel ring, followed by dip-coating of EL layer, hydrogel resin treatment, dip-coating of hydrogel resin, and dip-coating of PDMS. A tin-coated copper wire is inserted into the inner hydrogel core before the dip-coating of EL layer. This wire connects the inner hydrogel core to external power source. Meanwhile, this wire is also coated with EL layer during the EL layer dip-coating, so that it is insulated from the subsequently coated hydrogel layer to avoid short circuit. Similarly, another tin-coated copper wire is inserted into the hydrogel layer for electrical connecting before the PDMS coating. After the device fabrication, the coated EL layer and PDMS are carefully peeled off from the wires to allow electrical connections.

[0170] *Preparation of EL handbag*: The EL handbag is prepared by gluing two ends of a PAAm hydrogel fiber to a PAAm hydrogel cylinder. Subsequently, dip-coating processes and hydrogel resin treatment are conducted as previously described. The tip of the hanging belt is not treated with hydrogel resin, so that the hydrogel layer does not cover the tip. This makes the electrical connection to the inner hydrogel core and the hydrogel layer easier, and avoids short circuit.

[0171] *Preparation of EL "Tai Ji"*: The EL device showing a "Tai Ji" pattern is fabricated via layer-by-layer assembling. An EL layer is spin-coated on a Perspex sheet at a speed of 450 rpm for 60 s and put in a 65 °C oven for overnight. The resulting EL layer thickness is ~300 μm. Three pieces of 3 mm thick PAAm hydrogel are synthesized via molding. After curing, the EL layer is peeled off from the substrate and the hydrogels are released from the mold, and are assembled to form a "Tai Ji" pattern. The device is sealed at room temperature for 24 hours. After that, the device is taken out and illuminated under a voltage.

[0172] *Preparation of multi-color HILFs*: The fabrication processes of multi-color HILFs are identical to those previously described except that different ZnS particles are used for the

EL layer. In all cases, the weight ratio of ZnS particles to PDMS is fixed at 1:1. Three types of ZnS particles (blue: B, orange: O, green: G) and the mixture of them in certain weight ratios (O:B=7:3, O:B=8:2, O:G=9:1) are adopted to achieve six colors.

[0173] *Microscopic characterizations*: Optical microscopic images are taken using a binocular microscope (Nikon, Me600) at a bright field with an analyzer. SEM images are taken using a FESEM (Zeiss, ultra 55). Before subjecting to SEM analysis, samples are air-dried, and then treated with liquid nitrogen, followed by immediate freeze-drying inside a freeze-drier (VirTis Freeze Dryer, Lyophilizer), and coated with 10 nm Pt/Pd using a dual head sputter coater (EMS 300T, Quarum/EMS).

[0174] *XPS analysis*: Samples for XPS are air-dried and treated with liquid nitrogen, followed by immediate freeze-drying inside a freeze-drier (VirTis Freeze Dryer, Lyophilizer) for 24 hours. XPS analysis is conducted using a XPS system (K-Alpha, Thermo Scientific).

[0175] *Emission spectra measurement*: Emission spectra measurement is carried out by placing the device in front of an integrating sphere which is connected to spectrometer (Ocean Optics, USB 2000+) via an optical fiber. A sinusoidal voltage of amplitude 300 V and frequency 1 kHz is applied to illuminate the device. The intensity data are collected with the software SpectraSuite, and are used to calculate the chromaticity coordinates according to the CIE 1931 standard color-matching functions.

Circuit Analysis

[0176] In a HILF, the inner hydrogel core was connected to a voltage source and the outer hydrogel layer to the ground using tin-coated copper wires. As the voltage is applied, ions of opposite polarities accumulate at the interfaces between hydrogels and EL layer, forming electric double layers as shown in FIG. 9A. Electric double layers also form at the interfaces between hydrogel and metal. The radius of inner hydrogel is a, the external radius of the EL layer is b, the external radius of the outer hydrogel is c, and the length of the HILF is l. The equivalent circuit of the HILF under an applied voltage V is shown in FIG. 9B. Two plane-parallel capacitors due to the electric double layers between hydrogels and metals, two resistors due to the resistivity of hydrogels, and one coaxial cylindrical capacitor due to the EL layer are in series.

[0177] In series circuit, the voltage dropped over each load is proportional to the amplitude of the load. The electric double layer between hydrogel and metal has a large capacitance per unit area, ~10^{-1} F m^{-2}, and the area in the experiments is on the order of 10^{-5} m^2, giving a C_{EDL} of 10^{-6} F. Under a frequency of 1000 Hz, the equivalent impedance is calculated as

$$|Z_{EDL}| = \left| \frac{1}{j\omega C_{EDL}} \right| \sim 160\Omega$$

[0178] For the hydrogels, they are treated as pure resistors and their resistance R is proportional to the resistivity ρ, the length l and the reciprocal of the cross-sectional area S:

$$R = \rho \frac{l}{S}$$

[0179] For the polyacrylamide hydrogel containing 8 M lithium chloride, the resistivity is measured to be on the order of 10^{-1} Ω m.

[0180] The cross-sectional area of inner hydrogel is

$$S_{in} = \pi a^2$$

[0181] The cross-sectional area of outer hydrogel is

$$S_{in} = \pi \left(c^2 - b^2 \right)$$

[0182] In the experiments described herein, representative values are a = 1 mm, b = 1.1 mm, c = 1.5 mm, and l = 10 cm. It is estimated that the resistance of inner hydrogel is R_{in} ~3.2 kΩ, and the resistance of outer hydrogel R_{out} is ~3.1 kΩ. The equivalent impedance of hydrogels is $R_{hydrogel}$ ~6.3 kΩ.

[0183] For the EL layer, it behaves like a coaxial cylindrical capacitor with capacitance of per unit length c_{EL} scale as

$$c_{EL} = \frac{2\pi\varepsilon_r\varepsilon_0}{\ln b/a},$$

where ε_r is the relative dielectric constant of EL layer and ε_0 the vacuum permittivity, 8.85×10^{-12} F m^{-1}.

[0184] Thus, the capacitance of the HILF of length l is

$$C_{EL} = \frac{2\pi\varepsilon_r\varepsilon_0 l}{\ln b/a}.$$

[0185] Using representative values in the experiments described herein, ε_r ~5.5 which is averaged from ε_{PDMS} ~2.5 and ε_{ZnS} ~8.5, it is estimated that the capacitance of EL layer is C_{EL} = 2.9×10^{-10} F, and the equivalent impedance under a frequency of 1000 Hz is:

$$|Z_{EL}| = \left|\frac{1}{j\omega C_{EL}}\right| \sim 5.5 \times 10^5\ \Omega.$$

[0186] Comparing the equivalent impedances, it is concluded that the voltage applied on the HILF drops mostly across the EL layer, while the drop is negligible across the EDLs between hydrogel and metal, and the hydrogels. Even for an applied voltage of amplitude 1000 V, which is beyond the range in the experiments, the voltage drops over each EDL between hydrogel and metal is ~0.29 V, which is still lower than the electrochemical window of hydrogel (typically within $\pm$1 V). Thus, the HILF can operate stably without electrolyzing the hydrogels.

[0187] The fabric display consists of multi rows and columns, and is one type of array display. An array display is commonly controlled by passive-matrix addressing technique. Briefly, a passive matrix addressing scans through the rows in order, driving the selected row first. Then it selectively drives the column electrodes to turn them off or turn them on depending on whether the corresponding segment in the selected row is on or off.

[0188] The performance of the fabric display is determined by several factors, including the *RC* delay of the device, the response of EL materials, and the resolution of the passive matrix addressing.

[0189] *RC* delay. The RC delay of fabric display is determined by resistance of PAAm hydrogel fibers, and capacitance of EL layer and PDMS layer. For the PAAm hydrogel containing 8.0 M lithium chloride, resistivity is ~10^{-1} Ω m. Thus, resistance of PAAm hydrogel is calculated as:

$$R_{Gel} = 2\rho\frac{l}{S} = \frac{0.8l}{\pi D^2}.$$

The factor of 2 is because every pixel is formed by two hydrogel fibers.

[0190] For the capacitance, the large capacitance of EDLs is neglected since it is in series with the EL layer capacitance and the PDMS layer capacitance. The small distributed capacitance of the air is neglected since it is in parallel. It is assumed that the contact between the EL layer-coated hydrogel fiber and the PDMS layer-coated hydrogel fiber is firm, and the contact area scales as D^2. The EL layer capacitance and the PDMS capacitance are in series. The capacitance of one fabric display pixel is determined as:

$$C_{pixel} = \frac{C_{EL}C_{PDMS}}{C_{EL}+C_{PDMS}} = \frac{\varepsilon_{EL}\varepsilon_{PDMS}}{\varepsilon_{EL}+\varepsilon_{PDMS}}\frac{D^2}{d} = 1.52\times10^{-11}\frac{D^2}{d}.$$

Thus,

$$\tau_{RC} \sim R_{Gel}C_{pixel} = 3.87\times10^{-12}\frac{l}{d}.$$

[0191] *RC* delay of the fabric display is independent of the hydrogel fiber diameter. Such independence is understood as follows: when the diameter of hydrogel fiber, D, becomes smaller, the resistance of hydrogel becomes larger and scales as $1/D^2$, while the capacitance of EL layer and PDMS layer becomes smaller and scales as D^2. These two changes cancel each other, so that *RC* delay is independent of the hydrogel fiber diameter.

[0192] Typical number for the PAAm hydrogel fiber length, l, ranges from 0.1-10 m, and typical thickness of coating layer, d, is on the order of 100 μm. The delay time τ_{RC} ranges from 10^{-9}-10^{-7} s. This is much smaller than the common response time of the EL materials (ZnS particles), which is on the order of 100 Hz to 10 kHz.

[0193] It is further noted that for the signal transmission through the hydrogel fiber, signal decay should be also taken into account. For an ionic cable, the signal decay is negligible as long as $l^2\omega/D_{signal}<<1$, where ω is frequency of the signal and D_{signal} is signal diffusivity in the ionic cable. For the EL device using ZnS particles, ω is commonly on the order of 100 Hz to 10 kHz. For ionic cable, D_{signal} can reach 10^7 m^2 s^{-1} due to the low permittivity of the dielectric. Thus, for the fabric display dimension on the order of 1 m, the signal decay is negligible.

[0194] Resolution of the passive matrix addressing. In a passive matrix display, each row is sequentially scanned by a pulse. For the period of a frame T_{frame}, the pulse lasts for the duration of T_{on} at one row. T_{on} relates to the number of rows, N, as $T_{on}=T_{frame}/N$. During this pulse, the signal for a row is applied to the columns. The pulse duration T_{on} is the so-called refresh rate. To avoid flicker for eyes, the refresh rate is usually set above 50 Hz, i.e. T_{frame} is set below 20 ms. For the period of 20 ms, the number of rows is limited by the pulse width T_{on}, $N=T_{frame}/T_{on}$. For a pulse width of 20 μs, the number of rows can be as high as 1000. However, the resolution in passive matrix is inevitably restricted by ghosting effect (or crosstalk), and cannot be higher than 320×240.

[0195] It has been experimentally confirmed that the EL device can be illuminated with frequency 1 kHz and pulse width 20 μs, or frequency 200 Hz and pulse width 50 μs. For the former case, T_{frame} equals to 1 ms, giving a maximum resolution of 50×50. For the latter case, T_{frame} equals to 5 ms, giving a maximum resolution of 100×100.

[0196] Response of EL materials. During the operation of EL devices using ZnS particles, electrons and holes are generated upon the application of high electric field. The separated electrons and holes recombine and produce light. When the frequency of the electric field is too high, the electrons and holes cannot respond. Typically, a ZnS based EL device operates in a frequency range between 100 Hz to 10 kHz. This frequency range allows flexible passive matrix designs.

[0197] From the above, it is concluded that: 1) RC delay does not influence the performance of fabric display. 2) Resolution of fabric display can reach the upper limit of passive matrix addressing. 3) Response of EL materials does not limit the fabric display designs.

[0198] It will be appreciated that while one or more particular materials or steps have been shown and described for purposes of explanation, the materials or steps may be varied in certain respects, or materials or steps may be combined, while still obtaining the desired outcome. Additionally, modifications to the disclosed embodiment and the invention as claimed are possible and within the scope of this disclosed invention.

CLAIMS:

1. A luminescent device comprising:

a fiber-shaped core comprising a first hydrogel comprising a first hydrogel polymer, wherein the fiber-shaped core has an elongated body and a side-wall surface along the elongated body;

a luminescent layer comprising a first elastomeric polymer and a luminescent material, coaxially disposed with the fiber-shaped core, and surrounding the fiber-shaped core's side-wall surface;

a hydrophilic layer comprising a second hydrogel comprising a second hydrogel polymer, coaxially disposed with the fiber-shaped core, and surrounding the luminescent layer; and

an elastomeric layer comprising a second elastomeric polymer, coaxially disposed with the fiber-shaped core, and surrounding the hydrophilic layer.

2. The luminescent device of claim 1, wherein the hydrophilic layer is a hydrogel layer.

3. The luminescent device of claim 1, wherein at least one of the first and second hydrogels further comprises a salt.

4. The luminescent device of claim 3, wherein the salt is selected from the group consisting of LiCl, NaCl, KCl, $MgCl_2$, $NaNO_3$, KNO_3, CH_3COOK, Na_2SO_4, K_2SO_4, $Na_2B_4O_7$, and a combination thereof.

5. The luminescent device of any one of the preceding claims, wherein the first and second hydrogel polymers are each independently selected from the group consisting poly(hydroxyethylmethacrylate) (PHEMA), poly(acrylamide) (PAAm), poly(dimethylacrylamide) (PDMA), poly(N-isopropylacrylamide) (PNIPAM), sodium polyacrylate (NaPAA), [2-(Acryloyloxy)ethyl] trimethylammonium chloride (PDMAEA), alginate, chitosan, cellulose, polyvinyl alcohol (PVA), poly(lactic acid) (PLA), hyaluronic acid, poly (ethylene glycol) (PEG), and a combination thereof.

6. The luminescent device of any one of the preceding claims, wherein the first and second hydrogel polymers are both poly(acrylamide) (PAAm).

7. The luminescent device of any one of the preceding claims, wherein the fiber-shaped core has two end surfaces and a cross-section surface each independently having a shape

selected from the group consisting of circle, oval, square, triangle, rectangle, diamond, trapezoidal, pentagon, hexagon, heptagon, and octagon.

8. The luminescent device of any one of the preceding claims, wherein the first and second elastomeric polymers are each independently selected from the group consisting of polydimethylsiloxane (PDMS), Ecoflex, polyurethane (PU), poly (isoprene), and poly (butadiene).

9. The luminescent device of any one of the preceding claims, wherein the first and second elastomeric polymers are each polydimethylsiloxane (PDMS).

10. The luminescent device of any one of the preceding claims, wherein the luminescent material is selected from the group consisting of ZnS doped with copper (Cu), aluminum (Al), chloride (Cl), bromine (Br), iodine (I), or manganese (Mn), ZnSe doped with Cu or Cl, ZnCdS doped with Cu, Cl, Mn, or silver (Ag), ZnSSe doped with Cu or Cl, and a combination thereof.

11. The luminescent device of any one of the preceding claims, wherein the luminescent layer adheres to the fiber-shaped core.

12. The luminescent device of claim 11, wherein the first hydrogel polymer comprises a first coupling agent, the first elastomeric polymer comprises a second coupling agent, and covalent bonds formed by reacting the first and second coupling agents adhere together the luminescent layer and the fiber-shaped core.

13. The luminescent device of claim 12, wherein the covalent bond is a siloxy bond (Si-O-Si) and the first and second coupling agents each comprises a molecular moiety comprising a silicon atom linked to a functional group selected from a group consisting of OH, Cl, Br, I, OPh, ester, and sulfonate ester.

14. The luminescent device of claim 13, wherein the first hydrogel polymer is cross-linked.

15. The luminescent device of claim 13, wherein the first elastomeric polymer is cross-linked.

16. The luminescent device of any one of the preceding claims, wherein the hydrophilic layer adheres to the luminescent layer.

17. The luminescent device of claim 16, wherein the second hydrogel polymer comprises a third coupling agent, the first elastomeric polymer comprises a fourth coupling agent, and covalent bonds formed by reacting the third and fourth coupling agents adhere together the hydrophilic layer and the luminescent layer.

18. The luminescent device of claim 17, wherein the covalent bond is a siloxy bond (Si-O-Si) and the third and fourth coupling agents each comprises a molecular moiety comprising a silicon atom linked to a functional group selected from a group consisting of OH, Cl, Br, I, OPh, ester, and sulfonate ester.

19. The luminescent device of claim 16, further comprising a first adhesion polymeric network comprising a plurality of first adhesion polymer chains joined together by a bonding force and interwoven with the second hydrogel polymer to adhere together the luminescent layer and the hydrophilic layer; wherein the first adhesion polymeric network is covalently bonded to the first elastomeric polymer while topologically bonded to the second hydrogel polymer.

20. The luminescent device of claim 19, wherein each of the first adhesion polymer chains is independently selected from the group consisting of poly(4-aminestyrene), chitosan, alginate, cellulose, poly(N-isopropylacrylamide), polymers containing silane groups, polymers containing catechol groups, polymers containing both silane and catechol groups, a copolymer thereof, a terpolymer thereof, and a block copolymer thereof.

21. The luminescent device of claim 19, wherein at least one of the second hydrogel polymer and the first elastomeric polymer is cross-linked.

22. The luminescent device of any one of the preceding claims, wherein the elastomeric layer adheres to the hydrophilic layer.

23. The luminescent device of claim 22, wherein the second hydrogel polymer comprises a fifth coupling agent, the second elastomeric polymer comprises a sixth coupling agent, and covalent bonds formed by reacting the fifth and sixth coupling agents adhere together the hydrophilic layer and the elastomeric layer.

24. The luminescent device of claim 23, wherein the covalent bond is a siloxy bond (Si-O-Si) and the fifth and sixth coupling agents each comprises a molecular moiety comprising a silicon atom linked to a functional group selected from a group consisting of OH, Cl, Br, I, OPh, ester, and sulfonate ester.

25. The luminescent device of claim 24, wherein the silicon atom is linked to OH.

26. The luminescent device of claim 24, wherein the silicon atom is linked to Cl.

27. The luminescent device of claim 19, wherein the bonding force results from a bond or interaction selected from the group consisting of hydrogen bond, ionic bond, van der Waals interaction, covalent bond, π–π stacking, cation-π interaction, host-guest interaction, and a combination thereof.

28. The luminescent device of any one of the preceding claims, wherein the luminescent layer further comprises a hydrophilic polymer covalently bonded to the first elastomeric polymer.

29. The luminescent device of claim 28, wherein the hydrophilic polymer comprises a seventh coupling agent, the first elastomeric polymer comprises an eighth coupling agent, and the covalent bonds are formed by reacting the seventh and the eighth coupling agents.

30. The luminescent device of claim 28 or 29, wherein the hydrophilic polymer is the second hydrogel polymer.

31. The luminescent device of claim 29 or 30, wherein the covalent bond is a siloxy bond (Si-O-Si) and the seventh and eighth coupling agents each comprises a molecular moiety comprising a silicon atom linked to a functional group selected from a group consisting of OH, Cl, Br, I, OPh, ester, and sulfonate ester.

32. The luminescent device of any one of the preceding claims, wherein the fiber-shaped core further comprises a first electrode and the hydrophilic layer further comprises a second electrode.

33. The luminescent device of claim 32, wherein at least one of the first and second electrodes is made from carbon or an inert metal.

34. The luminescent device of any one of the preceding claims, wherein the first elastomeric polymer and the luminescent material have a weight ratio of about 1:1.

35. The luminescent device of any one of the preceding claims, wherein one or more of the fiber-shaped core, the hydrophilic layer, and the elastomeric layer are transparent.

36. The luminescent device of any one of the preceding claims, wherein the luminescent device is soft, stretchable, or both soft and stretchable.

37. The luminescent device of any one of the preceding claims, wherein the luminescent device is stretchable to 1.5, 2, 3, 4, or 5 times of its original length.

38. The luminescent device of any one of the preceding claims, wherein the fiber-shaped core is a hydrogel core.

39. A method of providing luminescence, comprising:

providing a luminescent device of any one of the preceding claims;

applying a voltage between the fiber-shaped core and the hydrophilic layer; and

activating the luminescent material to emit luminescence.

40. The method of claim 39, wherein the fiber-shaped core further comprises a first electrode and the hydrophilic layer further comprises a second electrode, and the voltage is applied to the first and second electrodes.

41. The method of claim 39, wherein the voltage is an alternating voltage.

42. The method of claim 39, wherein the voltage ranges from 100 volts to 1 kilovolt.

43. A method of fabricating the luminescent device of any one of claims 1-38, comprising:

(1) providing the fiber-shaped core comprising the first hydrogel comprising the first hydrogel polymer;

(2) disposing the luminescent layer comprising the first elastomeric polymer coaxially with the fiber-shaped core and surrounding the fiber-shaped core's side-wall surface;

(3) disposing the hydrophilic layer comprising the second hydrogel polymer coaxially with the fiber-shaped core and surrounding the luminescent layer; and

(4) disposing the elastomeric layer coaxially with the fiber-shaped core and surrounding the hydrophilic layer.

44. The method of claim 43, wherein step (3) further comprises coating the luminescent layer with a coating comprises a hydrophilic polymer.

45. The method of claim 44, wherein in step (3), the hydrophilic layer is disposed onto and surrounding the coating comprising the hydrophilic polymer.

46. The method of claim 44 or 45, wherein the hydrophilic polymer comprises a ninth coupling agent, the first elastomeric polymer comprises a tenth coupling agent, and the method comprises forming covalent bonds by reacting the ninth and tenth coupling agents.

47. The method of claim 46, wherein the ninth and tenth coupling agents each comprises a molecular moiety comprising a silicon atom linked to a functional group selected from a group consisting of OH, Cl, Br, I, OPh, ester, and sulfonate ester.

48. The method of any one of claims 45-47, wherein the hydrophilic polymer forms covalent bonds with the second hydrogel polymer, topologically entangled with the second hydrogel polymer, or both.

49. The method of any one of claims 45-48, wherein the hydrophilic polymer is the second hydrogel polymer.

50. The method of any one of claims 44-49, further comprising providing a first electrode into the fiber-shaped core and providing a second electrode into the hydrophilic layer.

51. A method of increasing hydrophilicity of a hydrophobic polymer's surface, comprising:

providing a hydrophobic polymer comprising an eleventh coupling agent;

providing a hydrophilic polymer comprising a twelfth coupling agent; and

reacting the eleventh coupling agent and the twelfth coupling agent to form covalent bonds.

52. The method of claim 51, wherein the covalent bond is a siloxy bond (Si-O-Si) and the eleventh and twelfth coupling agents each comprises a molecular moiety comprising a silicon atom linked to a functional group selected from a group consisting of OH, Cl, Br, I, OPh, ester, and sulfonate ester.

53. The method of claim 51 or 52, wherein the hydrophobic polymer is selected from the group consisting of polydimethylsiloxane (PDMS), Ecoflex, polyurethane (PU), poly (isoprene), and poly (butadiene).

54. The method of any one of claims 51-53, wherein the hydrophilic polymer is selected from the group consisting poly(hydroxyethylmethacrylate) (PHEMA), poly(acrylamide) (PAAm), poly(dimethylacrylamide) (PDMA), poly(N-isopropylacrylamide) (PNIPAM), sodium polyacrylate (NaPAA), [2-(Acryloyloxy)ethyl] trimethylammonium chloride

(PDMAEA), alginate, chitosan, cellulose, polyvinyl alcohol (PVA), poly(lactic acid) (PLA), hyaluronic acid, poly (ethylene glycol) (PEG), and a combination thereof.

55. A luminescent device comprising:

one or more first composite fibers each comprising:

a first fiber-shaped core comprising a first hydrogel comprising a first hydrogel polymer, wherein the first fiber-shaped core has an elongated body and a side-wall surface along the elongated body; and

a luminescent layer comprising a first elastomeric polymer and a luminescent material, coaxially disposed with the first fiber-shaped core, and surrounding the first fiber-shaped core's side-wall surface; and

one or more second composite fibers each comprising:

a second fiber-shaped core comprising a second hydrogel comprising a second hydrogel polymer, wherein the second fiber-shaped core has an elongated body and a side-wall surface along the elongated body; and

an elastomeric layer comprising a second elastomeric polymer, coaxially disposed with the second fiber-shaped core, and surrounding the second fiber-shaped core's side-wall surface;

wherein at least one of the first composite fibers and at least one of the second composite fibers are disposed at an angle such that the first and second composite fibers at least partially overlap.

56. The luminescent device of claim 55, wherein the angle is less than 180 degrees and more than 0 degree.

57. The luminescent device of claim 55 or 56, wherein at least one of the first and second hydrogels further comprise a salt.

58. The luminescent device of any one of claims 55-57, wherein the first and second hydrogel polymers are each independently selected from the group consisting poly(hydroxyethylmethacrylate) (PHEMA), poly(acrylamide) (PAAm), poly(dimethylacrylamide) (PDMA), poly(N-isopropylacrylamide) (PNIPAM), sodium polyacrylate (NaPAA), [2-(Acryloyloxy)ethyl] trimethylammonium chloride (PDMAEA),

alginate, chitosan, cellulose, polyvinyl alcohol (PVA), poly(lactic acid) (PLA), hyaluronic acid, poly (ethylene glycol) (PEG), and a combination thereof.

59. The luminescent device of any one of claims 55-58, wherein at least one of the first and second fiber-shaped cores each have two end surfaces and a cross-section surface each having a shape independently selected from the group consisting of circle, oval, square, triangle, rectangle, diamond, trapezoidal, pentagon, hexagon, heptagon, and octagon.

60. The luminescent device of any one of claims 55-59, wherein the first and second elastomeric polymers are each independently selected from the group consisting of polydimethylsiloxane (PDMS), Ecoflex, polyurethane (PU), poly (isoprene), and poly (butadiene).

61. The luminescent device of any one of claims 55-60, wherein the luminescent material is selected from the group consisting of ZnS doped with copper (Cu), aluminum (Al), chloride (Cl), bromine (Br), iodine (I), or manganese (Mn), ZnSe doped with Cu or Cl, ZnCdS doped with Cu, Cl, Mn, or silver (Ag), and ZnSSe doped with Cu or Cl.

62. The luminescent device of any one of claims 55-61, wherein the luminescent layer adheres to the first fiber-shaped core.

63. The luminescent device of any one of claims 55-62, wherein the elastomeric layer adheres to the second fiber-shaped core.

64. The luminescent device of any one of claims 55-63, wherein the first fiber-shaped core further comprises a first electrode and the second fiber-shaped core further comprises a second electrode.

65. The luminescent device of any one of claims 55-64, wherein the luminescent device is soft, stretchable, or both soft and stretchable.

66. The luminescent device of any one of claims 55-65, wherein the luminescent device comprises a plurality of the first composite fibers parallel to each other, a plurality of the second composite fibers parallel to each other; and wherein the first and second composite fibers form a grid.

67. The luminescent device of claim 66, wherein the angle is less than 180 degrees and more than 0 degree.

68. A method of providing luminescence, comprising:

providing a luminescent device of any one of claims 55-67;

applying a voltage between the first and second fiber-shaped cores; and

activating the luminescent material to emit luminescence at the area wherein the first and second composite fibers partially overlap.

69. The method of claim 68, wherein the first fiber-shaped core further comprises a first electrode and the second fiber-shaped core further comprises a second electrode, and the voltage is applied to the first and second electrodes.

70. The method of claim 69, wherein the voltage is an alternating voltage.

71. The method of claim 70, wherein the voltage ranges from 100 volts to 1 kilovolt.

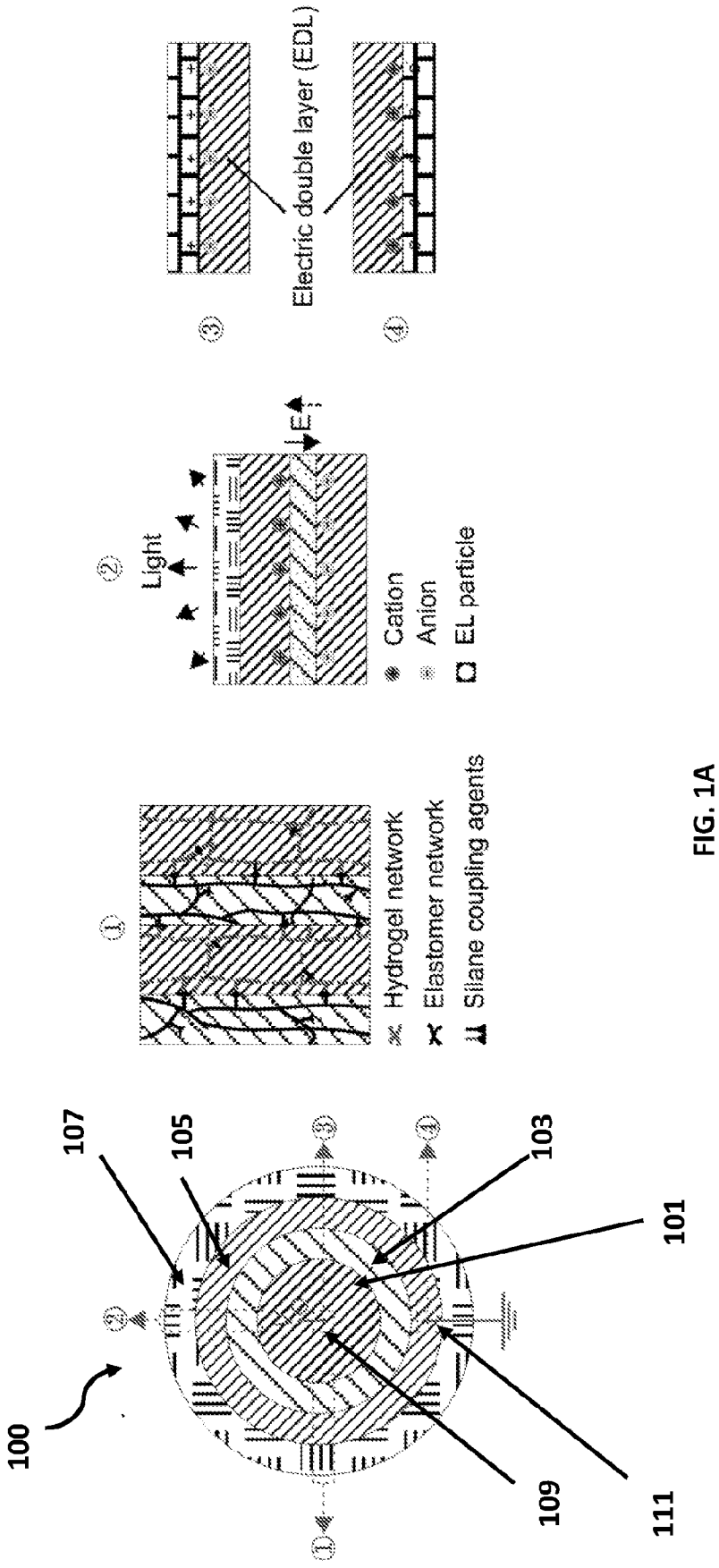

100
107
105
103
101
109
111
Hydrogel network
Elastomer network
Silane coupling agents
Cation
Anion
EL particle
Light
Electric double layer (EDL)

FIG. 1A

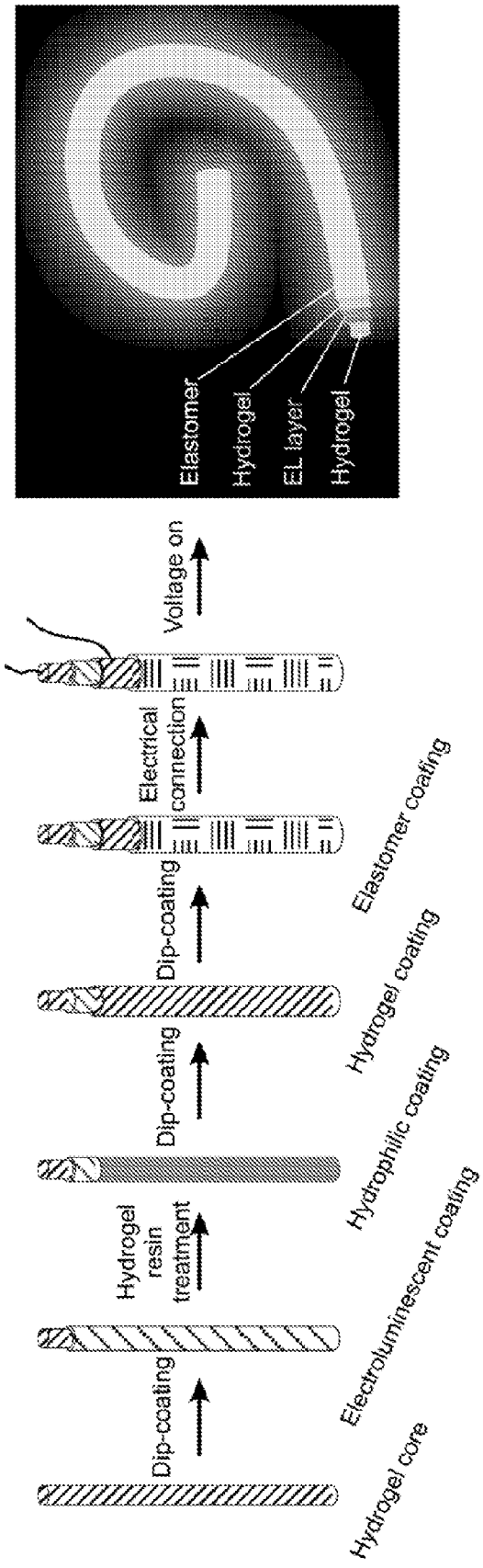

Elastomer
Hydrogel
EL layer
Hydrogel
Voltage on
Electrical connection
Dip-coating
Dip-coating
Hydrogel resin treatment
Dip-coating
Elastomer coating
Hydrogel coating
Hydrophilic coating
Electroluminescent coating
Hydrogel core

FIG. 1B

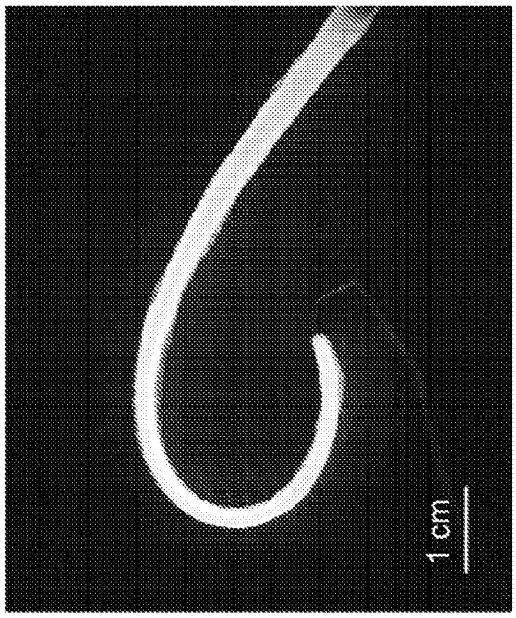


FIG. 1E

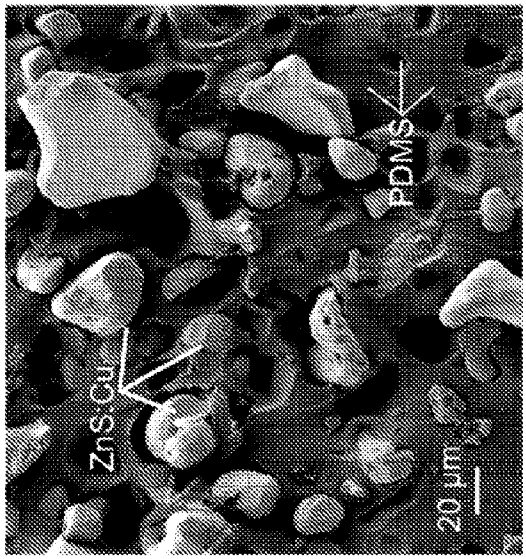


FIG. 1D

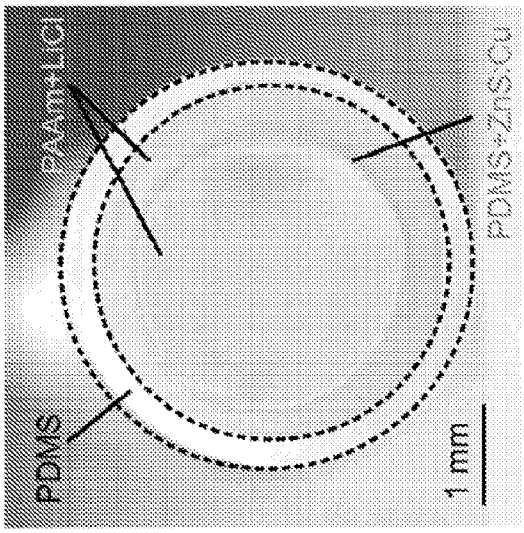


FIG. 1C

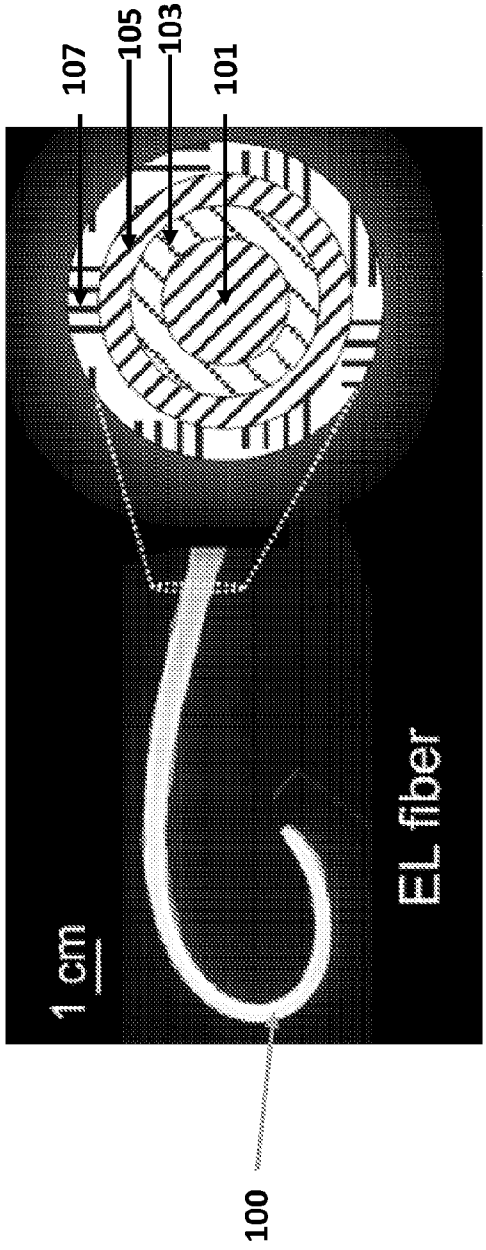


FIG. 1F

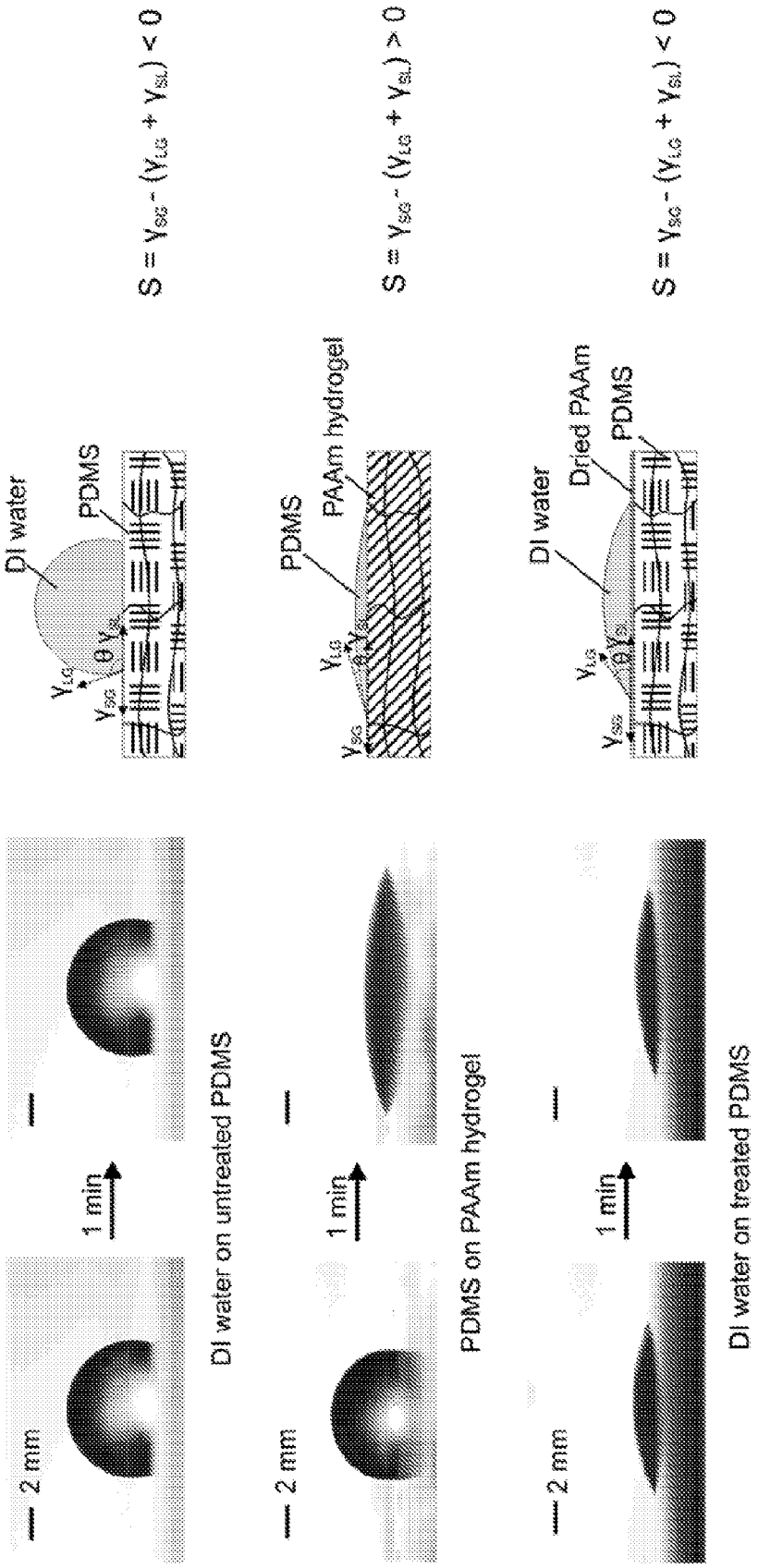


FIG. 2A

FIG. 2B

FIG. 2C

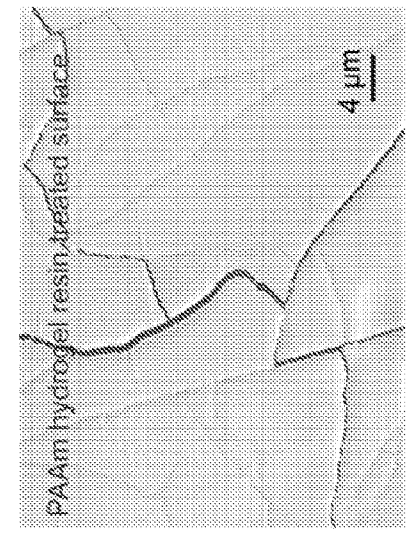


FIG. 2F

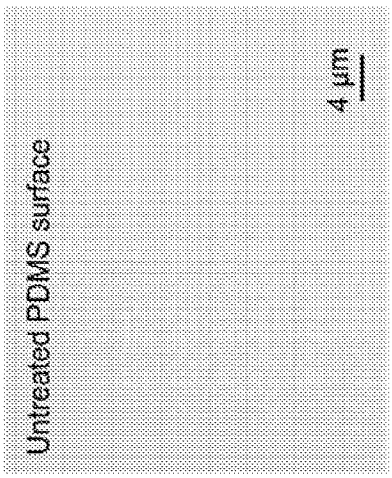


FIG. 2E

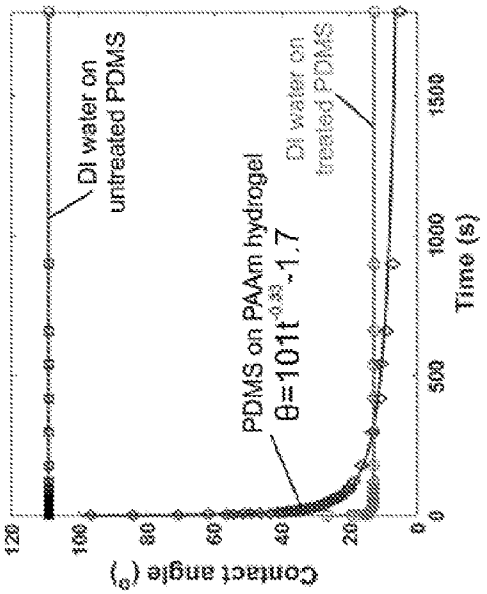


FIG. 2D

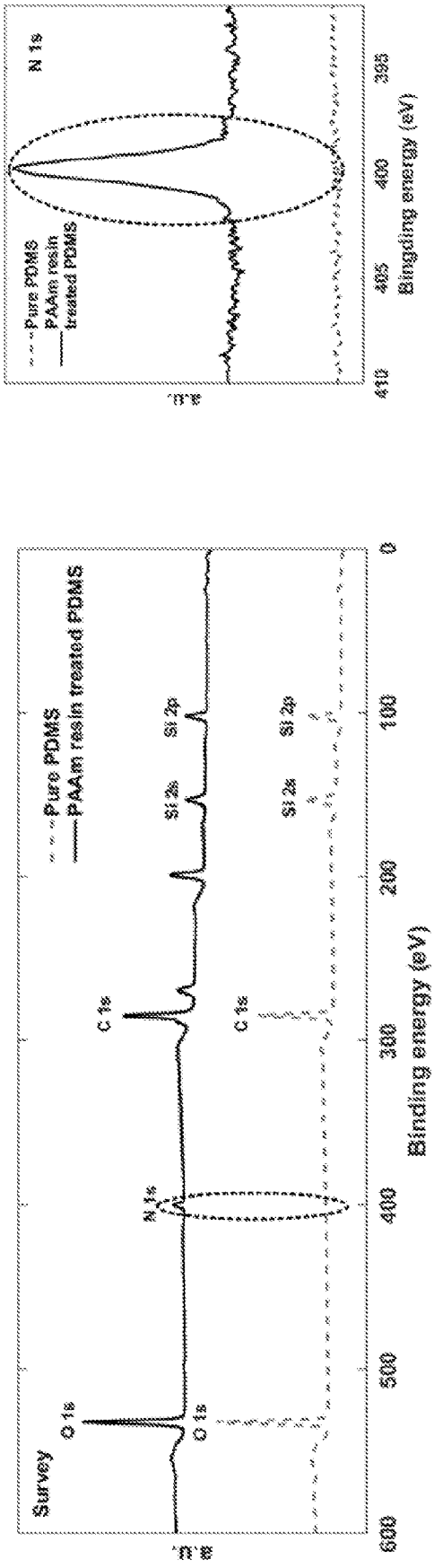

Survey
O 1s
O 1s
N 1s
C 1s
Si 2s
Si 2p
C 1s
Si 2s
Si 2p
Pure PDMS
PAAm resin treated PDMS
Binding energy (eV)
0
100
200
300
400
500
600
a.u.
N 1s
Pure PDMS
PAAm resin treated PDMS
Binding energy (eV)
395
400
405
410
a.u.

FIG. 2G

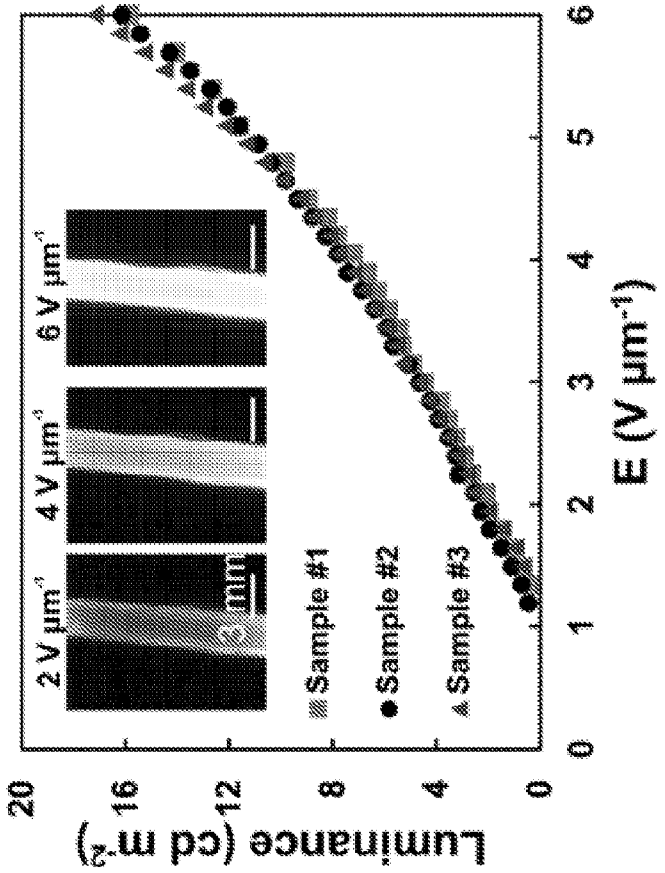

Luminance (cd m^{-2})
E (V µm^{-1})
Sample #1
Sample #2
Sample #3
2 V µm^{-1}
4 V µm^{-1}
6 V µm^{-1}
1 mm

FIG. 3B

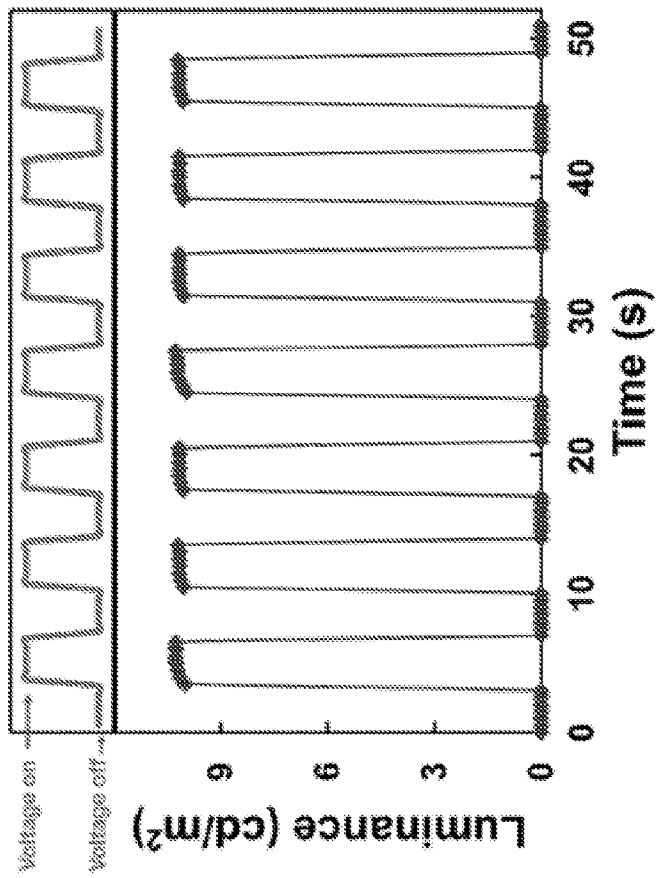

Luminance (cd/m^2)
Time (s)
Voltage on
Voltage off

FIG. 3A

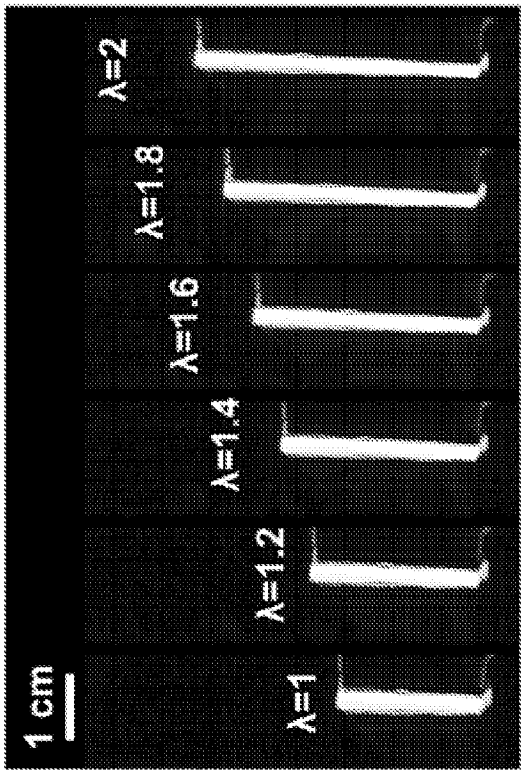

1 cm
λ=1
λ=1.2
λ=1.4
λ=1.6
λ=1.8
λ=2

FIG. 3D

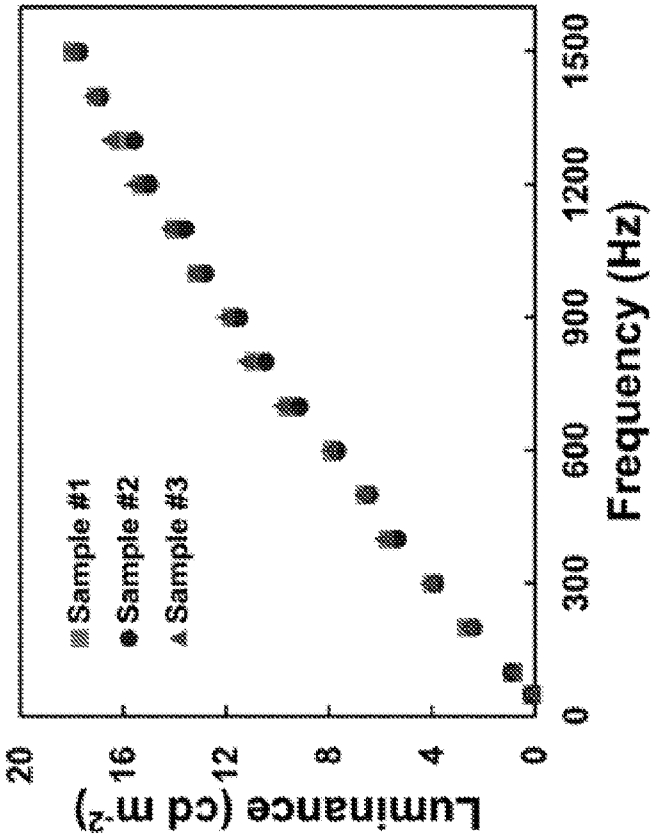

Luminance (cd m⁻²)
Frequency (Hz)
Sample #1
Sample #2
Sample #3
0
4
8
12
16
20
0
300
600
900
1200
1500

FIG. 3C

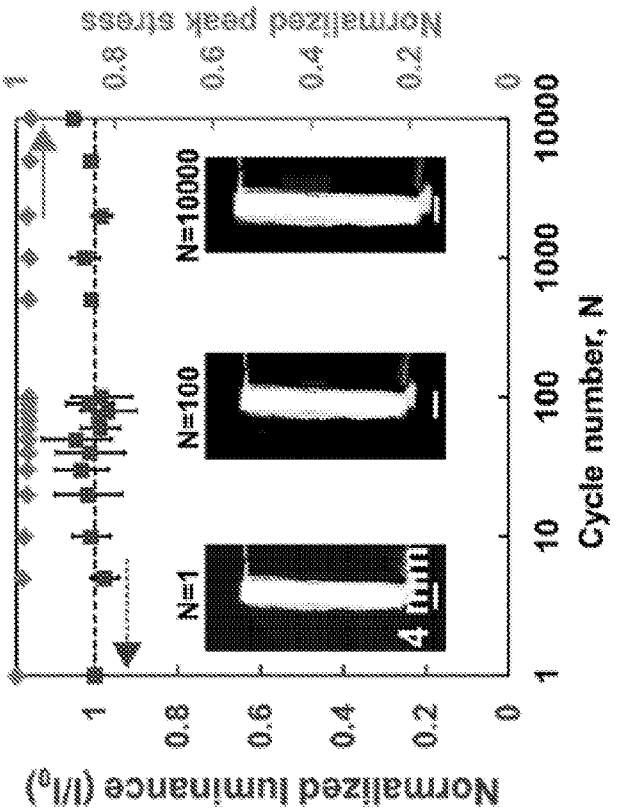

Normalized luminance (I/I0)
Normalized peak stress
Cycle number, N
N=1
N=100
N=10000
4 mm

FIG. 3F

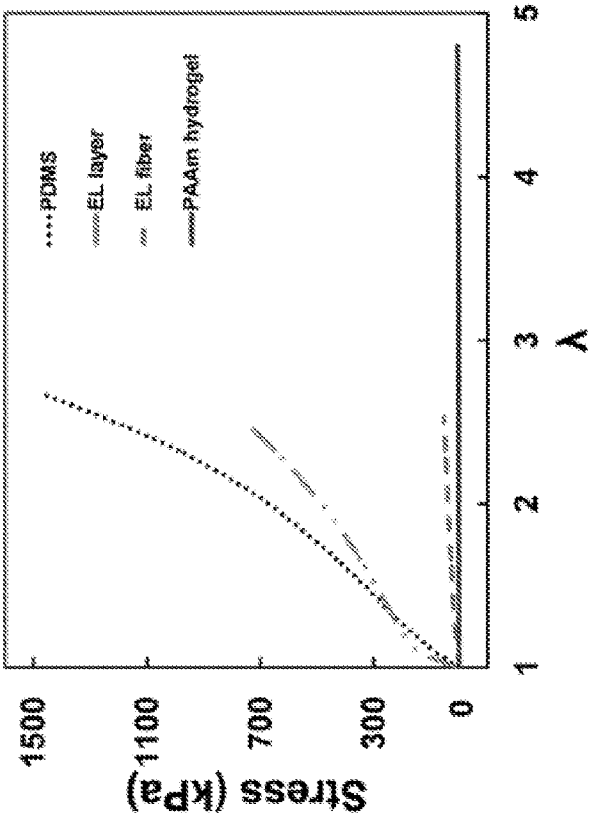

Stress (kPa)
λ
PDMS
EL layer
EL fiber
PAAm hydroget

FIG. 3E

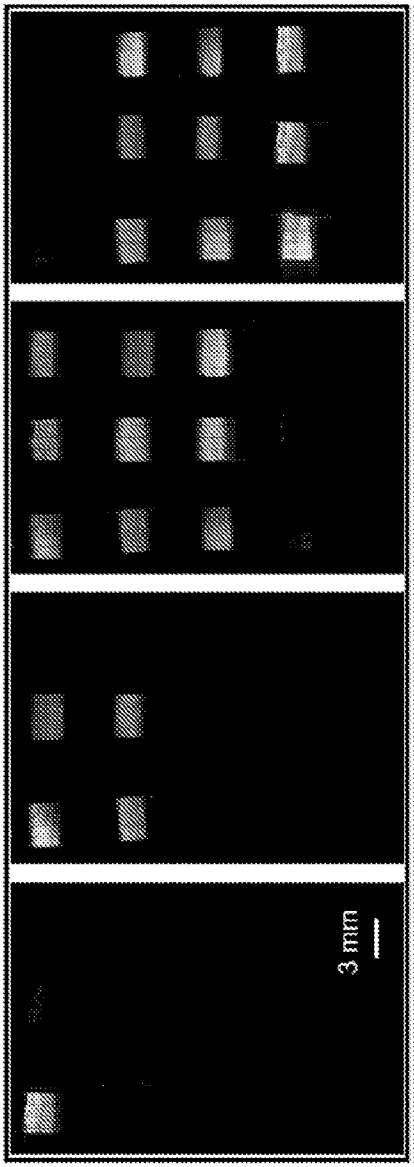


FIG. 4B

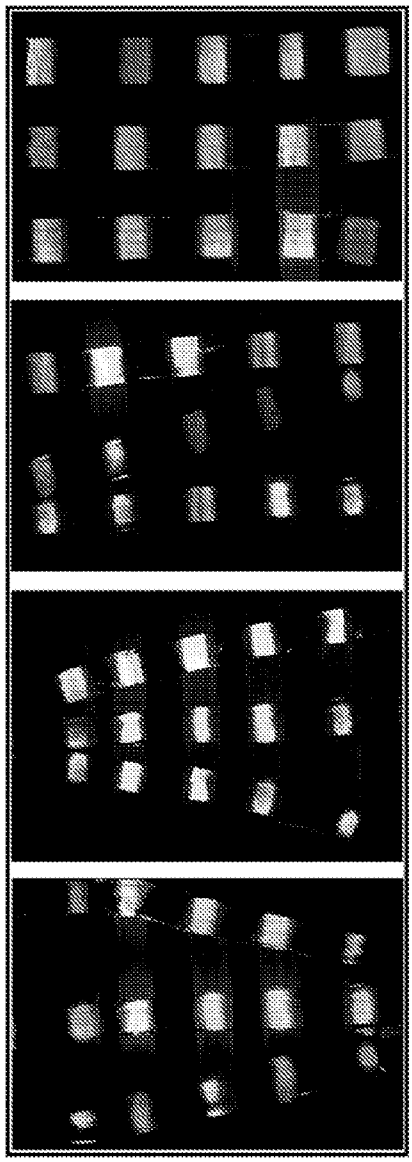


FIG. 4C

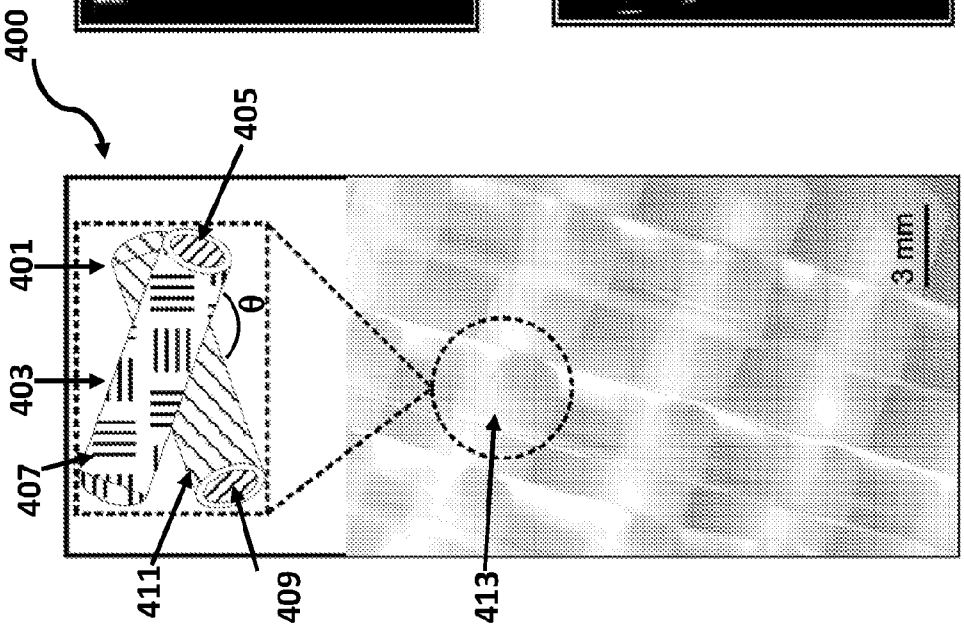


FIG. 4A

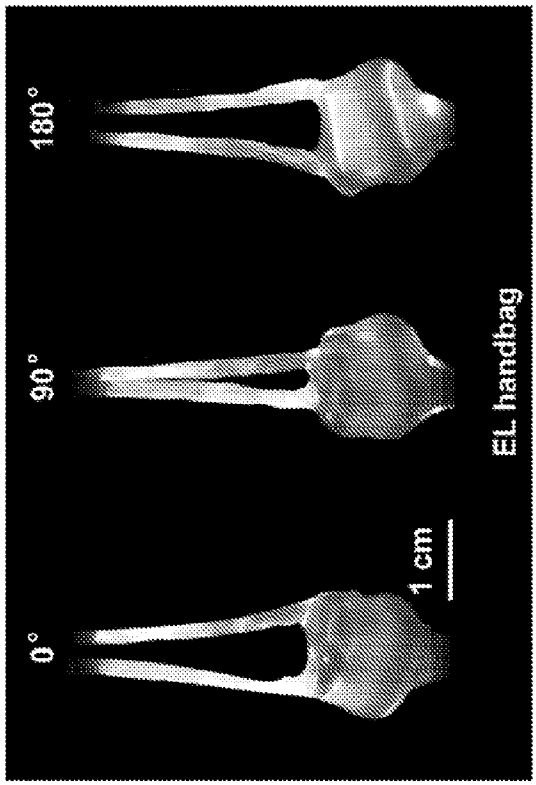

0°
90°
180°
1 cm
EL handbag

FIG. 4E

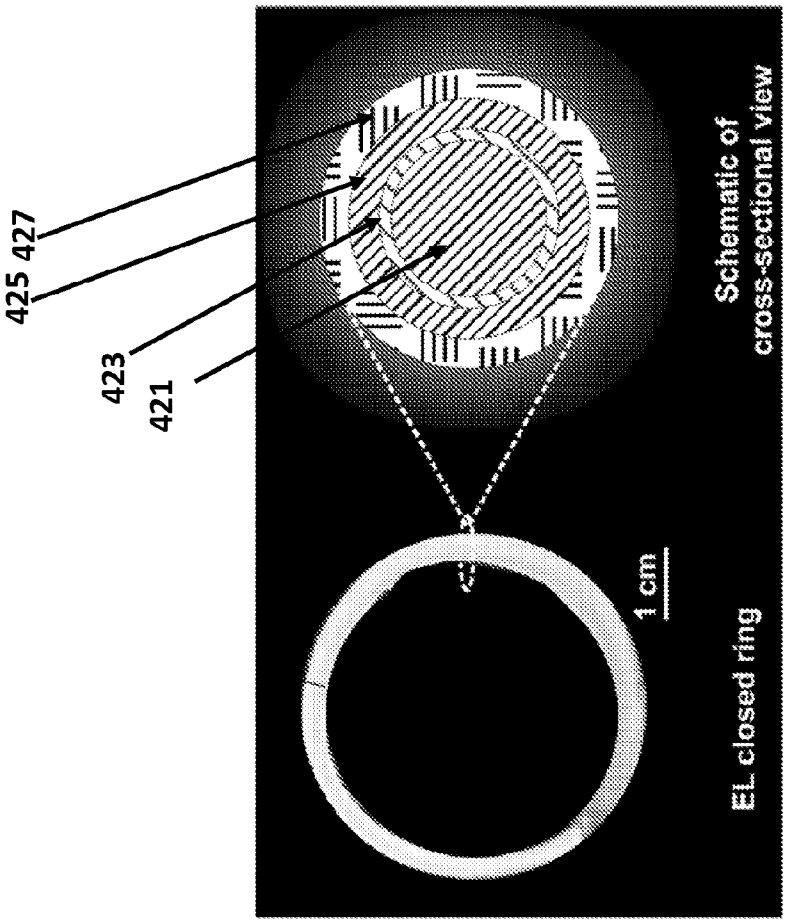
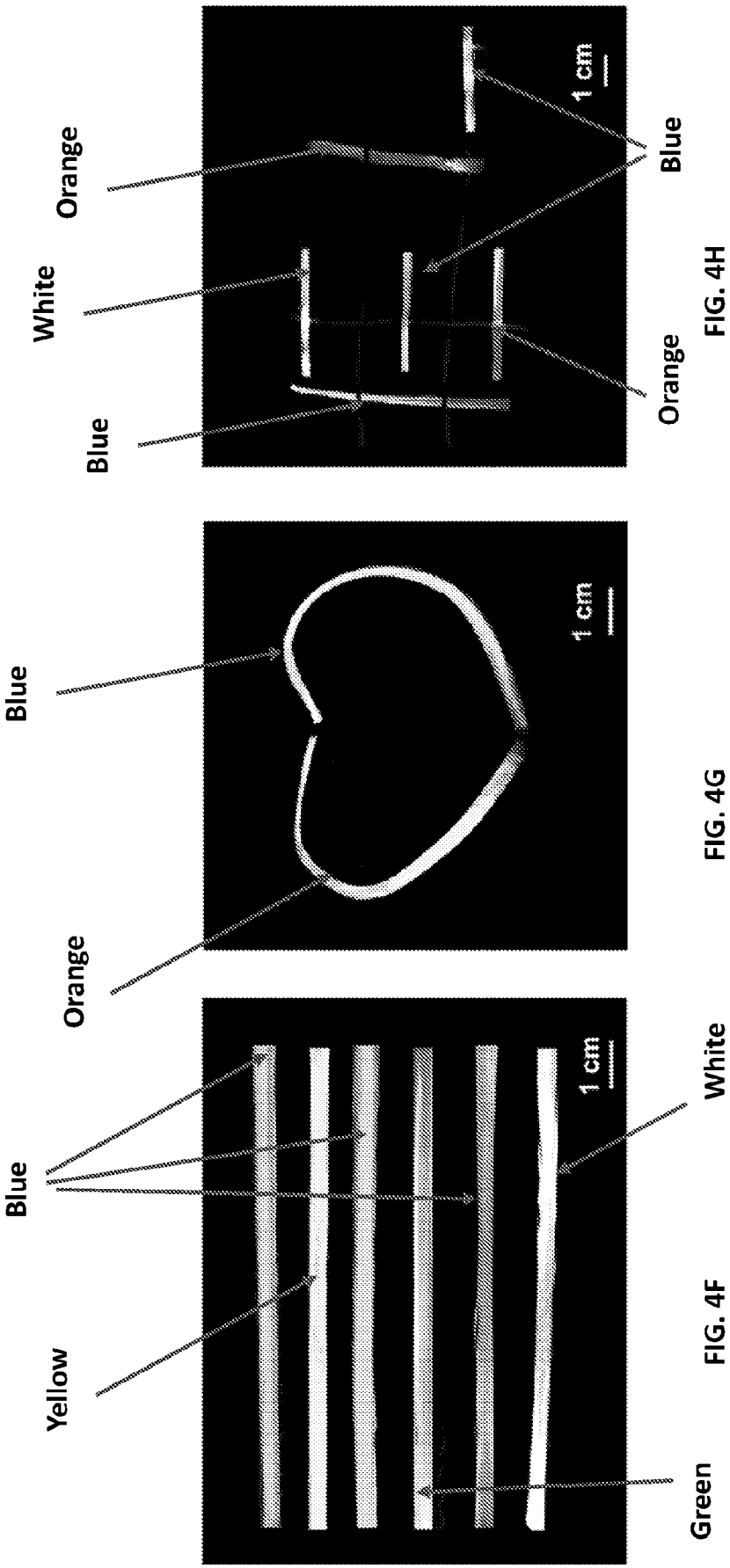

425 427
423
421
Schematic of cross-sectional view
1 cm
EL closed ring

FIG. 4D


Blue
Yellow
1 cm
Green
White
FIG. 4F
Blue
Orange
1 cm
FIG. 4G
Orange
White
Blue
1 cm
Blue
Orange
FIG. 4H

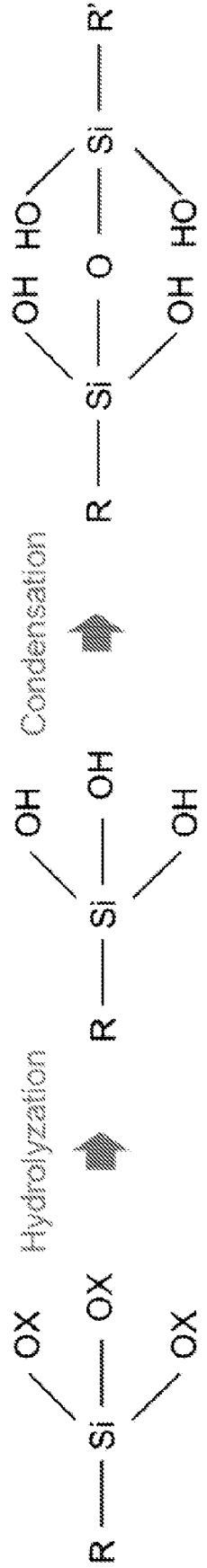


FIG. 5A

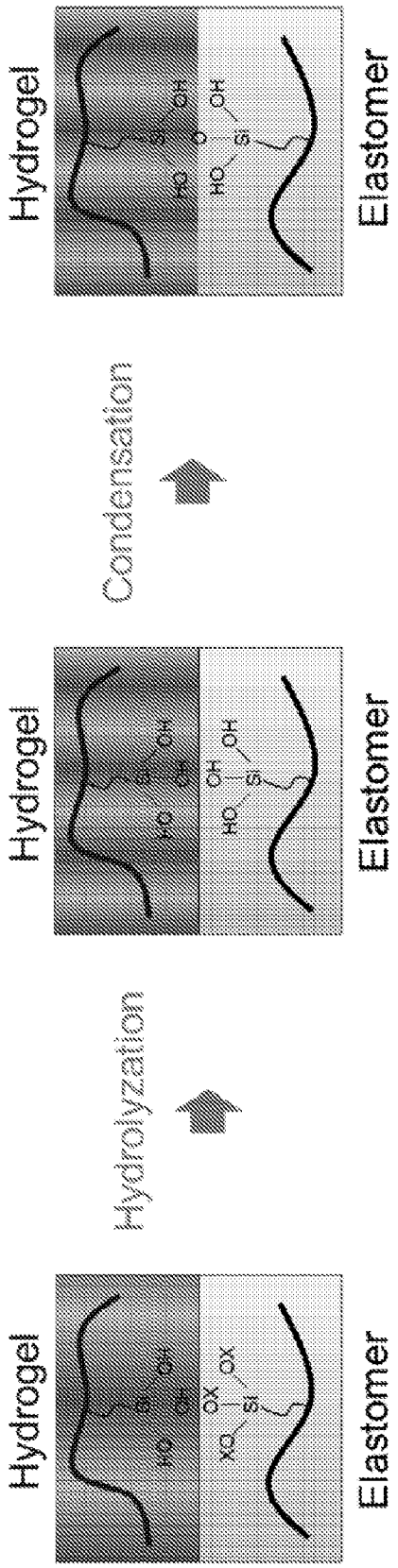

Hydrogel
Elastomer
Hydrolyzation
Hydrogel
Elastomer
Condensation
Hydrogel
Elastomer

FIG. 5B

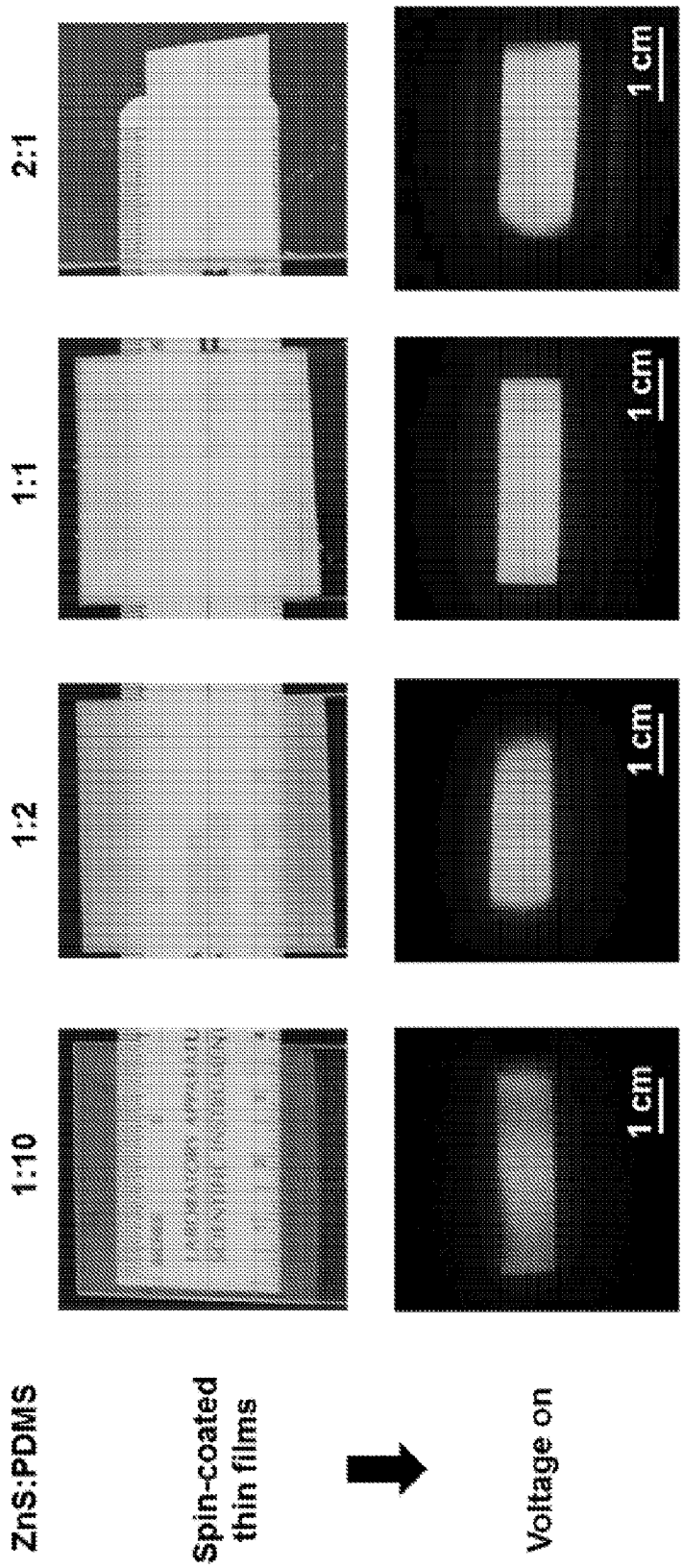
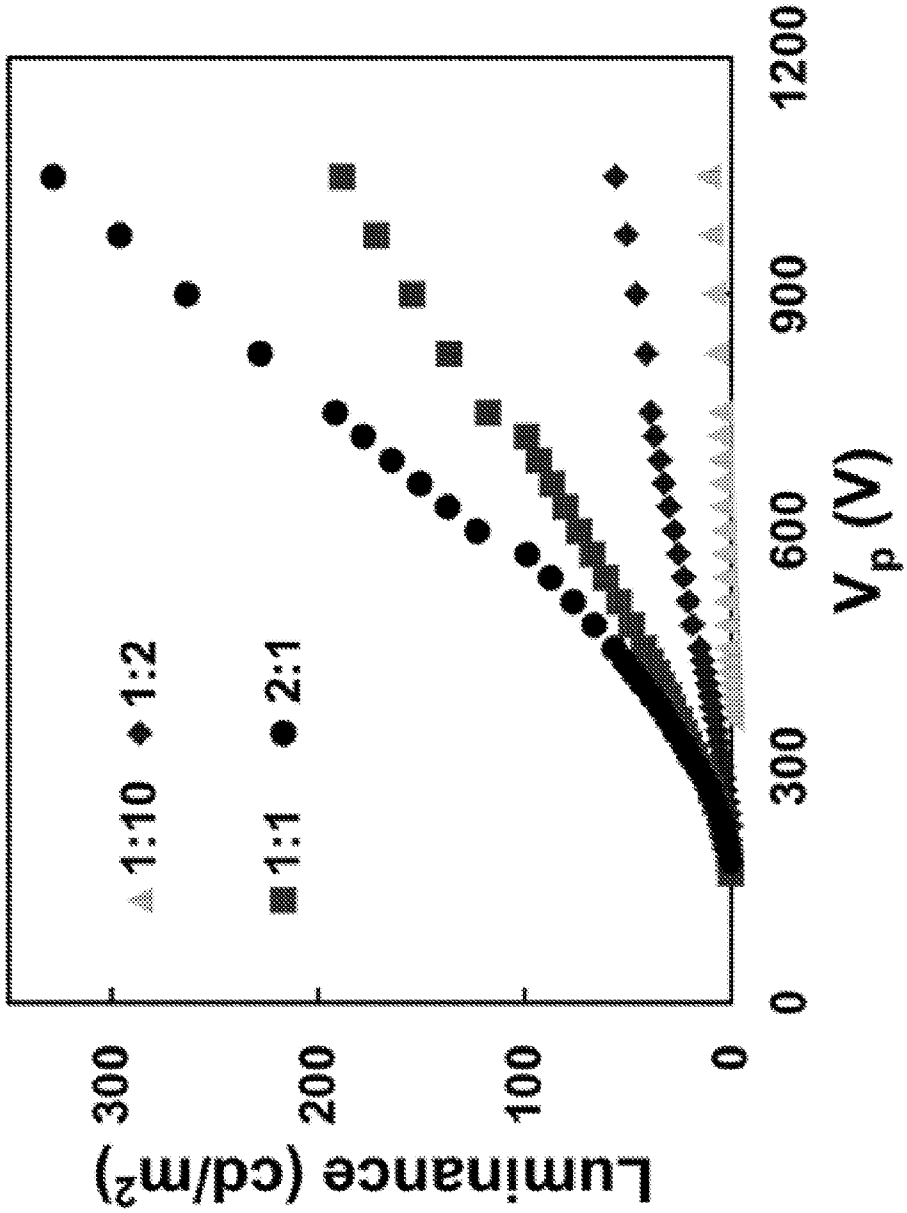

ZnS:PDMS
1:10
1:2
1:1
2:1
Spin-coated thin films
Voltage on
1 cm
1 cm
1 cm
1 cm

FIG. 6A



FIGS. 6B

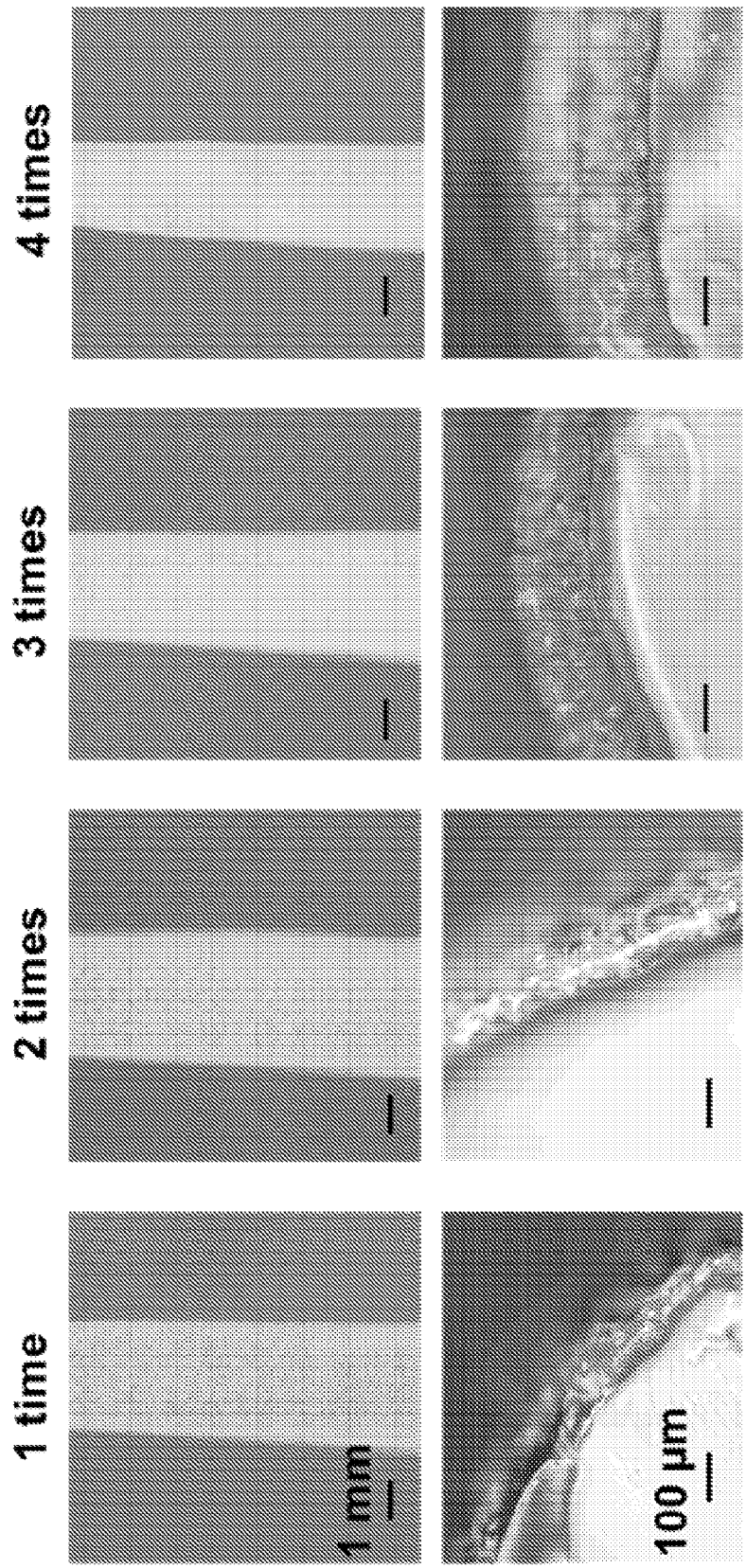


FIG. 7A

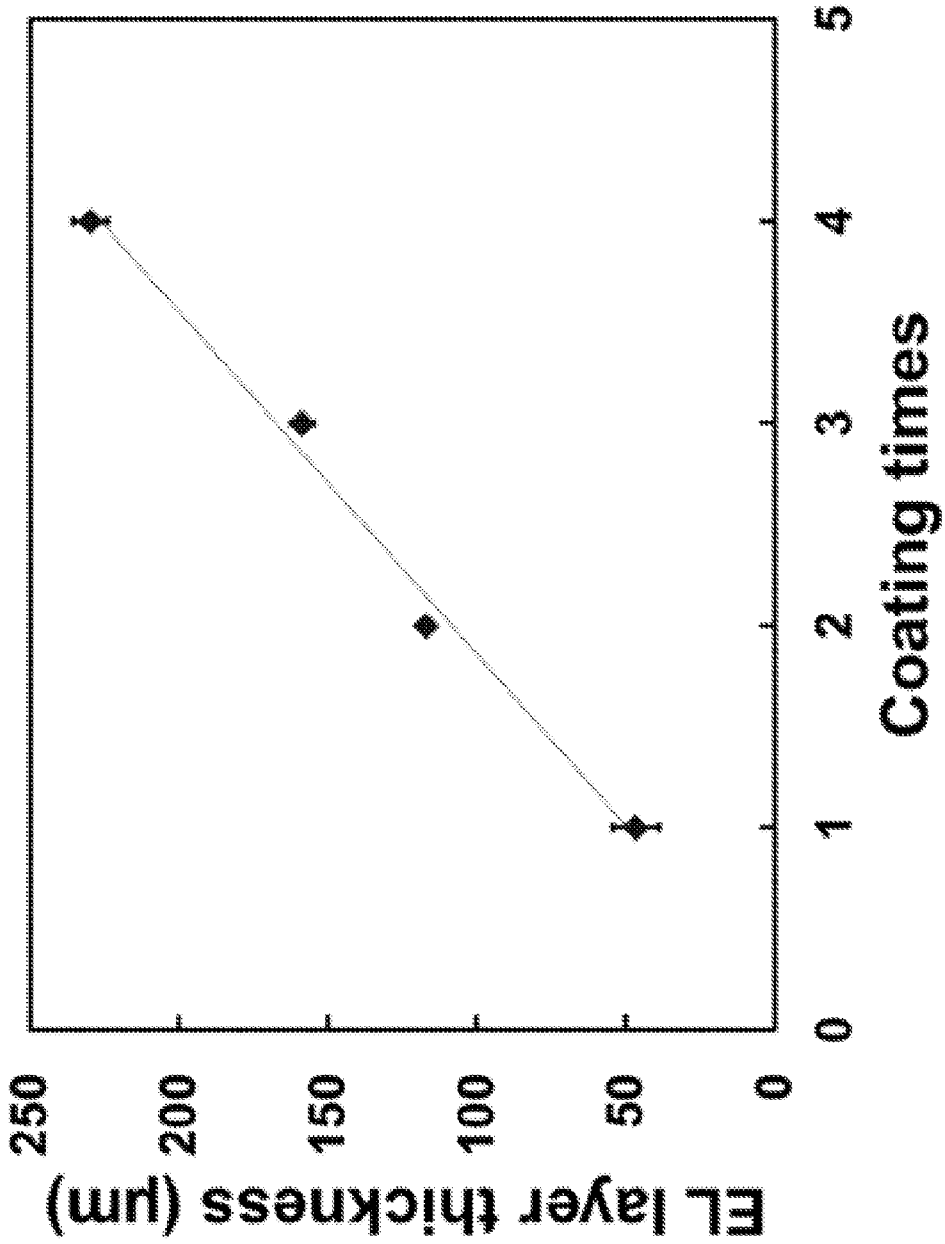

EL layer thickness (μm)
250
200
150
100
50
0
0
1
2
3
4
5
Coating times

FIG. 7B

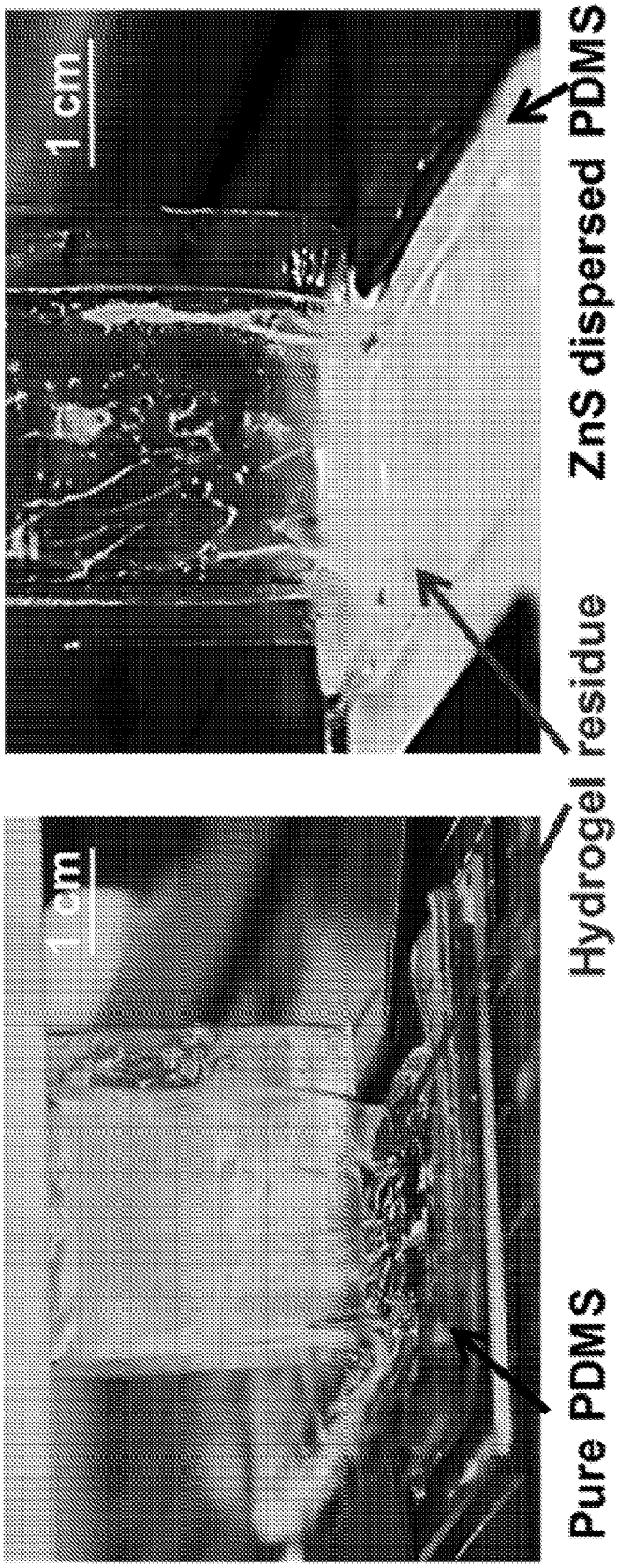


FIG. 8A

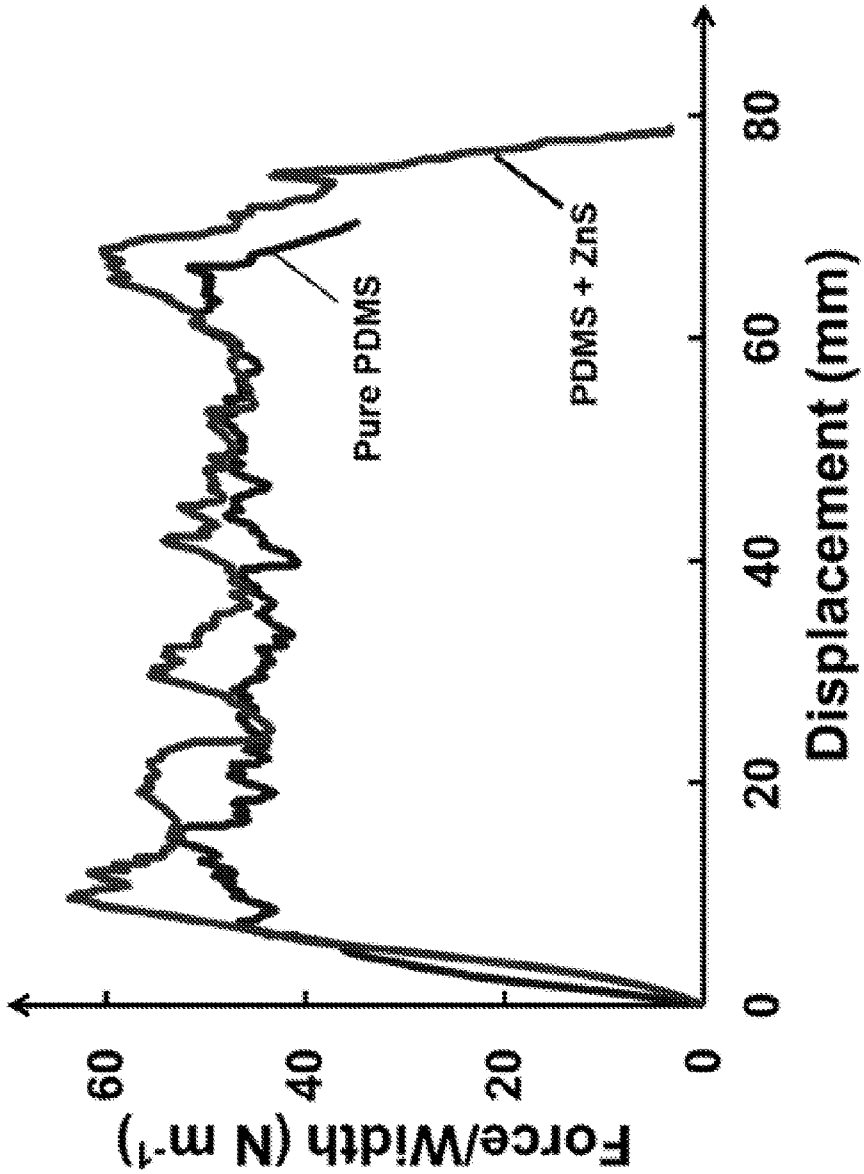

Force/Width (N m-1)
0
20
40
60
0
20
40
60
80
Displacement (mm)
Pure PDMS
PDMS + ZnS

FIG. 8B

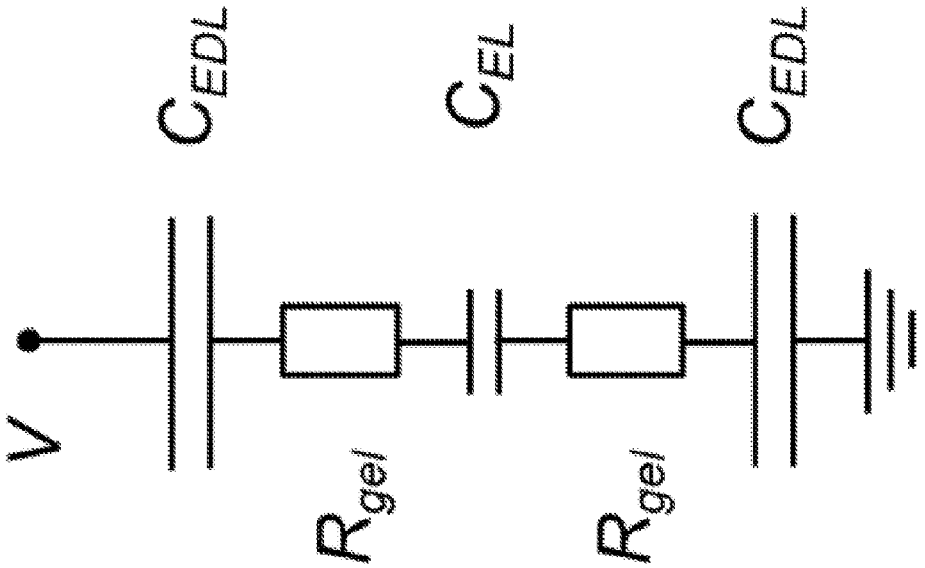

C_{EDL}
C_{EL}
C_{EDL}
V
R_{gel}
R_{gel}

FIG. 9B

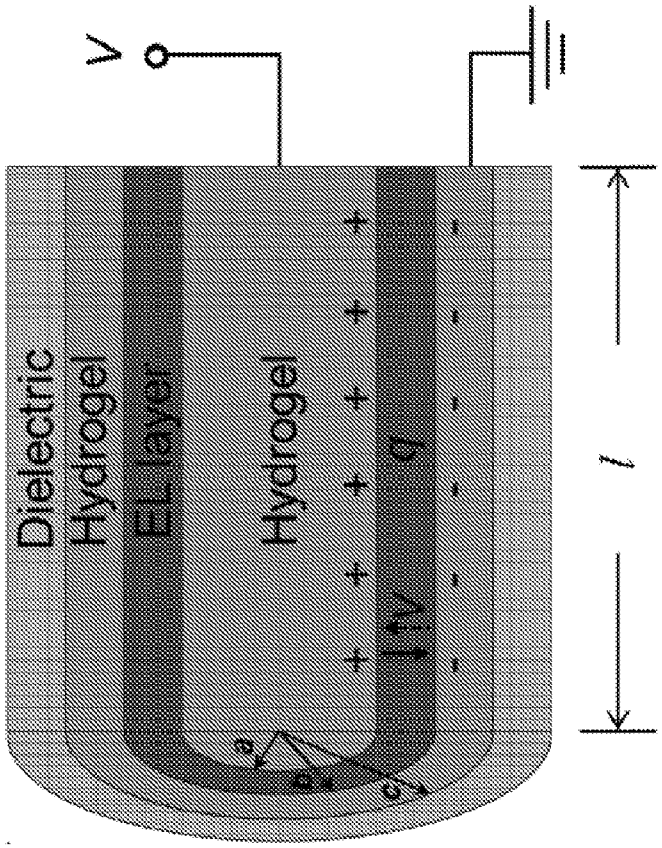

V
Dielectric
Hydrogel
EL layer
Hydrogel
q
l
a
b
c

FIG. 9A

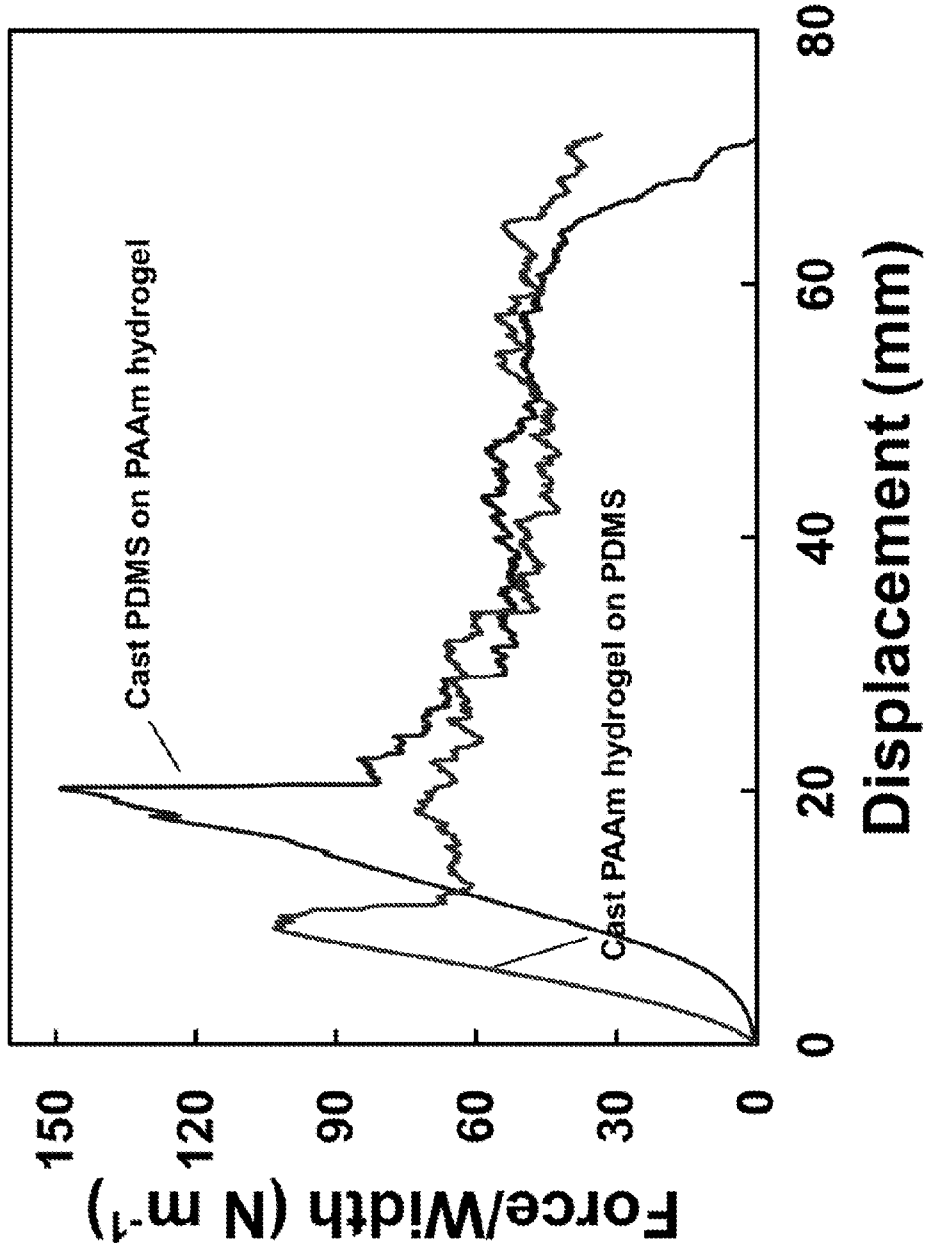

Force/Width (N m-1)
150
120
90
60
30
0
0
20
40
60
80
Displacement (mm)
Cast PDMS on PAAm hydrogel
Cast PAAm hydrogel on PDMS

FIG. 10

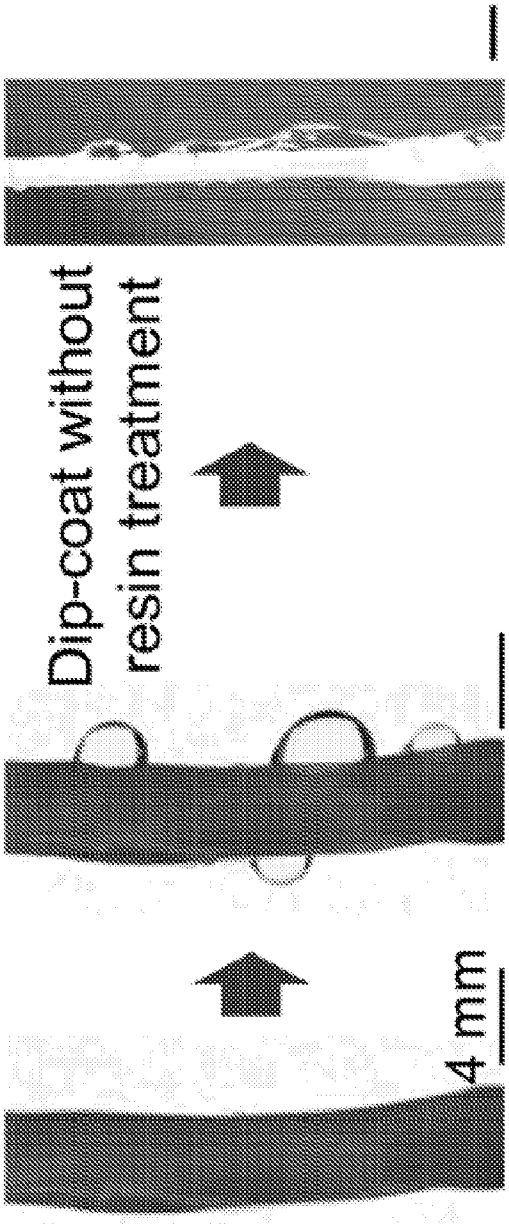


FIG. 11A

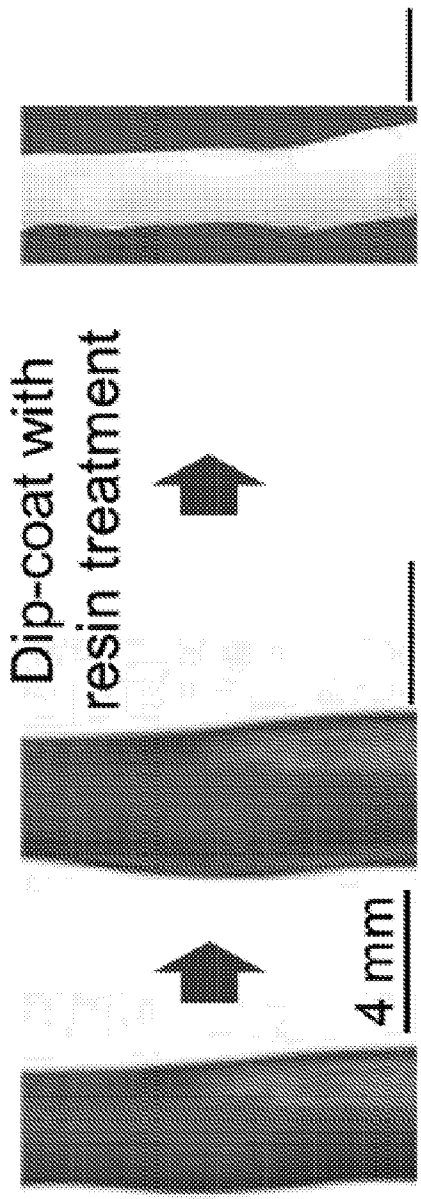


FIG. 11B

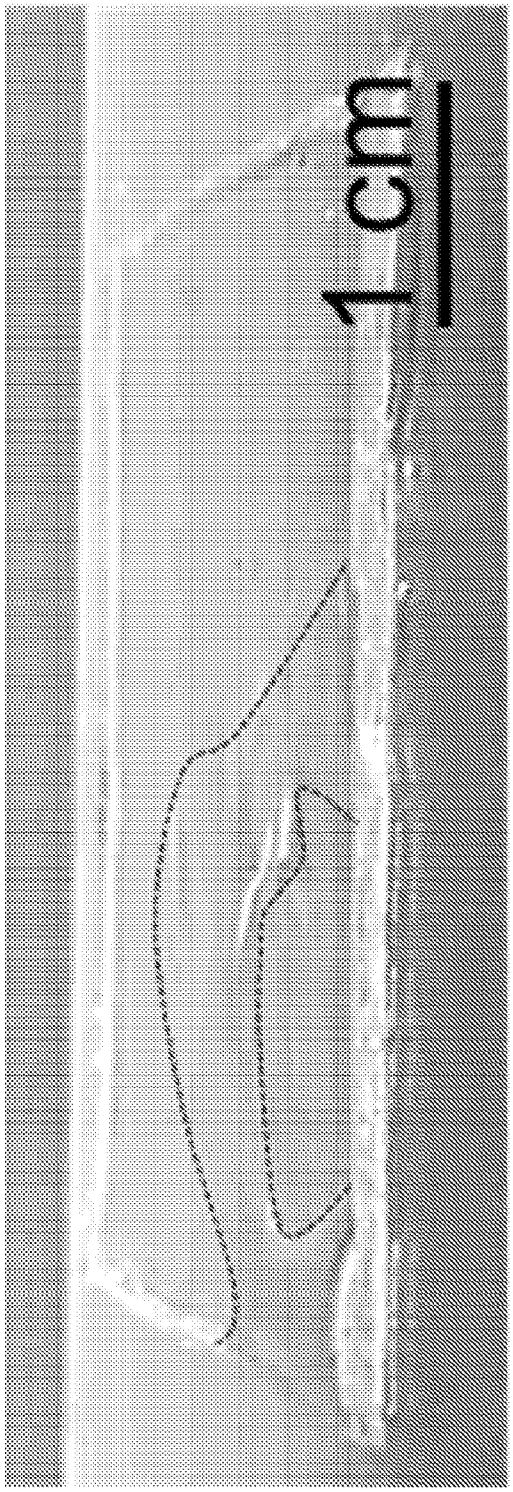


FIG. 12

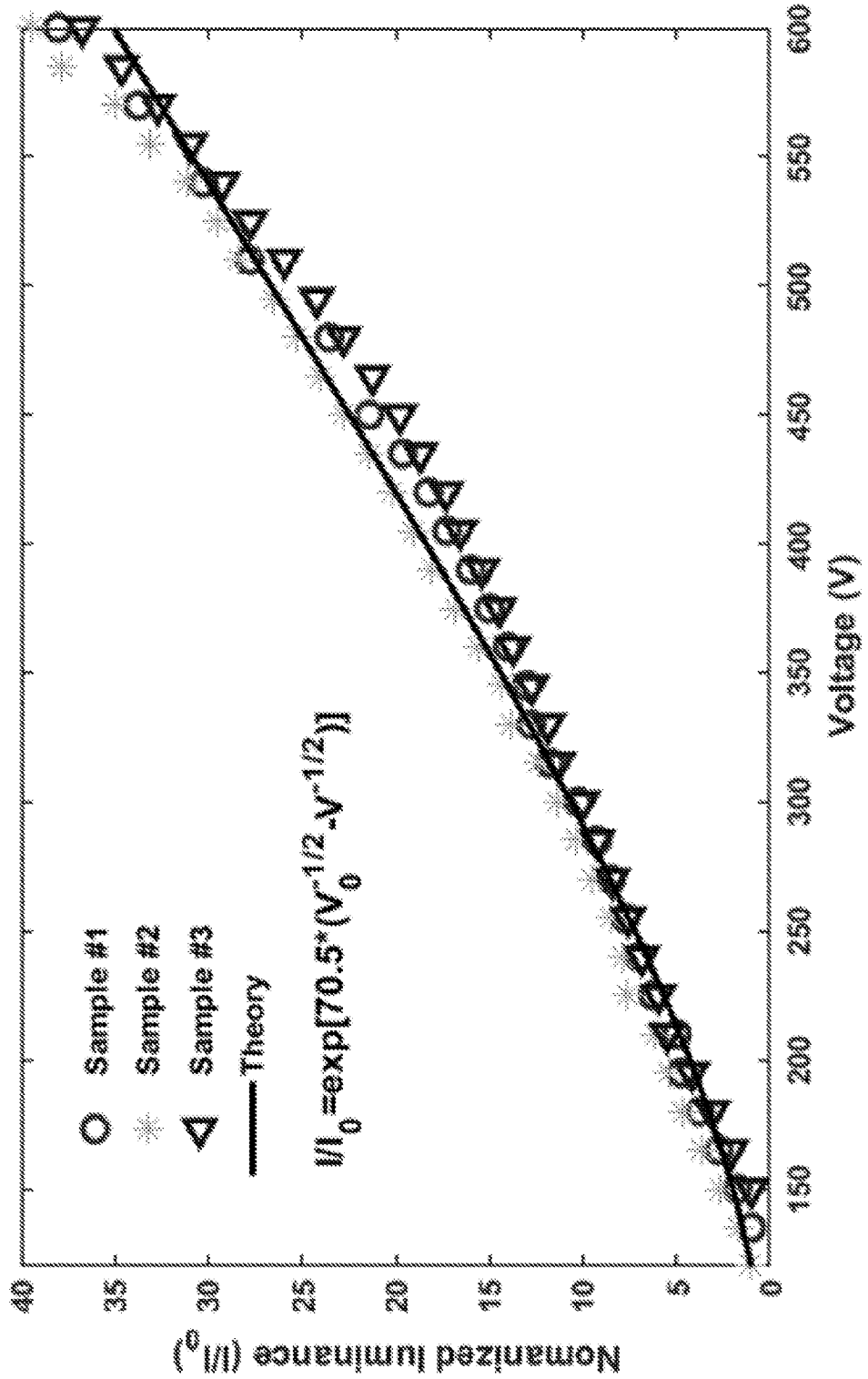

Nomanized luminance (I/I0)
Voltage (V)
Sample #1
Sample #2
Sample #3
Theory
I/I0=exp[70.5*(V0^-1/2-V^-1/2)]
0
5
10
15
20
25
30
35
40
150
200
250
300
350
400
450
500
550
600

FIG. 13

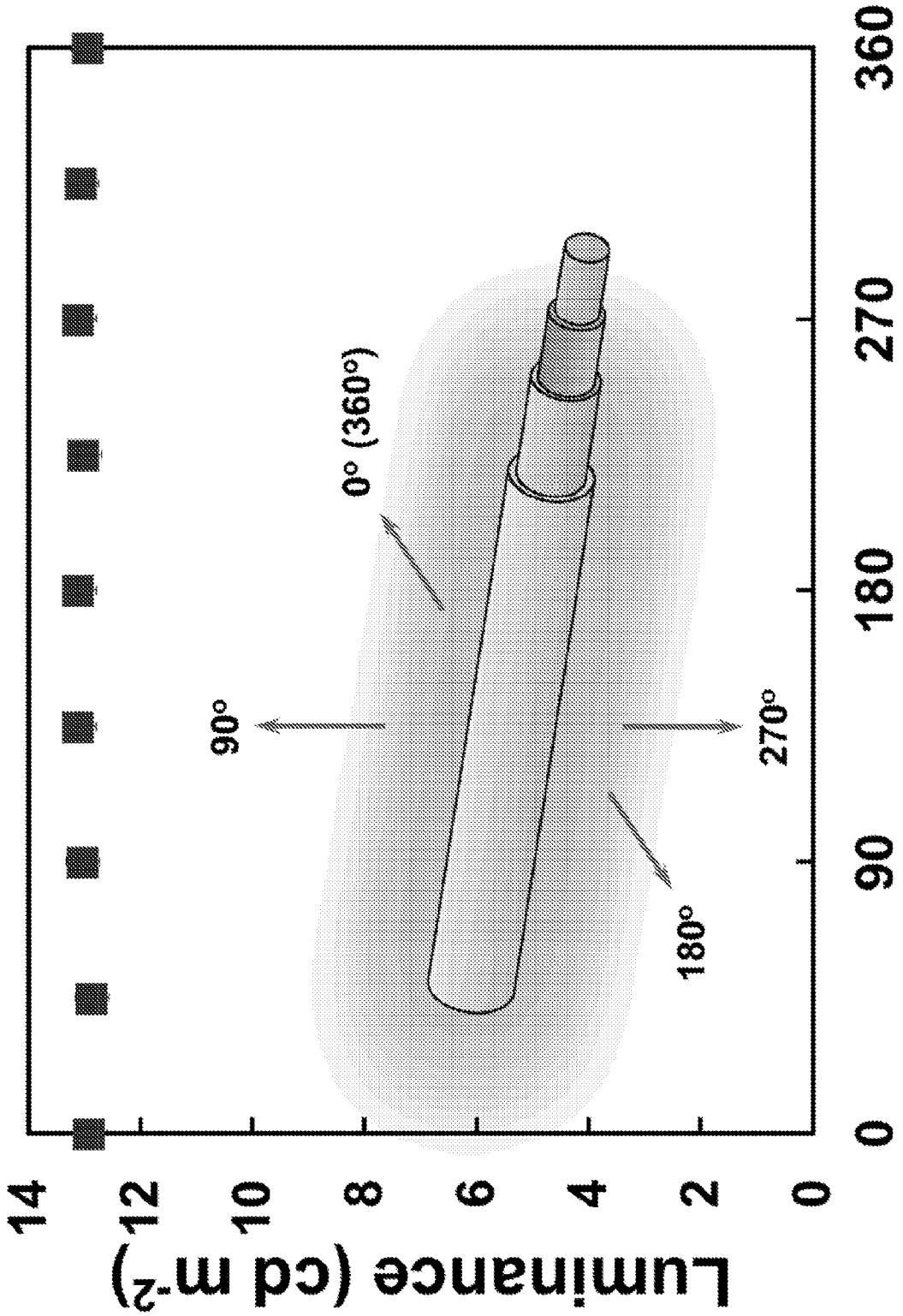

Luminance (cd m-2)
0
2
4
6
8
10
12
14
View angle (°)
0
90
180
270
360
0° (360°)
90°
180°
270°

FIG. 14

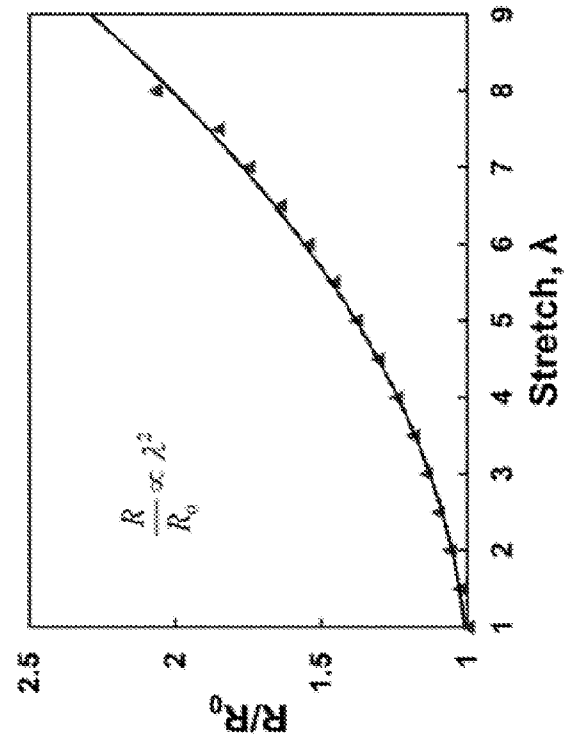


FIG. 15B

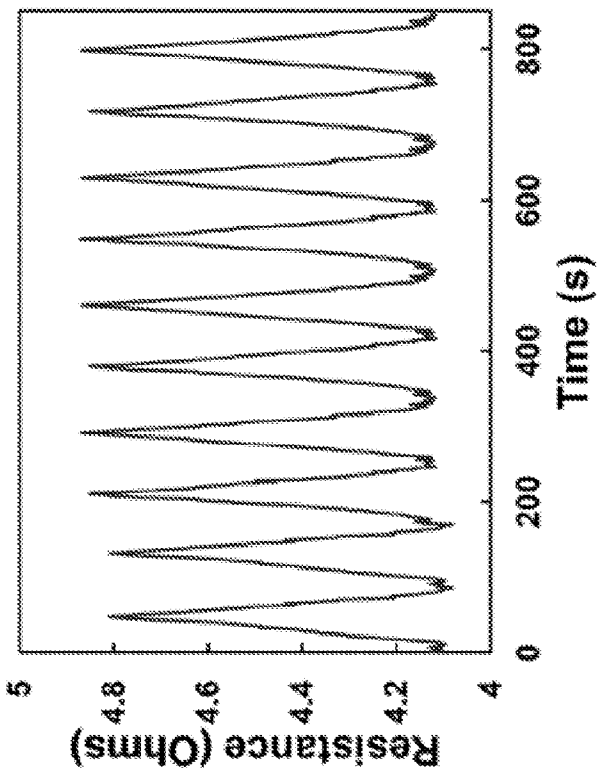


FIG. 15A

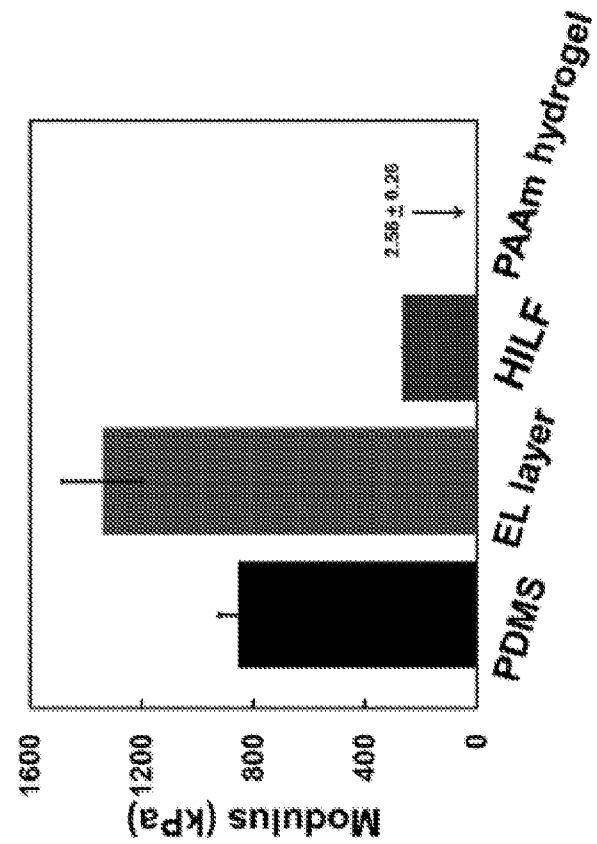


FIG. 16B

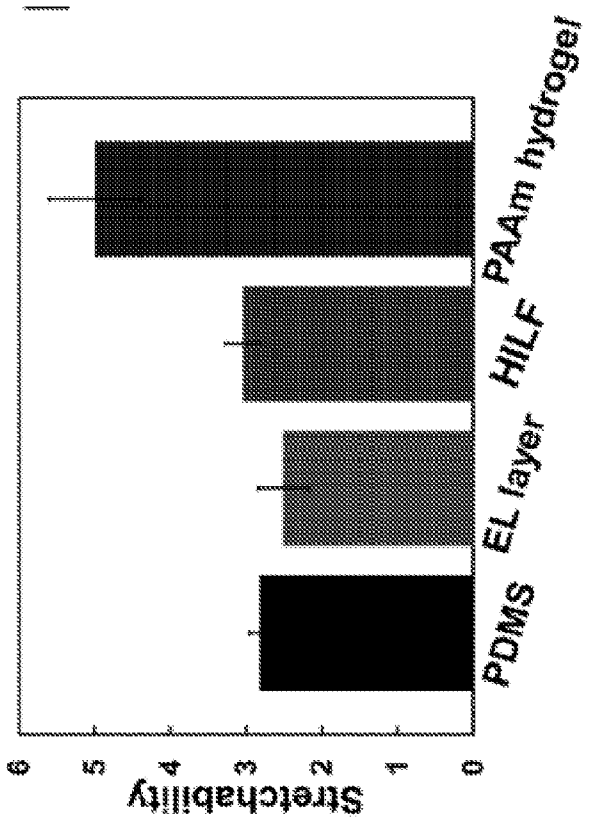
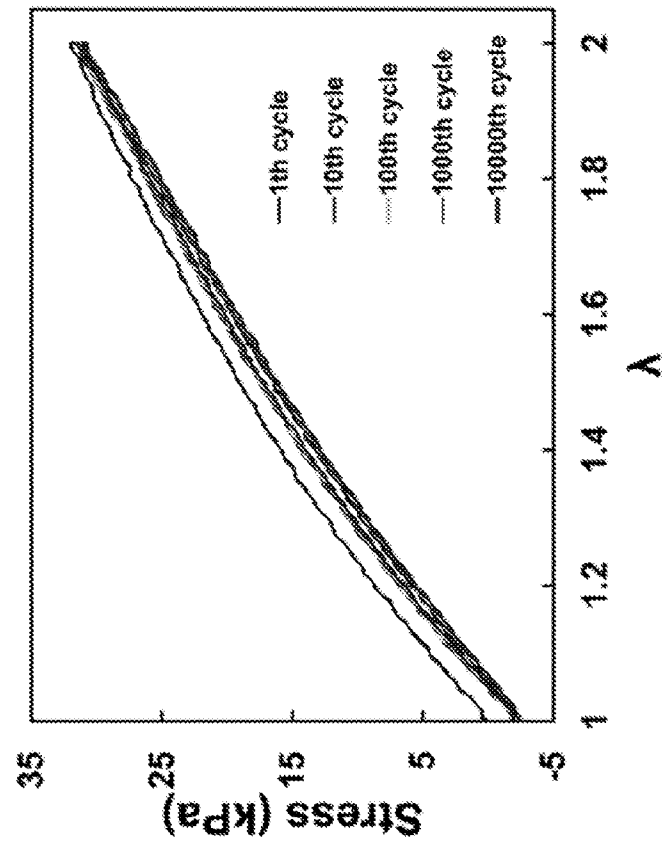


FIG. 16A


Stress (kPa)
35
25
15
5
-5
1
1.2
1.4
1.6
1.8
2
λ
1th cycle
10th cycle
100th cycle
1000th cycle
10000th cycle

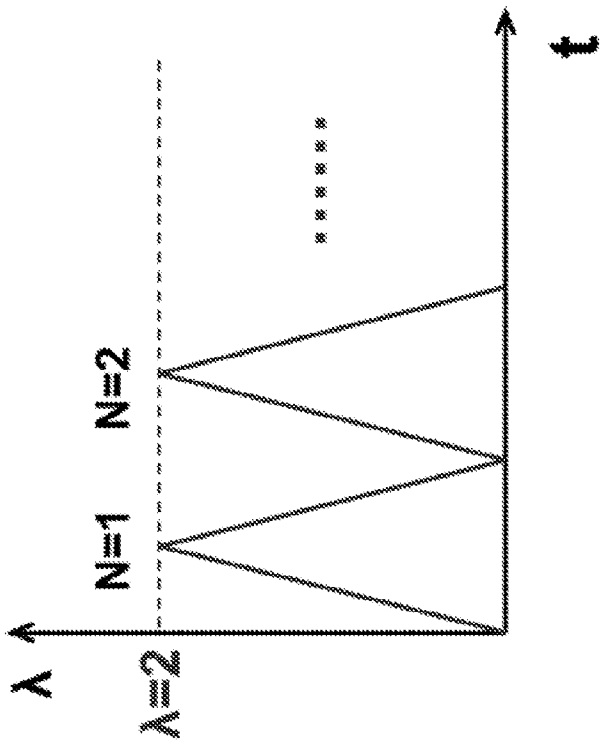

λ
λ=2
N=1
N=2
t

FIG. 17

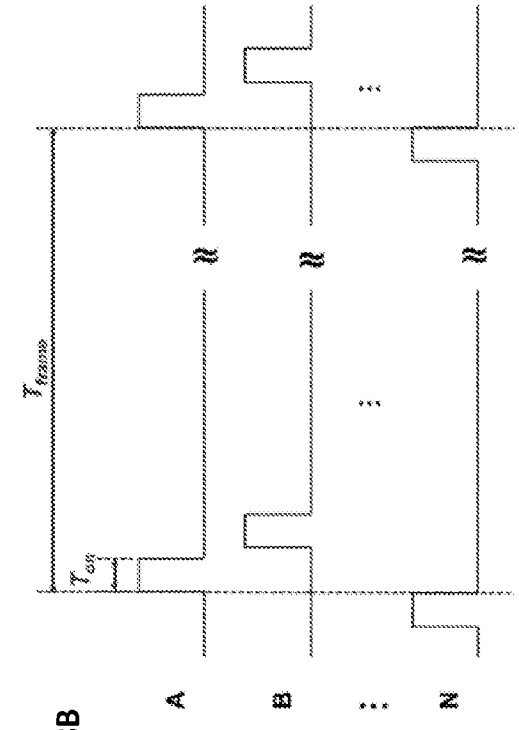


FIG. 18B

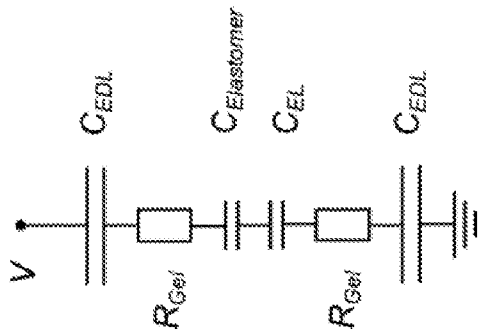


FIG. 18D

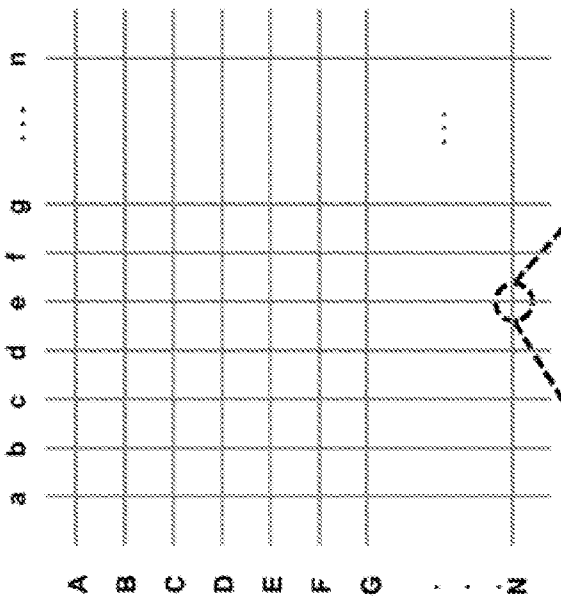


FIG. 18A

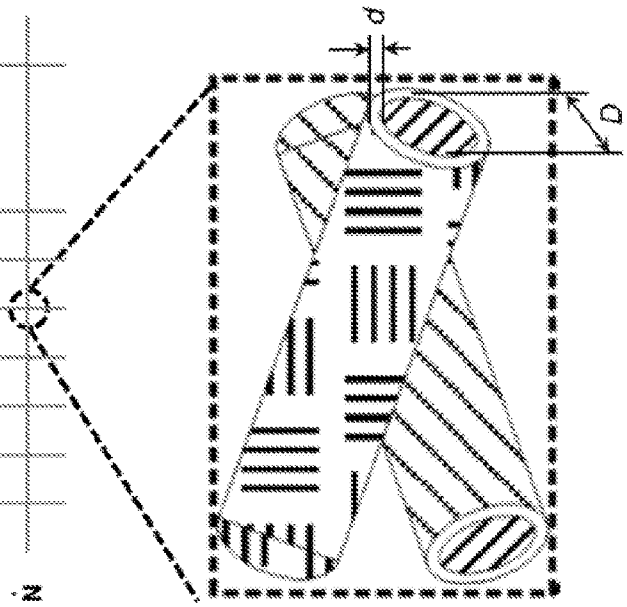


FIG. 18C

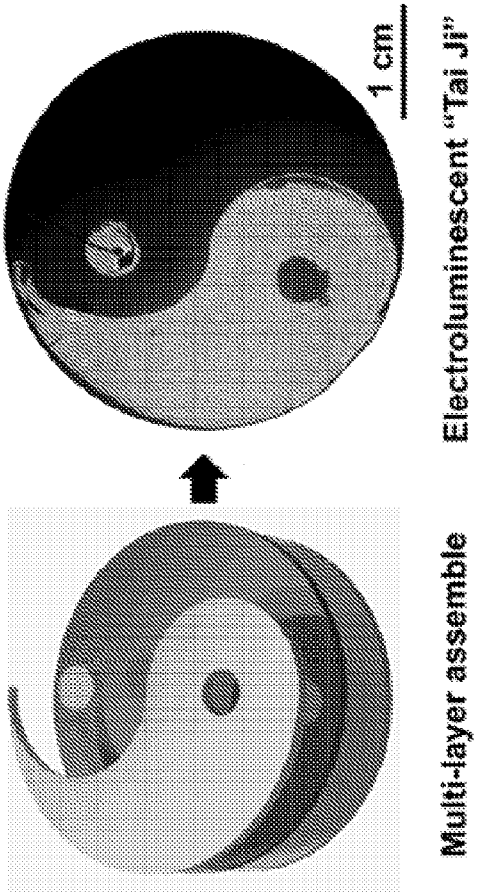


FIG. 19A

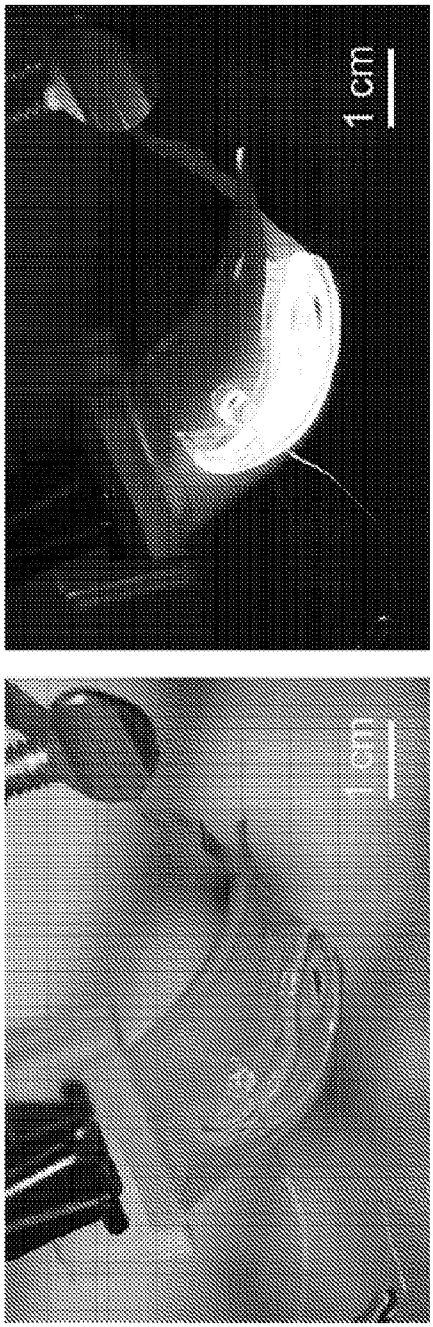


FIG. 19B

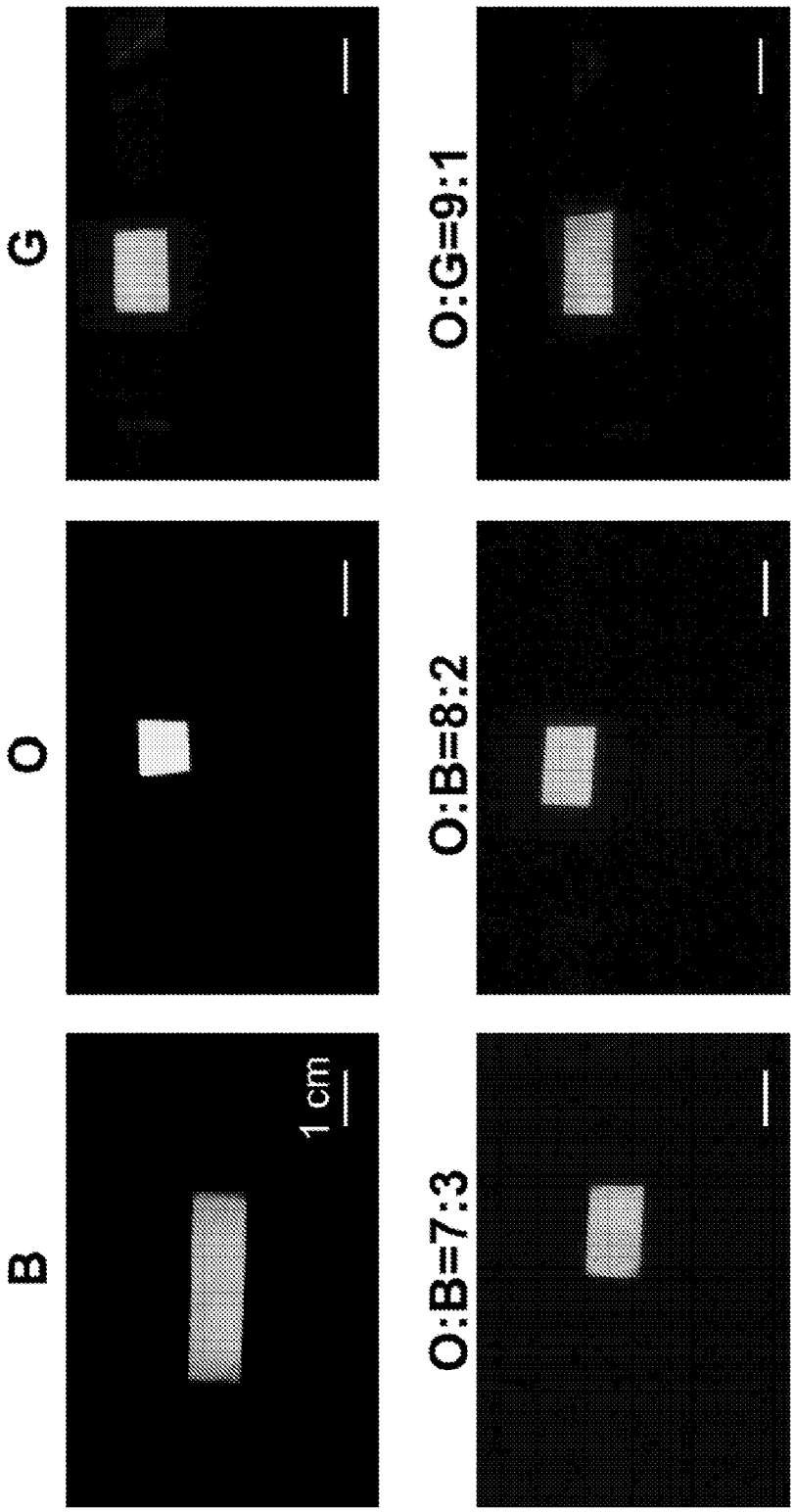


FIG. 20

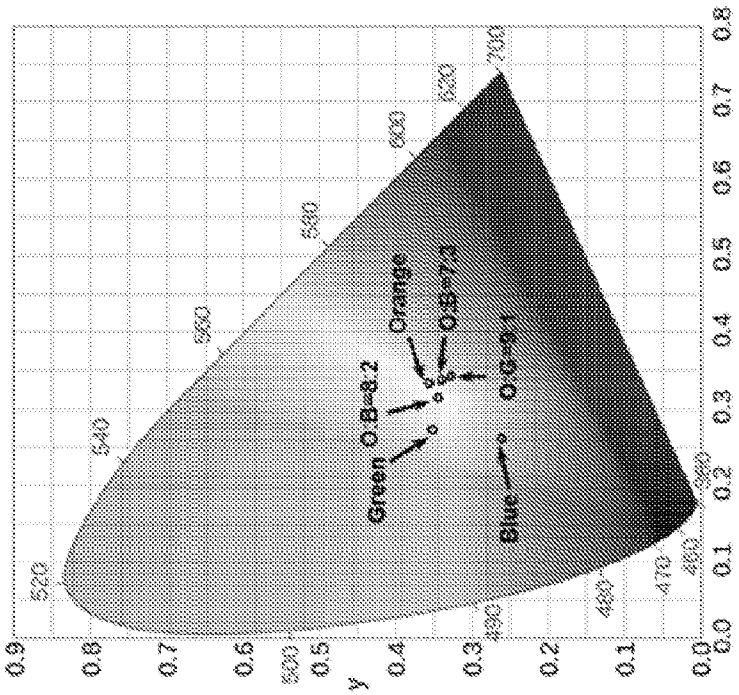


FIG. 21B

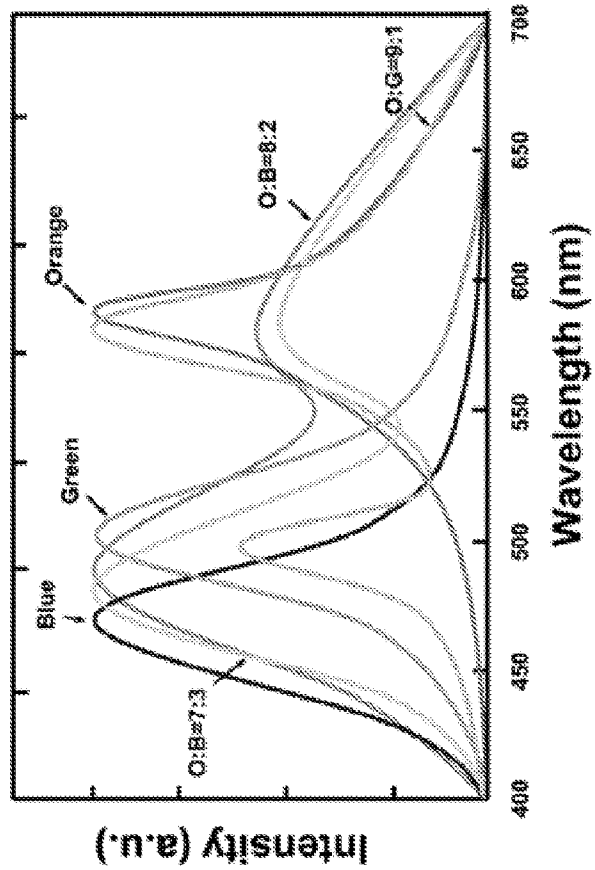


FIG. 21A

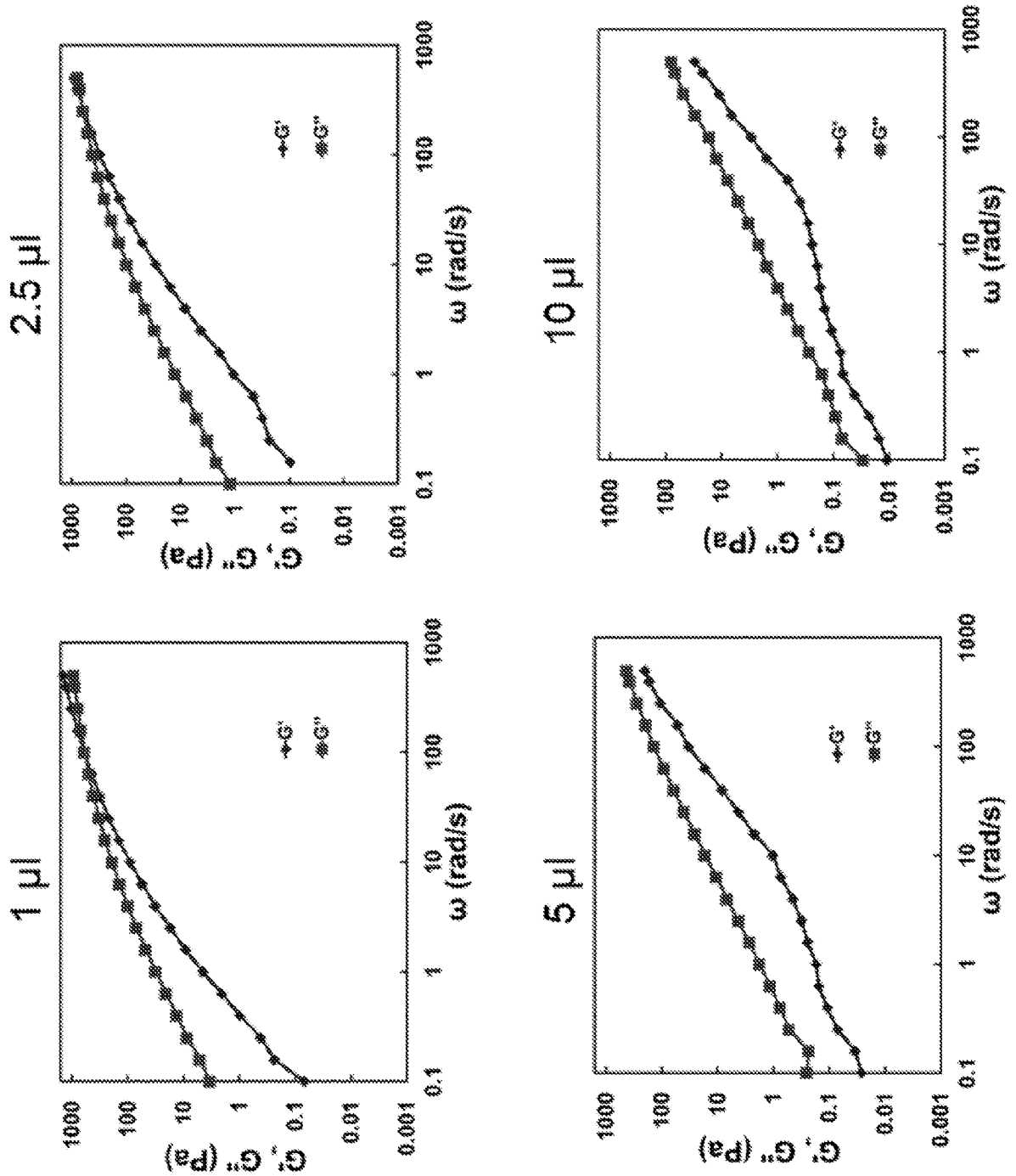

1 µl
2.5 µl
5 µl
10 µl
G', G'' (Pa)
ω (rad/s)
G'
G''
1000
100
10
1
0.1
0.01
0.001
0.1
1
10
100
1000

FIG. 22

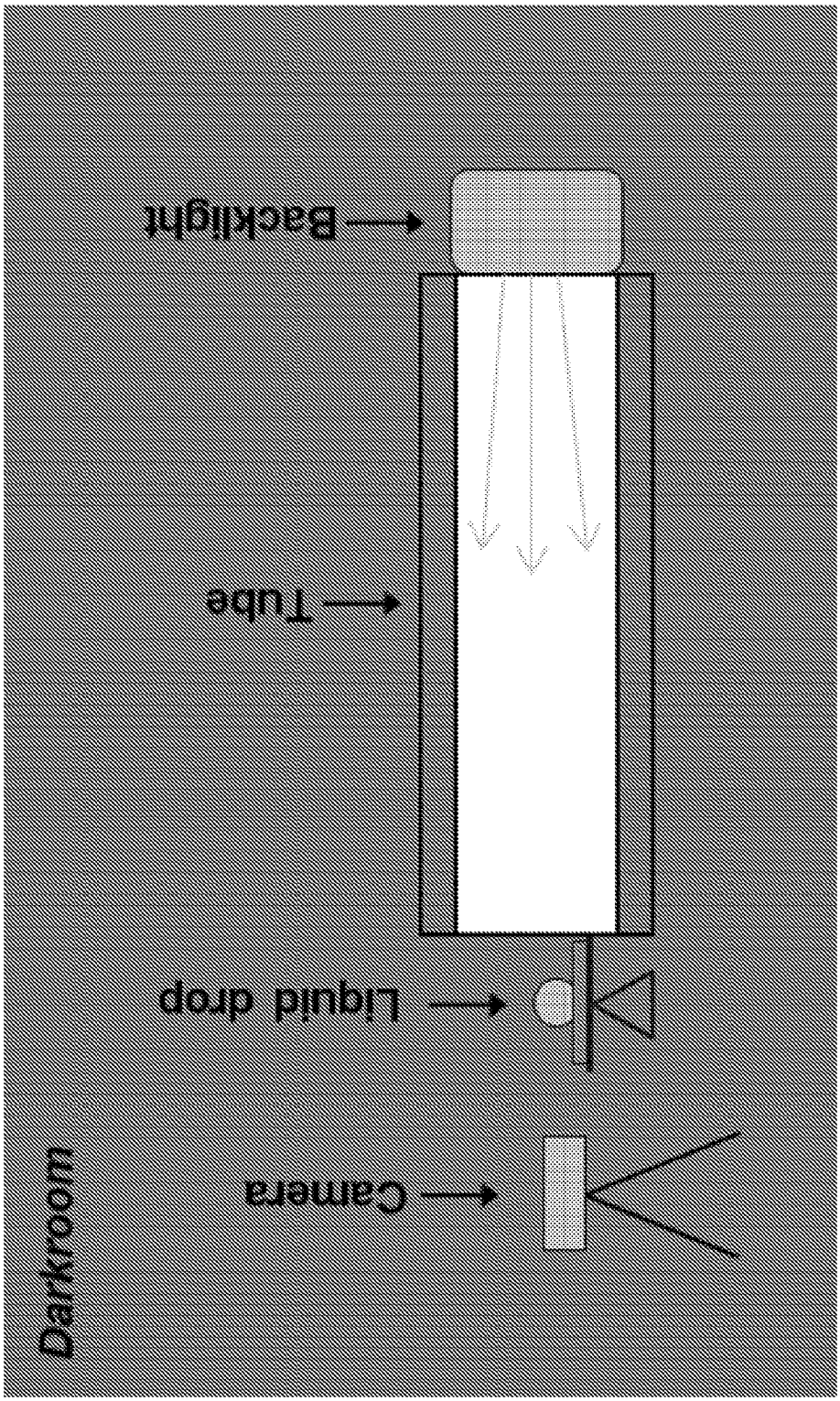


FIG. 23

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 19/30398

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - H01L 51/00 (2019.01)
CPC - H01L 51/5012, Y10S 428/917, A61L 27/52, B21C 37/047, Y10T 442/3057

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
See Search History Document

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 5,824,093 A (RAY et al.) 20 October 1998 (20.10.1998) the entire document, and more specifically: col 3, ln 21-24 and ln 55-56; col 4, ln 19-61; col 8, ln 14-33; abstract; figures 1-2 and 10	1-5 and 55-57
A	US 2014/0170920 A1 (SASIKANTH MANIPATRUNI et al.) 19 June 2014 (19.06.2014) the entire document, and more specifically: para [0017], [0023], [0019], [0035], [0058]-[0059]; figure 9	1-5 and 55-57
A	US 2005/0169958 A1 (HUNTER et al.) 4 August 2005 (04.08.2005); the entire document	1-5 and 55-57
A	US 2011/0027458 A1 (BOOCK et al.) 3 February 2011 (03.02.2011); the entire document	1-5 and 55-57
A	US 4,747,662 A (FITZ) 31 May 1988 (31.05.1988): the entire document	1-5 and 55-57
A	GUO et al., "Highly Stretchable, Strain Sensing Hydrogel Optical Fibers"; Advanced Materials, Volume 28, Issue 46 (December 2016), pg 10244-10249 (the entire document)	1-5 and 55-57

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 June 2019	15 JUL 2019
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 19/30398

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.: 6-54 and 58-71
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.