



(43) International Publication Date
6 October 2016 (06.10.2016)

(51) International Patent Classification:

G02F 1/15 (2006.01) *G02C 7/08* (2006.01)
G02F 1/157 (2006.01)

(21) International Application Number:

PCT/US2016/025679

(22) International Filing Date:

1 April 2016 (01.04.2016)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/142,728 3 April 2015 (03.04.2015) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH,

[Continued on next page]

(54) Title: OPTICAL APPARATUS WITH CONDUCTIVE POLYMERIC COMPOSITION

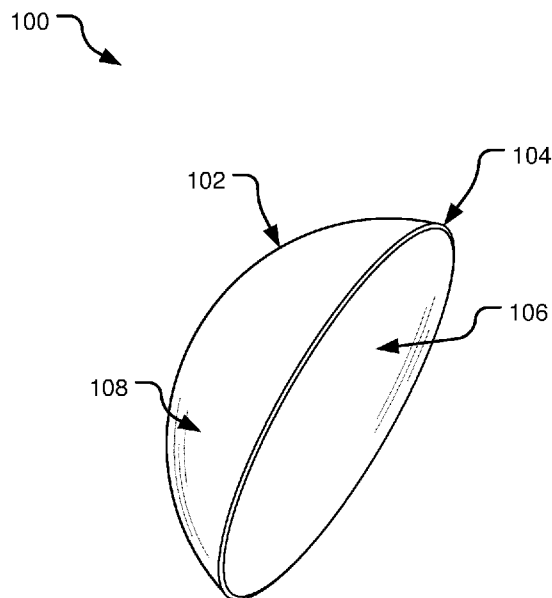


FIG. 1

(57) Abstract: Conductive polymeric compositions, and methods of manufacturing and using conductive polymer compositions, particularly for optical devices and ophthalmic applications. As an example, an opto-electrochemical device comprises a substrate having an electrochromic coating thereon, the coating comprising a conductive composition. The coating is operably connected to a voltage source, such that the electrochromic coating has a first absorption state at a first voltage level and a second absorption state at a second voltage level. In some implementations, at the first absorption state the device has a first focal length and at the second absorption state the device has a second focal length different than the first focal length.





GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT,
LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE,

SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

OPTICAL APPARATUS WITH CONDUCTIVE POLYMERIC COMPOSITION**CROSS-REFERENCE**

This PCT application claims priority to U.S. provisional application 62/142,728, filed April 3, 2015. For U.S. purposes, this application is a continuation-in-part application of U.S. provisional application 62/142,728, filed April 3, 2015.

TECHNICAL FIELD

This disclosure is directed to conductive polymeric compositions for use in optical applications, such as lenses.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

None.

BACKGROUND

Medical devices have a diverse array of properties. In order to perform acceptably, and, e.g., to minimize the trauma to the patient, not be rejected, etc., the device and its surface are designed with the application in mind. For example, many medical devices require a combination of properties such as strength, thermal stability, structural stability, flexibility, opacity, radio-opacity, storage stability, lubricity, stability to sterilization treatment, etc., and of course, biocompatibility, in order to be effective for their intended purpose. Some devices, such as those for ophthalmic purposes, need to be clear and/or have a proper index of refraction.

Organic and inorganic electrochromic (EC) materials, reversibly change their absorption spectrum in response to a voltage-driven redox reaction, have been used in electrochromic devices. The result is a voltage driven change in color in the material, as well as additional material property changes such as conductivity.

SUMMARY

The present disclosure is directed to conductive polymeric compositions, and methods of manufacturing and using conductive polymer compositions. Specifically, the disclosed technology includes customizing conductive compositions, including conductive polymers and nanogels, with a range of physical, mechanical and optical properties tailored to various applications, particularly for optical and ophthalmic applications.

In one particular implementation, this disclosure provides an opto-electrochemical device comprising a substrate having an electrochromic coating thereon, the coating comprising a conductive composition. The coating is operably connected to a voltage source, such that the electrochromic coating has a first absorption state at a first voltage level and a second absorption state at a second voltage level. In some implementations, at the first absorption state the device has a first focal length and at the second absorption state the device has a second focal length different than the first focal length.

These and various other features and advantages will be apparent from a reading of the following detailed description.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a perspective view of a contact lens.

FIG. 2 is a perspective view of an intraocular lens.

FIG. 3 is a perspective view of a smart contact lens.

FIG. 4 is a schematic diagram of a switchable Fresnel lens plate in an “off” condition and an “on” condition.

FIG. 5 is a side view schematic diagram of a switchable Fresnel lens plate.

FIG. 6 is a side view schematic diagram of an example polymer Fresnel lens plate.

FIG. 7 is a schematic diagram of two examples of binary Fresnel zone plate lenses.

DETAILED DESCRIPTION

Iontronics are devices utilizing conductive polymers and other materials that interface between electrical and ionic environments. Electro-ionic interactions occur at time scales of human physiological processes, and have a rich and biocompatible chemistry. Iontronics can interface with the aqueous, ionic environment of the body, and include transistors for processing signals and computing logic operations, optics for modulating and diffracting light, and provide transport of ionic species for drug delivery. Computing can be performed

in vivo in response to internal or external stimulus. Devices embedded in the body can communicate with a device outside of the body to leverage data analytics and powerful algorithms for smart biomedical devices.

The present disclosure describes various conductive polymeric compositions, methods of manufacturing the conductive polymeric compositions, and various applications for conductive polymeric compositions with iontronics. Specifically, the disclosed technology includes customization of conductive polymeric compositions, which includes conductive polymers and nanogels, with a full range of physical and mechanical properties for use in various applications. The conductive polymers and nanogels described herein can be synthesized from modified commercially available polymers (including monomers) or nanogels. This customization provides for actuating, modulating, and controlling a system, and doing so externally from the body with iontronics. The conductive polymers and nanogels described herein can be synthesized to specification or intended use.

The present disclosure is directed to conductive polymeric compositions that particularly suited for optical applications such as medical lenses (e.g., intraocular lenses and contact lenses) and other lenses (e.g., Fresnel lenses). The conductive compositions are particularly suited as coatings on, fillers in, or fillers in coatings on optical devices (e.g., lenses), since in some implementations the conductive compositions are transparent. The conductive compositions enable a specific parameter of a device or material to be altered (such as the refractive index of a lens, equilibrium water content, tackiness, flexibility, durability, etc.) without impacting any other material properties. The conductive compositions can also be specifically designed with a charge, such as anionic or cationic.

The conductive compositions described herein can include an electrically conductive polymer or combination of polymers selected from polyfluorenes, polyphenylenes, polypyrenes, polyazulenes, polynaphthalenes, polypyrroles, polycarbazoles, polyindoles, polyazepines, polyanilines, polythiophenes, polyacetylenes, and copolymers thereof. In a more particular implementation, the electrically conductive polymer is selected from poly(3,4-ethylenedioxythiophene) (PEDOT), polyaniline (PANI), polypyrrole (PPy), poly(phenylene vinylene) (PPV), poly(arylene), polyspirobifluorene, poly(3-hexylthiophene) (P3HT), poly(o-methoxyaniline) (POMA), poly(o-phenylenediamine) (PPD), or poly(p-phenylene sulfide). The conductive polymers can also include functionalized PEDOT with additional functional groups on the end of the polymer chain (e.g., PEDOT-TMA (PTMA), PEDOT-PEG, and PEDOT block PEG).

In several examples in this disclosure, the conductive polymer poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) is used. PEDOT is an organic semiconductor while PSS is a “dopant” material (provides the charge carrier to the semiconductor, making the layer electrically conductive) as well as providing ancillary
5 benefits such as increased solubility. PEDOT:PSS is solution processable (e.g., for spin coating thin films), has good electrical conductivity (10-1000 S/cm), is hygroscopic, ionically conductive, electrochemically active, and electrochromic. However, other polymer compositions customized with improved and optimized properties may be used in the disclosed technology.

10 For example, a polymer composition may include a PEDOT derivative, a nanogel, or a combination of both, that could optimize one material property at the expense of another. For example, an implementation could have reduced electrical conductivity with increased ionic conductivity, and the polymer composition can be used as either an electrolyte or as an ion transport material.

15 In some implementations, customization of a system can include incorporation of a customized nanogel. Nanogels are polymer ensembles that can be used to mix hydrophobic and hydrophilic materials, with novel chemical, mechanical, and optical properties. Nanogels can be charged, behave like ions in solution, and can be transported inside conductive polymer films. Nanogels can be cross-linked to form solid layers with large water content,
20 opening up the possibility of novel solid electrolytes and other device layers. By using nanogels, in some implementations, either with conductive polymers or in place of conductive polymers, there may be more system capabilities.

In some implementations the reactive pendent group of the nanogel is an acrylate or an isocyanate. In some implementations, the nanogels are siloxane nanogels, having been
25 formed from a composition including a siloxane acrylate. In some implementations, the composition includes a siloxane acrylate and an acrylate, such as a urethane-based acrylate. Urethane-based acrylate(s) enable secondary interactions (reversible hydrogen bonding) within the composition. In some implementations, other monomer, polymer or copolymer material(s) may be used in place of the urethane-based acrylate(s), as long as they provide
30 secondary interactions (reversible hydrogen bonding) in the composition and meet the criteria for an intraocular lens. In other implementations, the composition includes a siloxane acrylate and a hydrophilic monomer, such as a hydrophilic acrylate.

In a particular implementation, this disclosure provides switchable, thin film diffractive optical gratings and Fresnel zone plate lenses fabricated using a micro-patterned

electrochromic polymer and gel electrolyte. Electrochemically switching the conductive polymer (e.g., PEDOT:PSS) causes the patterned layer to change between a low-absorption to high-absorption state, acting as an amplitude diffractive optical element. The switchable lens and gratings can include a patterned (e.g., lithographically patterned) electrochromic polymer, a gel electrolyte, and a transparent conductive oxide (e.g., indium tin oxide (ITO), zinc oxide (ZnO)) coated glass substrate. Electrochemically actuated diffractive optics have many potential applications in low power and implantable biomedical devices.

In another implementation, a conductive polymer composition can be used in or on devices implanted in a user. In some implementations, the device is a medical device implanted in the patient. As an example, the implanted device can be an ophthalmic device, such as an intraocular lens. As another example, the implanted device can be a “smart” lens, whose focal power or focal distance can be modified.

As indicated above, the conductive compositions of this disclosure are particularly suited for ophthalmic devices and other ophthalmic purposes, at least because the optical properties of conductive compositions can be dynamically changed using electro-ionic signals. The optical properties can be controlled by electrochemically modulating the water content, refractive index, the absorption spectrum, or the thickness of the polymer layer. These conductive compositions can be used to make refractive or diffractive optical elements including diffraction gratings, Bragg holograms, diffractive optical elements, waveplates or other retarders, waveguides, prisms or lenses with dynamic properties. Combining these optical actuators with the computing, sensing, and communication interface capabilities of ionic transistors further enhances their utility.

In the following description, reference is made to the accompanying drawing that forms a part hereof and in which are shown by way of illustration at least one specific implementation. The following description provides additional specific implementations. It is to be understood that other implementations are contemplated and may be made without departing from the scope or spirit of the present invention. The following detailed description, therefore, is not to be taken in a limiting sense. While the present invention is not so limited, an appreciation of various aspects of the invention will be gained through a discussion of the examples provided below.

As used herein, the singular forms “a”, “an”, and “the” encompass implementations having plural referents, unless the content clearly dictates otherwise. As used in this specification and the appended claims, the term “or” is generally employed in its sense including “and/or” unless the content clearly dictates otherwise.

Spatially related terms, including but not limited to, “lower”, “upper”, “beneath”, “below”, “above”, “on top”, etc., if used herein, are utilized for ease of description to describe spatial relationships of an element(s) to another. Such spatially related terms encompass different orientations of the device in addition to the particular orientations depicted in the figures and described herein. For example, if a structure depicted in the figures is turned over or flipped over, portions previously described as below or beneath other elements would then be above or over those other elements.

Turning to FIG. 1, a contact lens 100 is illustrated. Lens 100 has a flexible body 102 that has a domed shape in a quiescent state, a peripheral edge 104, and a first side 106 and a second side 108. In this illustrated implementation, the first side 106 is the side that is closer to the eye when inserted in an eye and has a concave shape, and second side 108 is the outer surface and has a convex shape. The lens 100 is non-tacky, biocompatible, has acceptable refractive index, and is free of visible imperfections and glistening. The lens 100 is sufficiently flexible and durable to survive multiple bending and unbending cycles while remaining undamaged. The lens 100 can be hydrophobic, hydrophilic, or neutral.

In FIG. 2, an intraocular lens (IOL) 200 is illustrated. Similar to the contact lens 100 of FIG. 1, the IOL 200 has a body 202 with a domed shape, a peripheral edge 204, and a first side 206 and an opposite second side (not shown). IOL 200 also has opposing arms 209, to facilitate handling of the IOL 200. Unlike the contact lens 100, however, the IOL 200 is fairly rigid.

The lens 100 and the IOL 200 are formed from a polymeric composition that may include any number of additives, fillers, etc. The conductive polymeric compositions of this disclosure are particularly conducive as the lens 100 or the IOL 200, or as a coating on the lens 100 or the IOL 200. Similarly, the nanogels of this disclosure are particularly conducive to being used as an additive (e.g., filler) in any polymeric composition used to form the lens 100 or the IOL 200. The nanogels can be used to modify or affect the physical structural properties of the lens 100 or the IOL 200 and/or the surface properties.

In FIG. 3, a “smart” contact lens 300 is illustrated. Similar to the contact lens 100 of FIG. 1, the contact lens 300 has a body 302 with a domed shape and a peripheral edge 304. Centrally located on the body 302 is a Fresnel zone plate 305 that has a variable focus, for near vision correction and far vision correction. Proximate peripheral edge 304 is an antenna (e.g., RF power antenna) 306 operably connected to the Fresnel zone plate 305 via circuitry 308. Circuitry 308 controls the power to Fresnel zone plate 305 to

adjust its focus. The lens 300, particularly the circuitry 308 and thus the Fresnel zone plate 305, can be controlled wirelessly.

A Fresnel zone plate (FZP), such as the Fresnel zone plate 305 of FIG. 3, can be formed by an electrically conductive composition, such as an electrochromic material, of this technology. Electrochromic materials reversibly change their absorption spectrum in response to a voltage-driven redox reaction. The electrochromic effect is characteristically observed in response to an applied voltage as an ion exchange between the electrochromic material and an electrolyte which changes the oxidation state of the electrochromic material. The result is a voltage driven change in color in the material, as well as additional material property changes such as conductivity.

Poly(3,4-ethylene-dioxythiophene) doped with poly(styrene-sulfonate) (PEDOT:PSS) is one example of a suitable electrochromic material. Among conductive polymers, PEDOT:PSS has high chemical stability, flexibility and has a relatively high conductivity of > 1000 S/cm. In the case of PEDOT:PSS, the electrochemical redox reaction will dope (oxidize) or dedope (reduce) the material thereby changing its conductivity and shifting its absorption spectrum from the infrared into visible wavelengths, which is observed as a darkening of the material. This shift can be exploited in applications that range from electrochemical displays to transistors. Electrochromic materials such as PEDOT:PSS have intrinsic advantages over other thin-film optical materials such as liquid crystals (LCs), including low voltage DC actuation, ease of processing on flexible substrates, aqueous electrolytes, and demonstrated biocompatibility. The explicitly ionic electrochemical actuation mechanism of PEDOT:PSS also enables the materials to interface seamlessly with physiological environments.

Using diffractive optics, Fresnel lenses and/or FRPs can be made using thin, planar patterns that focus light similar to traditional refractive lenses but have the added advantage of utilizing thin substrates to attain similar optical properties. Diffractive optics use spatially varying amplitude or phase modulation to interfere light and control the power distribution of the transmitted light beam. For example, an amplitude FZP lens can be generated from a structure of concentric rings of alternately low and high absorption segments with varying pitch without the volume and mass of material that would be needed to manufacture a similar refractive lens from conventional dielectric material. FZP micro-lens arrays on thin, flexible substrates have been optimized for wide-field imaging in bio-inspired compound eyes.

The conductive compositions provide the ability to dynamically alter the focal length of a device by switching a diffractive optical element 'on' or 'off' using an external electrical

signal; this has significant applications for a range of optical devices such as lenslet arrays and switchable focus optics, including biomedical ophthalmic devices such as electrically switchable focus IOLs. By combining the advantages of diffractive optics with active electrochromic materials, a platform in which switchable diffractive optics with the ability to dynamically alter the focus of a lens can be developed. Patterned electrochromic layers can be combined with traditional refractive optics to enable a device to repeatedly and reversibly switch the focal length of a lens in response to an electrical signal.

FIG. 4 schematically illustrates operation of a switchable FZP opto-electrochemical device (OECD) 400 during operation. OECD 400 includes a substrate 402 having a Fresnel-type active region 404 thereon, the active region 404 formed by an electrochromic polymeric material. When the OECD 400 is 'off' there is minimal contrast between the electrochromic active region 404 and inactive regions of the substrate 402 and the device 400 is a lens with infinite focal length. When the OECD 400 is 'on', the absorption of the active region 404 shifts and thus diffracts a portion of the incident light onto a focal spot. The focal length of the FZP lens is a function of the spacing between the concentric circles in the pattern of the active region 404.

FIG. 5 is a cross-section of an OECD, such as those of FIG. 4. OECD 500 has a first substrate 502 (e.g., glass substrate) on which is a transparent conductor 504 (e.g., ITO), and a second substrate 512 (e.g., glass substrate) on which is a transparent conductor 514 (e.g., ITO). On the first substrate 502 and conductor 504 is a patterned electrochromic layer 506 formed by active regions (e.g., PEDOT:PSS) 508 and inactive regions (e.g., over-oxidized regions) 509. Sandwiched between the two substrates 502, 512 is a gel electrolyte 515. The conductors 504, 514 are electrically connected to a voltage source.

When a positive voltage is applied to conductor 514 (counter electrode, relative to the conductor 504 as a working electrode), the cations in the gel electrolyte 515 are driven into electrochromic patterned regions (e.g., PEDOT:PSS) 508. Darkening of the active regions 508 is observed and the absorption spectrum shifts into the visible wavelengths.

The spacing of the concentric ring structure in an FZP, such as that of FIG. 4 and FIG. 5, decreases as $1/r^2$ where r is the radial distance from the center of the lens. The alternatingly electrochemically active regions (e.g., active regions 508) with switchable absorption and the chemically over-oxidized inactive regions (e.g., inactive regions 509) diffract light at an angle inversely proportional to the ring spacing such that the incident light is diffracted to a single focal point. In binary FZPs, some of the light is diffracted into higher order modes as

well, resulting in multiple foci. The power in higher order foci falls off as a function of m^{-2} , where $m = 1, 3, 5 \dots$ is the mode order.

In some designs, two or more different active regions can be present on the device. By having multiple unconnected active regions, one region can be activated at one point in time, another activated at a different time, etc., providing a device that has multiple finite focal points. The region to be activated can be selected depending on the focal length desired. Such a device can be readily implemented with repeating lines, such as concentric circles. Because the electrochromic feature is reversible, the device has a virtually infinite life.

Electrochromic materials, including PEDOT:PSS, are flexible and can be fabricated onto many different substrate materials, including flexible polymers and implantable devices. Electrochromic devices intrinsically work well in aqueous electrolyte environments, and most significantly can be made using biocompatible materials that are non-toxic and compatible with biological systems. Furthermore, PEDOT:PSS requires a low DC voltage to dynamically alter its absorption state. The ability to switch on-and-off a thin-film lens with a low DC voltage can be used to make varifocal contact and IOL devices, with the power supplied using, e.g., an RF coil and rectifier, or a small on-board power source. Contact lens 300, of FIG. 3, is such a variable focal lens.

An OECD, such as those of FIG. 4 and FIG. 5, are can fabricated by micro-patterning a layer of conductive polymer (e.g., PEDOT:PSS) on a conductive substrate (e.g., an ITO-coated glass substrate) using conventional lithographic patterning. FZP lenses and amplitude diffraction gratings devices of different sizes were made to characterize the operation and diffraction efficiency. We show that the focus power of a FZP lens can be changed by a factor of 8.2 at a voltage swing of 2 V, with a diffraction efficiency of up to 0.72%. We also examine the ultimate potential diffraction efficiency of OECDs and their potential as ophthalmic biomedical devices.

It was found that the diffraction efficiency can be controlled as a function of the applied voltage. By utilizing the electrochromism of conductive compositions such as PEDOT:PSS, a FZP lens can be switched between a nearly uniform low absorption (oxidized) “off” state with infinite focal length, to a pattern of alternating low and high absorption (reduced) rings in the “on” state with a finite focal length. For PEDOT:PSS, with an applied voltage of -1 V to 1 V, the diffraction efficiency of the switchable lens can be varied 4.1-fold between the “on” and “off” states.

FIG. 6 is another side-view schematic diagram of another example Fresnel zone plate (FZP) 600. FZP 600 has a substrate 602 (e.g., glass substrate) on which is a working electrode region 604 and a counter electrode region 606, both which are covered by a transparent conductor 608 (e.g., ITO). A scribe line 610, which is electrically insulating,
5 separates the working electrode region 604 and the counter electrode region 606. The working electrode region 604 is grounded through the conductor 608 and the counter electrode region 606 is connected to a voltage source. Above the conductor 608 and the work electrode region 604 is a patterned lens 612, e.g., a PEDOT:PSS Fresnel lens. A gel electrolyte 614 and glass coverslip 616 covers the lens 612 and the conductor 608.

10 When voltage is applied to the working electrode 604, ions from the gel electrolyte 614 electrochemically react with the electrochromic polymer (e.g., PEDOT) of the lens 612 causing a shift in the absorption spectrum, refractive index, water content and/or volume, thus changing the diffraction efficiency and/or focal length of the lens 612 (or vice-versa).

FIG. 7 shows two images of examples of binary Fresnel zone plate lenses 700A and
15 700B. The spacing of the rings determines the optical lens power based on the desired wavelength of light. Dark areas are patterned material and light areas are transparent. The lens 700B is a traditional zone plate and the lens 700A is a Spiral zone plate. The continuous patterned line of the spiral zone plate 700A makes electrical contact easier.

As indicated above, the pattern of active regions and inactive regions formed by
20 conductive, polymeric composition(s) that are formed by polymers and/or nanogels; this can include conductive photo-resist resins. As an example, by mixing a highly conductive PEDOT:PSS polymer with functionalized PEDOT:TMA or PEDOT nanogels, films can be made to cross-link to form a strong, robust polymer layer while still being conductive. The crossed-linked PEDOT:TMA or other functionalized polymer (e.g., PEG additive to
25 PEDOT:PSS) forms a polymer matrix that holds together the high conductivity PEDOT:PSS polymer chains. By adding a photoinitiator (e.g., TPO-L) the solution can be polymerized with UV light. By coating (e.g., spin-casting) a thin film layer of this solution, photolithography techniques can be used to selectively expose regions of the film to crosslink. As a result, the film behaves as a “negative tone” photoresist. The unexposed and
30 uncrosslinked parts of the film can be removed with post-exposure treatment (e.g., solvents, plasma, etc.). With this technology, various patterns can be formed.

In addition, the substrate of the thin film can be treated with some sort of functionalized coating (e.g., silane-based chemistry) to form functional groups on the substrate that can be cross-linked with the PEDOT:TMA to improve substrate adhesion.

Examples of electrically conductive polymers or combinations of polymers include one or more polyfluorenes, polyphenylenes, polypyrenes, polyazulenes, polynaphthalenes, polypyrroles, polycarbazoles, polyindoles, polyazepines, polyanilines, polythiophenes, polyacetylenes, and copolymers thereof. Particular electrically conductive polymers include
5 poly(3,4-ethylenedioxythiophene) (PEDOT), polyaniline (PANI), polypyrrole (PPy), poly(phenylene vinylene) (PPV), poly(arylene), polyspirobifluorene, poly(3-hexylthiophene) (P3HT), poly(o-methoxyaniline) (POMA), poly(o-phenylenediamine) (PPD), and poly(p-phenylene sulfide). Nanogels may be made from any of these polymers. For example, nanogels formed from dimethyl aminoethyl methacrylate (DMAEMA) or poly(3,4-
10 ethylenedioxythiophene)-tetramethacrylate (PTMA) are electrically conductive;

In some implementations, the nanogel polymeric composition includes at least one siloxane acrylate and may additionally include at least one acrylic copolymer, such as a urethane-based acrylic copolymer.

The nanogels allow crosslinked nanoscale structures to be formed from vastly
15 different monomers, for example, from a hydrophilic monomer (e.g., 2-hydroxyl ethyl acrylate or HEA) and a hydrophobic monomer (e.g., “Ebecryl”). The reactive nanogels formed have a backbone that includes the different monomers that go in to synthesizing them. After the nanogels are synthesized, the nanogels can be used as a filler, e.g., within another polymer or a solvent, or as coating. The nanogels can be homogeneously dispersed in any
20 matrix (e.g., solvent, polymer) and can be reacted within the matrix. If the matrix is optically clear, addition of the nanogels does not destroy the clarity of the matrix.

EXAMPLES

25 Switchable FZP lenses (OECDs) with alternately electrochemically active regions with switchable absorption and chemically over-oxidized inactive regions were made. The patterns for the binary FZP lenses were generated for optical powers of 1.5 and 3.0 diopters (focal lengths of 666 and 333 mm). Each lens has a diameter of 8 mm and was designed for an incident wavelength of 594 nm. The center circle was designed to be transparent while the
30 spacing between the outermost rings was 25 micrometers and 50 micrometers for the 3.0 and 1.5 diopter lenses, respectively. FZP lenses of higher power (shorter focal length) can trivially be fabricated by altering the concentric ring spacing within the constraints of optical lithography. The diffraction gratings were patterned lines of alternating inactive and active electrochromic regions. The gratings were designed with pitches of 10, 20, 30, and 40

micrometers and a nominal duty cycle of 50%, defined as the ratio of the width of the active lines to the grating pitch.

To fabricate the switchable OECD, ITO-coated 25 mm × 25 mm glass slides (from Sigma-Aldrich) with a resistivity of 8-12 Ω/sq. were used as substrates. The coated slides were cleaned in soap solution, acetone, and isopropanol in a sonicator (from Branson) and subsequently dried by blowing with N₂ gas. The electrochromic solution included PEDOT:PSS (Clevios PH-1000, from Heraeus), 5 v/v % glycerol, 0.5 v/v % dodecylbenzenesulfonic acid (DBSA, from Sigma-Aldrich), and 1 w/w % (3-glycidyloxypropyl)trimethoxysilane (GOPS, from Sigma-Aldrich) and was spin-coated onto the substrate at 1,000 rpm for 60 seconds. PEDOT:PSS was also spin-coated onto a blank glass microscope slide as a control in the absence of the ITO layer to measure the thickness and conductivity of the film.

The presence of glycerol enhanced the conductivity of the PEDOT:PSS formulation while the DBSA served as a secondary dopant and a surfactant. The monomer GOPS cross-linked the film to enhance the hydrolytic stability of the formulation and prevented delamination from the underlying substrate.

After spinning on the PEDOT:PSS solution, the device was baked on a hotplate at 120° C for 20 minutes to dry the film. A positive photoresist (AZ 4210, Futurrex) was spin-coated onto the PEDOT:PSS-coated ITO slide and patterned in a Karl Suss MJB3 mask aligner using a photomask with the patterns described above. The photoresist was developed according to the manufacturer's directions and the patterned device was exposed to a 150 W O₂ plasma for 30 seconds to descum the surface. The patterned device was subsequently soaked in a 1:4 solution of commercial bleach (Clorox™, 8.25 % sodium hypochlorite) and water for 5 seconds and then rinsed in DI water. This soak chemically over-oxidized the PEDOT:PSS and turned the exposed regions into a non-conductive, transparent, and electrochemically inactive film. The photoresist was removed with acetone and methanol and dried by blowing with N₂ gas.

The final device was assembled as a sandwiched structure composed of a gel electrolyte between the patterned PEDOT:PSS ITO glass slide and a blank ITO-coated glass slide (similar to that shown in FIG. 5). Copper tape with conductive adhesive (3M™ Copper Foil Shielding Tape) was wrapped around both the patterned and blank ITO-coated glass slide to make electrical contacts points around the device. The gel electrolyte solution was formulated using 40 w/w % of poly(sodium 4-styrenesulfonate) (Na:PSS, from Sigma-Aldrich) with an average molecular weight of 70,000 Da, 10 w/w % D-sorbitol, 10 w/w %

glycerol, and 40 w/w % DI water. This viscous formulation was then sandwiched between the patterned PEDOT:PSS ITO glass slide and the blank ITO-coated glass slide with the ITO side facing the electrolyte. A rubber shim with a thickness of 1/32 inch was used as a spacer for the electrolyte. The slides were clipped together and the sandwiched device was then left to dry overnight. Finally, wires were soldered onto the copper tape electrical contacts on the back of the slide for testing.

The thickness and conductivity of the PEDOT:PSS film on the control glass slide was measured using a Dektak profilometer and four-point probe respectively. The spin-coated PEDOT:PSS film thickness was measured to be 230 nm with a conductivity of 345 S/cm. The electrochromic contrast between the patterned regions was measured by viewing the grating device through a transmission microscope with a 594 nm bandpass filter and comparing the intensity registered by the CMOS camera pixels in the active and inactive (over-oxidized) areas of the device. The transmission contrast ΔT is defined as the difference in optical transmission between the active and inactive regions and was measured for each grating size at a voltage 0 V ('off' state, low absorption) and 1 V ('on' state, high absorption), as shown in Table 1. The transmission in each state was compared to the fully oxidized state at -1 V. The reduction in measured contrast between the regions for narrower gratings can also be attributed to lateral diffusion during the chemical over-oxidation patterning step, which is more severe for narrower gratings. Despite this lateral diffusion into the masked regions, the interface between the active and inactive regions is still sharp, so the assumption of a binary diffractive grating is valid.

Table 1

Diffraction grating performance

The 'On' state was measured at $V_L = 1$ V and the 'Off' state at $V_L = 0$ V. The transmission contrast is the difference in transmission between the active and inactive regions.

Pitch	Diffraction Efficiency, "on"	Diffraction Efficiency, "off"	Grating Contrast, "on"	Grating Contrast, "off"	Duty cycle
10 μm	0.037%	0.014%	6.50%	1.48%	48.1%
20 μm	0.17%	0.059%	18.5%	1.48%	38.2%
30 μm	0.40%	0.14%	20.0%	2.04%	44.3%
40 μm	0.52%	0.18%	24.8%	1.55%	45.5%

The above specification, examples, and data provide a complete description of the structure, features and use of exemplary implementations of the invention. Since many implementations of the invention can be made without departing from the spirit and scope of the invention, the invention resides in the claims hereinafter appended. Furthermore,

5 structural features of the different implementations may be combined in yet another implementation without departing from the recited claims.

WHAT IS CLAIMED IS:

1. An opto-electrochemical device comprising a substrate having an electrochromic coating thereon and operably connected to a voltage source, the electrochromic coating comprising a conductive composition and having a first absorption state at a first voltage level and a second absorption state at a second voltage level, wherein at the first absorption state the device has a first focal length and at the second absorption state the device has a second focal length different than the first focal length.
2. The opto-electrochemical device of claim 1 further comprising a transparent conductive oxide between the substrate and the conductive electrochromic coating.
3. The opto-electrochemical device of claim 2, wherein the transparent conductive oxide is ITO or ZnO.
4. The opto-electrochemical device of claim 1, wherein the conductive composition comprises at least one of PEDOT:PSS, P3HT, polypyrrole, and polyaniline.
5. The opto-electrochemical device of claim 1, wherein the conductive composition comprises a conductive nanogel.
6. The opto-electrical device of claim 1, the electrochromic coating further comprising a nanogel.
7. The opto-electrochemical device of claim 1, wherein the conductive polymer is present on the substrate as a pattern of active regions alternating with inactive regions.
8. The opto-electrochemical device of claim 7, wherein the active regions and the inactive regions are present as concentric circles.

9. The opto-electrochemical device of claim 7, wherein the active regions and the inactive regions are present as spirals.
10. The opto-electrochemical device of claim 7, wherein the conductive polymer defines multiple, unconnected active regions.
11. The opto-electrochemical device of claim 1, wherein the device is a Fresnel lens.
12. The opto-electrochemical device of claim 1 further comprising a voltage source.
13. The opto-electrochemical device of claim 12 further comprising an antenna.
14. The opto-electrochemical device of claim 13, wherein the device is a smart lens.
15. The opto-electrochemical device of claim 1, wherein the device is an implantable ophthalmic lens.
16. The opto-electrochemical device of claim 5 or 6, wherein the nanogel affects at least one of the refractive index, equilibrium water content, tackiness, flexibility, and durability of the device.
17. The opto-electrochemical device of claim 1, wherein the conductive composition changes the local refractive index of the electrochromic coating at the second voltage level compared to the first voltage level.
18. The opto-electrochemical device of claim 16, wherein the local refractive index changes due to changes in absorption.
19. The opto-electrochemical device of claim 1, wherein the conductive composition changes the local refractive index of the electrochromic coating by changing the thickness of the coating.

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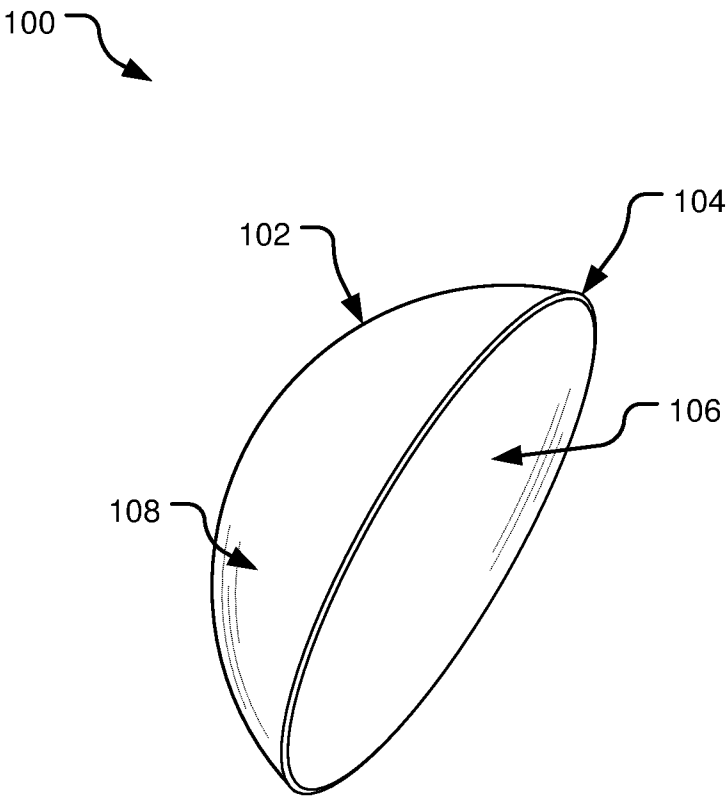


FIG. 1

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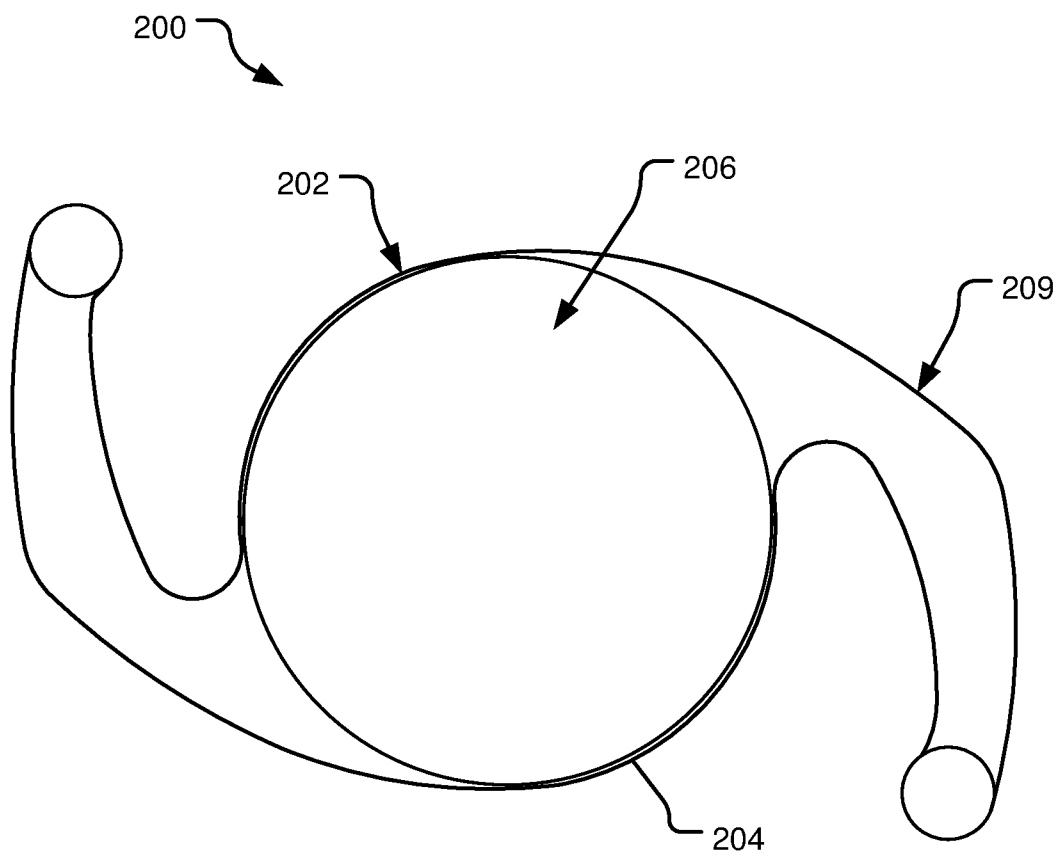


FIG. 2

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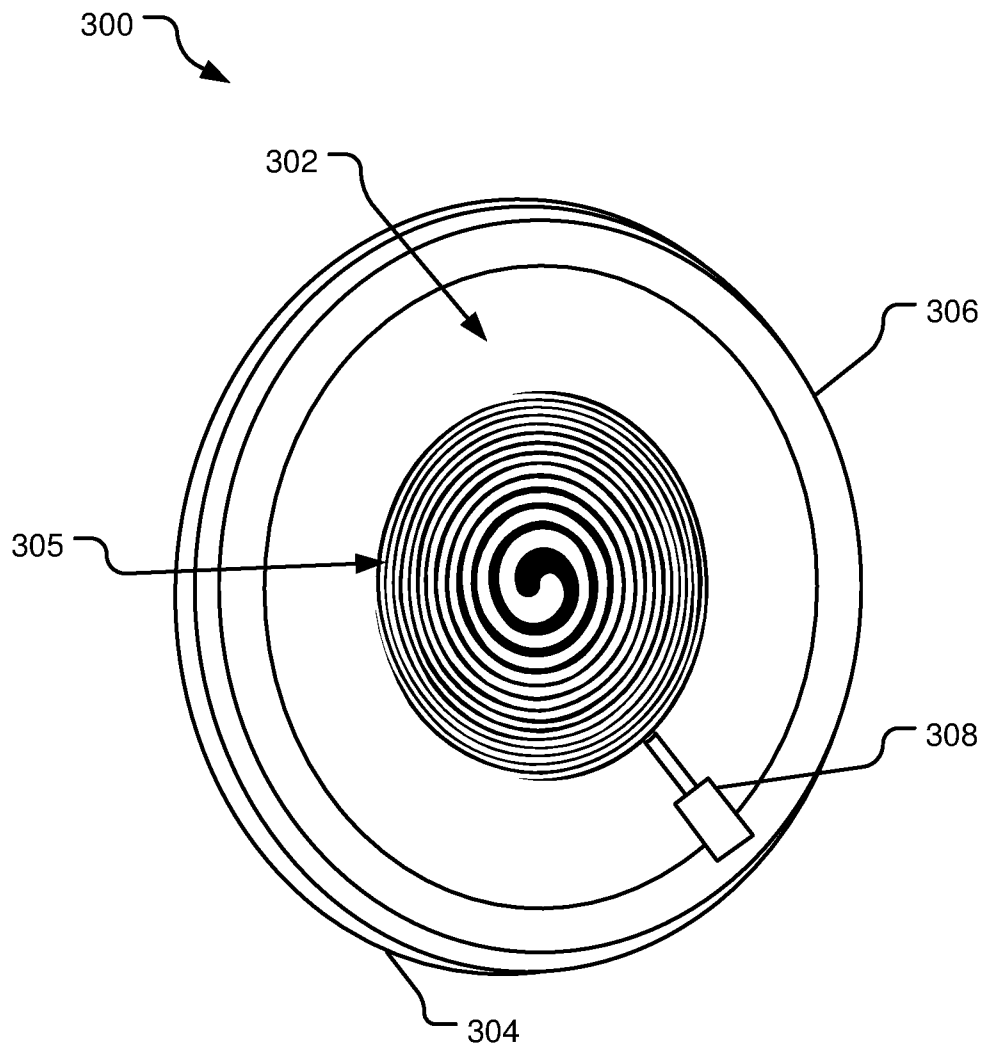


FIG. 3

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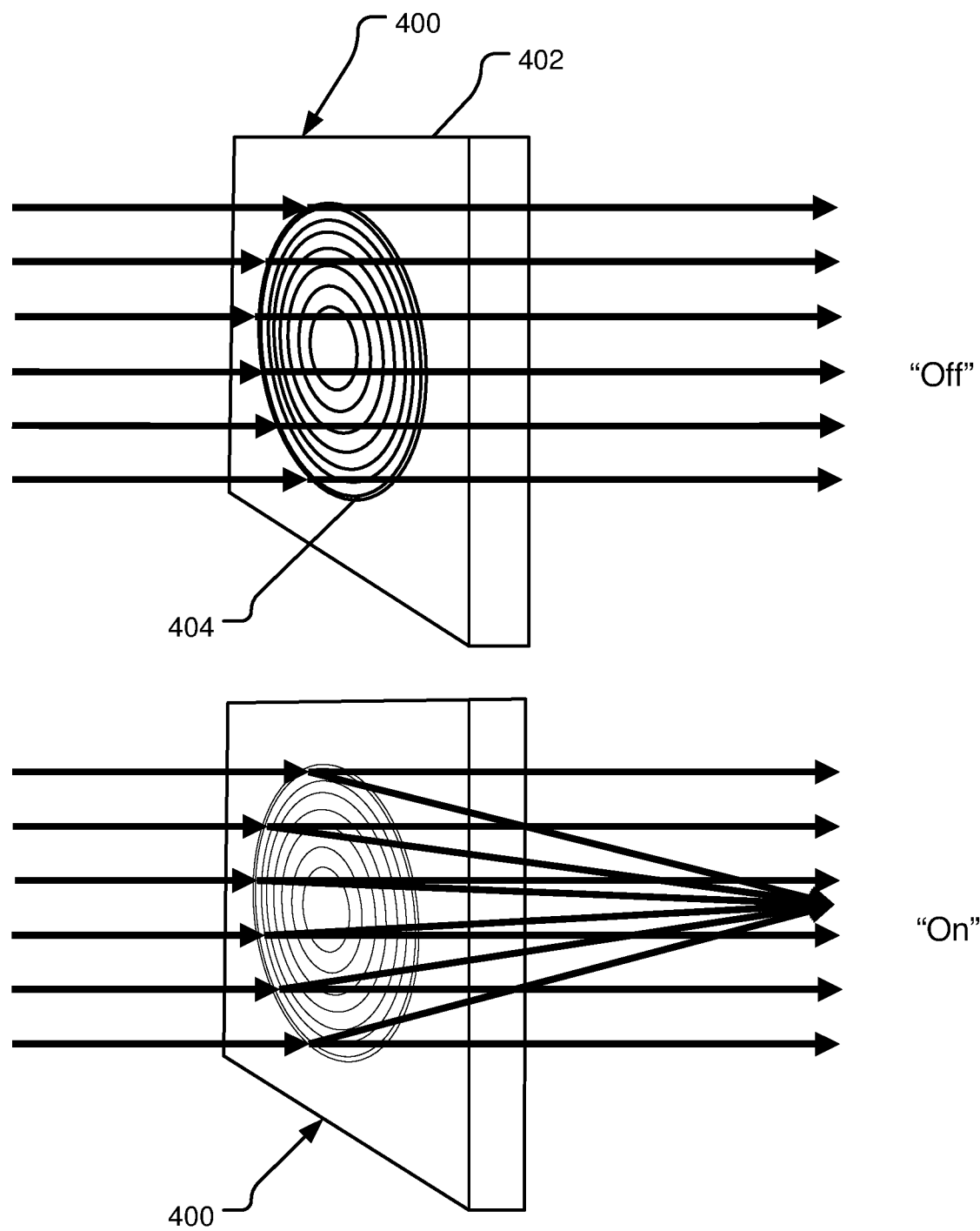


FIG. 4

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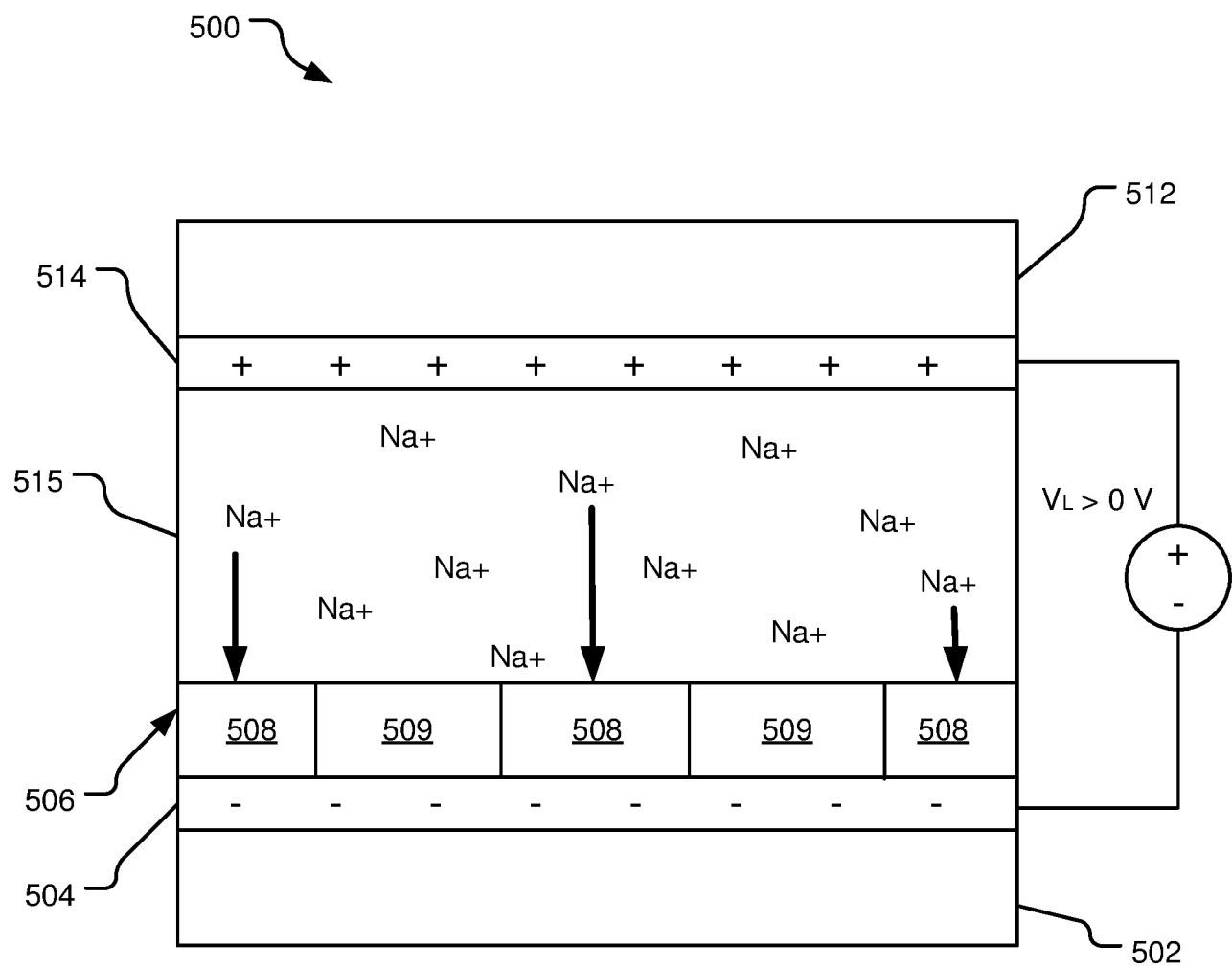


FIG. 5

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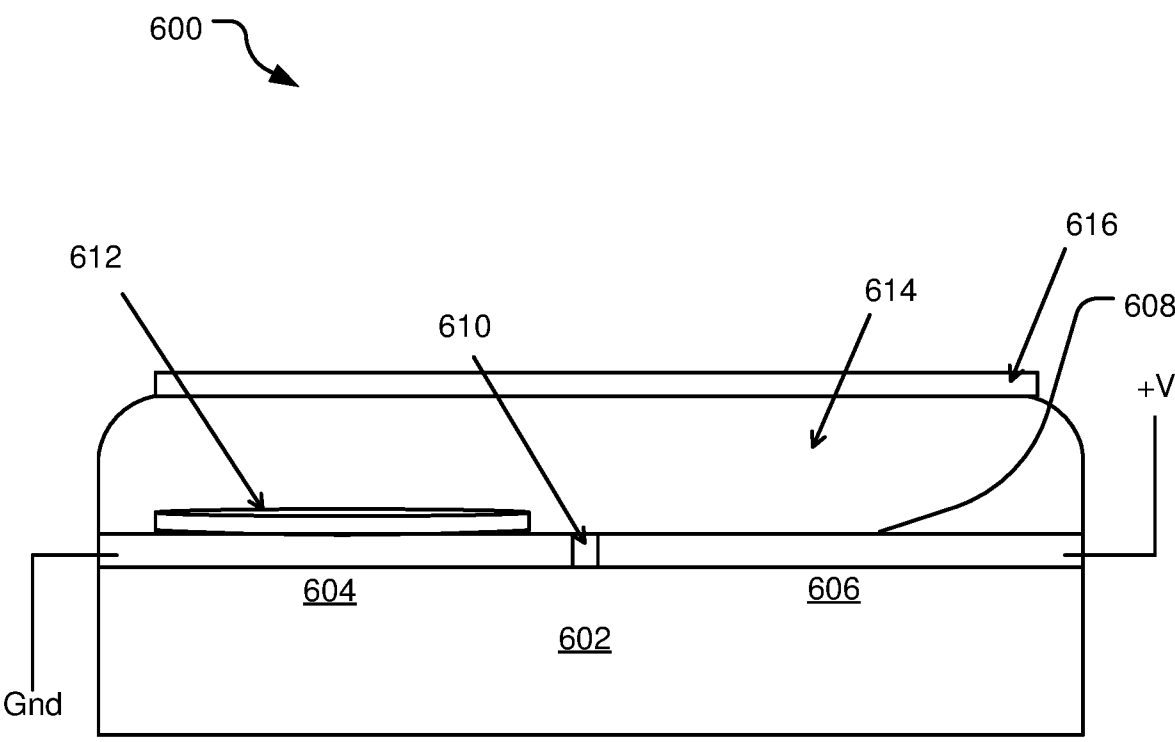
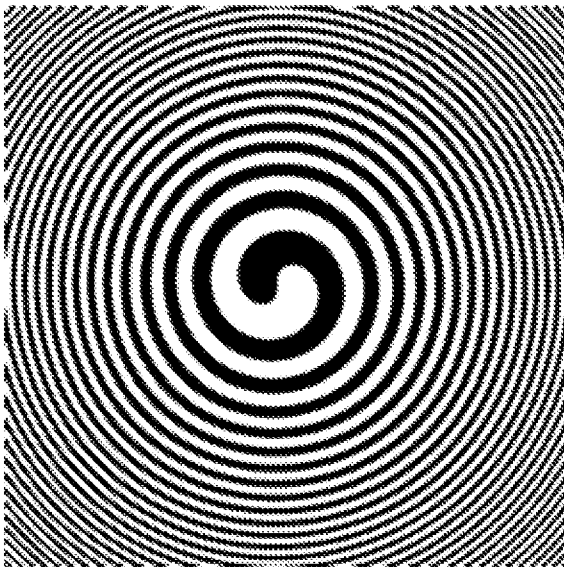


FIG. 6

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700A



700B

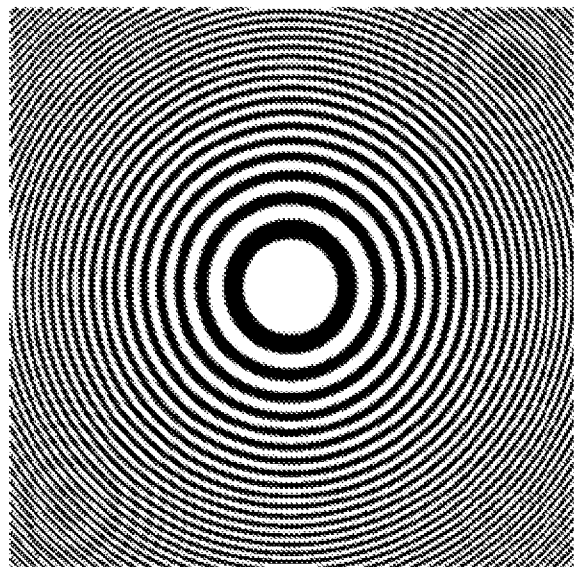


FIG. 7



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US16/25679

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - G02F 1/15, 1/157; G02C 7/08

CPC - G02F 1/15; G02C 7/101, 7/022

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8): G02F 1/061, 1/13, 1/15, 1/153, 1/155, 1/157, 1/63; G02C 7/02, 7/04, 7/06, 7/08, 7/10 (2016.01)

CPC: G02F 1/0018, 1/0063, 1/061, 1/137, 1/15, 2001/1515, 1/1533, 1/155, 1/157; G02C 7/022, 7/04, 7/06, 7/08, 7/101, 7/108

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatSeer (US, EP, WO, JP, DE, GB, CN, FR, KR, ES, AU, IN, CA, INPADOC Data); Google Scholar; EBSCO Discovery Service; IP.com;
Keywords: intra_ocular*, ophthalmic*, lens*, electro_chromic*, electro_active*, coating*, layer*, volt*, absorb*, PED:PSS, P3HT, polypyrrole*, polyaniline*, index*, refracti*, focus*, nanogel*

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 2003/0227664 A1 (AGRAWAL, A et al.) December 11, 2003; abstract; figures 1A and 7C; paragraphs [0004, 0069, 0080, 0142, 0162]	1-8, 10-12, and 15-18 --- 9, 13, 14, and 19
Y	US 2013/0271811 A1 (LAM, D et al.) October 17, 2013; figures 1-7; paragraphs [0079-0081, 0150, and 0151]	9
Y	US 8,870,370 B1 (OTIS, B et al.) October 28, 2014; abstract; figure 1; column 5, lines 55-67	13 and 14
Y	US 2006/0139570 A1 (BLUM, R et al.) June 29, 2006; paragraphs [0050, 0207, 0208]	19
A	US 2009/0279050 A1 (MCGINN, J et al.) November 12, 2009; entire document	1-19
A	US 2009/0204207 A1 (BLUM, R et al.) August 13, 2009; entire document	1-19
A	US 5,729,379 A (ALLEMAND, P et al.) March 17, 1998; entire document	1-19

☐ 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

31 May 2016 (31.05.2016)

Date of mailing of the international search report

24 JUN 2016

Name and mailing address of the ISA/

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