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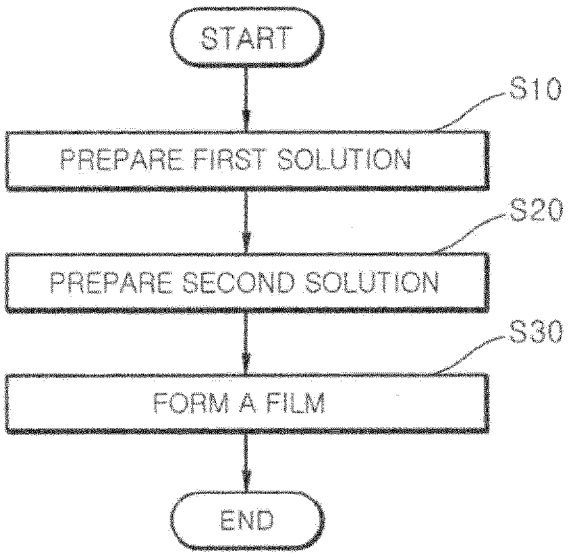
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(54) Title: METHOD OF PREPARING A FREE STANDING ULTRATHIN POROUS MEMBRANE AND FREE STANDING ULTRATHIN POROUS MEMBRANE MANUFACTURED USING THE SAME

(57) Abstract: Provided is a method of preparing a free standing ultrathin porous membrane and a free standing ultrathin porous membrane manufactured thereby. In one embodiment, the method comprises preparing a first solution by mixing nafion and an organic solvent; mixing the first solution and water to obtain a second solution; forming a film by applying the second solution onto a substrate followed by heat treatment at about 60 - 200 °C or room temperature; and separating the film from the substrate.

【FIG 1】



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[DESCRIPTION]

[Invention Title]

METHOD OF PREPARING A FREE STANDING ULTRATHIN POROUS MEMBRANE AND FREE STANDING ULTRATHIN POROUS MEMBRANE MANUFACTURED USING THE SAME

[Technical Field]

The present invention relates to a method of preparing a free standing ultrathin porous membrane and a free standing ultrathin porous membrane manufactured using the same

[Background Art]

Nafion is a sulfonated tetrafluoroethylene-based fluoropolymer-copolymer. It is the first synthetic polymer with ionic properties, which is called a perfluorinated sulfonic acid ionomer (PFSA) or an ionomer. Nafion has unique ionic properties, which are caused by introducing a perfluorovinyl ether group terminated with a sulfonate group (-SO_3H) onto a polytetrafluoroethylene (PTFE) backbone.

Meanwhile, to stabilize a nanometer-scale Nafion thin film, the interaction between bulk Nafion surfaces in a solvent, that is, the interaction between various compositions in the two components is essential.

Although synthetically independent on a solvent concentration, the transition of liquid Nafion to film-type Nafion occurs when excessive water and heat are present for initiating polymerization.

In Prior Art Document 2 (Henkensmeier et al., U.S. Unexamined Patent Publication No. 2016-0204459, published on July 14, 2016), a method of preparing a porous Nafion membrane with an unknown thickness and a very large pore size of about 10 μm is disclosed.

However, the Nafion membrane has a problem of reducing proton conductivity under low relative humidity (RH) conditions, which is pointed out as a chronic problem that the Nafion membrane must overcome. To this end, research on a process of manufacturing a free standing Nafion membrane, which has been widely used in numerous fields, is persistently required.

Therefore, the inventors suggest low-dimensional manufacture of free standing Nafion having multiple functions as a novel material that can be applied to numerous technical fields.

[Disclosure]

[Technical Problem]

One object of the present invention is to provide a free standing ultrathin porous membrane which has a free standing structure without a support, and has a nano-sized pore and thickness and a method thereof.

Another object of the present invention is to provide a free standing ultrathin porous membrane with excellent ion conductivity, moisture retention and structural stability and a method thereof.

Still another object of the present invention is to provide a free standing ultrathin porous membrane with excellent biocompatibility and an excellent separation property and a method thereof.

Still another object of the present invention is to provide a method of preparing a free standing ultrathin porous membrane which is stable even at a large size and is easy to handle thereby providing various applications.

[Technical Solution]

One aspect of the present invention relates to a method of preparing a free standing ultrathin porous membrane, comprising: preparing a first solution comprising nafion; mixing the first solution and water to obtain a second solution; forming a film by applying the second solution onto a substrate followed by heat treatment at about 60 - 200 ℃ or room temperature; and separating the film from the substrate.

In one embodiment, the film may have a thickness of about 800 nm or less and an average pore diameter of about 1 nm to about 10 nm.

In one embodiment, the heat treatment may be conducted at a temperature of about 120℃ to about 160 ℃.

In one embodiment, the first solution comprises the nafion only.

In another embodiment, the first solution comprises the nafion and organic solvent.

In one embodiment, the second solution comprises the nafion only.

In another embodiment, the second solution comprises comprises the first solution and water.

In one embodiment, the first solution may comprise the nafion and the organic solvent in a fixed volume of organic solvent between 5 to 20 with varying amounts of nafion (0.1 ~10).

In one embodiment, the second solution may comprise the first solution and water in a volume ratio of about 1: 30 (first solution : water).

In one embodiment, the organic solvent may include dimethyl sulfoxide.

In one embodiment, the film may be separated by hydrolysis of bonds formed at the interface of the film and the substrate.

Another aspect of the present invention relates to a free standing ultrathin porous membrane manufactured by the foregoing method.

In one embodiment, the free standing ultrathin porous membrane may have about 1500 or more pores having a diameter of about 1.5 nm to about 2.0 nm in 1300 x 1600 nm^2 area.

In one embodiment, the free standing ultrathin porous membrane may have a hydrogen ion conductivity, measured in 90 °C water, of about 0.01 mS/cm to about 0.3 mS/cm.

[Advantageous Effects]

A free standing ultrathin porous membrane manufactured according to the present invention can have a free standing structure without a support required for conventional ionomer precipitation, nano-sized pores and thickness, excellent ion conductivity, moisture retention and structural stability, and excellent biocompatibility and an excellent separation property.

[Description of Drawings]

FIG. 1 is a flowchart illustrating a method of preparing a free standing ultrathin porous membrane according to an exemplary embodiment of the present invention.

FIG. 2 schematically illustrates a method of preparing a free standing ultrathin porous membrane according to an exemplary embodiment of the present invention.

FIG. 3 is a graph showing transmission electron microscope (TEM) results of Examples.

FIG. 4 is a graph showing small angle X-ray scattering (SAXS) analysis results of Examples.

FIG. 5(a)(b) are AFM images of Examples measured by atomic force microscopy.

FIG. 6 is results of contact angle tests of M1~M7 films prepared by Examples 1~7 respectively.

FIG. 7 is a graph showing thermogravimetric analysis (TGA) results of Examples and Comparative Example.

FIG. 8A to 8C are graphs showing dynamic machine test results of Example 1.

FIG. 9A to 9C show the results of measuring zeta potentials of Example 1.

FIG. 10 is a graph showing XRD analysis results of Examples and Comparative Example 1.

FIG. 11 are images that show auto-fluorescence of the films.

FIG. 12 is test result of biocompatibility of the films of Examples 1-17.

FIG. 13 is optical image showing cell growth on the film of Example 7.

FIG. 14A to 14C are graphs showing cyclic voltammetry analysis results of Example 3 and Comparative Example 1.

FIG. 15A to 15E are ATR-FT-IR spectra of Examples and Comparative Example.

[Modes of the Invention]

To explain the present invention, when detailed description on the related art or configuration is determined to unnecessarily obscure the subject matter of the present invention, the detailed description will be omitted.

In addition, the terms to be described below are defined in consideration of functions in the present invention, and may vary according to a user, the intention or custom of an operator. Therefore, the definition should be based on the contents spanning the entire specification.

Method of preparing free standing ultrathin porous membrane

One aspect of the present invention relates to a method of preparing a free standing ultrathin porous membrane. FIG. 1 a flowchart illustrating a method of preparing a free standing ultrathin porous membrane according to an exemplary embodiment of the present invention, and FIG. 2 schematically illustrates a method of preparing a free standing ultrathin porous membrane according to an exemplary embodiment of the present invention.

Referring to FIGS. 1 and 2, the method of preparing a free standing ultrathin porous membrane includes: a step of preparing a first solution (S10); a step of preparing a second solution (S20); and a step of forming a film (S30). More particularly, the method of preparing a free standing ultrathin porous membrane includes: preparing a first solution by mixing nafion and an organic solvent (S10); mixing the first solution and water to obtain a second solution (S20); forming a film by applying the second solution onto a substrate followed by heat treatment at about 60 - 200 ℃ or room temperature (S30) and separating the film from the substrate..

Hereinafter, the method of preparing a free standing ultrathin porous membrane according to an exemplary embodiment will be described in detail, step by step.

Step of preparing a first solution (S10)

The step is to prepare a first solution as shown in FIG. 2(a).

In one embodiment, the first solution comprises the nafion only.

In another embodiment, the first solution comprises the nafion and organic solvent.

In one embodiment, the nafion may be perfluorinated sulfonic acid ionomer, for example, a bulk-state perfluorinated sulfonic acid ionomer, which does not contain a solvent.

The organic solvent may include dimethyl sulfoxide (DMSO), dimethylformamide, methylene chloride, trifluoroacetic acid, trifluoromethane sulfonic acid, primary alcohols, secondary alcohols and chloroform. Among them, DMSO is preferred. When the organic solvent is contained, the bulk-state perfluorinated sulfonic acid ionomer may be easily dissolved.

When the dimethyl sulfoxide is used as an organic solvent, the bulk perfluorinated sulfonic acid ionomer may be easily dissolved, thereby easily preparing

a first solution, and a film, which will be described below, may serve as a polymerization initiator.

In one embodiment, the first solution may comprise the nafion and the organic solvent in a fixed volume of organic solvent between 5 to 20 with varying amounts of nafion (0.1 ~10). Within this range, the nafion ionomer may be dissolved, thereby easily preparing the first solution. For example, the first solution may include the perfluorinated sulfonic acid ionomer and dimethyl sulfoxide in a volume ratio of about 1:0.5 to about 1:100. For example, these components may be included in a volume ratio of about 1:2 to about 1:4.

Step of preparing a second solution (S20)

This step is to prepare a second solution containing the first solution.

In one embodiment, the second solution comprises the nafion only.

In another embodiment, the second solution comprises comprises the first solution and water. For example, the second solution may be prepared by mixing the first solution and water.

The water serves as a gas diffusion template for imprinting a nano-sized pore onto a film to be described below.

In one embodiment, the second solution may contain the first solution and water in a volume ratio of about 1:0.1 to about 1:100. Within this range, the structural stability of a film may not be degraded, and a nano-sized pore may be easily formed in the film.

Step of forming a film (S30)

This step is to form a film by applying the second solution onto a substrate followed by heat treatment as shown in FIG. 2(b). The heat treatment is conducted at about 60 - 200 ℃ or room temperature. If the heat treatment is conducted under the temperature of 120 ℃, the structural stability of the film may be degraded, the nano-sized pore may not be formed in the structure, and it may be difficult to form the film with a nano-sized thickness. For example, the film may be formed by heat treatment of the second solution at about 120 ℃ to about 160 ℃ for about 1 to 3 hours.

For example, the thermal treatment temperature may be about 120, 121, 122, 123, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139,

140, 141, 142, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159 or 160 °C.

The substrate may include glass petri dish, silicon wafer, glass wafer and the like.

In an embodiment, the film may be easily deposited on a substrate surface, and identified with an interference fringe on the substrate surface.

In one embodiment, as shown in FIG. 2(c), the film may have a thickness of about 800 nm or less. The film is porous and may have an average pore diameter of about 1 nm to about 10 nm. For example, the film may have a thickness of about 50 nm to about 800 nm and an average pore diameter of about 1 nm to about 5 nm. For example, the film may have a thickness of about 190 nm to about 700 nm.

The pore diameter is associated with the scale of a small molecule having a critical influence on biomedical applications. The film with a nano-scale thickness may have a large surface area upon modification by adjusting the concentration of the first solution.

In one embodiment, the porosity of the film may be about 20% to about 85%. Under the above-mentioned porosity condition, excellent ion conductivity and structural stability may be exhibited.

Step of separating film (S40)

The film prepared from the step of (S30) is subjected to separation from the substrate.

For example, the film may be separated from a substrate by hydrolysis of bonds formed at the interface of the film and the substrate. The hydrolysis is initiated by using an agent such as ammonium hydroxide (NH_4OH), acetone, alcohol and the like.

The film may have a strong affinity to a substrate since a Si-O-C bond is formed at the interface of the film and the substrate. Therefore, when the agent is applied to the film, the film is detached from the bottom surface of the substrate, and thus freely floats on or is scattered in the solution according to a porosity level.

The ammonium hydroxide and alcohol serve as bond scissors between a glass substrate and surface-treated Nafion to easily separate the Nafion from the substrate while preventing damage to the film.

The alcohol may include an alcohol having 1 to 10 carbon atoms. For example, one or more of methanol, ethanol and propanol may be included.

It is technically important to manufacture an ultrathin low-dimensional meso-nanoporous free standing membrane. The ultrathin film manufactured using an ion-conductive polymer (ionomer) such as Nafion with a proton conductive property is useful for application to alternative energy fields, particularly, fuel cells and battery technology. Such a low-dimensional material provides excellent efficiency in both aspects of a reduction in production costs and accessibility to novel features in combination with low-dimensionality.

Meanwhile, the development and application of a synthesis strategy for achieving low cost production and stabilization of a thin membrane film still remain as technical challenges. Therefore, remarkable advances in synthetic technology depends on the availability of next generation material properties.

The improvement in the properties of a nanometer scale material has focused on the development of conductivity of a material, ion migration, porosity, miscibility, irradiation properties (thermal, electrical, pH, photoreactive and photonic properties).

When the manufacture of a conventional thin/ultrathin ionomer membrane is not achieved in a free standing form, to improve or expand the properties of the ionomer membrane such as Nafion, the surface modification of the ionomer membrane is essential.

Meanwhile, the free standing ultrathin porous membrane according to the present invention may have a nano-sized ultrathin thickness beyond the micrometer scale. In addition, crossing over to lower dimensions using the method of preparing a free standing ultrathin porous membrane according to the present invention provides novel physicochemical properties, and may manufacture a multifunctional ionomer membrane.

Since the free standing ultrathin porous membrane according to the present invention has high durability, physical and chemical properties thereof may be adjusted in a desired direction. In addition, since the membrane has a biocompatible property, it can be used in the field of biotechnology, and since it has a free standing property, it does not need a support for precipitating an ionomer as is conventional, thereby exhibiting excellent economic feasibility.

When the method of preparing a free standing ultrathin porous membrane according to the present invention is applied, controlled actuation may be allowed,

and the method may be applied to fields of manufacturing small chemicals (e.g., drugs) and biochemicals (e.g., aptamers) inducing a bio-related environment.

When the free standing membrane according to the present invention is applied to the field of biotechnology, an excellent economic effect is exhibited, and such a free standing membrane has not been manufactured until now.

The low-dimensional effect of the present invention may bring an abrupt change in an adsorption property by rapidly changing the porosity of the membrane. At the same time, the free standing ultrathin membrane shows auto fluorescence behavior as a result of a surface property change at nanometer-scale thickness.

In the present invention, the method of preparing a free standing ultrathin porous membrane exhibits a more excellent effect than a conventional process, and has the following characteristics.

(1) Free standing membrane: The manufacture of a conventional membrane film needs a support, and is not present in a free standing film or membrane.

(2) Nano-scale thickness: The thickness range of the membrane of the present invention is 800 nm or less.

(3) Nanoporosity: A 1 to 5-nm pore formed in the surface of the membrane and the biocompatible property open up numerous possibilities in biological and medical fields. This is because the pore size of the membrane is compatible with the sizes of a biomolecule and a small chemical molecule.

(4) Due to the confinement effect caused by the nano-sized pore and thickness of the membrane, autofluorescence occurs and thus may be applied to various fields.

Membrane manufactured by method of preparing membrane

Another aspect of the present invention relates to a free standing ultrathin porous membrane manufactured by the method of preparing an ionomer membrane described above.

The membrane obtained from the foregoing method is strong stable enough and easy to handle for various applications. For example, the membrane of the present invention can be easily mounted on the jig for further process such as coating or cell experiments. Further, the membrane of the present invention is almost wrinkle free.

In one embodiment, the ionomer membrane has a plurality of pores with an average size of about 1 to 10 nm, and a thickness of about 800 nm or less.

In one embodiment, the ionomer membrane may have a hydrogen ion conductivity, measured in 90 °C water, of about 0.01 mS/cm to about 0.3 mS/cm.

The ionomer membrane according to the present invention allows the hierarchical assembly of more complicated structures by combining size dependency with the stand-alone property thereof.

For example, a colloid solution consisting of a semiconductor metal (e.g., TiO_2 quantum dots), graphene and a composite thereof, other interesting metals such as magnesium, manganese and silver nanoparticles may be adsorbed onto a surface or chemically mixed by a conventional surface chemical method. This means that the present invention can impart optical properties, conductive properties, platinum for ionic polymer-metal composite (IPMC) technology and magnetic nanoparticles for magnetically-driven properties in combination.

The ionomer membrane of the present invention has the following properties:

(a) Excellent ion conductivity

(b) Excellent moisture retaining property

(c) Stability over a long composition range

(d) Wide range of autofluorescence

(e) Biocompatibility

The ionomer membrane of the present invention may be applied to the following technical fields:

(a) Biomedical field

(b) Fuel cell field

(c) Sensor field

(d) Separation technology field

In addition, the ionomer membrane of the present invention may be applied to the following technical fields:

- used for gas sensing property using porosity
- suitable for use in environmental toxicity test
- used for bio-detection of phytotoxic material
- used for moisture sensor in plant due to various moisture retaining properties

Hereinafter, configurations and actions of the present invention will be described in further detail with reference to exemplary examples of the present invention. However, these examples are merely provided as preferable examples,

and it is to be understood that the present invention is not limited to the following examples in any way. Since the contents not described herein can be easily inferred technically by those of skilled in the art, the description thereof will be omitted.

Examples and Comparative Examples

Example 1

Manufacture of ionomer membrane: A first solution was prepared by dissolving a bulk-state perfluorinated sulfonic acid ionomer (Nafion 211) in dimethyl sulfoxide (DMSO). The volume ratio of perfluorinated sulfonic acid ionomer to dimethyl sulfoxide was 1:2. Then, the first solution was mixed with water to obtain a second solution. The second solution has a volume ratio to water of 1: 30 (first solution : water). The second solution was applied onto a glass petri dish followed by heat treatment at 140 ℃. Afterward, the film was separated from glass petri dish by applying 1M ammonium hydroxide (NH_4OH) or acetone or ethanol to the film.

In example 1, the ratio is 0.1: 10 (nafion : organic solvent).

Example 2

A film was prepared by the same method as described in Example 1, except that a first solution comprising perfluorinated sulfonic acid ionomer and dimethyl sulfoxide in a volume ratio of 0.25:1 was used and the reaction condition was changed based on Table 1.

Example 3

A film was prepared by the same method as described in Example 1, except that a first solution comprising perfluorinated sulfonic acid ionomer and dimethyl sulfoxide in a volume ratio of 0.5:1 was used and the reaction condition was changed based on Table 1.

Example 4

A film was prepared by the same method as described in Example 1, except that a first solution comprising perfluorinated sulfonic acid ionomer and dimethyl sulfoxide in a volume ratio of 0.35:1 was used and the reaction condition was changed based on Table 1.

Example 5

A film was prepared by the same method as described in Example 1, except that a first solution comprising perfluorinated sulfonic acid ionomer and dimethyl sulfoxide in a volume ratio of 1:1 was used and the reaction condition was changed based on Table 1.

Example 6

A film was prepared by the same method as described in Example 1, except that a first solution comprising perfluorinated sulfonic acid ionomer and dimethyl sulfoxide in a volume ratio of 2:1 was used and the reaction condition was changed based on Table 1.

Example 7

A film was prepared by the same method as described in Example 1, except that a first solution comprising perfluorinated sulfonic acid ionomer and dimethyl sulfoxide in a volume ratio of 1:2 was used and the reaction condition was changed based on Table 1. The solution compromising of either no organic solvent in the presence of polymer or organic and polymer containing a lower content of solvent and the final polymer-organic solution to water ratio was increased 1: 100 altering the degree of polymerization.

The results are shown in Table 1:

[Table 1]

	Volume ratio (Nafion: DMSO)	Volume ratio (first solution: water)	Heat treatment temp.(℃)	Thickness (nm)
Example 1(M1)	1:2	1: 30	140	630
Example 2(M2)	0.25:1	1: 30	120	398.4
Example 3(M3)	0.5: 1	1: 30	130	360
Example 4(M4)	0.35:1	1: 30	150	356
Example 5(M5)	1:1	1: 30	125	703.1
Example 6(M6)	2:1	1: 30	135	425
Example 7(M7)	1:2 (ultrathin)	1: 100	160	93

The thicknesses and pore sizes of the ionomer membranes in Examples 1 to 7 were measured by SEM, and are determined to exist in the range of 15 nm to 800 nm (micro- to cm sized membranes) and 1.5 nm to 10 nm with respect to thickness and pore size.

FIG. 3 is a graph showing transmission electron microscope (TEM) results of Example 1, and FIG. 4 is a graph showing small angle X-ray scattering (SAXS) analysis results of Example 1. Referring to FIGs. 3 and 4, it can be seen that the ionomer membranes of the examples had a pore size in a range of 1 to 10 nm.

FIG. 5A and 5B are AFM images of Examples measured by atomic force microscopy. By measurement of thickness with AFM, the thickness of the membranes prepared from Examples ranges from 15 nm to 580 nm.

The films prepared from Examples and Comparative Examples were evaluated as to hydrophilic to hydrophobic tenability, dynamic mechanical test, zeta potential, structural microstructural variations, auto-fluorescence, biocompatibility, cyclic voltammetry analysis and functional group variation. The results are shown in Figs 4~11.

FIG. 6 is results of contact angle tests of M1~M7 films prepared by Examples 1~7 respectively. The results of the time of complete collapse of droplet of M1-M7 films are shown in Table 2 below:

[Table 2]

	Time of collapse(min)
Example 1(M1)	90
Example 2(M2)	60
Example 3(M3)	45
Example 4(M4)	40
Example 5(M5)	30
Example 6(M6)	20
Example 7(M7)	0.1

The film M1 was the most hydrophobic and M7 was the most hydrophilic.

FIG. 7 is a graph showing thermogravimetric analysis (TGA) results of Examples 1-4 and Comparative Example 1(pure nafion). Referring to FIG. 7, it can be seen that the examples exhibited excellent thermal stability compared to

Comparative Example 1, and the excellent thermal stability is maintained until 400 ℃.

The water absorption test of Examples 1-3 and Comparative Example 1(unmodified) was conducted and the results(after 84 hours and 12 hours respectively) are shown in Table 3 and 4 below.

[Table 3]

	Water absorption (after 12hr, %)
Example 1(M1)	21
Example 2(M2)	83.36
Example 3(M3)	92.95
Comparative Example 1 (unmodified)	2

[Table 4]

	Water absorption with time (%)	
	After 12 hr	After 84 hr
Example 2(M2)	83.36	85.59
Comparative Example 1 (unmodified)	2	52

Referring to Table 3, it can be seen that the Examples exhibited higher water absorption than Comparative Example 1(unmodified). Particularly, Example 3(M3) exhibited the best performance. Referring to Table 4, Comparative Example 1 reached only 52%(after 84 hours) and 2 % (after 12 hours). That is, Comparative Example 1 did not reach the level of Example 1 even after water absorption for 84 hours.

FIG. 8A to 8C are graphs showing dynamic machine test results of Example 1. Referring to FIG. 8A to 8C, it can be seen that, as an oscillatory force increased, the elastic regime increased (20-fold increase), and as the frequency increased, the elastic regime decreased.

FIG. 9 shows the results of zeta potentials of Example 1. Referring to FIG. 9, it can be seen that the film of Example 1 has no surface charge.

FIG. 10 is a graph showing XRD analysis results of Examples 1-3 (M1~M3) and Comparative Example 1(Pure NF). Referring to FIG. 10, it can be confirmed that Comparative Example 1 had some microstructural differences among various compositions (components). In Fig. 10, deconvolution of peaks suggest that lattice of the films are distorted due to the thermal treatment and composition variations. The membrane of Comparative Example 1 showed elongation of the lattice parameters as compared to the reported values which are possible due to heating Comparative Example 1.

FIG. 11 are images that show auto-fluorescence of the films. From the fluorescence test, the films of Examples may have wide range of auto fluorescence property.

FIG. 12 is test result of biocompatibility of the films of Examples 1-17. Ctrl represents cells without membranes, M is medium alone, B is empty wells. As shown in Fig 12, cells grew well on the surface of membranes of the Examples and no cell toxicity was visible after 48 hrs of incubation.

FIG. 13 is an optical image showing cell growth on the film of Example 7. As shown in Fig. 13, cell growth was done on free standing nano membrane and healthy cells were able to grow well. No cytotoxicity was observed.

FIG. 14A to 14C are graphs showing cyclic voltammetry analysis results of Example 3 and Comparative Example 1. FIG. 14A, FIG. 14B and FIG. 14C represent the electrochemical properties of Example 3 showing electron transfer under oxidative and reductive (reverse current) conditions as a function of the applied potential range. Referring to FIG. 15, Comparative Example 1 exhibited considerably lower electrochemical activity, compared to Example 3, and Example 3 exhibited a much higher capacity and faraday current, and was in a μA range exhibiting a higher faraday potential and capacity, compared to Comparative Example 1.

FIG. 15A to 15E are ATR-FTIR spectra of Examples and Comparative Example showing functional group variation. Functional group variations are shown depending on the volume ratio between nafion and organic solvent.

As above, the present invention was described with reference to examples. It will be understood by those of ordinary skill in the art that the present invention can be implemented in modified forms without departing from the essential features of the present invention. Therefore, the disclosed embodiments should be considered in a descriptive aspect, rather than a limiting aspect. The scope of the present invention is shown in the claims rather than the foregoing description, and all differences within the equivalent range thereto will be construed as being included in the present invention.

[CLAIMS]

[Claim 1]

A method of preparing a free standing ultrathin porous membrane, comprising:

preparing a first solution comprising nafion;

preparing a second solution comprising the first solution;

forming a film by applying the second solution onto a substrate at 60 - 200 ℃ or RT; and separating the film from the substrate.

[Claim 2]

The method of claim 1, wherein the film has a thickness of about 800 nm or less and an average pore diameter of about 1 nm to about 10 nm.

[Claim 3]

The method of claim 1, wherein the heat treatment is conducted at a temperature of about 120℃ to about 160 ℃.

[Claim 4]

The method of claim 1, wherein the first solution comprises the nafion only.

[Claim 5]

The method of claim 1, wherein the first solution comprises the nafion and organic solvent

[Claim 6]

The method of claim 1, wherein the second solution comprises the nafion only.

[Claim 7]

The method of claim 1, wherein the second solution comprises the first solution and water.

[Claim 8]

The method of claim 1, wherein the organic solvent includes dimethyl sulfoxide.

[Claim 9]

The method of claim 1, wherein the film is separated by hydrolysis of bonds formed at the interface of the film and the substrate.

[Claim 10]

A free standing ultrathin porous membrane prepared by the method according to any one of claims 1 to 7.

[Claim 11]

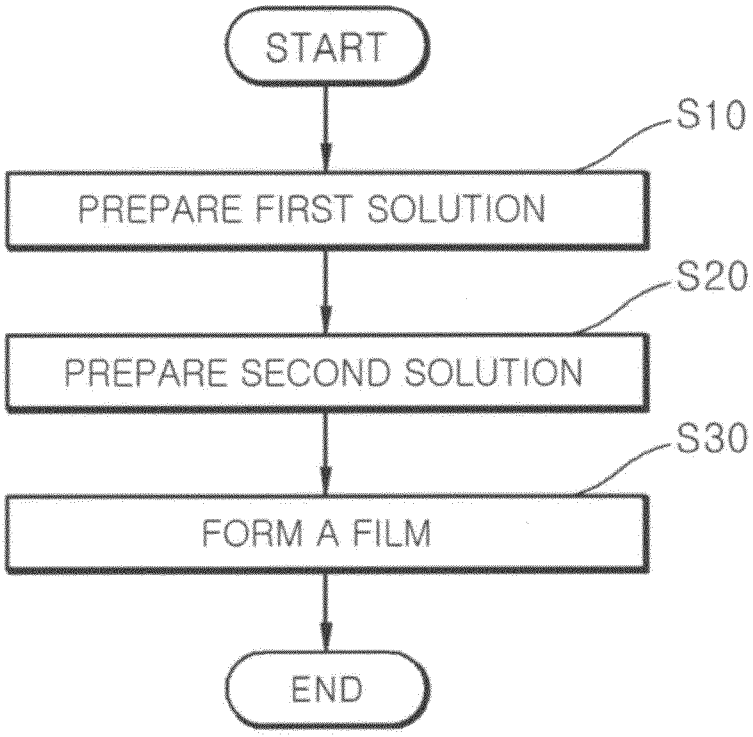
The free standing ultrathin porous membrane of claim 8, wherein the membrane has about 1500 or more pores having a diameter of about 1.5 nm to about 2.0 nm in 1300 x 1600 nm^2 area.

[Claim 12]

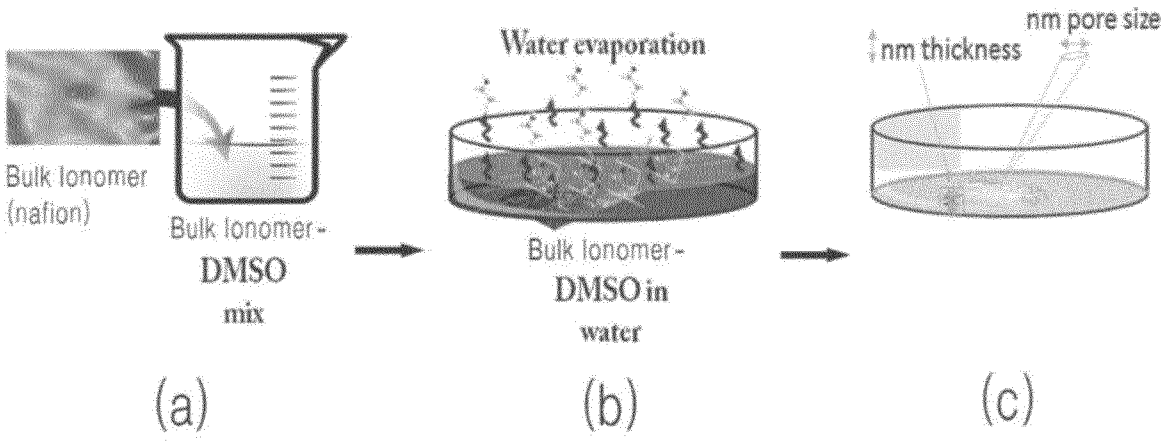
The free standing ultrathin porous membrane of claim 9, wherein the membrane has a hydrogen ion conductivity, measured in 90 °C water, of about 0.01 mS/cm to about 0.3 mS/cm.

【DRAWINGS】

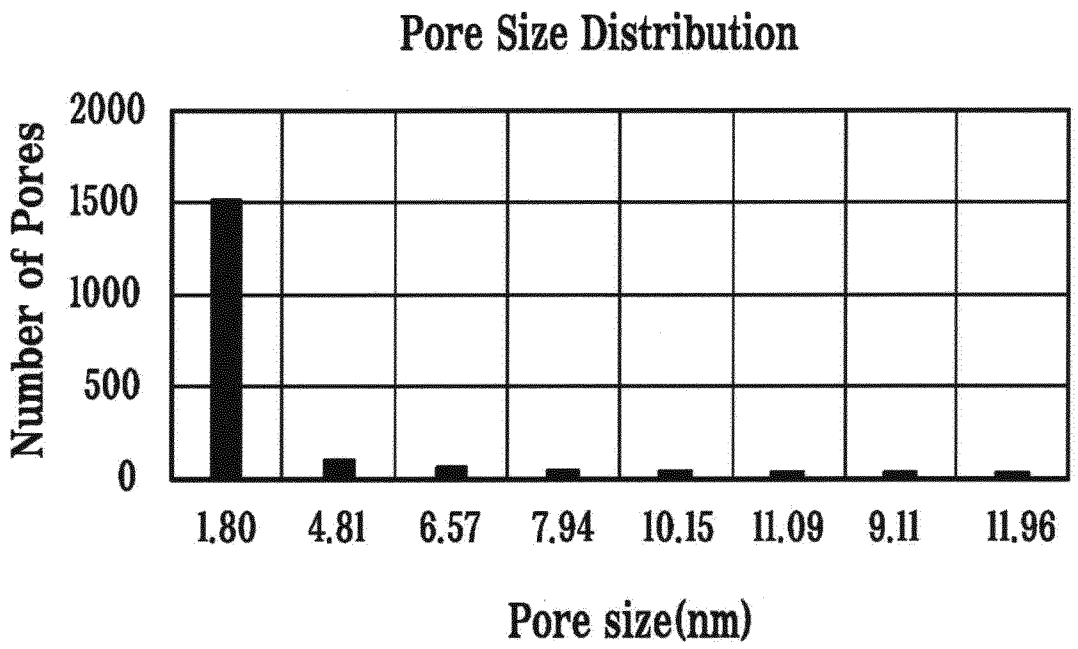
【FIG 1】



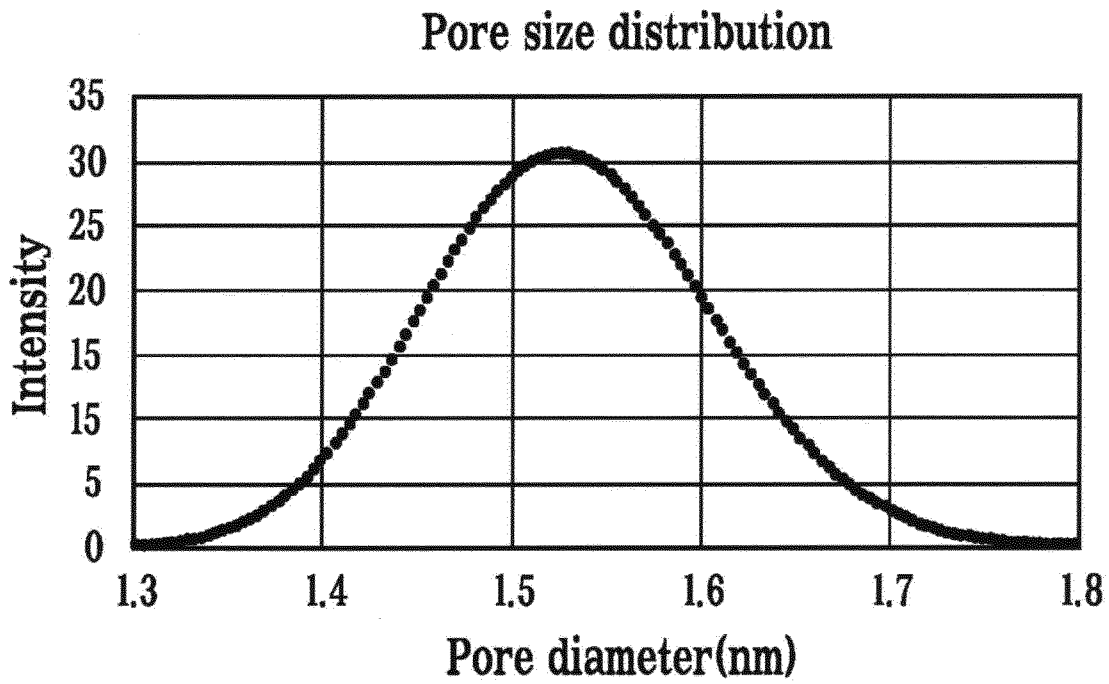
【FIG 2】



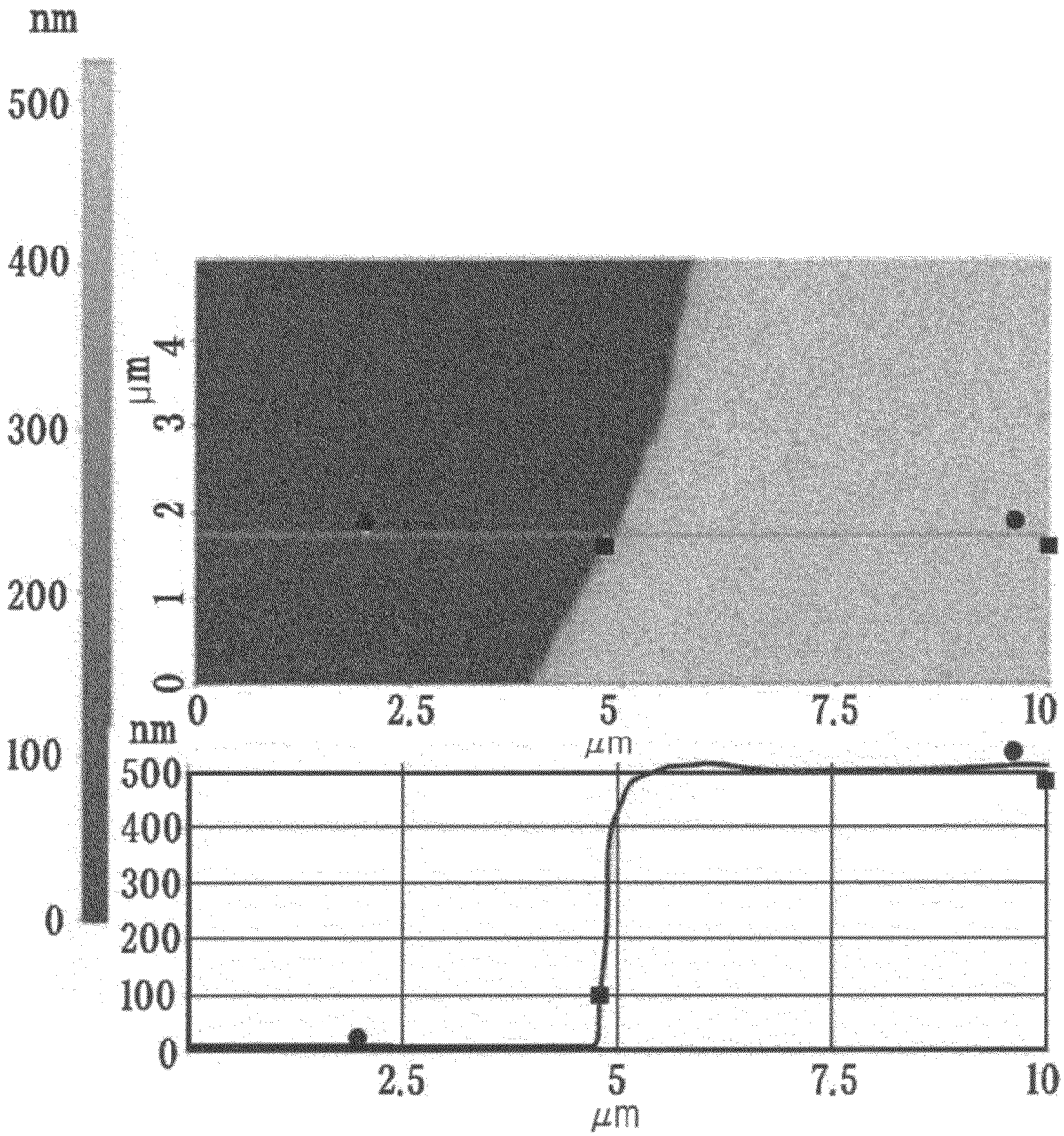
【FIG 3】


Pore Size Distribution
Number of Pores
2000
1500
1000
500
0
1.80
4.81
6.57
7.94
10.15
11.09
9.11
11.96
Pore size(nm)

【FIG 4】

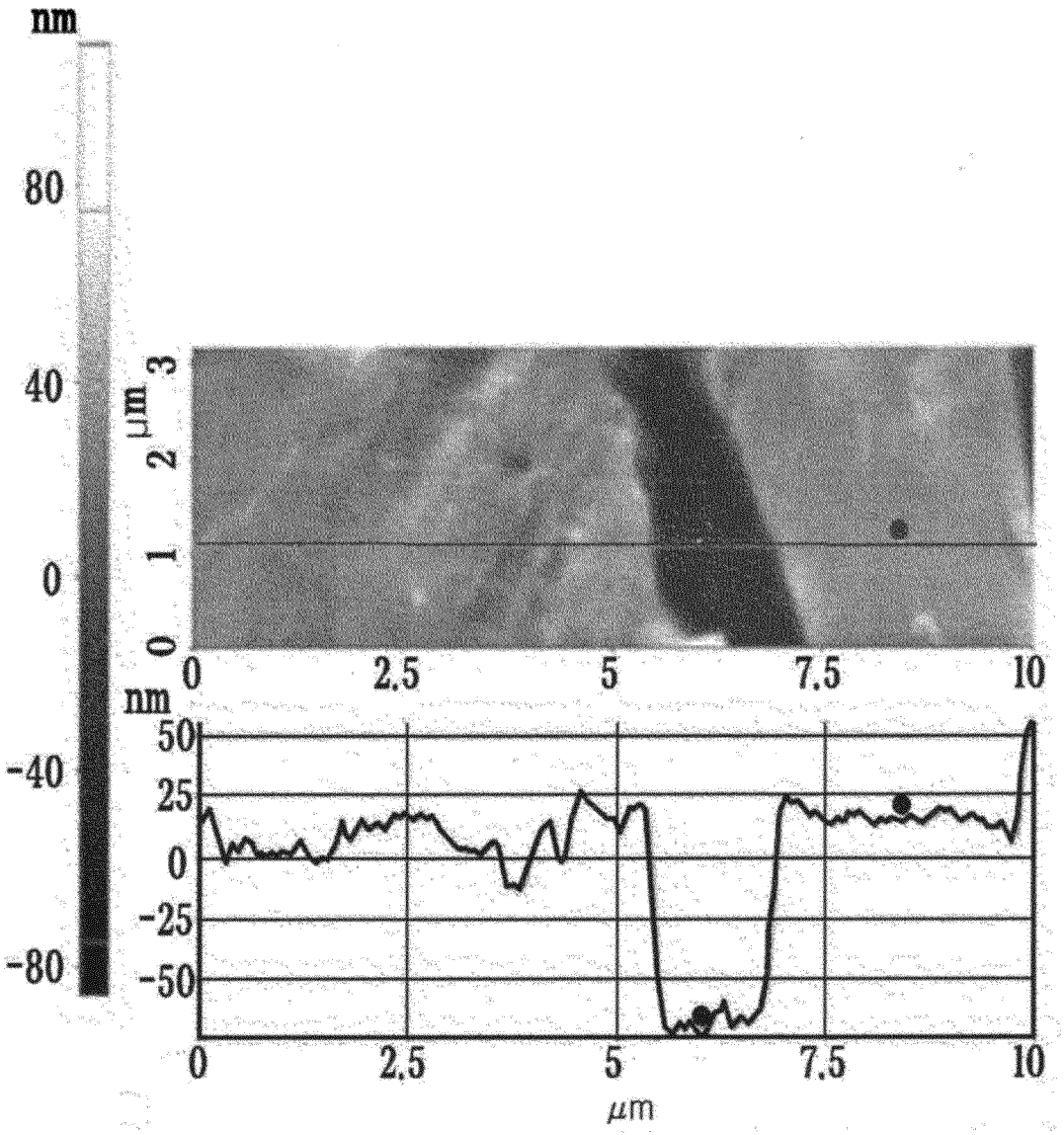

Pore size distribution
Intensity
35
30
25
20
15
15
5
0
1.3
1.4
1.5
1.6
1.7
1.8
Pore diameter(nm)

【FIG 5A】



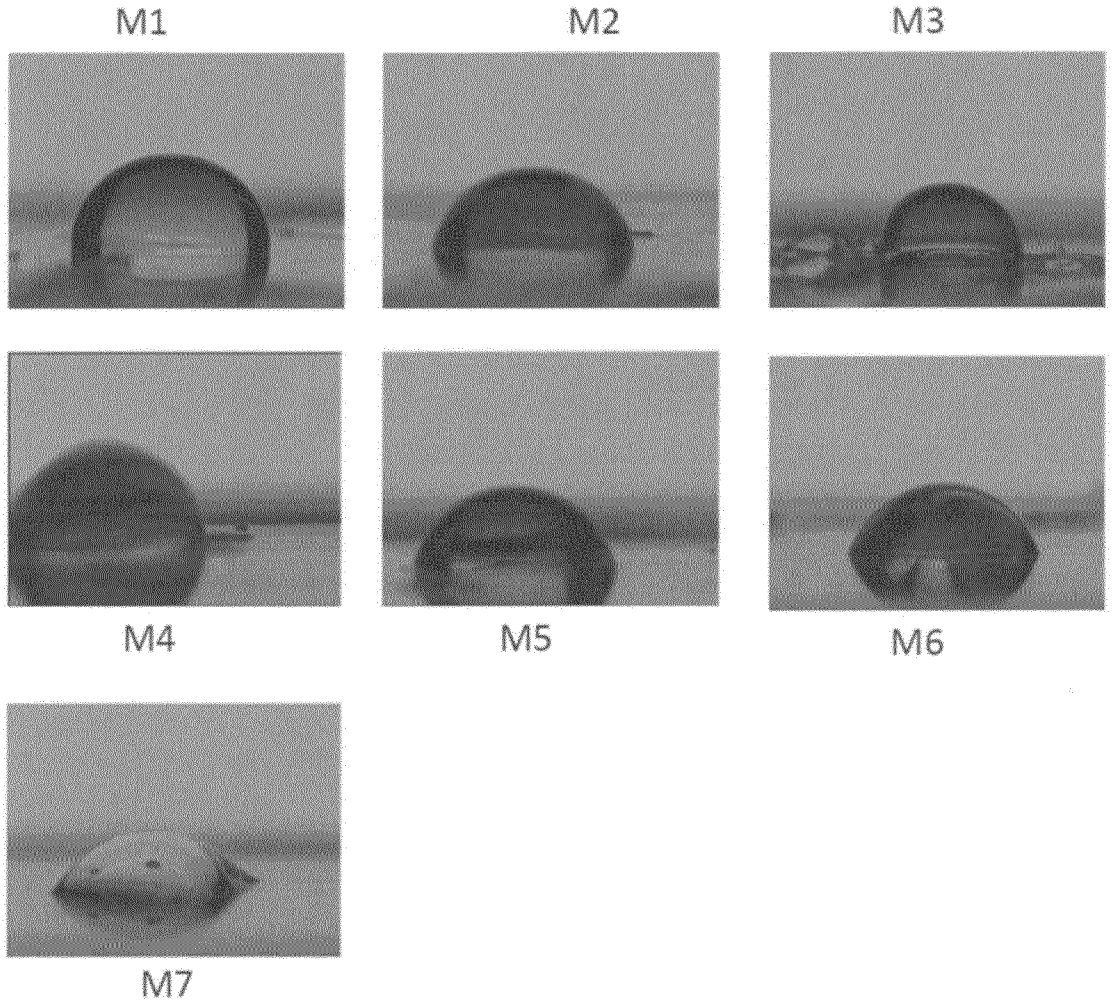
Cursor	ΔX(μm)	ΔY(nm)	Angle(deg)
●	7.630	507.786	3.808
■	5.195	385.734	4.246

【FIG 5B】

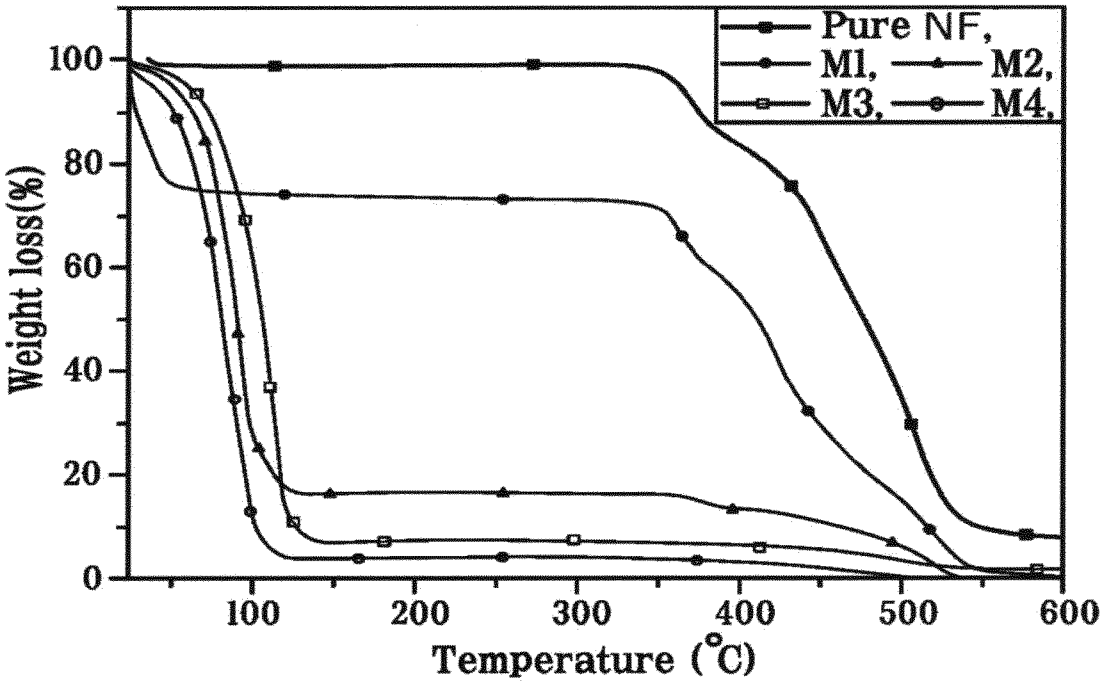


Cursor	ΔX(μm)	ΔY(nm)	Angle(deg)
●	2.385	86.978	2.089

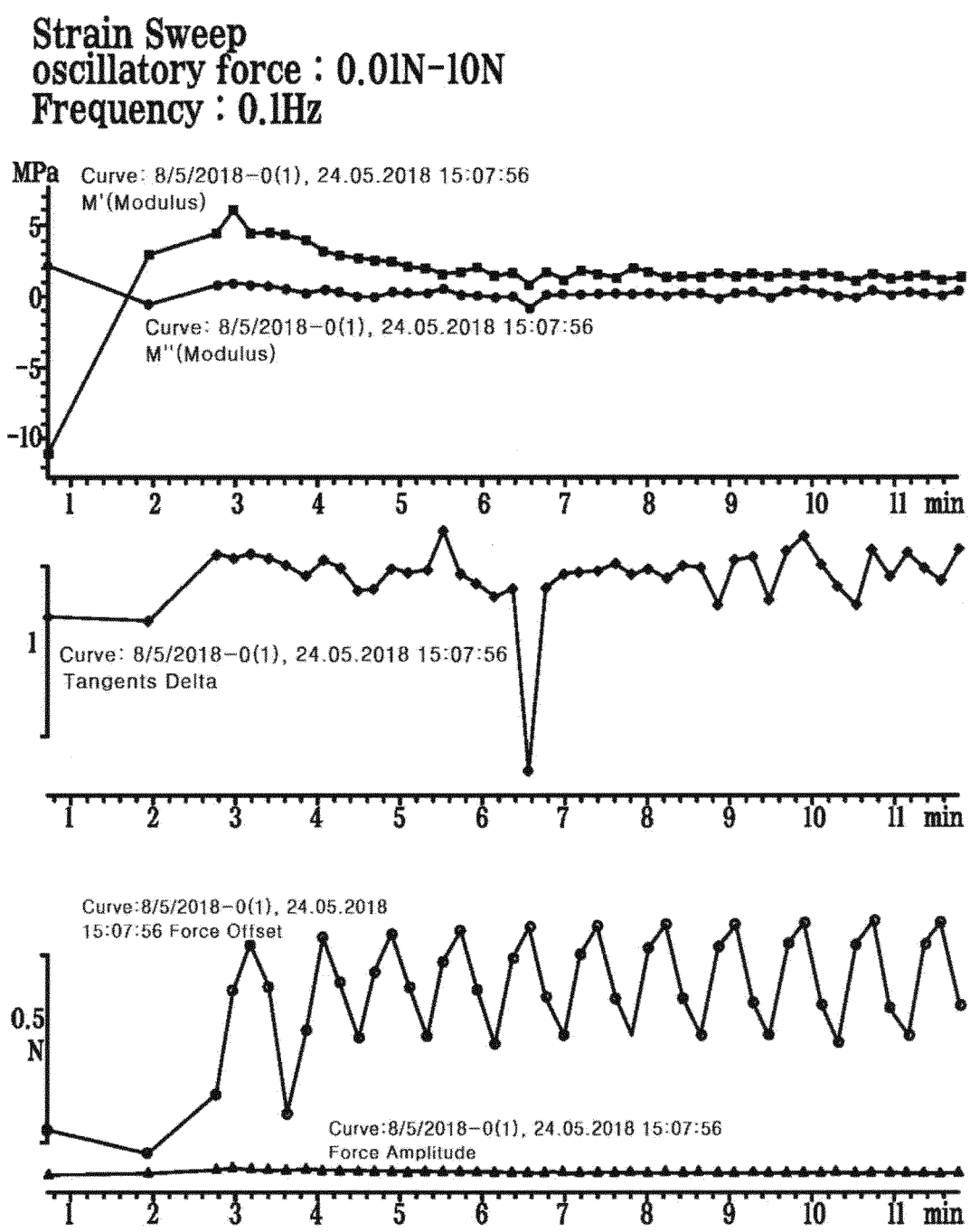
【FIG 6】



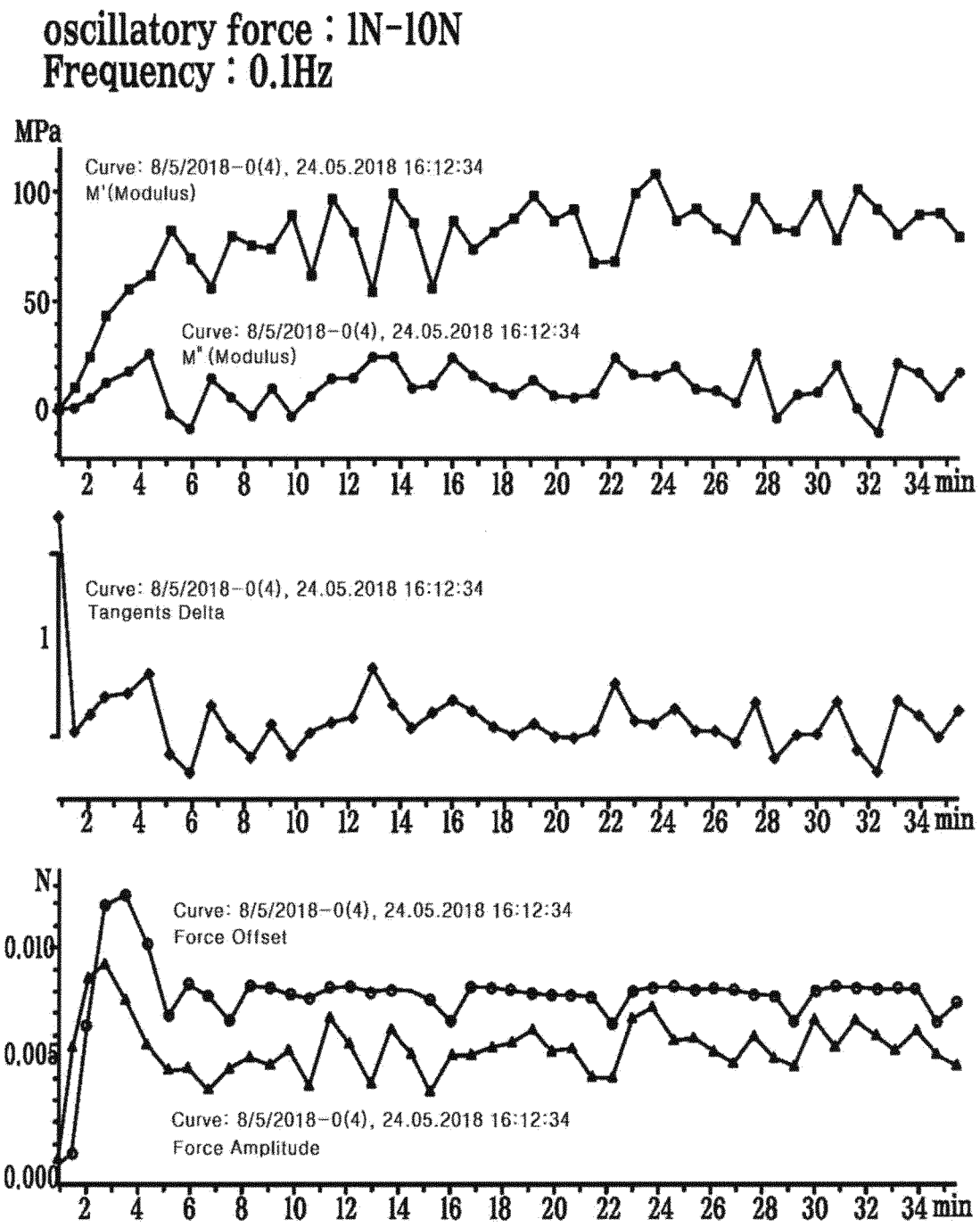
【FIG 7】


Pure NF,
M1,
M2,
M3,
M4,
Weight loss(%)
100
80
60
40
20
0
100
200
300
400
500
600
Temperature (°C)

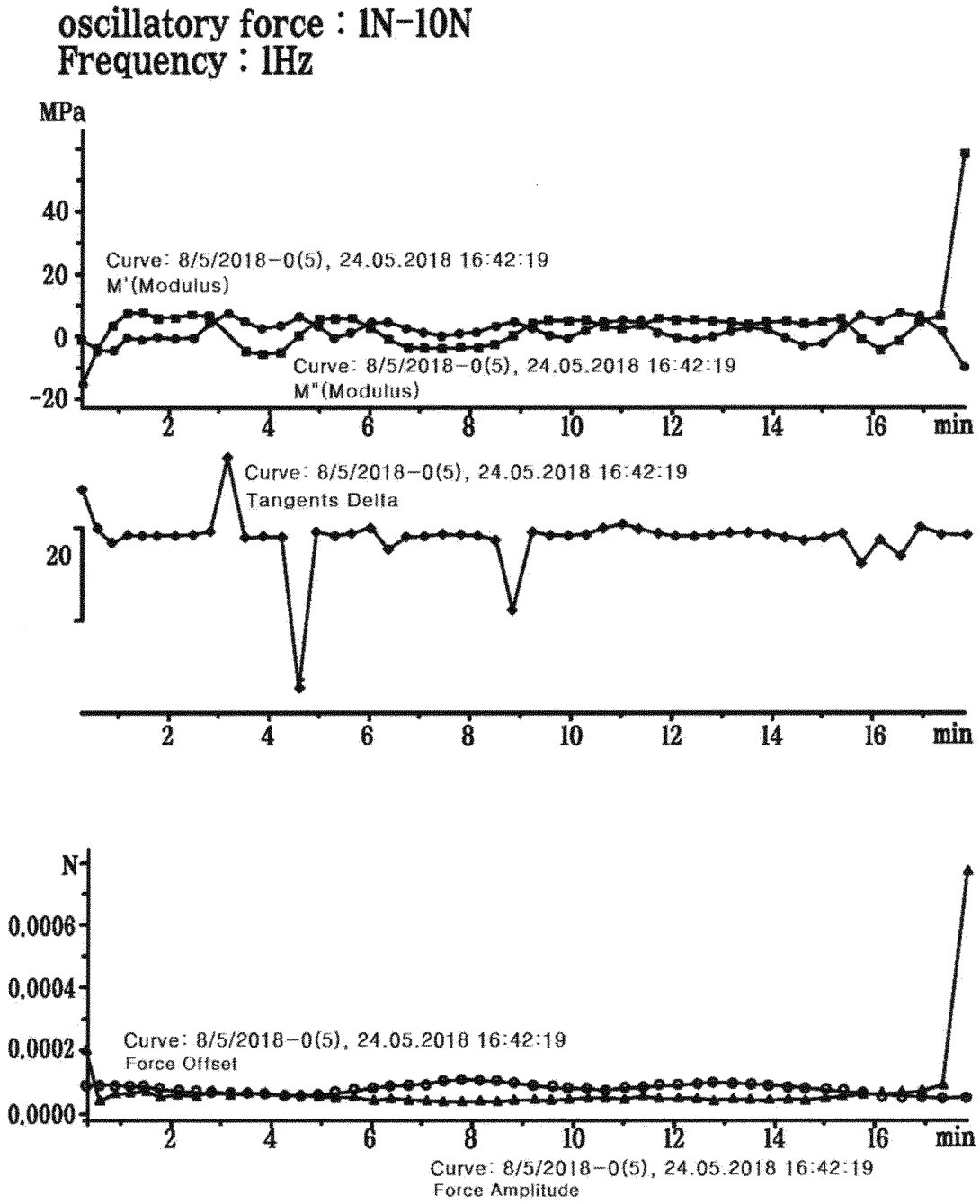
【FIG 8A】


Strain Sweep
oscillatory force : 0.01N-10N
Frequency : 0.1Hz
MPa
Curve: 8/5/2018-0(1), 24.05.2018 15:07:56
M'(Modulus)
5
0
-5
-10
Curve: 8/5/2018-0(1), 24.05.2018 15:07:56
M''(Modulus)
1 2 3 4 5 6 7 8 9 10 11 min
1
Curve: 8/5/2018-0(1), 24.05.2018 15:07:56
Tangents Delta
1 2 3 4 5 6 7 8 9 10 11 min
Curve:8/5/2018-0(1), 24.05.2018
15:07:56 Force Offset
0.5
N
Curve:8/5/2018-0(1), 24.05.2018 15:07:56
Force Amplitude
1 2 3 4 5 6 7 8 9 10 11 min

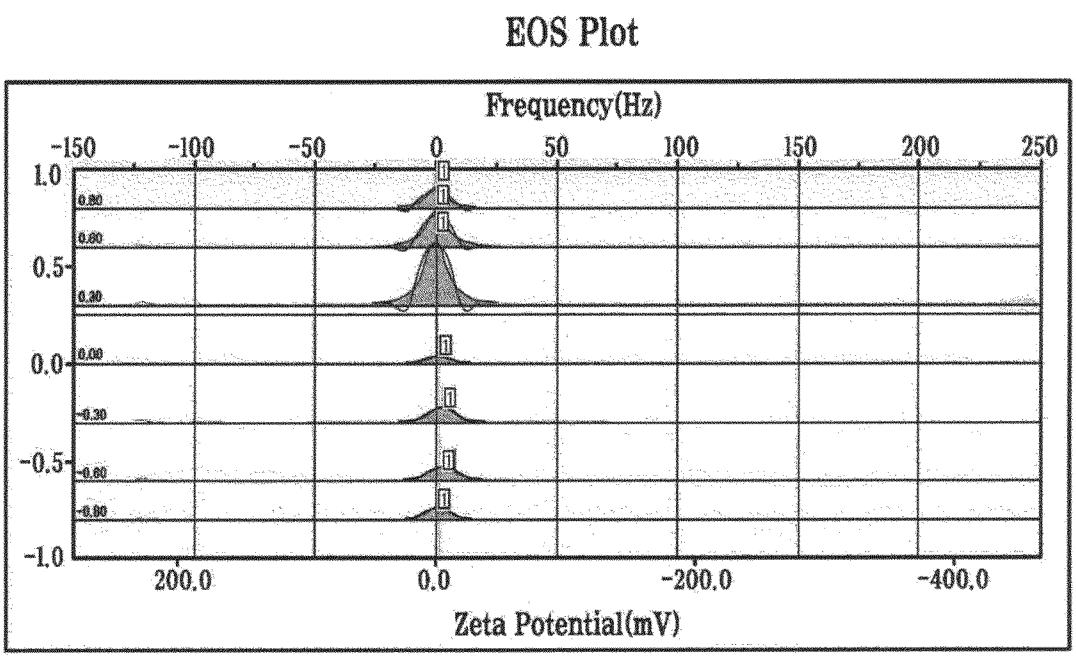
【FIG 8B】


oscillatory force : 1N-10N
Frequency : 0.1Hz
MPa
100
50
0
Curve: 8/5/2018-0(4), 24.05.2018 16:12:34
M'(Modulus)
Curve: 8/5/2018-0(4), 24.05.2018 16:12:34
M" (Modulus)
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 min
1
Curve: 8/5/2018-0(4), 24.05.2018 16:12:34
Tangents Delta
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 min
N
0.010
0.005
0.000
Curve: 8/5/2018-0(4), 24.05.2018 16:12:34
Force Offset
Curve: 8/5/2018-0(4), 24.05.2018 16:12:34
Force Amplitude
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 min

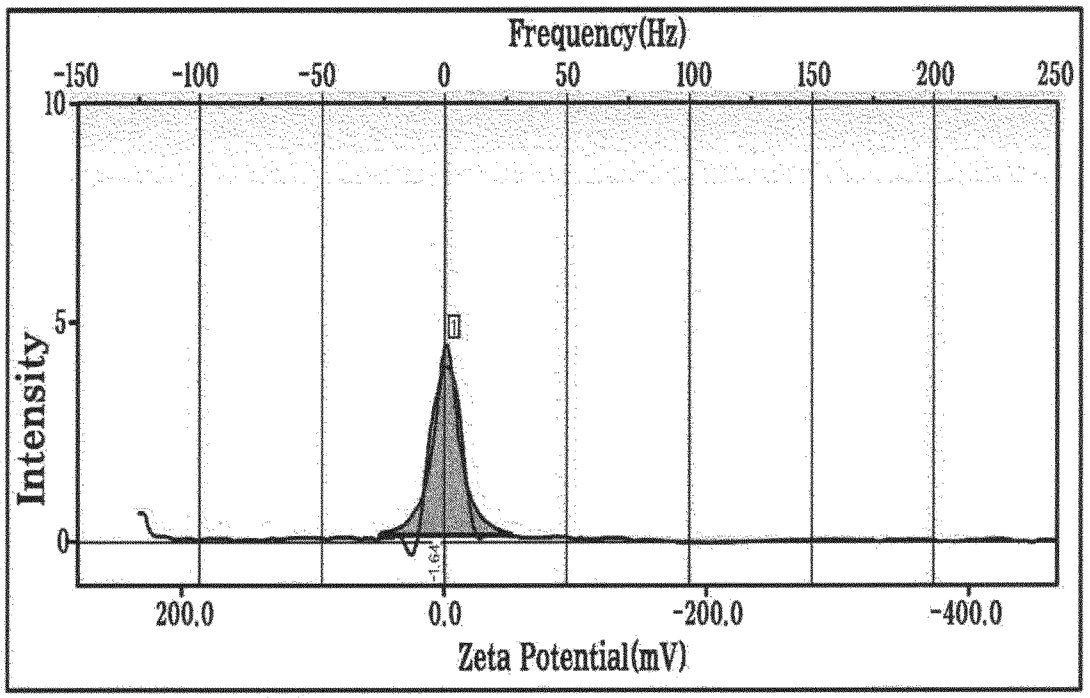
【FIG 8C】


oscillatory force : 1N-10N
Frequency : 1Hz
MPa
40
20
0
-20
Curve: 8/5/2018-0(5), 24.05.2018 16:42:19
M'(Modulus)
Curve: 8/5/2018-0(5), 24.05.2018 16:42:19
M"(Modulus)
2
4
6
8
10
12
14
16
min
Curve: 8/5/2018-0(5), 24.05.2018 16:42:19
Tangents Delta
20
2
4
6
8
10
12
14
16
min
N
0.0006
0.0004
0.0002
0.0000
Curve: 8/5/2018-0(5), 24.05.2018 16:42:19
Force Offset
2
4
6
8
10
12
14
16
min
Curve: 8/5/2018-0(5), 24.05.2018 16:42:19
Force Amplitude

【FIG 9A】


EOS Plot
Frequency(Hz)
-150
-100
-50
0
50
100
150
200
250
1.0
0.5
0.0
-0.5
-1.0
0.80
0.60
0.30
0.00
-0.30
-0.60
-0.90
200.0
0.0
-200.0
-400.0
Zeta Potential(mV)

【FIG 9B】


Mobility Distribution
Frequency(Hz)
-150
-100
-50
0
50
100
150
200
250
10
5
0
Intensity
-1.64
200.0
0.0
-200.0
-400.0
Zeta Potential(mV)

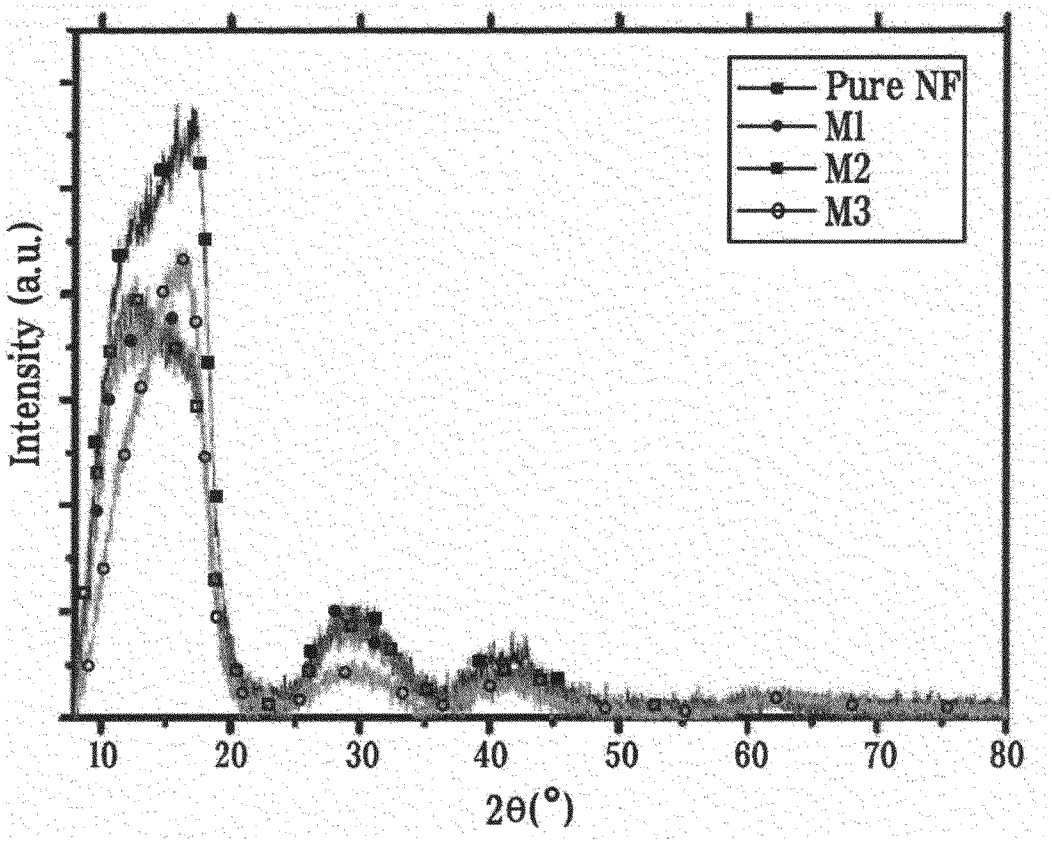
【FIG 9C】

Measurement Results

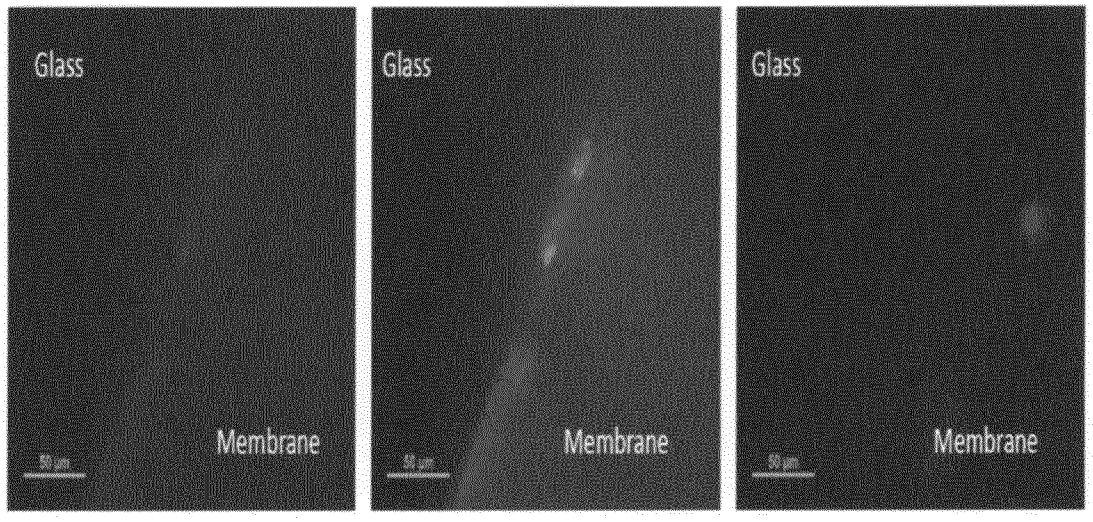
Zeta Potential	: -1.64	(mV)	Doppler shift	: 0.88	(Hz)
Mobility	: -1.278e-005	(cm^2/Vs)	Base Frequency	: 124.9	(Hz)
Conductivity	: 0.0257	(mS/cm)	Conversion Equation	: Smoluchowski	

Zeta Potential of Cell			Diluent Properties		
Flat Surface of Sample	: -3.65	(mV)	Diluent Name	: WATER	
Lower Surface	: 1.47	(mV)	Temperature	: 25.0	(°C)
Cell Condition			Refractive Index	: 1.3328	
Cell Type	: Flat Surface Cell		Viscosity	: 0.8878	(cP)
Avg. Electric Field	: -14.23	(V/cm)	Dielectric Constant	: 78.3	
Avg. Current	: -0.02	(mA)			

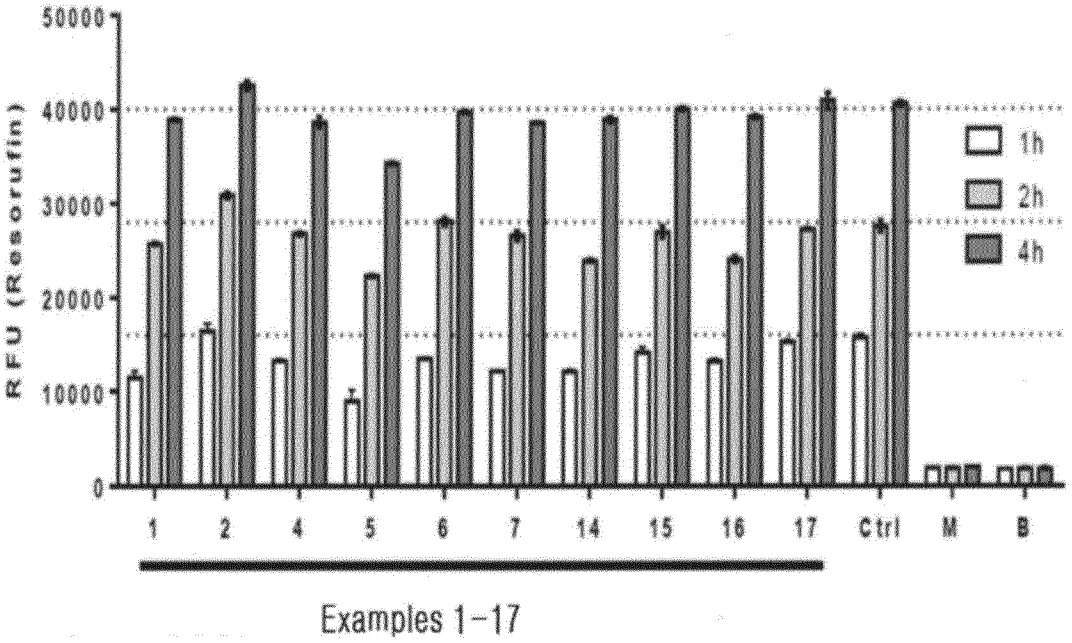
【FIG 10】



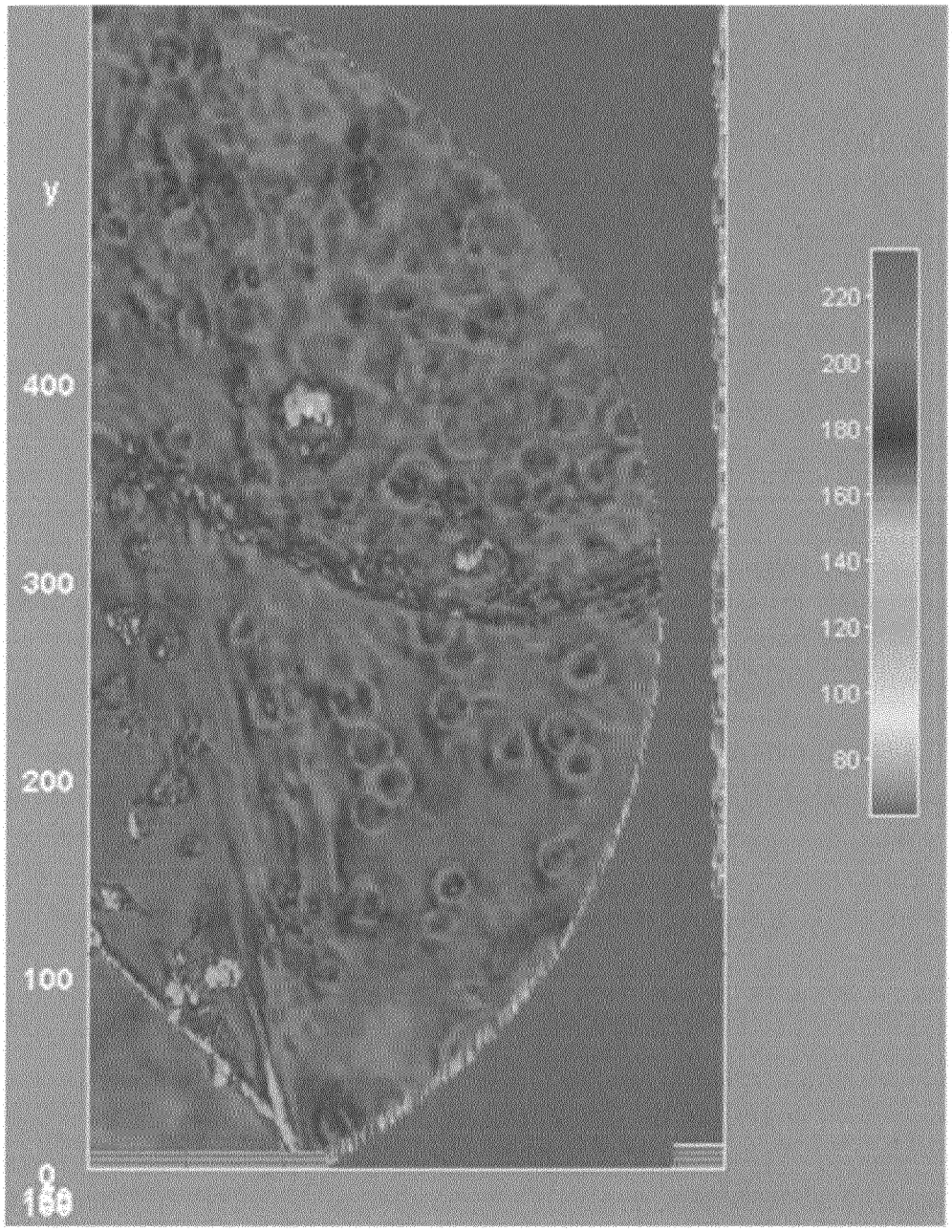
【FIG 11】


Glass
Membrane
Glass
Membrane
Glass
Membrane
Red-fluorescence
Green-fluorescence
Blue-fluorescence

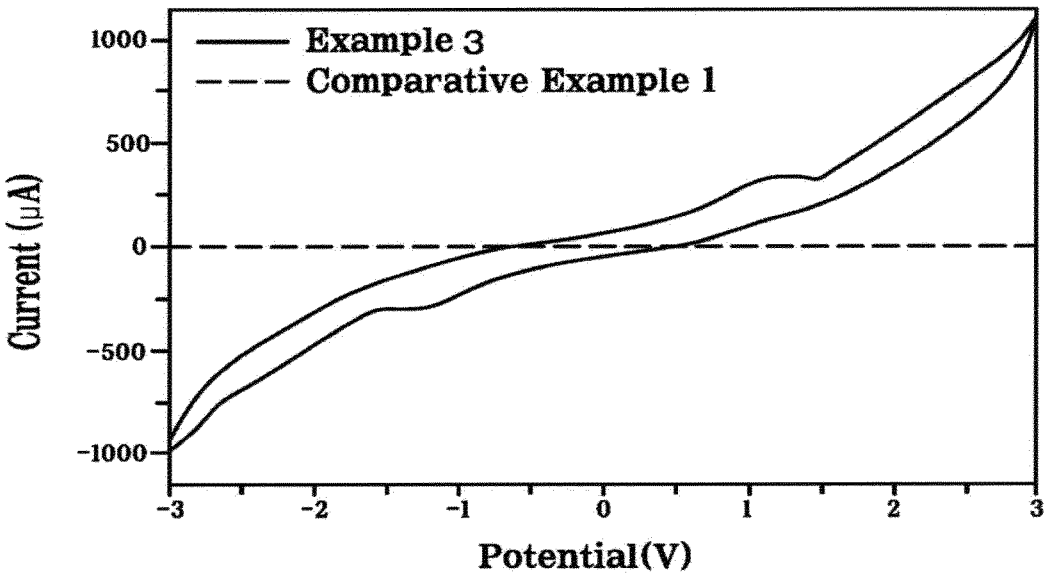
【FIG 12】


RFU (Resorufin)
50000
40000
30000
20000
10000
0
1h
2h
4h
1
2
4
5
6
7
14
15
16
17
Ctrl
M
B
Examples 1-17

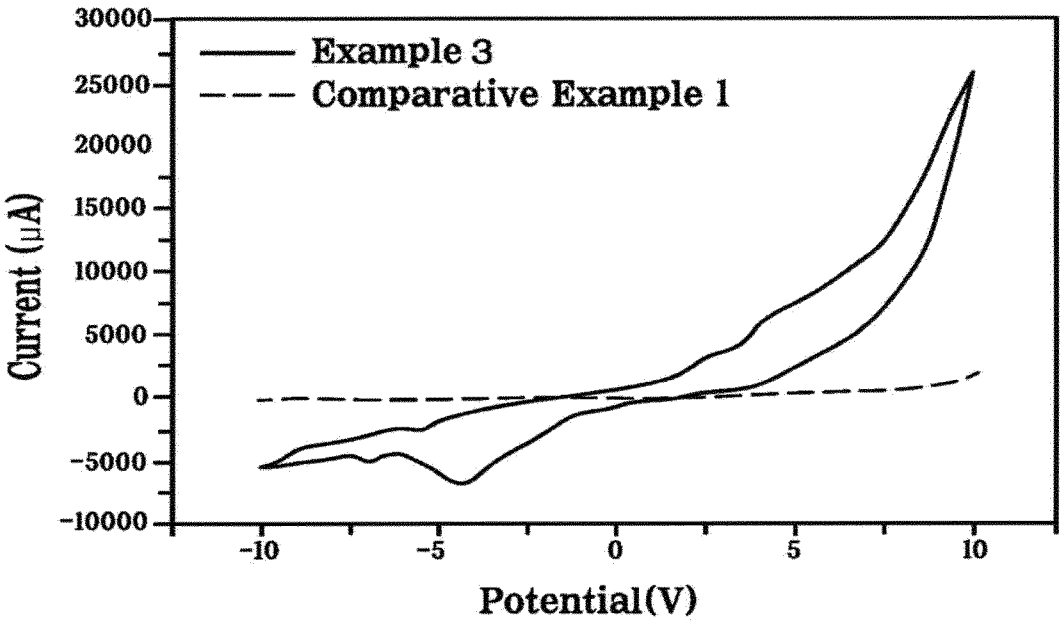
【FIG 13】



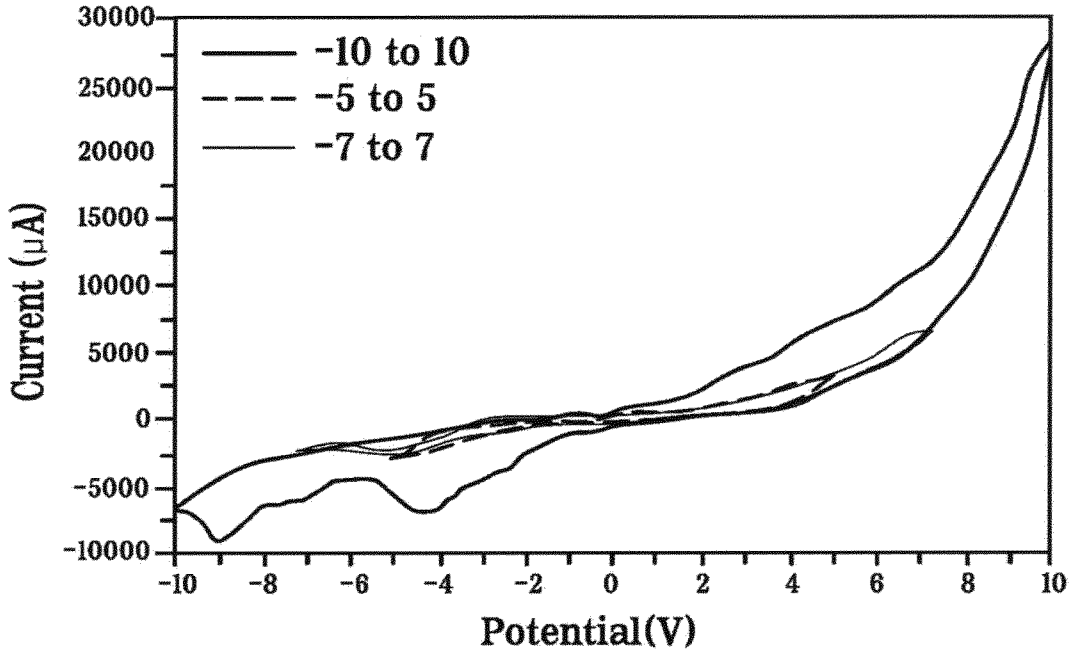
【FIG 14A】



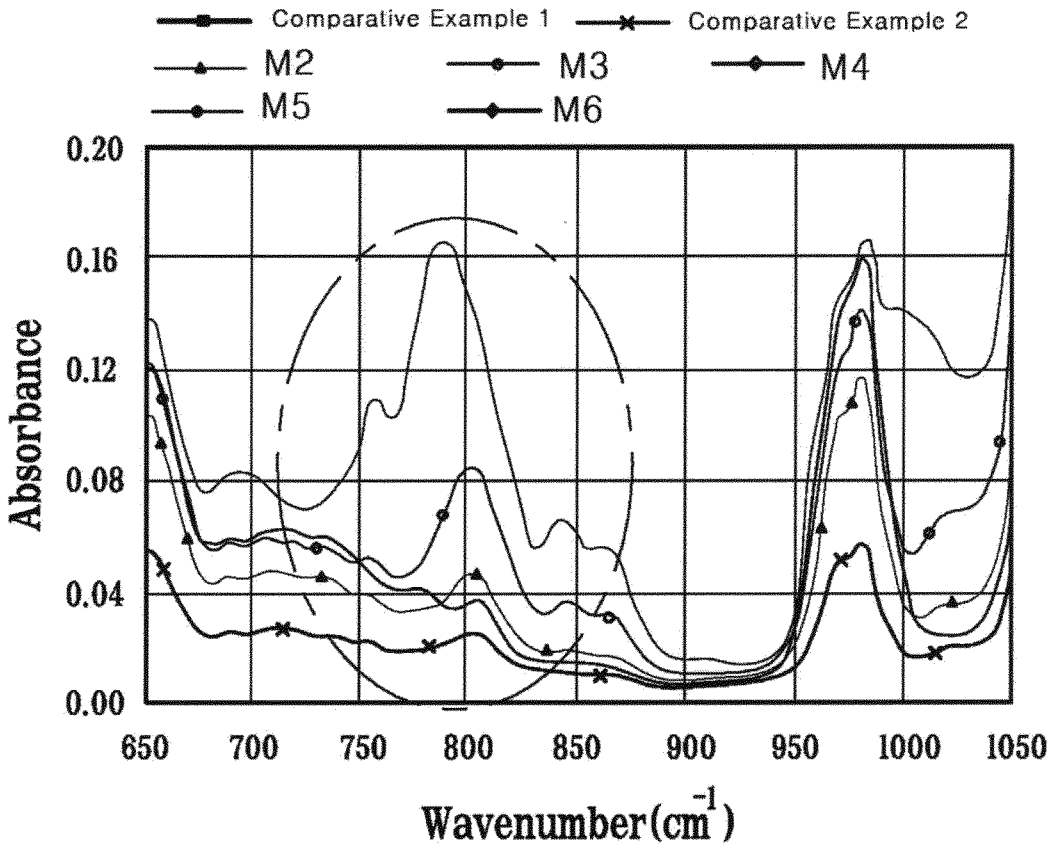
【FIG 14B】



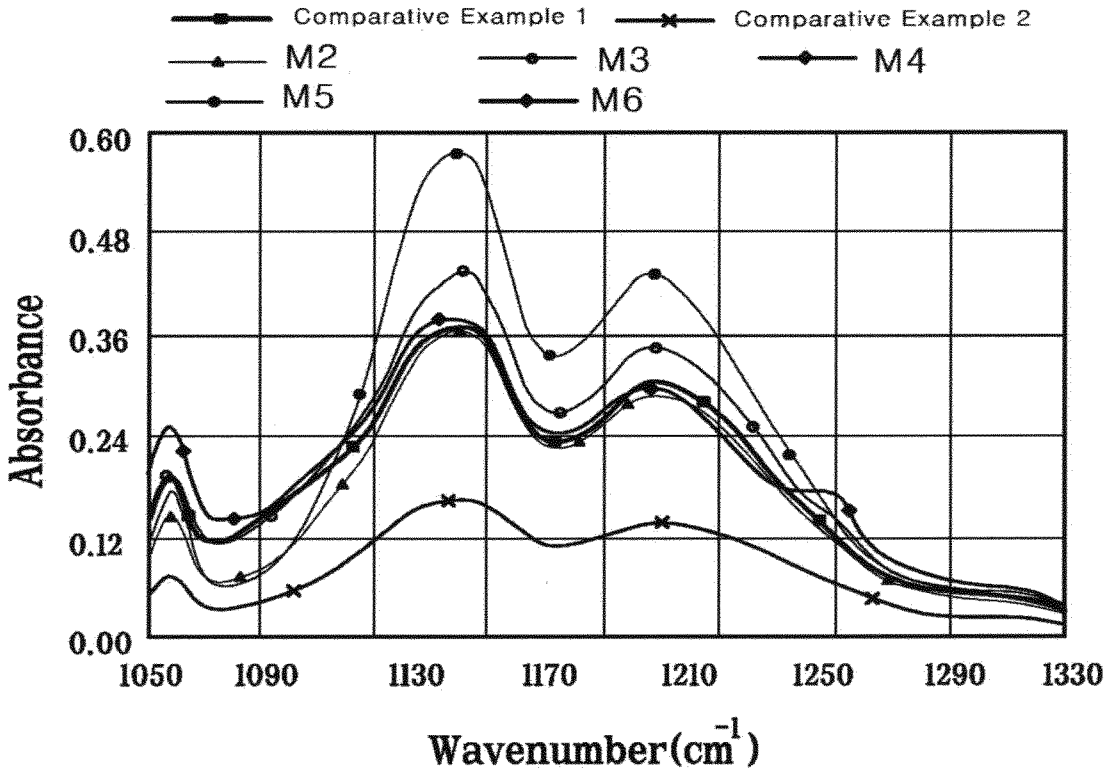
【FIG 14C】



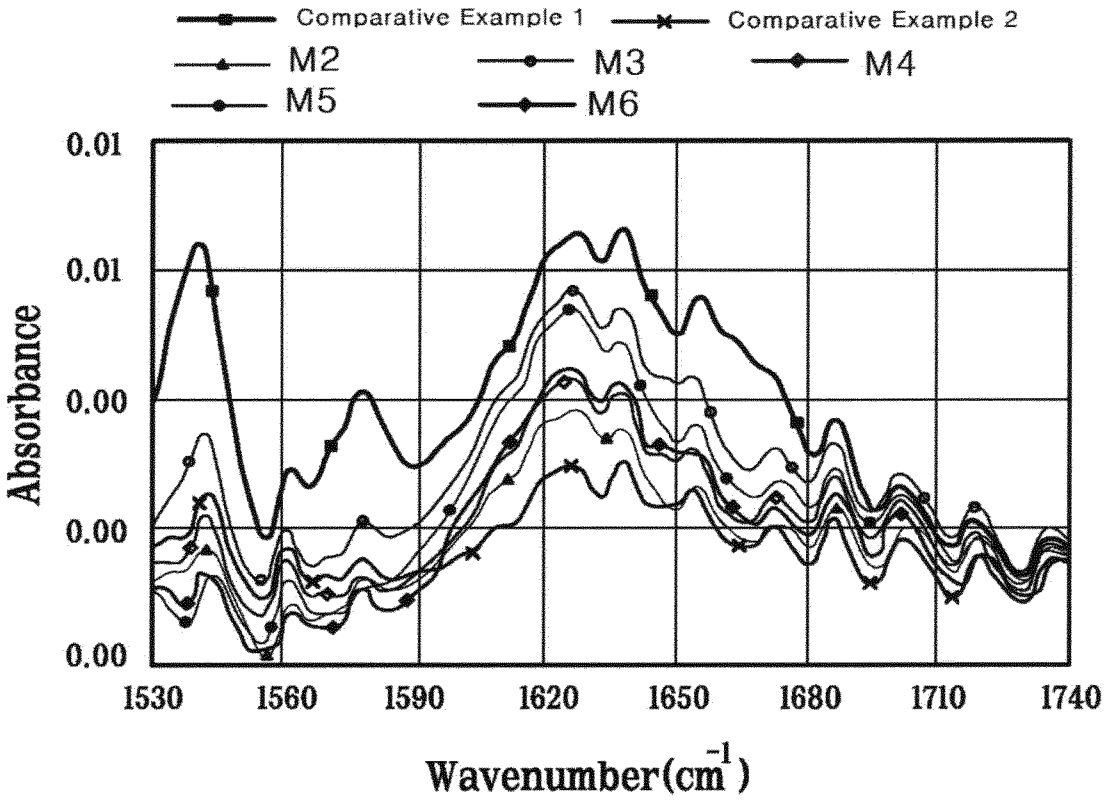
【FIG 15A】



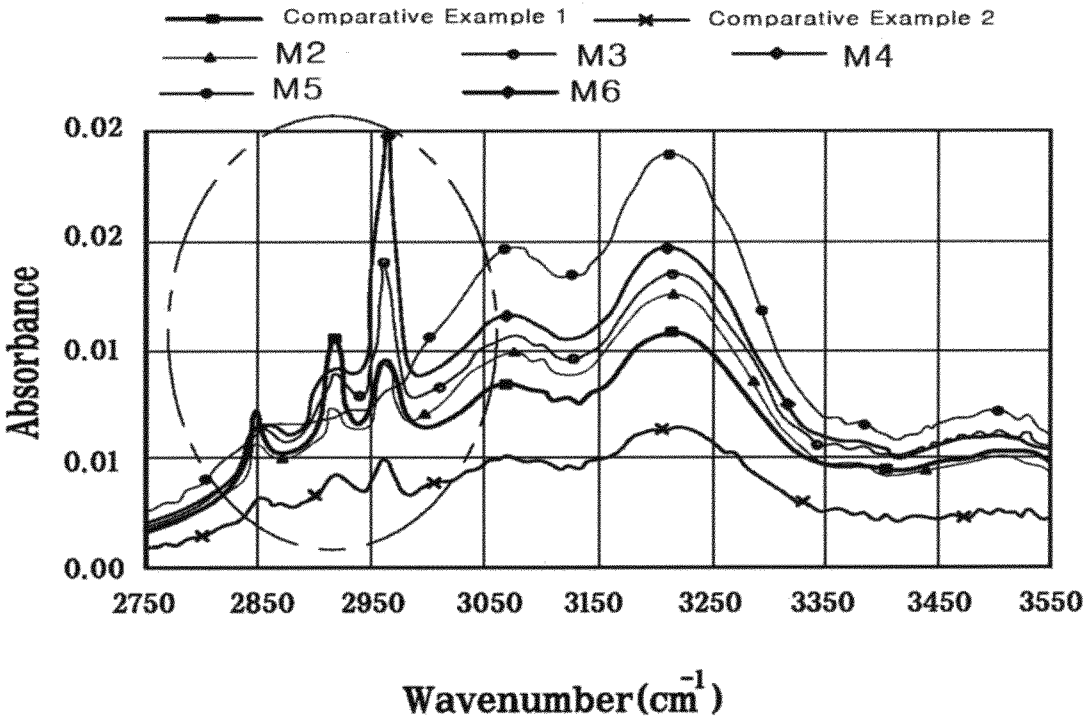
【FIG 15B】



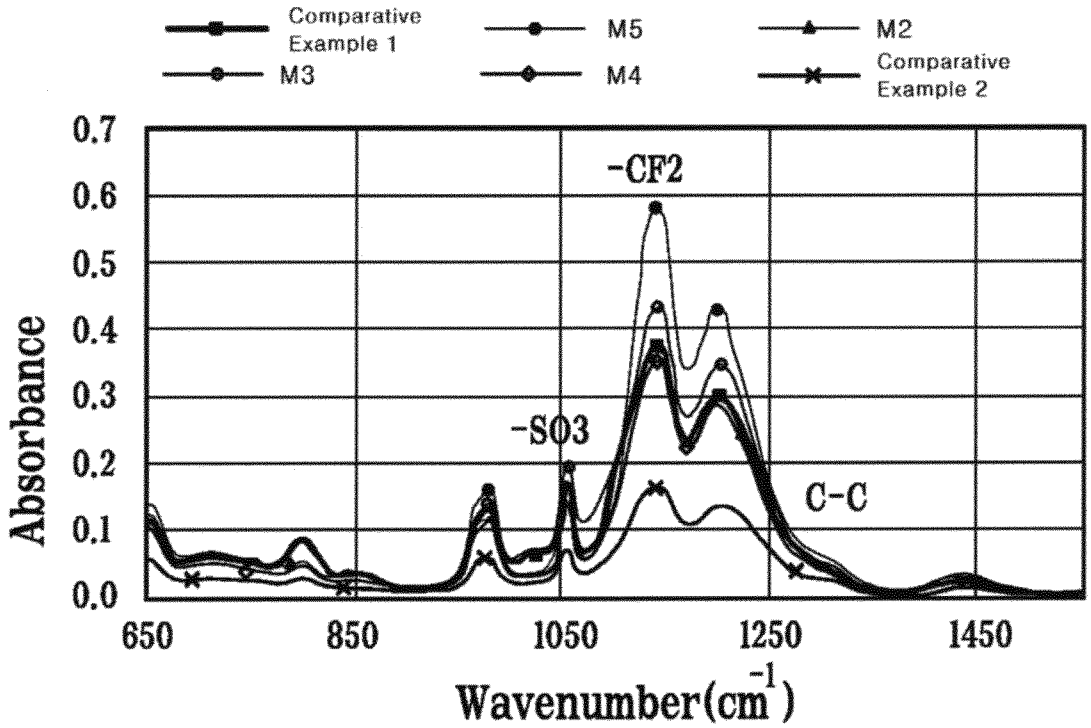
【FIG 15C】



【FIG 15D】



【FIG 15E】



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2020/001209

A. CLASSIFICATION OF SUBJECT MATTER

C08J 5/22(2006.01)i

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)
C08J 5/22; B01D 61/02; B01D 69/12; C08J 5/18; C08K 9/02; G01N 33/00; H01M 8/10

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: free standing, ultrathin porous membrane, nafion, substrate, separating, hydrolysis, ionomer

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KR 10-2016-0087214 A (KOREA INSTITUTE OF SCIENCE AND TECHNOLOGY) 21 July 2016 See paragraphs [0001], [0003], [0054]; and claims 1, 12.	1-12
Y	US 2015-0056399 A1 (TAKEOKA, SHINJI et al.) 26 February 2015 See paragraph [0073]; and claims 15, 16.	1-12
A	WO 2017-083703 A1 (GETPREECHARSAWAS, JIRACHAI et al.) 18 May 2017 See the whole document.	1-12
A	KR 10-2014-0007164 A (SUNGSHIN WOMENS UNIVERSITY INDUSTRY ACADEMIC COOPERATION FOUNDATION) 17 January 2014 See the whole document.	1-12
A	KR 10-2005-0048080 A (AJOU UNIVERSITY INDUSTRY COOPERATION FOUNDATION) 24 May 2005 See the whole document.	1-12

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

☒ See patent family annex.

* Special categories of cited documents:
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"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
19 May 2020 (19.05.2020)	**20 May 2020 (20.05.2020)**

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2020/001209

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