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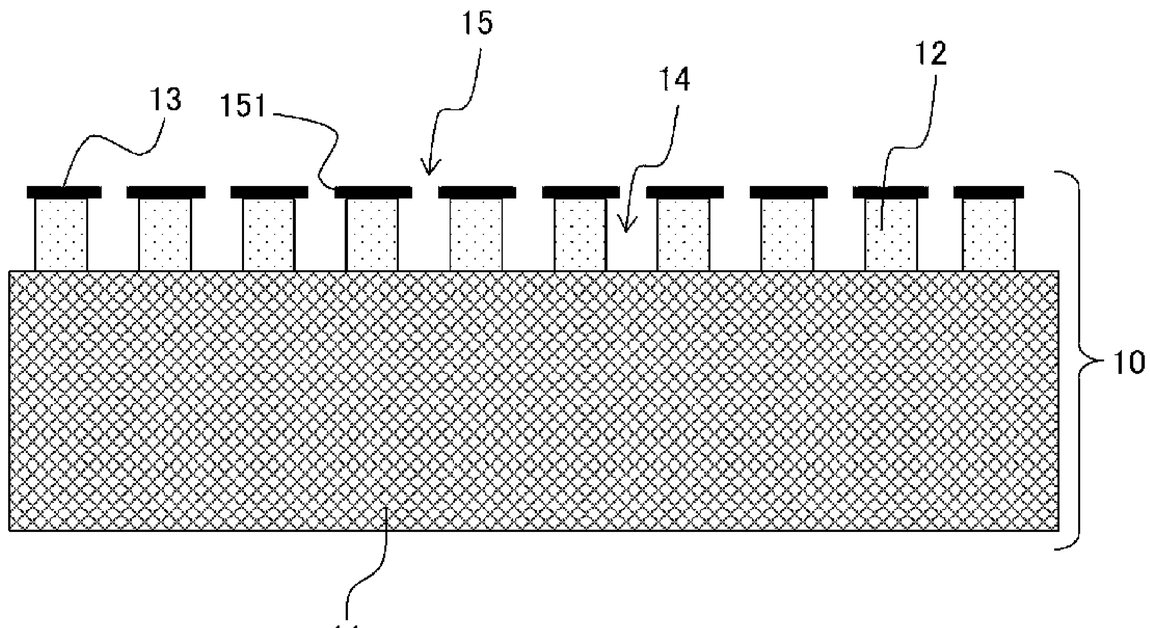
(54) **Title:** SEPARATION MEMBRANE AND METHOD FOR MANUFACTURING SEPARATION MEMBRANE

(54) 発明の名称： 分離膜及び分離膜の製造方法



(57) **Abstract:** The present invention provides a separation membrane having excellent durability. In order to solve this problem, a separation membrane 10 includes: a supporting body 11 that has water permeability; a matrix layer 12 that is supported on the supporting body 11 and has first holes 14; and a graphene layer 13 that is supported on the matrix layer 12, includes a graphene material including at least one of graphene and graphene oxide, and has second holes 15 which overlap with the first holes 14. The density of openings of the first holes 14 and

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the second holes 15 is individually 0.1×10^3holes/μm^2 or more and 10×10^3holes/μm^2 or less.

(57) 要約：耐久性に優れた分離膜を提供する。この課題の解決のため、分離膜１０は、通水性を有する支持体１１と、支持体１１に支持され、第１孔１４を有するマトリクス層１２と、マトリクス層１２に支持されるとともにグラフェン又は酸化グラフェンの少なくとも一方を含むグラフェン材料を含み、第１孔１４と重なる第２孔１５を有するグラフェン層１３とを含む。第１孔１４及び第２孔１５の開口密度は、それぞれ独立して、０．１×１０^{3}個／μｍ^{2}以上１０×１０^{3}個／μｍ^{2}以下である。

DESCRIPTION

Title of Invention: SEPARATION MEMBRANE AND METHOD FOR PRODUCING SEPARATION MEMBRANE

Technical Field

[0001]

The present disclosure relates to a separation membrane and a method for producing a separation membrane.

Background Art

[0002]

Due to the growing shortage of fresh water sources, there is a need by many countries for solutions that can convert seawater into clean drinking water. A filter such as a reverse osmosis membrane (RO) is used for desalination of seawater, and most of current commercially available RO membranes have a structure in which a thin aromatic polyamide selective layer is formed on a porous support layer. There is a high demand for novel membrane materials to improve the performance (separation performance, water permeability, and the like) of RO membranes.

[0003]

From this viewpoint, a carbon-based material has attracted attention. PTL 1 discloses that "a method for producing a filter molded body having a layer of graphene as

a filter medium, the method including: a step of forming a layer of a support 3 on a surface of a layer of graphene 1 formed on initial substrates 2 and 9 for graphene; a step of forming a water permeation hole in the layer of the support 3; a step of removing the initial substrates 2 and 9 for graphene; and a step of forming a water permeation hole by heating and holding the layer of graphene 1 at a low temperature for a predetermined time in air containing oxygen of 160 to 250°C".

Citation List

Patent Literature

[0004]

PTL 1: JP 2019-162635 A (Abstract)

Summary of Invention

Technical Problem

[0005]

PTL 1 discloses a separation membrane including a resist layer and graphene (FIG. 1 (6)). When an aqueous solution is treated using this separation membrane, a high pressure is applied to the separation membrane to some extent in order to allow the separation membrane to permeate therethrough. Therefore, there is a problem in durability of the separation membrane.

The problem to be solved by the present disclosure is

to provide a separation membrane having excellent durability and a method for producing the separation membrane.

Solution to Problem

[0006]

The separation membrane of the present disclosure includes a support having water permeability, a matrix layer supported by the support and having a first hole, and a graphene layer supported by the matrix layer and having a second hole that contains a graphene material containing at least one of graphene or graphene oxide and overlaps with the first hole. Other solutions will be described later in embodiments for carrying out the invention.

Advantageous Effects of Invention

[0007]

According to the present disclosure, it is possible to provide a separation membrane having excellent durability and a method for producing the separation membrane.

Brief Description of Drawings

[0008]

[FIG. 1] FIG. 1 is a cross-sectional view of a separation membrane of the present embodiment.

[FIG. 2] FIG. 2 is a perspective view of the separation

membrane of the present embodiment.

[FIG. 3] FIG. 3 is a top view of the separation membrane of the present embodiment.

[FIG. 4] FIG. 4 is a flowchart illustrating a method for producing the separation membrane of the present embodiment.

Description of Embodiments

[0009]

Hereinafter, modes (referred to as embodiments) for carrying out the present disclosure will be described with reference to the drawings. In the following description of one embodiment, another embodiment applicable to one embodiment will also be described as appropriate. The present disclosure is not limited to the following one embodiment, and different embodiments may be combined or may be modified in any manner as long as the effects of the present disclosure are not significantly impaired. In addition, the same members are denoted by the same reference numerals, and redundant description will be omitted. Furthermore, those having the same function are denoted by the same names. The illustrated contents are merely schematic, and for convenience of illustration, an actual configuration may be changed within a range not significantly impairing the effects of the present disclosure, or

illustration of some members may be omitted or modified between the drawings.

[0010]

FIG. 1 is a cross-sectional view of a separation membrane 10 of the present embodiment. The separation membrane 10 can be used, for example, to remove a solute such as an ion or a predetermined molecule from a solution containing the solute. For example, the solute can be removed by making a primary side a high pressure and flowing the solution to a secondary side. In addition, the separation membrane 10 can also be used to remove the dispersion from the slurry containing the dispersion.

[0011]

The separation membrane 10 can stand on its own and is excellent in handleability. The separation membrane 10 has a rectangular shape (FIG. 2) in the illustrated example, but the shape of the separation membrane 10 is not limited to the illustrated example. The separation membrane 10 includes a support 11, a matrix layer 12, and a graphene layer 13. The separation membrane 10 may include any layer other than these layers.

[0012]

The support 11 supports the matrix layer 12 and the graphene layer 13, and has water permeability. By providing the support 11, the separation membrane 10 can be made self-

standing, the strength of the separation membrane 10 can be improved, and for example, the durability to high pressure can be improved. The specific configuration of the support 11 is not particularly limited, but is preferably made of, for example, a porous material capable of performing water permeation. By using a porous material, water can permeate the support 11 and the strength of the support 11 can be improved, so that the strength of the separation membrane 10 as a whole can be improved. An opening formed of the porous material may extend only in one direction along the thickness direction (water permeation direction) of the support 11, or may extend on a zigzag inside the support 11.

[0013]

In the case of using the porous material, it is preferable that the pressure loss of the support 11 is small at the time of water permeation. Therefore, it is preferable to increase the porosity of the porous material within a range in which the strength of the support 11 can be maintained. In this case, an opening diameter of the opening (not shown) of the support 11 is preferably 1 μm or more and 100 μm or less. The opening diameter can be measured using a scanning electron microscope (SEM) or the like. The porosity is preferably, for example, 40% or more and 80% or less. The porosity can be measured by an Archimedes method or the like.

[0014]

The material of the support 11 is not particularly limited, and examples thereof include at least one of polymer materials such as polypropylene, polyethylene, polysulfone, polyethersulfone, polytetrafluoroethylene (PTFE), cellulose acetate, polyvinylidene fluoride (PVDF), and polyacrylonitrile; and ceramic materials such as silica, alumina, titania, and zirconia. Among them, the support 11 preferably contains at least one selected from the group consisting of polyethylene, polypropylene, polycarbonate, polytetrafluoroethylene, polyethersulfone, polysulfone, and cellulose acetate. By containing at least one of these, the weight of the separation membrane 10 can be reduced, and the strength of the separation membrane 10 can be improved.

[0015]

The shape of the support 11 is also not particularly limited, and can be, for example, a mesh shape, a woven fabric shape, a nonwoven fabric shape, or the like.

[0016]

The support 11 may appropriately coat at least the arrangement side of the matrix layer 12 in order to improve adhesion with the matrix layer 12. A coating material to be used is not particularly limited, and examples thereof include at least one of polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP), and the like. The coating material may

be obtained by crosslinking different coating materials.

[0017]

The matrix layer 12 has a first hole 14. By providing the matrix layer 12, defects (an example of an opening whose size is not controlled) and the like originally present in the graphene layer 13 can be closed, and unintended permeation of the separation membrane 10 can be suppressed. In addition, even when a defect or the like larger than the second hole 15 (described later) of the graphene layer 13 is present, the first hole 14 can suppress permeation of the separation membrane 10 through the defect. Thus, the separation performance by the separation membrane 10 can be secured. In addition, a substance having a size corresponding to the opening diameter of the first hole 14 can flow.

[0018]

The opening density of the matrix layer 12, that is, the number of the first holes 14 per unit area in a plane in a direction perpendicular to the water permeation direction is not particularly limited. The opening density of the matrix layer 12 is a factor that affects the maximum value of the opening density of the graphene layer 13. The opening density is a factor that affects the water permeability of the separation membrane 10, and is preferably higher, and in particular, the opening density is preferably 0.1×10^3

pieces/μm^2 or more and 10×10^3 pieces/μm^2 or less. By setting the number of particles to 0.1×10^3 particles/μm^2 or more, the water permeability can be improved. On the other hand, by setting the density to 10×10^3 pieces/μm^2 or less, a function as a mask by the matrix layer 12 can be easily exhibited although details will be described later. The opening density can be determined based on the number of the first holes 14 measured using, for example, a scanning electron microscope (SEM).

[0019]

The opening diameter of the first hole 14 is not particularly limited, and may be appropriately set according to the size of the target permeate. However, the opening diameter of the first hole 14 is preferably 5 nm or more and 20 nm or less. Within this range, the effect of blocking defects and the like present in the graphene layer 13 can be increased. In addition, the opening density can be improved, and the water permeability can be improved. Furthermore, the accuracy at the time of patterning (to be described later) can be improved. The opening diameter of the first hole 14 can be measured using, for example, a scanning electron microscope (SEM).

[0020]

FIG. 2 is a perspective view of the separation membrane 10 of the present embodiment. FIG. 3 is a top view of the

separation membrane 10 of the present embodiment. The first holes 14 are arranged in a diffused manner, for example, but a specific form thereof is not particularly limited. For example, the first hole 14 is a first hole group 141 in which the first holes 14 are continuously arranged linearly at equal intervals, and the plurality of first hole groups 141 can be arranged in parallel at equal intervals. Further, a 60° staggered arrangement in which the angle θ formed by the three adjacent first holes 14 is 60°, a 45° staggered arrangement in which the angle θ formed by the three adjacent first holes 14 is 45°, and the like are also exemplified. The angle θ formed here is an angle formed by two line segments L connecting the centers P of three adjacent first holes 14, and is the smallest angle.

[0021]

The arrangement pattern of the first holes 14 is preferably a 60° staggered arrangement illustrated in FIGS. 2 and 3 from the viewpoint of increasing the opening density. In the case of the 60° staggered arrangement, the opening diameter of the first hole 14 can be, for example, 5 nm or more and 20 nm or less, and the distance between the adjacent first holes 14 (center-to-center distance, length of one line segment) can be, for example, 2 times or more and 4 times or less (for example, 10 nm or more and 80 nm or less) the opening diameter of the first hole 14.

[0022]

Returning to FIG. 1, the matrix layer 12 supports the entire graphene layer 13 other than the first hole 14. As a result, even if an unintended defect or the like exists in the graphene layer 13, the size of the permeate can be controlled by the second hole 15 of the matrix layer 12.

[0023]

The thickness (film thickness) of the matrix layer 12 is not particularly limited. For example, the thickness is preferably 5 nm or more and 50 nm or less. When the thickness is 5 nm or more, the first hole 14 can be easily formed, and the second hole 15 of the graphene layer 13 can be easily formed. When the thickness is 50 nm or less, the pressure loss of the matrix layer 12 can be reduced.

[0024]

A constituent material of the matrix layer 12 is not particularly limited. Examples of the constituent material of the matrix layer 12 include at least one of positive or negative photoresist materials, a block copolymer, specifically, a polystyrene (PS)-polymethyl methacrylate (PMMA) copolymer, or a polysilsesquioxane methacrylate (PMAPOSS)-polymethyl methacrylate copolymer, and ceramic materials such as mesoporous silica and porous alumina.

[0025]

Among them, the matrix layer 12 preferably contains at

least one selected from the group consisting of a block copolymer, mesoporous silica, and porous alumina. By constituting the matrix layer 12 with such a material, the matrix layer 12 capable of supporting the graphene layer 13 can be formed. Among them, the matrix layer 12 preferably contains a block copolymer. By containing such a material, the opening diameter and the opening density of the first holes 14 can be easily controlled by changing the molecular weight ratio of each constituent element.

[0026]

The graphene layer 13 is supported by the matrix layer 12, contains a graphene material containing at least one of graphene and graphene oxide, and has the second hole 15. The graphene layer 13 usually includes graphene oxide.

[0027]

The graphene layer 13 includes one or more unit layers made of a sheet of a graphene material, and the second hole 15 is formed so as to penetrate the unit layers. In this way, even in a case where there is one unit layer, separation can be performed by the separation membrane 10, and in a case where there is a plurality of unit layers, the size of the permeate can be controlled by controlling the opening diameter of the second hole 15 regardless of the interlayer distance between adjacent unit layers.

[0028]

The second hole 15 is formed to overlap with the first hole 14. "Overlapping" refers to a state in which the first hole 14 and the second hole 15 communicate with each other so that a permeate such as a solute or a dispersion can flow. As a degree of overlapping, the second hole 15 does not need to completely overlap (that is, for example, as illustrated in FIG. 1, the opening diameter of the second hole 15 is smaller than the opening diameter of the first hole 14) the first hole 14, and the second hole 15 may overlap at least a part of the first hole 14. Note that, although details will be described later, the second hole 15 of the graphene layer 13 is formed using the matrix layer 12 as a mask. Therefore, the opening diameter of the second hole 15 and the opening diameter of the first hole 14 are usually substantially the same (or may be completely the same).

[0029]

The opening density of the second holes 15 in the graphene layer 13, that is, the number of the second holes 15 per unit area in a plane in a direction perpendicular to the water permeation direction is not particularly limited. The opening density of the graphene layer 13 is a factor that affects the water permeability of the separation membrane 10, and is preferably higher, and in particular, the opening density is preferably 0.1×10^3 pieces/μm^2 or more and 10×10^3 pieces/μm^2 or less. By setting the number

of particles to 0.1×10^3 particles/μm^2 or more, the water permeability can be improved. On the other hand, by setting the density to 10×10^3 pieces/μm^2 or less, for example, a function as the graphene layer 13 having high strength can be easily exhibited. The opening density can be determined based on the number of the second holes 15 measured using, for example, an atomic force microscope (AFM), a transmission electron microscope (TEM), a scanning electron microscope (SEM), or the like.

[0030]

The opening diameter of the second hole 15 is not particularly limited, and may be appropriately set according to the size of the target permeate. For example, the thickness is preferably, for example, 2 nm or more and 100 nm or less when relatively large molecules such as polymers are removed from the aqueous solution, and is preferably, for example, 0.1 nm or more and 2 nm or less when relatively small molecules such as low molecules and ions are removed. The opening diameter of the second hole 15 can be measured by the same method as the first hole 14 using, for example, an atomic force microscope (AFM), a transmission electron microscope (TEM), a scanning electron microscope (SEM), or the like.

[0031]

Assuming that the opening diameter (inner diameter) of

the first hole 14 is dM and the opening diameter (inner diameter) of the second hole 15 is dG, it is preferable to control the opening diameters of the first hole 14 and the second hole 15 so as to satisfy the following Formula (1).

$$0.02 \times dM \leq dG \leq 1.0 \times dM \quad \text{... Formula (1)}$$

By controlling the opening diameters of the first hole 14 and the second hole 15 so as to satisfy Formula (1), the second hole 15 can be easily formed, and the strength of the graphene layer 13 can be improved.

[0032]

As described above, the second hole 15 of the graphene layer 13 is formed using the matrix layer 12 as a mask. Therefore, the maximum value of the opening diameter dG of the second hole 15 coincides with the opening diameter dM of the matrix layer 12 which is usually a mask. On the other hand, the minimum value is about 0.5 nm assuming a structure in which one six-membered ring of graphene or graphene oxide is removed, and is about 0.02 times or more and 0.1 times or less dM. Therefore, by controlling the opening diameters of the first hole 14 and the second hole 15 so as to satisfy the above (1), the second hole 15 can be easily formed.

[0033]

The graphene material constituting the graphene layer 13 usually contains graphene oxide, and a first functional group constituting an inner wall 151 (including the opening)

of the second hole 15 is usually an oxygen-containing functional group such as a hydroxyl group, a carboxyl group, or an epoxy group contained in graphene oxide. The first functional group is preferably molecularly modified with a second functional group capable of bonding to the first functional group. As for the first functional group, in particular, although details will be described later, the graphene material is oxidized at the time of forming the second hole 15, and these oxygen-containing functional groups are easily generated on the inner wall of the second hole 15. By being modified with the second functional group, a substance that permeates through the second hole 15 can be selected depending on the type of the second functional group, or the size of the permeate passing through the second hole 15 can be controlled depending on the size of the second functional group.

[0034]

The second functional group is not particularly limited as long as it can react with and bond to the first functional group. The second functional group includes, for example, a reactive functional group capable of being bonded to the first functional group and a functional group capable of being bonded to the first functional group and further expressing a function such as opening diameter control.

Examples of the reactive functional group include at

least one of an alkoxysilyl group, a chlorosilyl group, an amino group, a carboxyl group, and a hydroxyl group.

Examples of the functional group include at least one of an alkyl group (methyl group, ethyl group, propyl group, butyl group, pentyl group, hexyl group, heptyl group, and the like), a functional group derived from polyethylene glycol (PEG), an acrylic group, a methacrylic group, an acrylamide group, a fluoroalkyl group, a functional group containing a zwitterion (phosphorylcholine, sulfobetaine, carboxybetaine, and the like), and derivatives thereof.

[0035]

Among them, the second functional group preferably contains at least one selected from the group consisting of an alkyl group, a functional group derived from polyethylene glycol, an acrylic group, a methacrylic group, an acrylamide group, a fluoroalkyl group, a functional group containing a zwitterion, and derivatives thereof. By containing at least one of these, the second functional group can be bonded toward the center side of the second hole 15 to exhibit various functions.

[0036]

FIG. 4 is a flowchart illustrating a method for producing the separation membrane 10 (FIG. 1) of the present embodiment. Hereinafter, FIG. 4 will be described with reference to FIG. 1 as appropriate. The method for producing

the separation membrane 10 usually includes a graphene layer forming step S1, a first arrangement step S2, a first hole forming step S3, a second hole forming step S4, a modification step S5, and a second arrangement step S6 in this order.

[0037]

The graphene layer forming step S1 is a step of forming a graphene layer 13 containing a graphene material containing at least one of graphene or graphene oxide on a substrate. The graphene layer forming step S1 may not be performed, and in a case where the graphene layer forming step S1 is not performed, for example, an optional graphene layer 13 may be separately purchased and prepared.

[0038]

The substrate may be any substrate as long as it can form the graphene layer 13 and separate the graphene layer 13 from the substrate, and examples thereof include a metal foil such as a copper foil. The metal foil may be appropriately formed on another substrate such as a silicon substrate or a sapphire substrate. The graphene layer 13 can be formed on the substrate by, for example, a chemical vapor deposition method (CVD). The graphene layer 13 is preferably a single-layer graphene having only one unit layer made of a sheet of a graphene material, but may be a multilayer graphene including a plurality of unit layers.

When the single-layer graphene is used, a single-crystal graphene having a large crystal size and few crystal grain boundaries is preferable from the viewpoint of film strength.

[0039]

The first arrangement step S2 is, for example, a step of arranging the matrix layer 12 on the surface of the graphene layer 13 formed in the graphene layer forming step S1 using a matrix material. As the matrix material, for example, a positive or negative photoresist material, a block copolymer, ceramic materials such as mesoporous silica and porous alumina, or the like can be used. The block copolymer is one molecule obtained by covalently linking a plurality of polymers.

[0040]

Among them, the matrix material preferably contains a block copolymer. By containing the block copolymer, one polymer can be removed by microphase separation to form the second holes 15, and the matrix layer 12 made of the other polymers can be formed as a balance. Examples of the block copolymer include at least one of a copolymer of polystyrene (PS) and polymethyl methacrylate (PMMA), and a copolymer of polysilsesquioxane methacrylate (PMAPOSS) and PMMA.

[0041]

A method for arranging the matrix material on the graphene layer 13 is not particularly limited, and for

example, the matrix material can be formed by applying a solution or slurry containing the matrix material and drying or solidifying the solution or slurry.

[0042]

The first hole forming step S3 is a step of forming the first holes 14 in the matrix layer 12 arranged in the graphene layer 13. A method for forming the first hole 14 is not particularly limited, and can be performed, for example, as follows. For example, when a photoresist material is used as the matrix material, the first hole 14 can be formed by forming a film of the photoresist material, exposing the film to light using ultraviolet light, X-rays, electron beams, or the like, and then treating the film with a developer.

[0043]

When a block copolymer is used as the matrix material, microphase separation is caused by performing a post-film-formation heat treatment, one polymer (corresponding to the second polymer) is then crosslinked and insolubilized by irradiation with ultraviolet rays, and the other polymer (corresponding to the first polymer) is removed, whereby the first hole 14 can be formed. When the block copolymer is used, the opening diameter and the opening density can be controlled by changing at least one of the molecular weights of one polymer and the other polymer or the ratio between

the molecular weights. For example, by increasing the molecular weight of the polymer corresponding to the first polymer, the opening diameter of the first hole 14 can be increased.

[0044]

When a ceramic material is used as the matrix material, for example, in the case of mesoporous silica, a film may be formed using a solution containing a SiO_2 precursor such as tetraethoxysilane (TEOS) and a surfactant such as cetyltrimethylammonium bromide, and then heated at a predetermined temperature. Thereafter, the first hole 14 can be formed by removing the surfactant by washing. The opening diameter and the opening density of the first hole 14 can be controlled by changing at least one of the type of the surfactant and the treatment conditions (temperature, solvent, and the like).

[0045]

The second hole forming step S4 is a step of forming the second hole 15 in the graphene layer 13 along the first hole 14 after the first hole forming step S3. A specific method for forming the second hole 15 is not particularly limited as long as the second hole is formed with respect to the graphene layer 13 exposed from the first holes 14 to the matrix layer 12 side, for example. For example, by using the matrix layer 12 having the first hole 14 as a mask, it

can be performed by at least one method such as a dry process such as oxygen plasma treatment or UV ozone treatment, or a wet process such as immersion in a potassium permanganate aqueous solution.

[0046]

The modification step S5 is a step of molecularly modifying the first functional group constituting the inner wall 151 constituting the second hole 15 with the second functional group capable of bonding to the first functional group. The inner wall 151 can be molecularly modified with the second functional group by the modification step S5, and at least one of the opening diameter of the second hole 15 and the material selectivity of the separation membrane 10 can be controlled. For example, when the second functional group is a long-chain alkyl group, a bulky functional group, or the like, the opening diameter of the second hole 15 can be made smaller than the opening diameter at the time of formation in the second hole forming step S4. As a result, when the opening diameter at the time of formation in the second hole forming step S4 is unintentionally increased, the opening diameter can be adjusted. The chemical modification can be performed, for example, by immersing separation membrane 10 in a solution of a compound having the second functional group. At this time, degassing treatment, heat treatment, and addition of a catalyst may be

performed as necessary.

[0047]

The modification step S5 is preferably performed, but may not be performed. Furthermore, the execution time of the modification step S5 may be during the formation of the second hole 15 or may be any time after the formation.

[0048]

The second arrangement step S6 is a step of arranging an integrated body of the matrix layer 12 and the graphene layer 13 in which the first hole 14 and the second hole 15 are formed, respectively, on the surface of the support 11 having water permeability so that the matrix layer 12 side is in contact. A specific method of the arrangement is not particularly limited, but for example, the matrix layer 12 and the support 11 can be arranged by being pressure-bonded to face each other. At this time, pressure-bonding may be performed using a vacuum laminating apparatus or the like. Thereafter, the separation membrane 10 can be obtained by immersing the separation membrane in, for example, a copper etching solution such as a ferric chloride aqueous solution, removing a metal foil such as a copper foil, washing with water, and drying. Note that the separation membrane 10 can also be obtained by etching and washing a metal foil such as a copper foil before being pressure-bonded to the support 11, and scooping an integrated product of the matrix layer

12 and the graphene layer 13 with the support 11 in water, for example.

[EXAMPLES]

[0049]

Hereinafter, the present disclosure will be described more specifically with reference to examples, but the present disclosure is not limited to the following examples.

[0050]

<Example 1>

The separation membrane 10 illustrated in FIG. 1 was prepared along the flowchart illustrated in FIG. 4 (here, the modification step S5 was not performed). A film of polysulfone was prepared as the support 11, and a block copolymer of polystyrene (number average molecular weight: 46100) and polymethyl methacrylate (number average molecular weight: 21000) was prepared as a matrix material. A graphene layer 13 made of single-layer graphene was formed on a copper foil by a CVD method (graphene layer forming step S1).

[0051]

A block copolymer material was applied and solidified on the graphene layer 13 to form a matrix layer 12 (first arrangement step S2). The whole was heated in vacuum (230°C for 1 hour or more) to cause microphase separation in the matrix material, so that the cylindrical domain of polymethyl methacrylate formed an upright structure. Thereafter, a

polystyrene region was insolubilized by ultraviolet irradiation in nitrogen for 1 minute, and polymethyl methacrylate was removed by immersion in acetic acid for 2 minutes, thereby forming the first hole 14 in the matrix layer 12 (first hole forming step S3).

[0052]

According to the observation of the matrix layer 12 using a scanning electron microscope, the opening diameter of the first hole 14 was 20 nm, and the opening density was $0.75 \times 10^3/\mu m^2$.

[0053]

After the first hole 14 was formed, the whole was subjected to oxygen plasma treatment, and oxygen plasma was brought into contact with the graphene layer 13 through the first hole 14 to form the second hole 15 along the first hole 14 (second hole forming step S4). Further, the graphene in the graphene layer 13 was partially changed to graphene oxide by the oxygen plasma treatment. The oxygen plasma treatment time was adjusted so that the opening diameter of the second hole 15 was 1 nm or less. After the UV ozone treatment, the resultant was immersed in an aqueous iron chloride solution to remove the copper foil, washed with water, and press-bonded to the support 11 (second arrangement step S6), thereby obtaining the separation membrane 10 of Example 1.

[0054]

The opening density of the graphene layer 13 was 0.5 × 10^3 pieces/μm^2 by observation using a transmission electron microscope.

[0055]

<Example 2>

A separation membrane 10 of Example 2 was prepared in the same manner as in Example 1 except that in the middle of preparing the separation membrane 10 in the same manner as in Example 1, the modification step S5 was further performed between the second hole forming step S4 and the second arrangement step S6. The modification step S5 was performed by immersing the whole material including the copper foil after the UV ozone treatment in methoxydimethyloctylsilane at room temperature for 24 hours. In the modification step S5, for example, a hydroxyl group (first functional group) bonded to the inner wall 151 of the second hole 15 was molecularly modified with an alkylsilane group (second functional group).

[0056]

The opening density of the graphene layer 13 was 0.5 × $10^3/\mu m^2$ by observation using a scanning electron microscope.

[0057]

<Comparative Example 1>

A commercially available reverse osmosis membrane was

prepared and used as a separation membrane of Comparative Example 1.

[0058]

<Comparative Example 2>

A separation membrane of Comparative Example 2 was prepared in the same manner as in Example 1 except that the support 11 was not provided.

[0059]

<Performance Evaluation>

A fluorescent dye aqueous solution (2×10^{-5} mol/L porphyrin derivative (5,10,15,20-tetrakis (4-sulfophenyl) porphyrin; TPPS) aqueous solution) was passed through each of the separation membranes 10 of Examples 1 and 2 and the separation membranes of Comparative Examples 1 and 2, and the dye blocking ability and the water permeation rate were evaluated. A cross-flow filtration device was used for evaluation. This filtration device was provided with a support part (not shown) for supporting the separation membrane, and each separation membrane was supported by the support part to perform a test.

[0060]

When the aqueous fluorescent dye solution was caused to pass through the separation membranes 10 of Examples 1 and 2 while being pressurized, colorless and transparent permeates were obtained visually. Therefore, it was

possible to transmit water molecules smaller than the opening diameters of the first hole 14 and the second hole 15 without transmitting TPPS larger than the opening diameters thereof regardless of the presence or absence of modification by the second functional group.

[0061]

Even in the case of allowing water to permeate the separation membrane of Comparative Example 1, a colorless and transparent permeate was visually obtained, similarly to the separation membranes 10 of Examples 1 and 2. However, in the case of using the separation membrane of Comparative Example 1, the pressure applied to the fluorescent dye aqueous solution for water permeation was 10 times the pressure applied when water permeates the separation membranes 10 of Examples 1 and 2. Therefore, it was found that by using the separation membranes 10 of Examples 1 and 2, water can permeate at a lower pressure as compared with water permeation using the separation membrane of Comparative Example 1, that is, a reverse osmosis membrane existing in the related art. With this, the pressure applied to the separation membrane 10 can be reduced, so that the durability of the separation membrane 10 can be improved.

[0062]

In the separation membrane of Comparative Example 2, when the applied pressure was gradually increased, the

graphene layer 13 was damaged before the pressure applied at the time of water permeation of the separation membranes 10 of Examples 1 and 2 reached, and thereby water permeation was not performed. Therefore, it was found that the separation membrane of Comparative Example 2 had poor durability and was difficult for water to permeate. Also from this point of view, it has been found that the separation membrane 10 of the present disclosure is superior in durability to the separation membrane of Comparative Example 2, and exhibits the same high water permeation performance as the reverse osmosis membrane.

[0063]

Although the separation membrane using the graphene according to the present disclosure has been described in detail with reference to the embodiments and examples, the gist of the present disclosure is not limited thereto, and various modifications are included. For embodiment, the above-described embodiments are described in detail in order to describe the present disclosure in an easy-to-understand manner, and are not necessarily limited to those having all the described configurations. Further, a part of the configuration of one embodiment can be replaced with the configuration of another embodiment, and the configuration of another embodiment can be added to the configuration of one embodiment. Furthermore, it is possible to add, delete,

and replace other configurations for a part of the configuration of each embodiment.

Reference Signs List

[0064]

10 separation membrane

11 support

12 matrix layer

13 graphene layer

14 first hole

141 first hole group

15 second hole

151 inner wall

S1 graphene layer forming step

S2 first arrangement step

S3 first hole forming step

S4 second hole forming step

S5 modification step

S6 second arrangement step

CLAIMS

[Claim 1]

A separation membrane comprising:

a support having water permeability;

a matrix layer supported by the support and having a first hole; and

a graphene layer supported by the matrix layer and having a second hole that contains a graphene material containing at least one of graphene or graphene oxide and overlaps with the first hole.

[Claim 2]

The separation membrane according to claim 1, wherein opening densities of the first hole and the second hole are each independently $0.1 \times 10^3/\mu m^2$ or more and $10 \times 10^3/\mu m^2$ or less.

[Claim 3]

The separation membrane according to claim 1 or 2, wherein

the graphene material contains graphene oxide, and

a first functional group constituting an inner wall of the second hole is molecularly modified with a second functional group capable of bonding to the first functional group.

[Claim 4]

The separation membrane according to claim 3, wherein

the second functional group contains at least one selected from the group consisting of an alkyl group, a functional group derived from polyethylene glycol, an acrylic group, a methacrylic group, an acrylamide group, a fluoroalkyl group, a functional group containing a zwitterion, and derivatives thereof.

[Claim 5]

The separation membrane according to claim 1 or 2, wherein when an opening diameter of the first hole is denoted by dM and an opening diameter of the second hole is denoted by dG, the following Formula (1) is satisfied.

$$0.02 \times dM \leq dG \leq 1.0 \times dM$$

[Claim 6]

The separation membrane according to claim 1 or 2, wherein the matrix layer contains at least one selected from the group consisting of a block copolymer, mesoporous silica, and porous alumina.

[Claim 7]

The separation membrane according to claim 6, wherein the matrix layer contains a block copolymer.

[Claim 8]

The separation membrane according to claim 1 or 2, wherein the support contains at least one selected from the group consisting of polyethylene, polypropylene, polycarbonate, polytetrafluoroethylene, polyethersulfone,

polysulfone, and cellulose acetate.

[Claim 9]

The separation membrane according to claim 1 or 2, wherein the support is made of a porous material.

[Claim 10]

The separation membrane according to claim 1 or 2, wherein

the graphene layer includes one or more unit layers made of a sheet of a graphene material, and

the second hole is formed so as to penetrate the unit layers.

[Claim 11]

The separation membrane according to claim 1 or 2, wherein the matrix layer supports the entire graphene layer other than the first hole.

[Claim 12]

A method for producing a separation membrane, comprising:

a first arrangement step of arranging a matrix layer on a surface of a graphene layer containing a graphene material containing at least one of graphene or graphene oxide using a matrix material;

a first hole forming step of forming a first hole in the matrix layer;

a second hole forming step of forming a second hole in

the graphene layer along the first hole after the first hole forming step; and

a second arrangement step of arranging an integrated body of the matrix layer and the graphene layer in which the first hole and the second hole are formed, respectively, on a surface of a support having water permeability such that a side of the matrix layer is in contact with the graphene layer.

[Claim 13]

The method for producing a separation membrane according to claim 12, further comprising:

a modification step of molecularly modifying the first functional group constituting an inner wall constituting the second hole with the second functional group capable of bonding to the first functional group.

[Claim 14]

The method for producing a separation membrane according to claim 12 or 13, wherein the matrix material contains a block copolymer.

FIG. 1

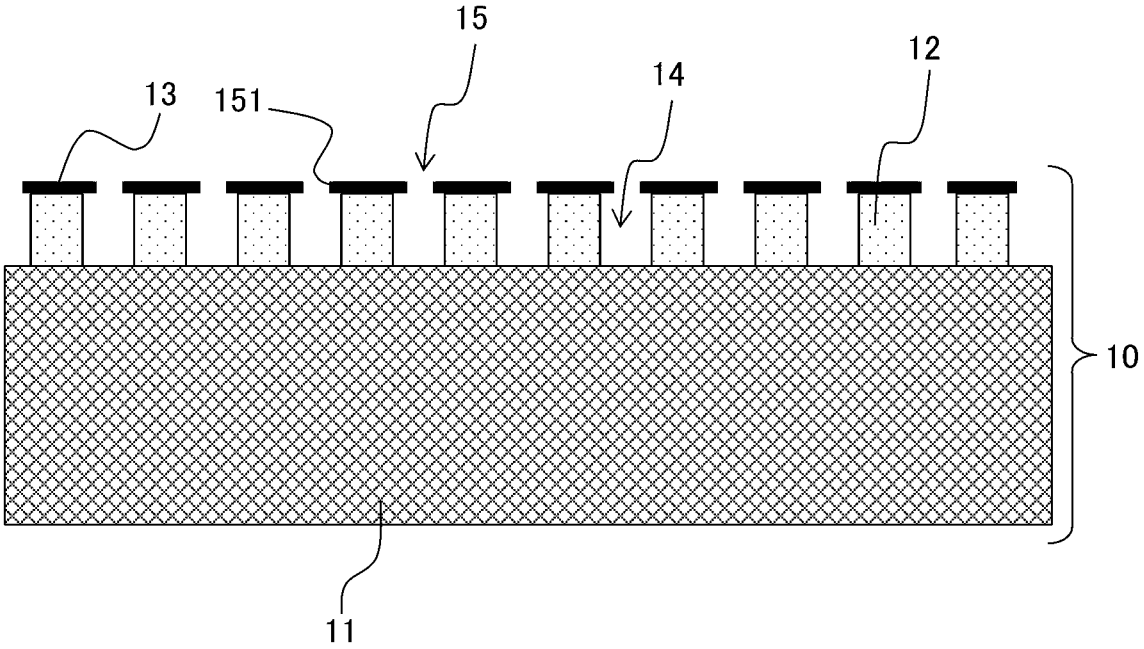


FIG. 2

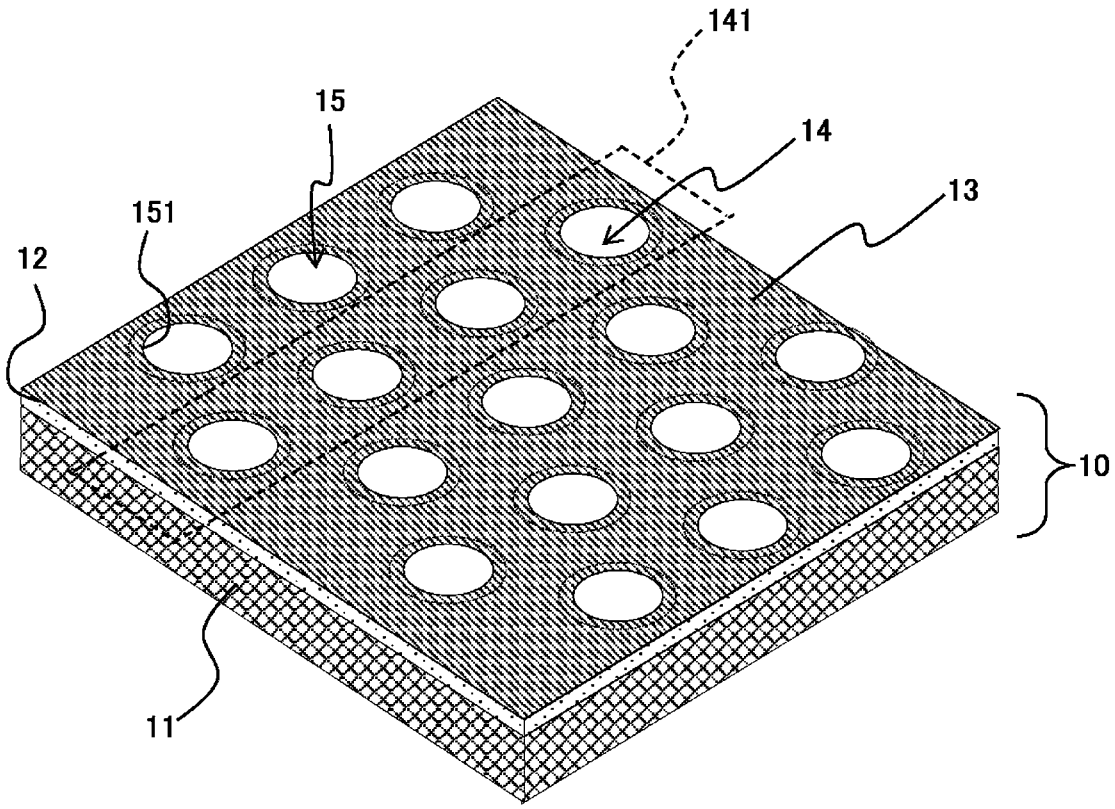


FIG. 3

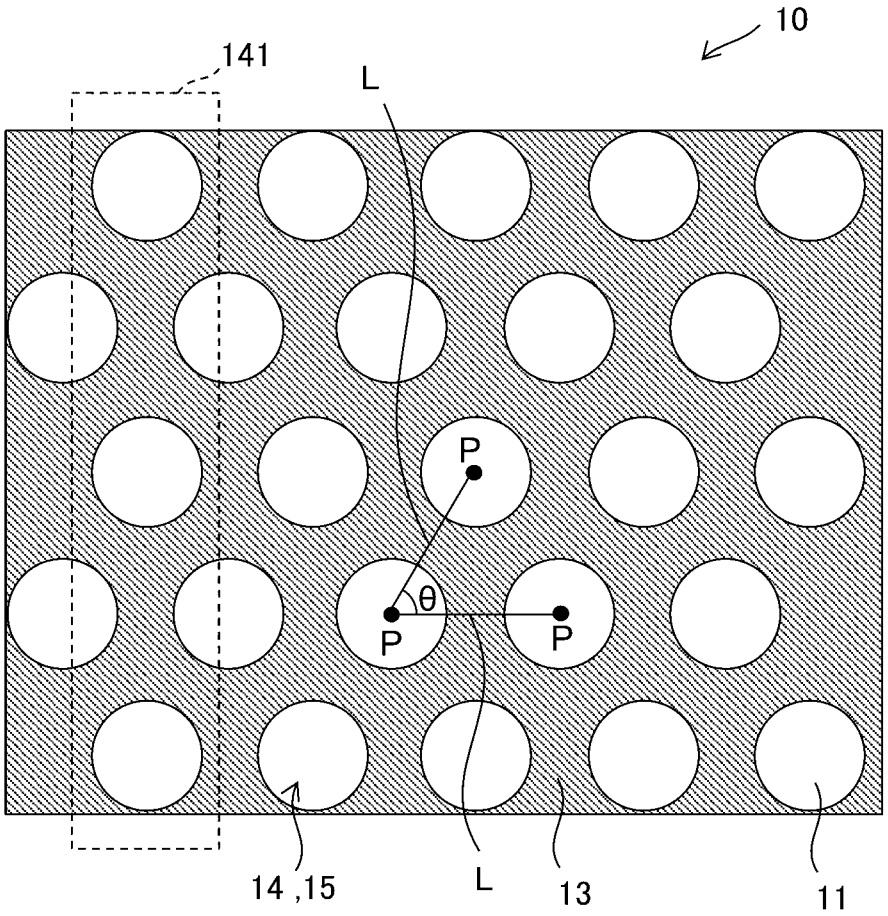
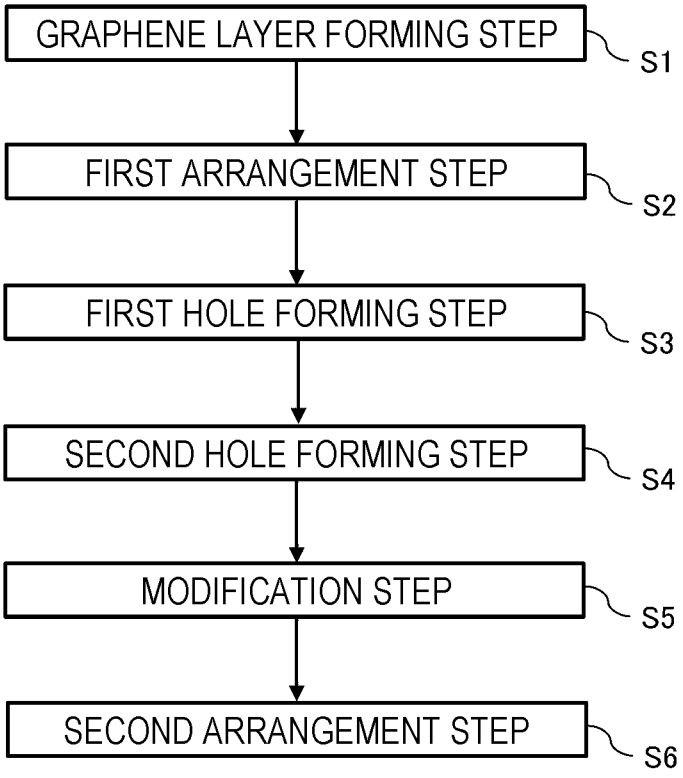


FIG. 4


GRAPHENE LAYER FORMING STEP
S1
FIRST ARRANGEMENT STEP
S2
FIRST HOLE FORMING STEP
S3
SECOND HOLE FORMING STEP
S4
MODIFICATION STEP
S5
SECOND ARRANGEMENT STEP
S6