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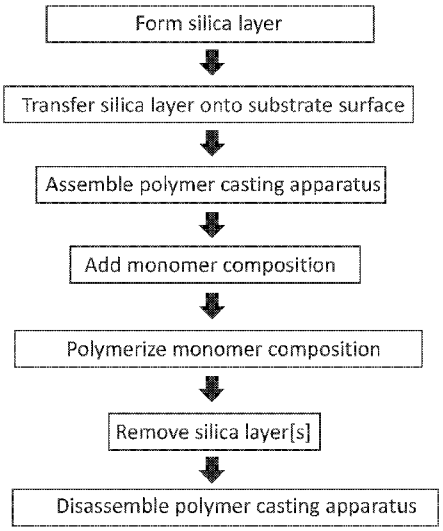

FIG. 1

(57) Abstract: Embodiments of the present disclosure provide for methods of detecting, sensors (e.g., chromogenic sensor), kits, compositions, and the like that related to or use tunable macroporous polymer. In an aspect, tunable macroporous materials as described herein can be used to determine the presence of a certain type(s) and quantity of liquid in a liquid mixture.

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Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

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METHODS AND SENSORS FOR DETECTION

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of and priority to U.S. Provisional Application Serial No. 62/507,294, having the title "METHODS AND SENSORS FOR DETECTION," filed on May 17, 2017, the disclosure of which is incorporated herein in by reference in its entirety.

FEDERAL SPONSORSHIP

This invention was made with government support under HDTRA1-15-1-0022 awarded by Department of Defense/Defense Threat Reduction Agency and under CMM11562861 awarded by the National Science Foundation. The government has certain rights in the invention.

BACKGROUND

Detection of liquid phase chemical such as ethanol, acetone, and benzene/toluene/xylene (BTX) requires materials with solvent stability and reliability. One of the barriers for sensors is the requirement of a semiconductor device powered by electric current. Hence, there is a need for a non-semiconductor sensing device.

SUMMARY

Embodiments of the present disclosure provide for methods of detecting, sensors (*e.g.*, chromogenic sensor), kits, compositions, and the like that related to or use tunable macroporous polymer.

An aspect of the present disclosure provides for a method of measuring the presence of a first liquid in a liquid mixture, comprising: providing a tunable polymer membrane; and exposing an area of the tunable polymer membrane to a liquid mixture, wherein the area of the tunable polymer membrane exposed to the liquid mixture changes color if the liquid mixture includes a first liquid.

An aspect of the present disclosure provides for a chromogenic sensor, comprising: a tunable polymer membrane, wherein an area of the tunable polymer membrane has the characteristic of changing color upon exposure to a first liquid if the first liquid is present in a liquid mixture.

An aspect of the present disclosure provides for a kit for testing the presence of a first liquid, comprising: a chromogenic sensor comprising a tunable polymer membrane, wherein an area of the tunable polymer membrane has the characteristic of changing color upon exposure to a first liquid if the first liquid is present in a liquid mixture; instructions for use of the chromogenic sensor to test for the presence of the first liquid in a liquid mixture.

An aspect of the present disclosure provides for a method of making a photonic structure, comprising: disposing nanoparticles onto a surface to form a three dimensional array of particles; introducing a prepolymer mixture to the array of particles; polymerizing the prepolymer mixture to form a polymer framework around the three dimensional array of particles; and removing the particles to form a three dimensional array of macropores to form a macroporous photonic crystal membrane, wherein the three dimensional polymer framework separates the macropores.

An aspect of the present disclosure provides for a tunable polymer membrane fabricated by the method described above and herein.

Other structures, kits, methods, features, and advantages will be or become apparent to one with skill in the art upon examination of the following drawings and detailed description. It is intended that all such additional structures, kits, methods, features and advantages be included within this description, be within the scope of the present disclosure, and be protected by the accompanying claims.

BRIEF DESCRIPTION OF THE DRAWINGS

Many aspects of the disclosed devices and methods can be better understood with reference to the following drawings. The components in the drawings are not necessarily to scale, emphasis instead being placed upon clearly illustrating the relevant principles. Moreover, in the drawings, like reference numerals designate corresponding parts throughout the several views.

FIG. 1 illustrates an embodiment of a method for fabricating macropoorus polymer membranes using a silica nanoparticle-based photonic crystal.

FIG. 2 illustrates a second embodiment of a method for fabricating macropoorus polymer membranes using a silica nanoparticle-based photonic crystal.

FIG. 3 illustrates a third embodiment of a method for fabricating macropoorus polymer membranes using a silica photonic crystal template.

FIG. 4 illustrates a fourth embodiment of a method for fabricating macropoorus polymer membranes using a silica multilayers or single template.

FIG. 5A is a photograph showing an example of the silica coating method described herein.

FIG. 5B depicts a photograph of a polyurethane membrane templated from FIG. 5A.

FIG. 6 illustrates normal-incidence transmission spectra obtained from the macroporous polymer film with different drying rates.

FIG. 7 illustrates a photograph of a macroporous polymer film dipping in a commercial ethanol-free fuel (TruFuel) blended with 2% of ethanol. Polymer film with deformation at the center before (A) and after (B). Scale bar: 5 mm.

FIGS. 8A-C illustrate typical SEM images of (FIG. 8A) Cross-section view of a greenish area from a macroporous polymer film. (FIG. 8B) Cross-section view of a deformed area. (FIG. 8C) Cross-sectional view of a recovered area.

FIG. 9 illustrates an image of chromogenic sensor for ethanol sensing.

FIG. 10 illustrates specular optical reflection spectra for detecting different concentrations of ethanol blended with octane.

FIG. 11 illustrates specular optical reflection spectra for detecting trace amount of ethanol blended with octane.

FIG. 12 illustrates specular optical reflection spectra for detecting ethanol vapor above ethanol-octane mixtures with different ethanol concentrations.

FIG. 13 illustrates a linear relationship between the positions of the optical reflection peaks and the ethanol concentrations in ethanol-octane mixtures.

FIGS. 14A-D illustrate specular optical reflection spectra for detecting ethanol in ethanol-free TruFuel, Shell gasoline, NyQuil medicine, and mouthwash liquids.

FIG. 15 illustrates schematics of smartphone-based sensor analysis procedure.

FIG. 16 illustrates a database of smartphone analysis to compare RGB data to ethanol concentration.

DETAILED DESCRIPTION

Before the present disclosure is described in greater detail, it is to be understood that this disclosure is not limited to particular embodiments described, as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting, since the scope of the present disclosure will be limited only by the appended claims.

Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit (unless the context clearly dictates otherwise), between the upper and lower limit of that range, and any other stated or intervening value in that stated range, is encompassed within the disclosure. The upper and lower limits of these smaller ranges may independently be included in the smaller ranges and are also encompassed within the disclosure, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the disclosure.

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. Although any methods and materials similar or equivalent to those described herein can also be used in the practice or testing of the present disclosure, the preferred methods and materials are now described.

As will be apparent to those of skill in the art upon reading this disclosure, each of the individual embodiments described and illustrated herein has discrete components and features which may be readily separated from or combined with the features of any of the other several embodiments without departing from the scope or spirit of the present disclosure. Any recited method can be carried out in the order of events recited or in any other order that is logically possible.

Embodiments of the present disclosure will employ, unless otherwise indicated, techniques of chemistry, inorganic chemistry, material science, and the like, which are within the skill of the art. Such techniques are explained fully in the literature.

The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how to perform the methods and use the compositions and compounds disclosed and claimed herein. Efforts have been made to ensure accuracy with respect to numbers (*e.g.*, amounts, temperature, etc.), but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in °C, and pressure is in atmosphere. Standard temperature and pressure are defined as 25 °C and 1 atmosphere.

Before the embodiments of the present disclosure are described in detail, it is to be understood that, unless otherwise indicated, the present disclosure is not limited to particular materials, reagents, reaction materials, manufacturing processes, or the like, as such can vary. It is also to be understood that the terminology used herein is for purposes of describing particular embodiments only, and is not intended to be limiting. It is also possible in the present disclosure that steps can be executed in different sequence where this is logically possible.

It must be noted that, as used in the specification and the appended claims, the singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a support" includes a plurality of supports. In this specification and in the claims that follow, reference will be made to a number of terms that shall be defined to have the following meanings unless a contrary intention is apparent.

Discussion

Embodiments of the present disclosure provide for methods of detecting, sensors (*e.g.*, chromogenic sensor), kits, compositions, and the like that related to or use tunable macroporous polymer. In an aspect, tunable macroporous materials as described herein can be used to determine the presence of a certain type(s) and quantity of liquid in a liquid mixture. Embodiments of the present disclosure are simple to use, provide robust results, and are re-useable while also being inexpensive.

In an aspect, the present disclosure provides for a unique macroporous structure that can be made by a simple and scalable nanoparticle self-assembly technology. This technology can result in unusual "cold" programming and subsequent room-temperature recovery, which can be cycled, for a large variety of polymers. The tunable properties are described herein. The flexibility of the methods and compositions described herein could expand and simplify the application scopes of new, tunable, materials that can be used as sensors or in methods of detecting the presence of and/or concentration of a liquid in a liquid mixture.

In an aspect, the present disclosure includes a method of measuring the presence and/or concentration of a first liquid (or multiple different types of liquids) in a liquid mixture. The liquid mixture (*e.g.*, an aqueous or non-aqueous mixture) can optionally include a first liquid (*e.g.*, an organic solvent). The tunable polymer membrane can be exposed to the liquid mixture in one or more ways. In an aspect, the tunable polymer membrane or a portion thereof can be dipped into the liquid mixture. In another aspect, an amount (*e.g.*, a drop or larger amount) of the liquid mixture can be disposed onto the surface of the tunable polymer membrane. In an aspect, an area of the tunable polymer membrane can be exposed to the vapor of the liquid mixture. In an aspect, the tunable polymer membrane or a portion of thereof can be dipped into the liquid mixture.

Upon exposure of the tunable polymer membrane to the liquid mixture, the tunable polymer membrane can change color, for example from a greenish color to a bluish color, yellowish color, or orange color, depending upon the concentration of the first liquid in the liquid mixture (See Example 1). The color and color change can be tuned based on the composition of the tunable polymer membrane and/or the method of making the tunable polymer membrane. In an aspect, the color change is detectable. In one aspect, the color change is perceptible by the human eye for those that can perceive the particular colors of the color change. It is understood that some individuals have degrees of color blindness, so the color change may not be perceived by those individuals. In another aspect, the color change can be evaluated using an analysis system to measure the color change from before to after or just after the change and correlate the color change using a known standard to the identity of the first liquid and/or the concentration of the first liquid. In an aspect, the analysis system can include a mobile device such as a cell

phone, tablet, or laptop, where a picture or image can be captured and subsequently be analyzed.

In an embodiment, the tunable polymer membrane can be used in a chromogenic sensor and kit to determine the presence of and/or concentration of a first fluid in the liquid mixture (*e.g.*, the liquid form, the vapor form, or both). For example, the method, chromogenic sensor, or kit can be useful for detecting the presence or concentration of a component in fuel. In an embodiment, the first liquid can be an organic solvent that can interact with the polymer such as an alcohol (e.g., ethanol) and the liquid mixture can be an aqueous mixture or a non-aqueous mixture such as a hydrocarbon mixture like gasoline. In this regard, the method, chromogenic sensor, or kit of the present disclosure can be used to measure the amount of ethanol in the gasoline, which can be useful in situations that require low or zero ethanol in the gasoline, such as in aircraft fuel.

In regard to the kit, the kit would have instructions and optionally a wipe(s) to clean off the surface of the tunable polymer membrane, gloves, a device to expose the liquid mixture to the tunable polymer membrane, and the like. The instructions would, among other things, provide guidance on how to perform the test, evaluate the test (*e.g.*, guide for what the color change means (*e.g.*, presence of a first liquid, concentration of the liquid, or the like)), clean the tunable polymer membrane, use the analysis system (*e.g.*, use the mobile device, the webpage to evaluate the results, and the like). The instructions may include other guidance as well to evaluate the contents of the liquid mixture in question.

Now having described the method, sensor, and kit, additional details will be provided that describe methods for preparing tunable materials. FIGs 1-3 are flowcharts depicting embodiments of methods described herein. FIG. 4 shows a further embodiment of a method for fabricating macroporous polymer membranes using a silica photonic crystal template

In an embodiment, the colloidal crystal of silica particles can be formed by first synthesis of silica particle. Monodispersed silica particles (*e.g.*, microspheres), with longest dimension (*e.g.*, a diameter for a spherical particle) of about 100 to 10,000 nm, were synthesized by the standard Stöber method or other appropriate method. Silica particles were self-assembled on a substrate such as a glass microslide, which is placed

in a clean scintillation vial including about 15 ml of ethanol with 1 vol% of silica particles, by the convective self-assembly technology to form colloidal crystals. Other monodispersed particles, such as polystyrene and poly(methyl methacrylate) (PMMA) particles, can also be used in assembling colloidal crystals using the convective self-assembly technology. These polymer latex particles can be selectively removed in organic solvents, such as toluene or acetone.

In an embodiment, a convective self-assembly method can enable the formation of ordered colloidal silica crystals on a glass substrate. Silica particles with a diameter of about 100 to 10,000 nm, which can be dispersed in an alcohol such as ethanol, can be assembled on the glass slides. The substrate can be varied in size depending of the desired applications.

After the silica layer or multilayer is applied, a polymer casting apparatus can be assembled. One or more substrates can be coated with a layer of silica particles as described above. In an embodiment, two or more substrates or a surface of two or more substrates can be coated with a silica layer. In an embodiment of a polymer casting apparatus, two or more coated substrates can be positioned in a container configured to hold a solvent in a sandwich-type configuration so that at least a surface of a first substrate coated with silica opposes a surface of a second substrate, uncoated or coated with silica. Other configurations can be realized with more than two coated substrates. In an embodiment, the coated substrates of the polymer casting apparatus are silica-coated glass.

In an embodiment, after assembly of the polymer casting apparatus, monomers or a monomer composition can be put in a space between two or more opposing silica coated surfaces of the two or more silica coated substrates. Monomers or a monomer composition that can form a polymer, a desired polymer, or a pre-determined polymer are described in more detail below.

After monomers are placed in the space, they can be polymerized by a polymerization method to form a tunable polymer membrane. The polymerization method can be photo-polymerization, wherein the monomers are polymerized by the application of light. In an embodiment, the light can be UV light and can be applied for a period of time.

The tunable polymer membrane can be made of a monomer, a monomer composition, or a polymer. In some embodiments, the monomers, monomer composition, or polymer can be a viscous and/or elastic polymer. The tunable polymer membrane can additionally be characterized by weak intermolecular forces. Further, the tunable polymer membrane can have a high Young's modulus and can still be reconfigurable via cold programming.

Following polymerization, the silica layers can be removed from the membrane and the membrane optionally washed. In an embodiment, the silica layer is removed by a solvent. In an embodiment, the silica is removed by 2% hydrofluoric acid (HF) aqueous solution. In an embodiment, the membrane can be washed by a wash solvent. In an embodiment, the wash solvent can be deionized water. The silica layers can be removed by a solvent that is placed in the container of the polymer casting apparatus in an embodiment. Selective removal of the silica layers can create macropores in the polymer. The polymer or tunable polymer membrane can be macroporous following removal of the templating silica layer.

In an embodiment, after removal of the silica monolayer (and optional wash), the polymer casting apparatus can be disassembled and the polymer membrane separated from the substrates that were previously silica coated. In an embodiment, the polymer membrane can be a tunable membrane.

The tunable polymer membrane can be configured to be modified such that the color of the tunable polymer membrane can vary in response to one or more liquids to which the tunable polymer membrane is exposed. The slow drying of liquid can cause a deformation of the tunable polymer membrane that changes the shape or configuration of the macropores in the tunable polymer membrane.

The color characteristics of the tunable membrane can be altered by drying after application of or cold programming. A solvent can alter the transparency by changing the shape of the macropores in the tunable polymer membrane through a mechanism such as capillary action.

The color change of the tunable polymer membrane can be cycled, or in other words is reversible. The color of the tunable polymer membrane as described herein can

changed by exposure to a liquid mixture (*e.g.*, ethanol in gasoline) and then returned to the original color by cold programming.

The methods and compositions described herein can use a large variety of shape memory polymers to form the tunable polymer membrane depending on the desired configuration of the tunable polymer membrane. Shape memory polymers as described herein can be elastic or glassy.

A "glassy" polymer can be a polymer or copolymer with glass transition temperature higher than room temperature. A "glassy" polymer can be optically transparent. A glassy polymer as used herein can have a glass transition state (T_g) higher than room temperature. In an embodiment, a glassy polymer has a T_g of about 120 °C. In an embodiment, the glassy polymer is poly(urethane) (with a typical T_g of about 90 °C), polyethylene terephthalate (PET) and polyethyleneoxide (PEO), epoxy, polyarylates, block copolymers containing polystyrene and poly(1,4-butadiene), and poly(2-methyl-2-oxazoline) and polytetrahydrofuran, polynorbornene, and other types of shape memory polymers.

In an embodiment, a polymer or tunable polymer membrane as used herein can be polymerized poly(urethane). In an embodiment, a polymer as used herein is a glassy membrane comprising poly(urethane)s. A coating as described herein can be a glassy membrane. A coating as described herein can be a glassy membrane comprising poly(urethane)s. In an embodiment, a glassy polymer can be used to form a membrane. In an embodiment, poly(urethane)s can be used to form a membrane.

A silica nanoparticle monolayer can be used as a structural template for fabricating macroporous polymer membranes. The templating layer can be multilayers of silica nanoparticles assembled by various methodologies, such as spin coating, dip coating, doctor blade coating, and so on. In an embodiment, the silica nanoparticles can be self-assembled or not be self-assembled and/or possess long-range ordering or not possess long-range ordering. Self-assembled silica nanoparticle monolayers can be used as described herein and can be created by a variety of methods, for example a simple and scalable Langmuir-Blodgett method as described above. As used and described herein, silica nanoparticles can be used for silica nanoparticle monolayers or multilayers. Silica

nanoparticles can be $Si_xO_yH_z$, synthesized by various methodologies, including the well-established Stöber method.

In an embodiment, the silica nanoparticles can be about 100 nm to about 10,000 nm. In an embodiment, silica nanoparticles are silicon dioxide (SiO_2). In an embodiment, a composition of silica nanoparticles has an average diameter of about 350 nm/particle. Silica nanoparticles as used herein can have a diameter of about 350 nm. In an embodiment, silica nanoparticles as used herein can be SiO_2 nanoparticles with a diameter of about 350 nm each.

EXAMPLES

Now having described the embodiments of the disclosure, in general, the examples describe some additional embodiments. While embodiments of the present disclosure are described in connection with the example and the corresponding text and figures, there is no intent to limit embodiments of the disclosure to these descriptions. On the contrary, the intent is to cover all alternatives, modifications, and equivalents included within the spirit and scope of embodiments of the present disclosure.

Example 1:

In this disclosure, a templating fabricated macroporous polymer photonic crystal that responds to selected compounds can be used as a chemical sensor with fast response and high sensitivity. The system is specifically designed to detect the presence and even measuring the target chemical in a multicomponent solution (ethanol in gasoline). The detection could be done by dipping the sensor in the liquid mixture as well as placing the sensor above the solution surface, which depends on the detection limit. The selective-interaction of a target compounds with the sensor provides a unique capability for chemical detection.

Silica particles were self-assembled on a glass microslide by the convective self-assembly technology to form colloidal crystals. Various thickness of resulting colloidal crystals (10-50 layers) were observed as a result of different particle volume fraction of the silica microspheres/ethanol suspension. The microslide with silica colloidal crystal was then allowed to stick to a blank microslide with a ~ 1 mm thick spacer in between.

Next, a viscous oligomer mixture (CN945A70, Sartomer) consisting of trifunctional acrylated urethane, tripropylene glycol diacrylate (TPGDA), and photoinitiator (Darocur 1173, 2-hydroxy-2-methyl-1-phenyl-1-propanone, BASF) was preheated to 90°C and then transferred into the space between the microslides. The capillary force assisted the infiltration of the oligomer mixture into the interstitial of silica microspheres and was evident as the oligomer mixture and silica particle index-matched and the sample cell turned transparent. The sample was then polymerized using a pulsed UV curing system (RC 742, Xenon) for 4 s. Last, the polymerized sample was removed from the glass microslide and subsequently soaked in a 1 vol% hydrofluoric acid aqueous solution for 24 h. The etched sample was rinsed with deionized water, ethanol and dried in air. The final product is in greenish diffractive color when observed at large viewing angles (>45°).

Cold programming experiments on the free-standing macroporous polymer film were performed where organic solvent (e.g., acetone and acetonitrile) was added dropwise on the film surface. Greenish diffractive color remained when the solvent was removed within 5 seconds using Kimwipes or air dry (Fig 6. blue-peak). The original diffractive colors were changed/lost after we leave the solvent on the surface and dried naturally in ~ 2 min (Fig. 6 orange-peak).

The bluish-iridescent color of the deformed areas is caused by the Bragg diffraction of visible light from the deformed macroporous film (see Fig 7B). Figure 8A shows the top-view SEM image of the greenish original area from the macroporous polymer film. Figure 8B is the cross-sectional SEM image of a bluish deformed area of the macroporous polymer film. The recovered of the macroporous 3-D order is shown by the cross-sectional SEM image in Figure 8C.

We utilized this unique cold programming cycle (deform and then recovery) with all-room-temperature-approach to design a chromogenic sensor, which uses the degree of recovery as a sensing parameter. A chromogenic sensor was fabricated to demonstrate the visible color change when in contact with different concentration of the analyte, which is ethanol in this case. In Figure 9, the sample changed from transparent to blue, yellow, then orange, when exposed to different concentrations of ethanol in gasoline (0 ppm, 2000 ppm, 3000 ppm, 4000 ppm, 5000 ppm, 6000 ppm, respectively). Furthermore, the response time of the chromogenic sensor was less than ~ 3 seconds.

The ethanol in gasoline (mostly alkanes) swells the SMP chromogenic sensor, and the degree of swelling is higher when the concentration of ethanol is greater. To further study the precise effect of swelling and ethanol concentration, we utilized a two-component system – ethanol in octane. By using a vis-NIR spectrometer, we could obtain a concentration dependence spectra due to the light diffraction of SMP with a response time of 5 s. The SMP begins at fully deformed state and then gradually recovers with increasing ethanol concentration. The SMP is fully recovered when the ethanol concentration is at 5500 ppm (Figure 10).

To further explore the sensitivity at low concentration, we experiment the SMP by allowing the sensor to response for 8 h under extremely low ethanol concentrations (Figure 11). The optical spectra show a distinct diffraction response for ethanol concentration as low as 10 ppm, magenta curve.

Low concentration aside, our chromogenic sensor could also detect ethanol at relatively high concentration. The idea is to distinguish ethanol concentration in gasoline by using its relative vapor pressure. Figure 12 shows the reflection spectra of the SMP when sensing the vapor of various gasoline with ethanol content ranging from 5 – 30 vol%. The SMP had a gradual red shift as the concentration of ethanol, hence the vapor pressure of ethanol, increased from 5% to 30%. Figure 13 illustrates an optical characterization of ethanol sensor with ethanol vapor when the concentration increases from 5 to 30 vol%.

Moreover, sensing experiments were performed using commercial products. The deformed polymer was used to test commercial product with ethanol and its control product that is ethanol-free. First, we investigate our sensor performance for gasoline. We first test the sensor with TruFuel, which is a commercially sold ethanol free gasoline with 92 octane number. The optical spectra show both flat curve in grey color (Figures 14A-D). Then, the sensors were separately deformed and triggered by using TruFuel with 1% of ethanol added and Shell gasoline in liquid and vapor respectively. Both shows orange iridescent peak ~ 630 nm (yellow and orange peak in Figures 14A and 14B, respectively). We then carried out a test for various pharmaceutical products. The chromogenic sensor shows no color change when triggered by ethanol free Nyquil. Whereas the sample triggered with regular Nyquil shows significant color change (dark

blue peak in Figure 14C). The same result is presented when the sensor use to distinguish daily supplies such as mouthwash. The sensor could differentiate commercially sold ethanol free Listerine to regular ones (Figure 14D).

Lastly, we developed a chromogenic sensor analysis tool using smartphones (Figure 15). We generated an RGB calorimetric profile database of the SM sensor when exposed to ethanol with known concentration (Figure 16). When a customer captured a new image for analysis, its RGB data will show in the app, and the results could be looked up in the database for analysis. We believe our unique SMP-based sensor and instant analysis system can be easily extended to the analysis of many more target chemicals in the desired system.

Ratios, concentrations, amounts, and other numerical data may be expressed in a range format. It is to be understood that such a range format is used for convenience and brevity, and should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. To illustrate, a concentration range of "about 0.1% to about 5%" should be interpreted to include not only the explicitly recited concentration of about 0.1 % to about 5 %, but also include individual concentrations (e.g., 1%, 2%, 3%, and 4%) and the sub-ranges (e.g., 0.5%, 1.1%, 2.2%, 3.3%, and 4.4%) within the indicated range. In an embodiment, the term "about" can include traditional rounding according to significant figure of the numerical value. In addition, the phrase "about 'x' to 'y'" includes "about 'x' to about 'y'".

Unless defined otherwise, all technical and scientific terms used have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. Although any methods and materials similar or equivalent to those described can also be used in the practice or testing of the present disclosure, the preferred methods and materials are now described.

Embodiments of the present disclosure will employ, unless otherwise indicated, techniques of separating, testing, and constructing materials, which are within the skill of the art. Such techniques are explained fully in the literature.

It should be emphasized that the above-described embodiments are merely examples of possible implementations. Many variations and modifications may be made to the above-described embodiments without departing from the principles of the present disclosure. All such modifications and variations are intended to be included herein within the scope of this disclosure and protected by the following claims.

CLAIMS

At least the following is claimed:

1. A method of measuring the presence of a first liquid in a liquid mixture, comprising:

providing a tunable polymer membrane; and

exposing an area of the tunable polymer membrane to a liquid mixture, wherein the area of the tunable polymer membrane exposed to the liquid mixture changes color if the liquid mixture includes a first liquid.

2. The method of claim 1, wherein the area changes from a greenish color to a bluish color, yellowish color, or orange color, depending upon the concentration of the first liquid in the liquid mixture.

3. The method of claims 1-2, wherein the color change is detectable.

4. The method of claims 1-3, wherein the first liquid is an organic solvent.

5. The method of claim 4, wherein the organic solvent is ethanol.

6. The method of claim 5, wherein the liquid mixture is gasoline.

7. The method of claims 1-6, wherein the color change is correlated to the concentration of the first liquid in the liquid mixture or vapor pressure of first liquid in the liquid mixture.

8. The method of claims 1-7, wherein the tunable polymer membrane is fabricated by the method of any of claims 19 to 40.

9. A chromogenic sensor, comprising: a tunable polymer membrane, wherein an area of the tunable polymer membrane has the characteristic of changing color upon exposure to a first liquid if the first liquid is present in a liquid mixture.

10. The chromogenic sensor of claim 9, wherein the area changes from a greenish color to a bluish color, yellowish color, or orange color, depending upon the concentration of the first liquid in the liquid mixture.

11. The chromogenic sensor of claims 9-10, wherein the color change is detectable.

12. The chromogenic sensor of claims 9-11, wherein the first liquid is a solvent.

13. The chromogenic sensor of claim 12, wherein the solvent is an alcohol and the liquid mixture is gasoline.

14. The chromogenic sensor of claims 9-13, wherein the liquid mixture is an aqueous mixture or a non-aqueous mixture.

15. The chromogenic sensor of claims 9-14, wherein the color change is correlated to the concentration of the first liquid in the liquid mixture or the vapor of the first liquid.

16. The chromogenic sensor of claims 9-15, wherein the tunable polymer membrane is fabricated by the method of any of claims 19-40.

17. A kit for testing the presence of a first liquid, comprising: a chromogenic sensor comprising a tunable polymer membrane, wherein an area of the tunable polymer membrane has the characteristic of changing color upon exposure to a first liquid if the first liquid is present in a liquid mixture; instructions for use of the chromogenic sensor to test for the presence of the first liquid in a liquid mixture.

18. The kit of claim 17, wherein the chromogenic sensor is one described in any one of claims 1-16.

19. A method of making a photonic structure, comprising:

disposing nanoparticles onto a surface to form a three dimensional array of particles;

introducing a prepolymer mixture to the array of particles;

polymerizing the prepolymer mixture to form a polymer framework around the three dimensional array of particles; and

removing the particles to form a three dimensional array of macropores to form a macroporous photonic crystal membrane, wherein the three dimensional polymer framework separates the macropores,

20. The method of claim 19, further comprising:

forming silica layer with silica nanoparticles; and

transferring the silica layer onto at least one surface of one or more substrates.

21. The method of claim 19, further comprising: disassembling the polymer casting apparatus.

22. The method of claim 19, further comprising: washing the tunable polymer membrane with a second solvent after removing the silica layers.

23. The method of claim 19, wherein the silica nanoparticles are SiO_2 nanoparticles with a longest dimension of about 100 nm to about 10,000 nm.

24. The method of claim 19, wherein the silica layer is a multilayer structure of colloidal silica crystals.

25. The method of claim 19, wherein the one or more substrates comprise glass.

26. The method of claim 19, wherein the monomer composition comprises a shape memory polymer.

27. The method of claim 19, wherein the first solvent is 2 vol% hydrofluoric acid.

28. The method of claim 27, wherein the second solvent is deionized water.

29. The method of claim 19, further comprising applying the tunable polymer membrane to a surface.

30. The method of claim 29, further comprising tuning the tunable polymer membrane by a first tuning method to create a tuned polymer membrane.

31. The method of claim 28, further comprising tuning the tuned polymer membrane with a second tuning method.

32. The method of claim 31, wherein the first tuning method is slow-evaporation of solvent.

33. The method of claim 31, wherein the second tuning method is fast-evaporation of solvent.

34. The method of claim 19, further comprising initiating a tuning cycle.

35. The method of claim 34, wherein the tuning cycle comprises a first tuning method to create a first tuning state of the tunable polymer membrane followed by a second tuning cycle to create a second tuning state.

36. The method of claim 35, further comprising repeating the tuning cycle.

37. The method of claim 35, wherein the first tuning method is selected from the group consisting of applying a force or immersing in a solvent and slow-drying.

38. The method of claim 35, wherein the first tuning method is selected from the group consisting of solvent and vapor.

39. The method of claim 35, wherein the tuning cycle alters the optical Bragg's diffraction peak from 400 – 700 nm.

40. The method of claim 19, wherein the polymer framework is made of polyurethane polymer.

41. A tunable polymer membrane fabricated by the method of any of claims 19-40.

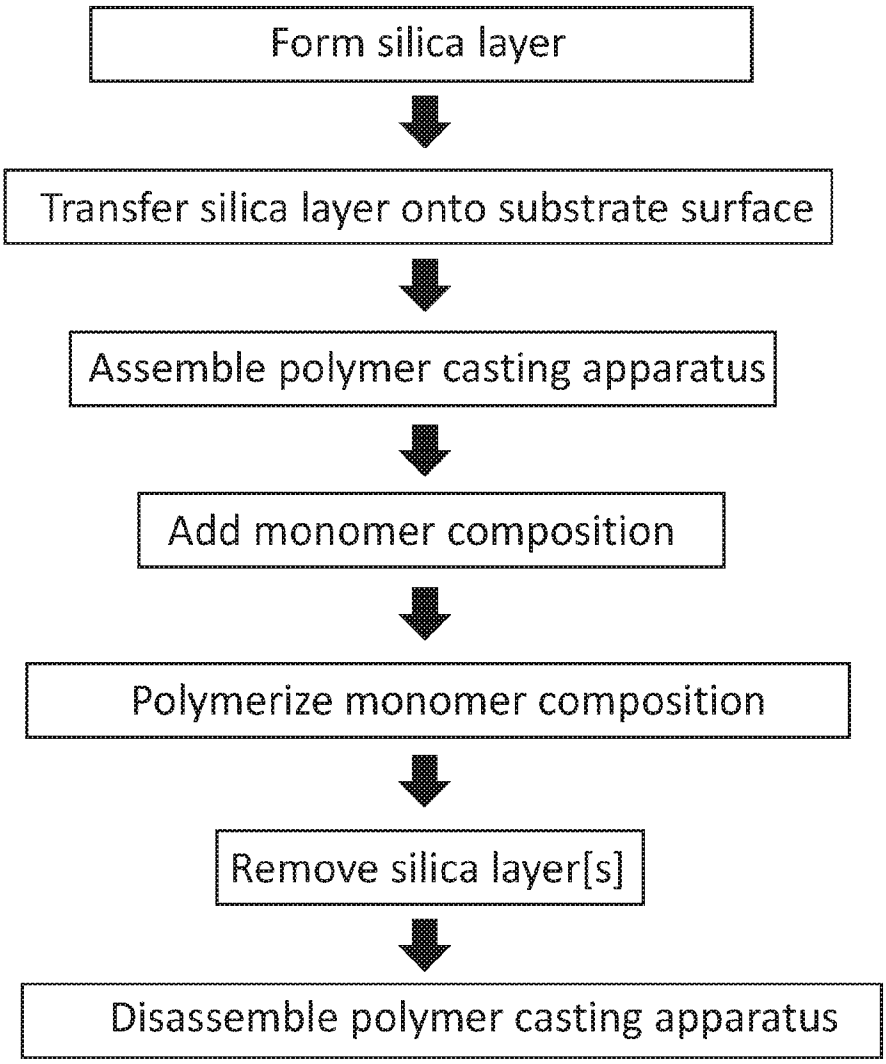
Form silica layer
Transfer silica layer onto substrate surface
Assemble polymer casting apparatus
Add monomer composition
Polymerize monomer composition
Remove silica layer[s]
Disassemble polymer casting apparatus

FIG. 1

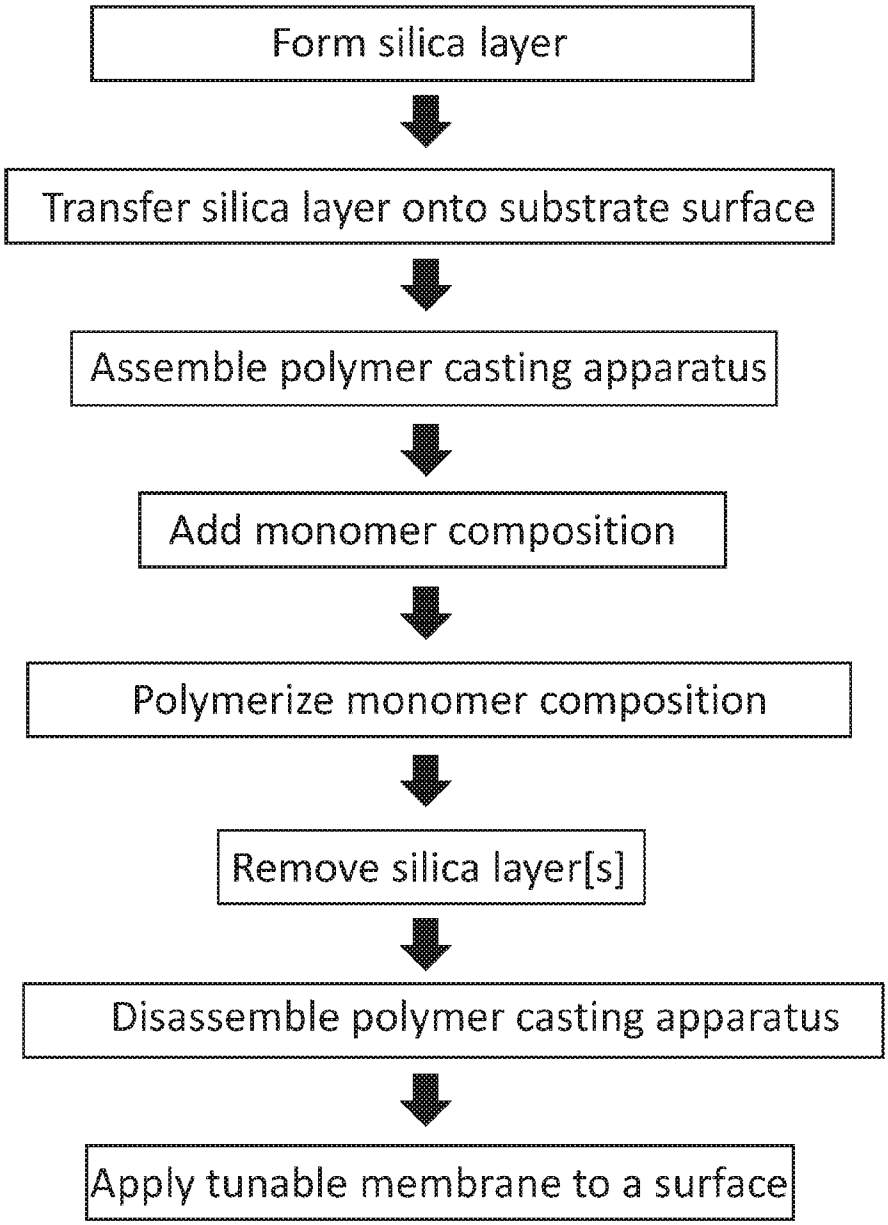
Form silica layer
Transfer silica layer onto substrate surface
Assemble polymer casting apparatus
Add monomer composition
Polymerize monomer composition
Remove silica layer[s]
Disassemble polymer casting apparatus
Apply tunable membrane to a surface

FIG. 2

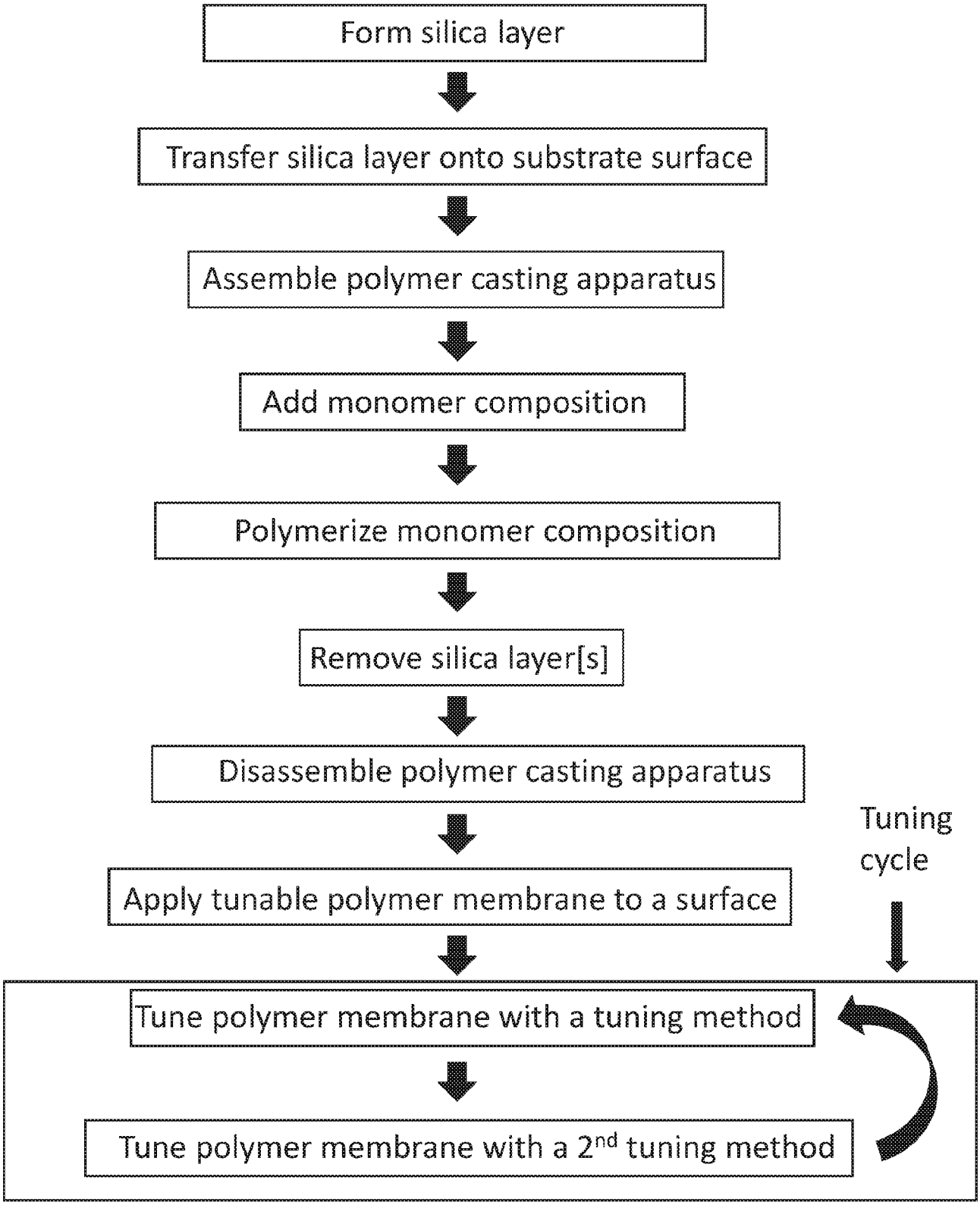
Form silica layer
Transfer silica layer onto substrate surface
Assemble polymer casting apparatus
Add monomer composition
Polymerize monomer composition
Remove silica layer[s]
Disassemble polymer casting apparatus
Apply tunable polymer membrane to a surface
Tune polymer membrane with a tuning method
Tune polymer membrane with a 2nd tuning method
Tuning cycle

FIG. 3

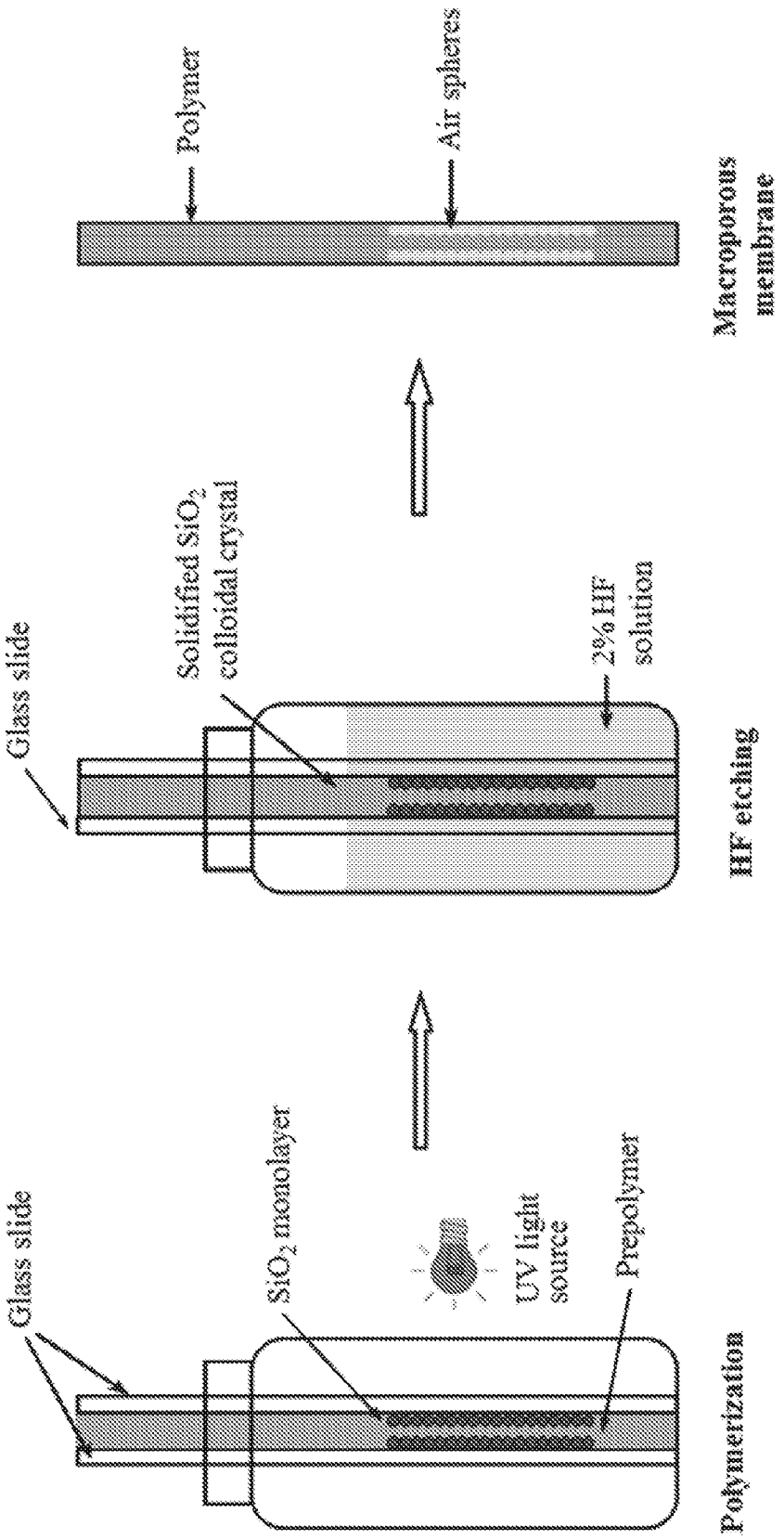
Polymer
Air spheres
Macroporous membrane
Glass slide
Solidified SiO_2 colloidal crystal
2% HF solution
HF etching
Glass slide
SiO_2 monolayer
UV light source
Prepolymer
Polymerization

FIG. 4

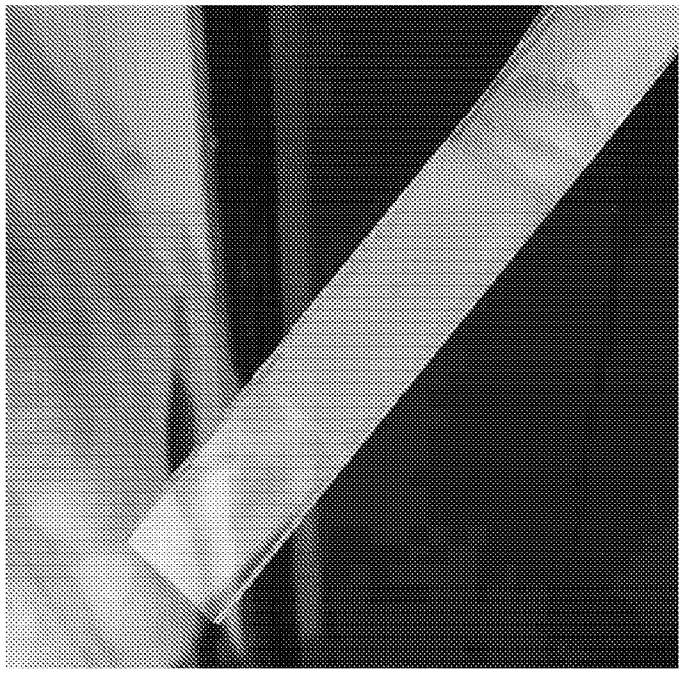

FIG. 5A

FIG. 5B

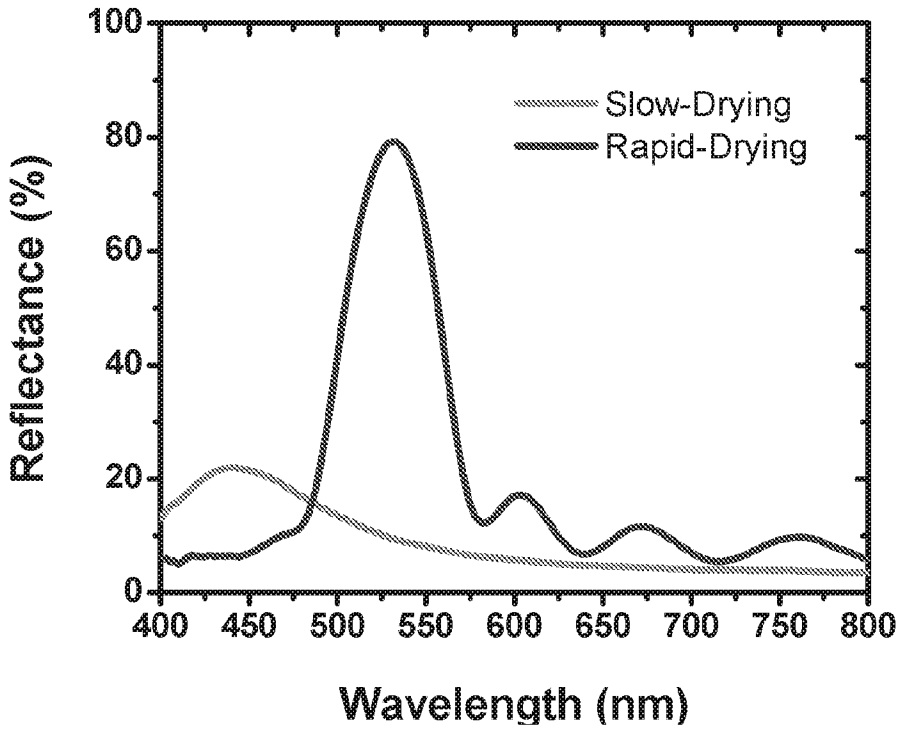
100
80
60
40
20
0
Reflectance (%)
Slow-Drying
Rapid-Drying
400
450
500
550
600
650
700
750
800
Wavelength (nm)

FIG. 6

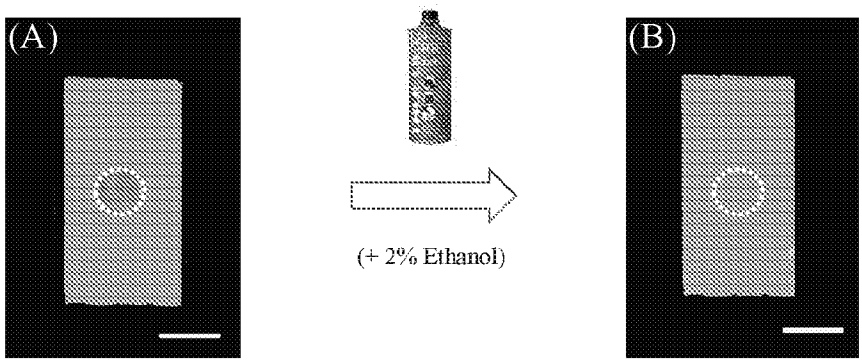
(A)
(+ 2% Ethanol)
(B)

FIG. 7

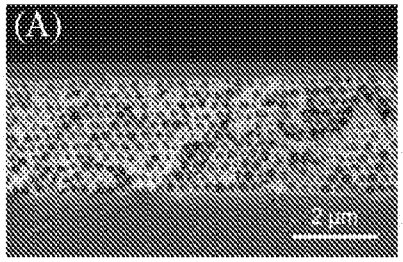

FIG. 8A

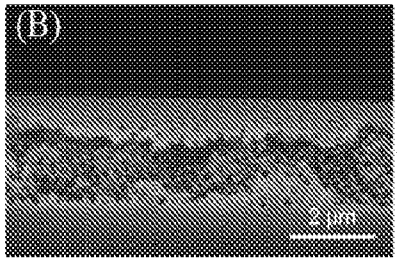

FIG. 8B

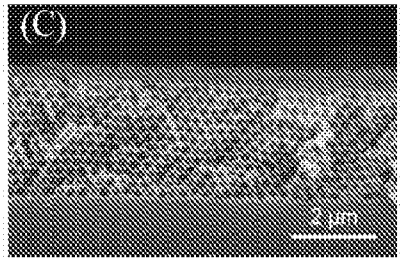

FIG. 8C

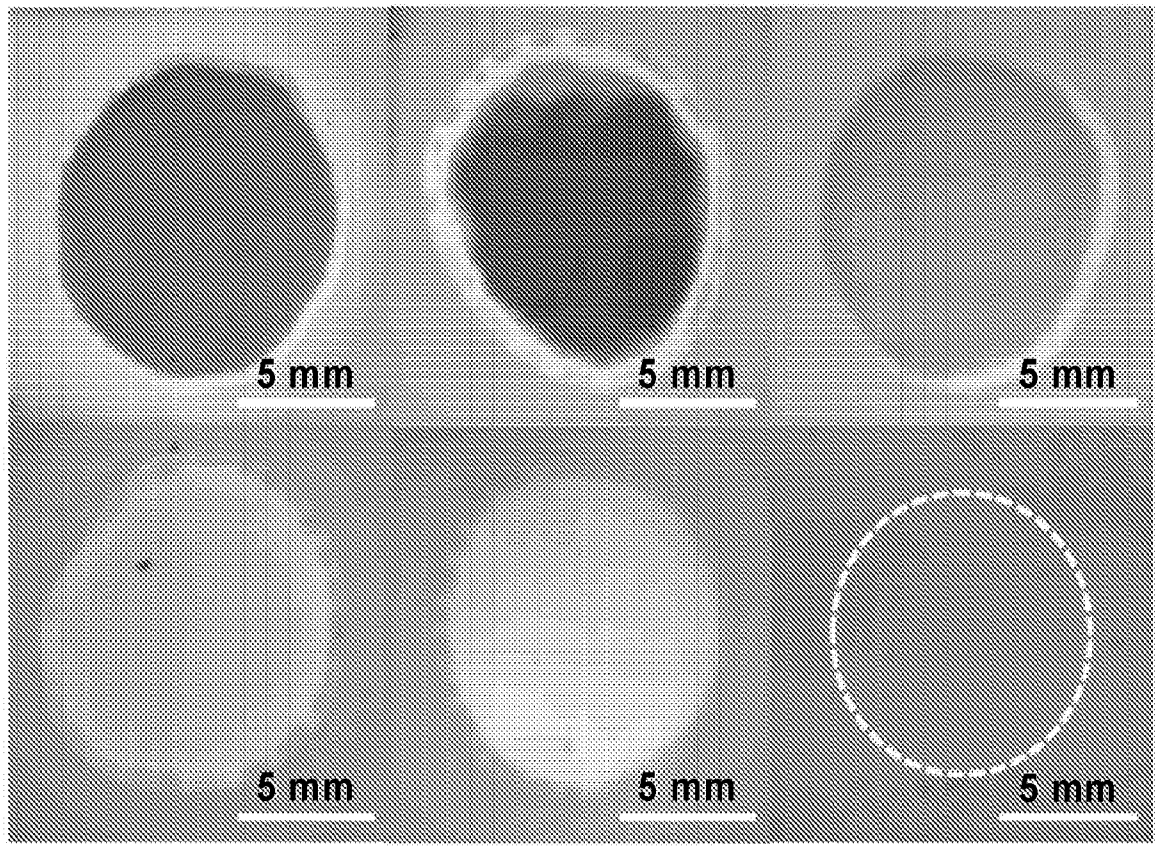

FIG. 9

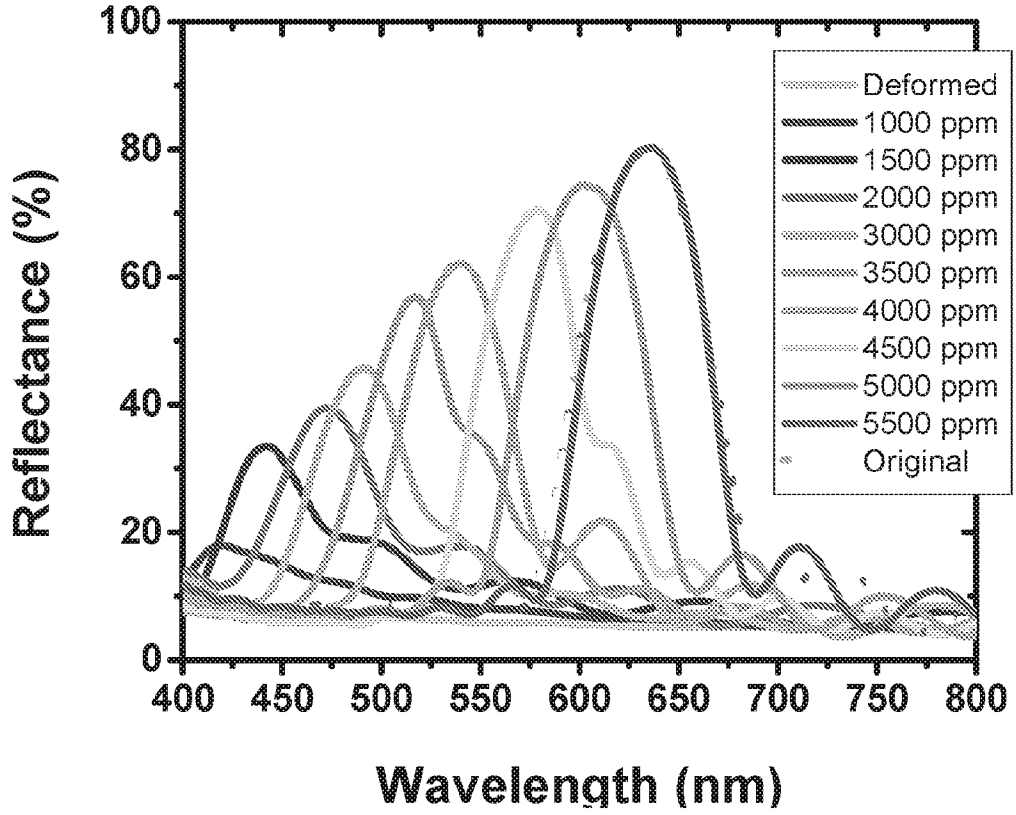
Reflectance (%)
Wavelength (nm)
Deformed
1000 ppm
1500 ppm
2000 ppm
3000 ppm
3500 ppm
4000 ppm
4500 ppm
5000 ppm
5500 ppm
Original

FIG. 10

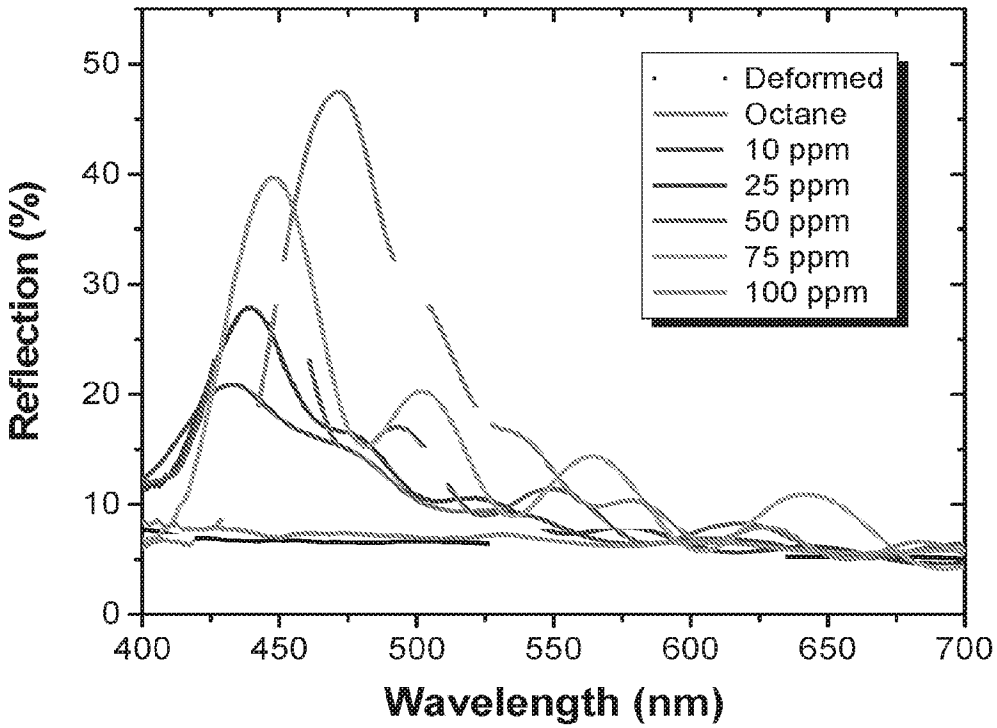
Reflection (%)
Wavelength (nm)
Deformed
Octane
10 ppm
25 ppm
50 ppm
75 ppm
100 ppm

FIG. 11

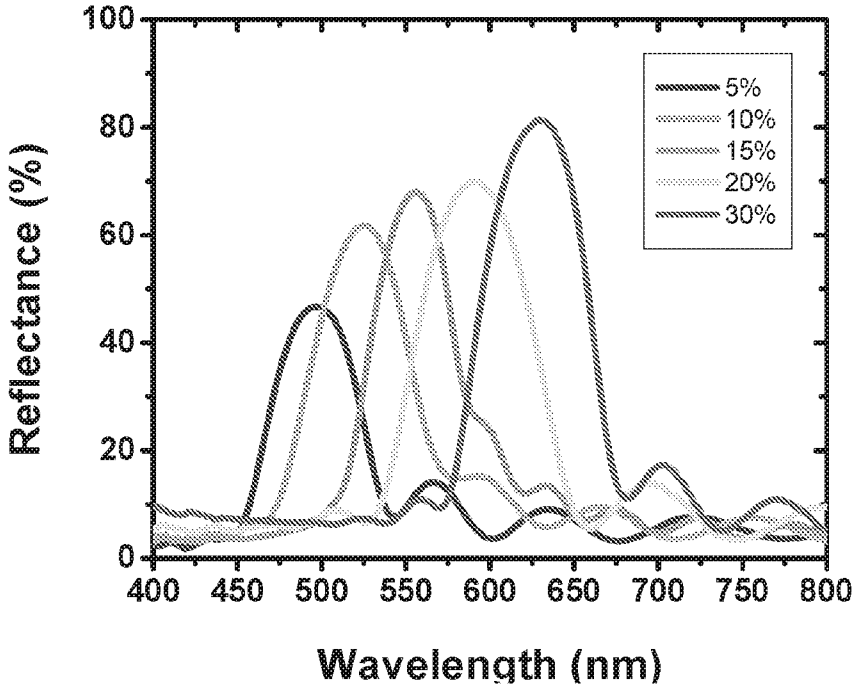
Reflectance (%)
Wavelength (nm)
5%
10%
15%
20%
30%
0
20
40
60
80
100
400
450
500
550
600
650
700
750
800

FIG. 12

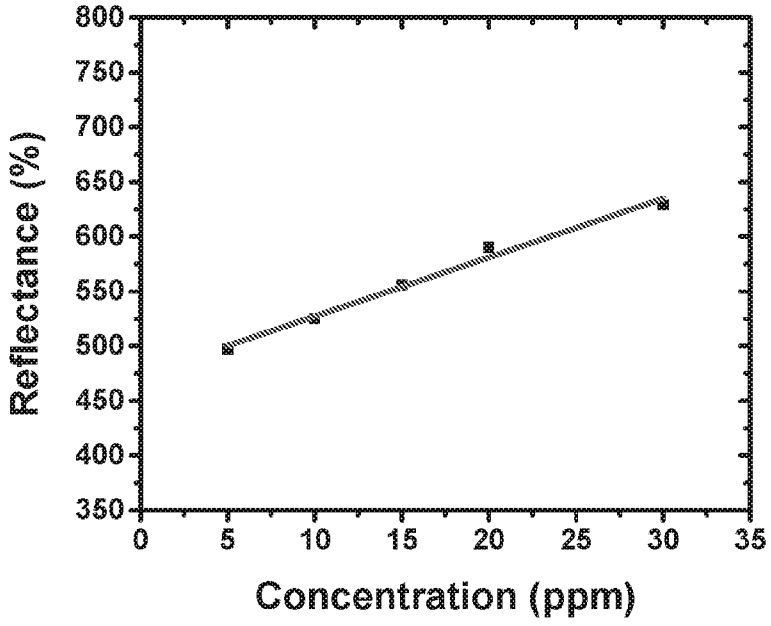
Reflectance (%)
Concentration (ppm)
350
400
450
500
550
600
650
700
750
800
0
5
10
15
20
25
30
35

FIG. 13

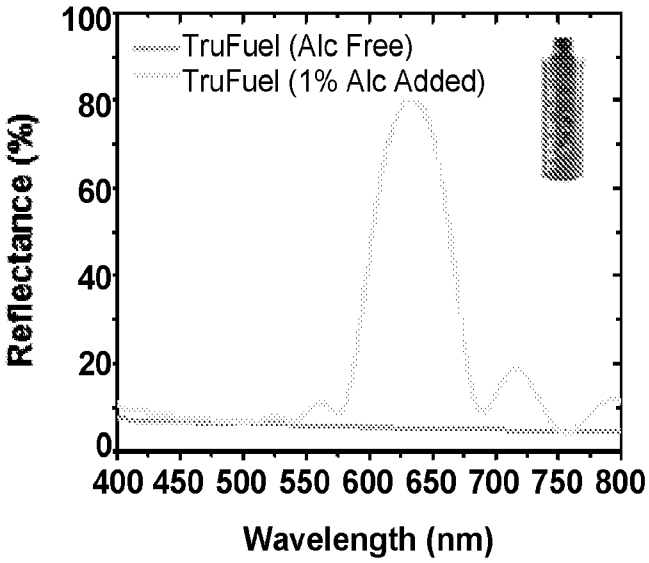

FIG. 14A

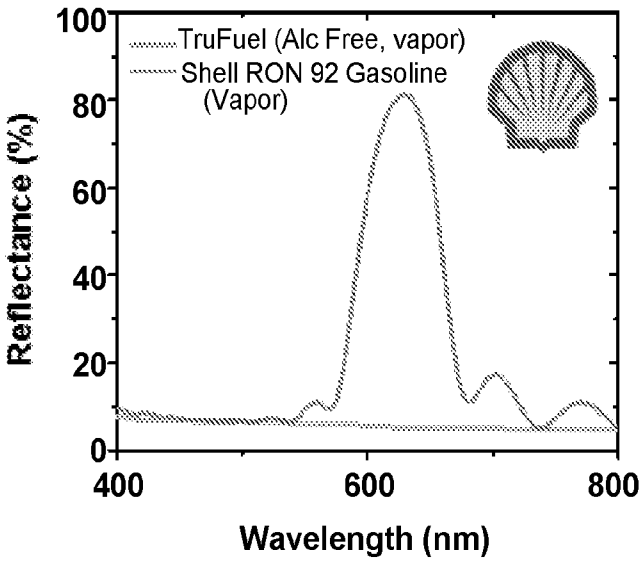

FIG. 14B

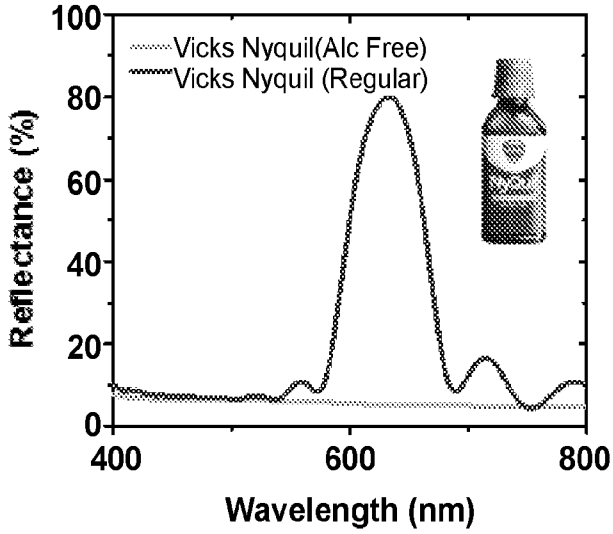

FIG. 14C

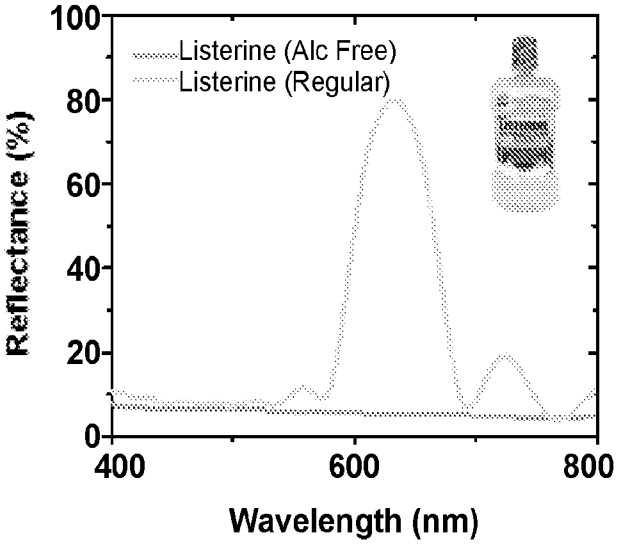

FIG. 14D

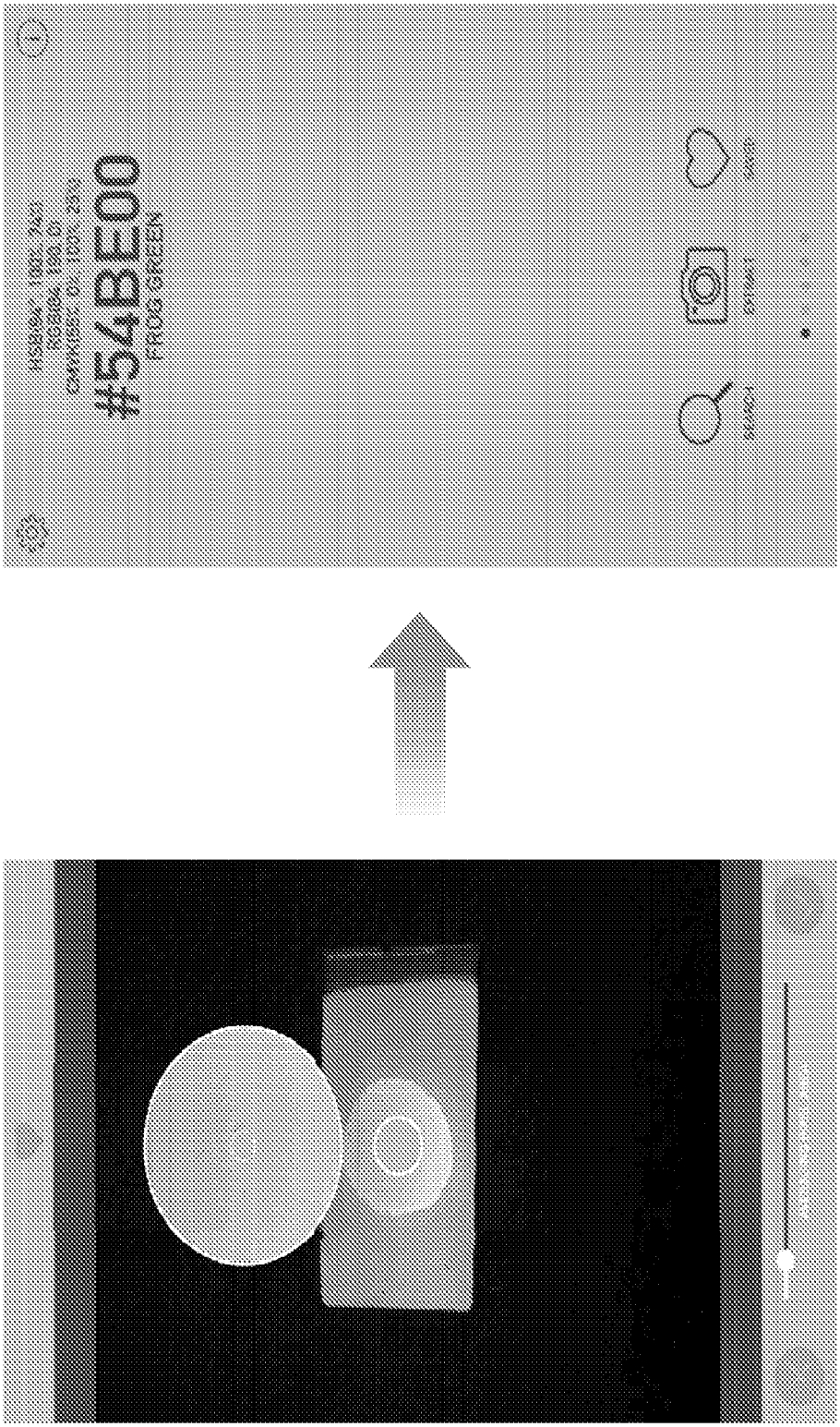

FIG. 15

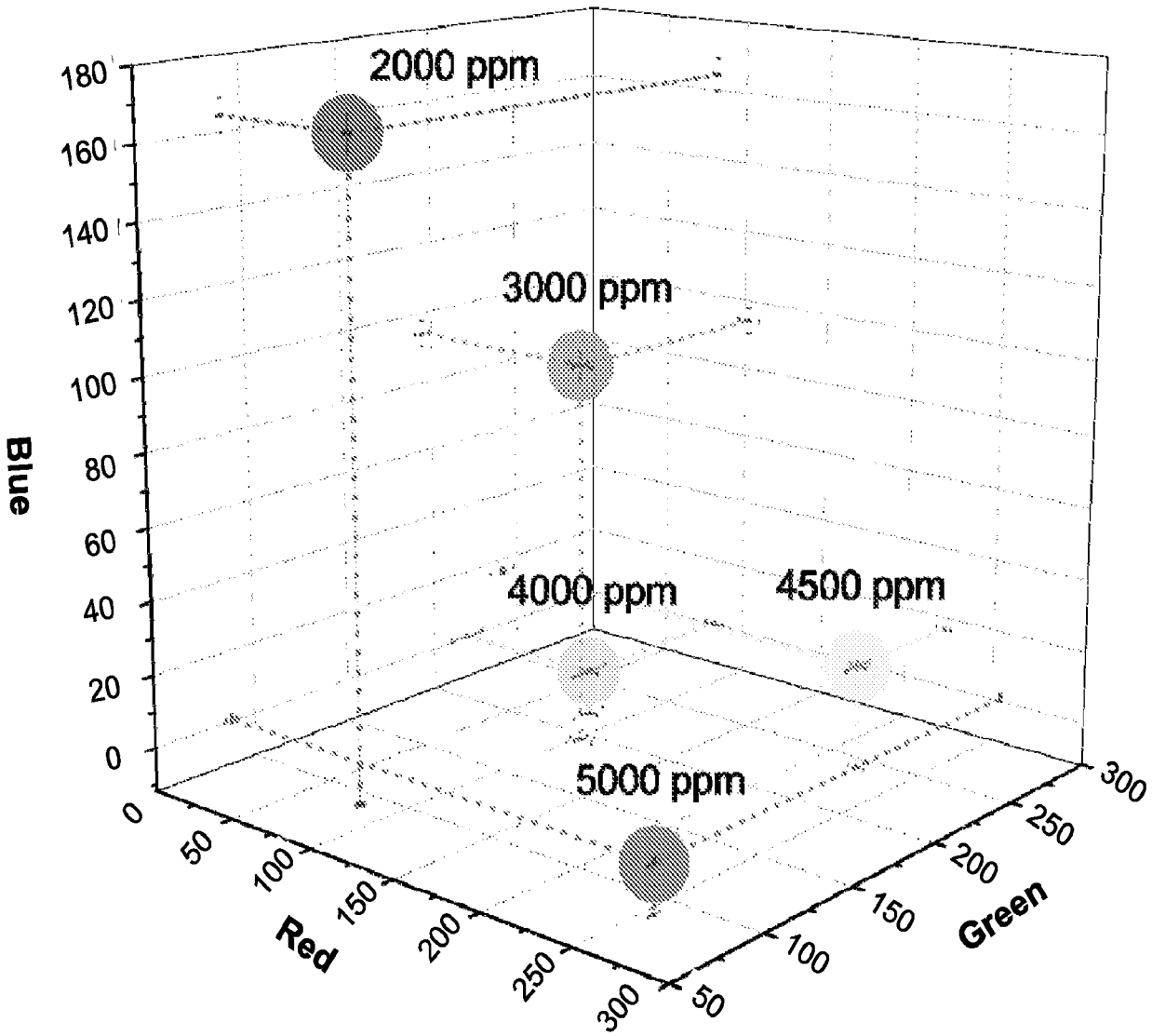
2000 ppm
3000 ppm
4000 ppm
4500 ppm
5000 ppm
Blue
Red
Green
180
160
140
120
100
80
60
40
20
0
0
50
100
150
200
250
300
50
100
150
200
250
300

FIG. 16