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(54) GRAPHENE MEMBRANE AND METHOD FOR MANUFACTURING THE SAME

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(57) ABSTRACT

Disclosed are a graphene membrane and a method for manufacturing the same. The graphene membrane includes a graphene layer having a porous pattern including a plurality of pores having a size of 5 to 100 nm and a supporter configured to support the graphene layer and including a plurality of pores having a greater size than the pores of the graphene layer.



FIG. 1







FIG. 3



FIG. 4



FIG. 5



FIG. 6



















FIG. 12



FIG. 13



FIG. 14



GRAPHENE MEMBRANE AND METHOD FOR MANUFACTURING THE SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] Pursuant to 35 U.S.C. § 119(a), this application claims the benefit of Korean Patent Application No. 10-2014-0051829, filed on Apr. 29, 2014, which is hereby incorporated by reference as if fully set forth herein.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention relates to graphene, and more particularly, to a graphene membrane and a method for manufacturing the same.

[0004] 2. Discussion of the Related Art

[0005] In general, membranes are key materials and parts to execute separation and purification in applied fields, such as water treatment, energy, medical science, food, pharmacy, gas and the like.

[0006] Conventional membranes may be manufactured mainly using materials, such as polymers, ceramics and metals, and be classified into sheet-type flat membranes and tube-type hollow fiber membranes. Membranes using polymers, which are easily formed and relatively inexpensive, have been mainly used now.

[0007] Material separation using a membrane is carried out by an action in which a material to be removed does not permeate open pores of the membrane and a fluid to be purified (water, air and the like) permeates the pores.

[0008] Since a fluid permeates a membrane in such a manner, as the thickness of the membrane decreases, the amount of the fluid permeating the membrane may increase and, as the sizes of pores formed on the membrane become more uniform, a removal rate may increase and material removal may be stable.

[0009] Graphene is a representative material known as a monolayer and has high electrical conductivity and strength and thus, research thereon as a new electronic material is underway.

[0010] Since graphene is manufactured as a monolayer and has high strength, if pores are formed on graphene, graphene may be implemented as an ideal membrane having high permeability.

[0011] Thereotical research or idea to implement graphene as a membrane is carried out recently. However, graphene is a material which is difficult to treat and thus, a technique to effectively increase a porosity using graphene is required.

SUMMARY OF THE INVENTION

[0012] Accordingly, the present invention is directed to a graphene membrane and a method for manufacturing the same that substantially obviate one or more problems due to limitations and disadvantages of the related art.

[0013] An object of the present invention is to provide a graphene membrane which may have a high surface porosity using graphene.

[0014] Another object of the present invention is to provide a method for manufacturing a graphene membrane having a high surface porosity which may be mass-produced.

[0015] Additional advantages, objects, and features of the invention will be set forth in part in the description which follows and in part will become apparent to those having

ordinary skill in the art upon examination of the following or may be learned from practice of the invention. The objectives and other advantages of the invention may be realized and attained by the structure particularly pointed out in the written description and claims hereof as well as the appended drawings.

[0016] To achieve these objects and other advantages and in accordance with the purpose of the invention, as embodied and broadly described herein, a graphene membrane includes a graphene layer having a porous pattern including a plurality of pores having a size of 5 to 100 nm and a supporter configured to support the graphene layer and including a plurality of pores having a greater size than the pores of the graphene layer.

[0017] Here, the surface porosity of the graphene layer may be 5 to 70%. The surface porosity may mean a ratio of an area occupied by the pores to the unit area of the graphene layer.[0018] The supporter may include a non-woven fabric or a polymer.

[0019] Further, the supporter may be configured to discontinuously support the graphene layer.

[0020] The graphene membrane may further include a bonding layer disposed between the graphene layer and the supporter.

[0021] Here, the bonding layer may include a pattern including a plurality of pores having a size which is equal to or greater than the pores of the graphene layer.

[0022] The mean size of the pores of the graphene layer may be 5 to 50 nm. More properly, the mean size of the pores of the graphene layer may be 10 to 30 nm.

[0023] In another aspect of the present invention, a method for manufacturing a graphene membrane includes preparing a graphene layer located on a supporter, forming a porous block copolymer pattern on the graphene layer, and forming a porous pattern on the graphene layer using the porous block copolymer pattern.

[0024] The formation of the porous block copolymer pattern may include self-assembling a block copolymer, in which a first polymer and a second polymer are covalently bonded to each other, on the graphene layer and developing the block copolymer so as to form the porous pattern.

[0025] The self-assembly of the block copolymer, in which the first polymer and the second polymer are covalently bonded to each other, on the graphene layer may include spin-coating the first polymer and the second polymer in a dissolving state on the graphene layer and executing heat treatment on the spin-coated first and second polymers.

[0026] The development of the block copolymer may include radiating ultraviolet light to the block copolymer and executing acid treatment on the block copolymer.

[0027] The development of the block copolymer may include executing ion beam etching on the block copolymer. **[0028]** The first polymer may be polystyrene and the second polymer may be PMMA.

[0029] The porous pattern may include a plurality of pores having a size of 5 to 100 nm.

[0030] The formation of the porous pattern on the graphene layer may include executing ion beam etching.

[0031] Here, the block copolymer may have a pattern of cylinder-shaped nano-structures.

[0032] The surface porosity of the graphene layer indicating a ratio of an area occupied by the pores to the unit area of the graphene layer may be 5 to 70%.

[0033] The method may further include removing the porous block copolymer pattern.

[0034] It is to be understood that both the foregoing general description and the following detailed description of the present invention are exemplary and explanatory and are intended to provide further explanation of the invention as claimed.

BRIEF DESCRIPTION OF THE DRAWINGS

[0035] The accompanying drawings, which are included to provide a further understanding of the invention and are incorporated in and constitute a part of this application, illustrate embodiment(s) of the invention and together with the description serve to explain the principle of the invention. In the drawings:

[0036] FIG. **1** is a schematic cross-sectional view illustrating a graphene membrane in accordance with one embodiment of the present invention;

[0037] FIG. **2** is a cross-sectional view illustrating a graphene membrane in accordance with another embodiment of the present invention;

[0038] FIG. **3** is a cross-sectional view illustrating a graphene membrane in accordance with yet another embodiment of the present invention;

[0039] FIGS. **4** to **13** are schematic cross-sectional views illustrating a process for manufacturing a graphene membrane in accordance with one embodiment of the present invention; and

[0040] FIG. **14** is a flowchart illustrating a process for manufacturing a graphene membrane in accordance with one embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0041] Hereinafter, embodiments of the present invention will be described in detail with reference to the accompanying drawings.

[0042] Reference will now be made in detail to the preferred embodiments of the present invention, examples of which are illustrated in the accompanying drawings. It will be appreciated that the technical spirit disclosed in the specification is not restricted by the accompanying drawings and includes various modifications, equivalents, and substitutions, without departing from the scope and spirit of the invention as disclosed in the accompanying claims.

[0043] If it is stated that an element is present "on" another element, it will be understood that the former may be directly present on the latter or other elements may be interposed between the two elements.

[0044] Further, in description of elements of the present invention, the terms "first", "second", etc. may be used. These terms are used only to discriminate one element, ingredient, area, layer and/or region from other elements, ingredients, areas, layers and/or regions, and the nature, order, or sequence of the corresponding element is not limited by these terms.

[0045] FIG. **1** is a schematic cross-sectional view illustrating a graphene membrane in accordance with one embodiment of the present invention.

[0046] As exemplarily shown in FIG. 1, the graphene membrane may include a graphene layer 10 located on a supporter 20 and have a porous pattern including a plurality of pores 11. [0047] Graphene has a structure in which carbon atoms form one atomic layer on a two-dimensional plane. The graphene layer **10** may form a state in which a single atomic layer is formed or plural atomic layers are stacked. Here, the respective atomic layers may be combined by binding force between molecules.

[0048] The porous pattern formed on such a graphene layer **10** may include a plurality of pores **10** having a size of 5 to 100 nm. The pores **11** may be formed in an about circular shape and thus, the size of the pores **11** may mean the diameter of the pores **11**. However, if the pores **11** are not formed in a circular shape, the size of the pores **11** may mean the greatest length of the pores **11**.

[0049] Further, the mean size of the pores 11 of the graphene layer 10 may be 5 to 50 nm. More properly, the mean size of the pores 11 of the graphene layer 10 may be 10 to 30 nm.

[0050] The surface porosity of the graphene layer **10** may be 5 to 70%. Here, a surface porosity means a ratio of an area occupied by the pores **11** to the unit area of the graphene layer **10**.

[0051] As described above, the graphene layer **10** may have the porous pattern including a plurality of pores **11** having a size of 5 to 100 nm while simultaneously having the above-described surface porosity.

[0052] That is, if the pores **11** have a size of 5 to 100 nm and a surface porosity of 5 to 70%, the graphene layer **10** may act as an excellent functional membrane.

[0053] The supporter **20** supports the graphene layer **10** so as to act as a membrane and may include a plurality of pores having a greater size than the pores **11** of the porous pattern formed on the graphene layer **10**.

[0054] Therefore, the supporter **20** may have a function of stably supporting the graphene layer **10** without an effect on the function of the graphene layer **10** as a membrane.

[0055] The supporter **20** may include a material having a net structure, for example, a non-woven fabric. Further, the supporter **20** may include a structure with a pattern of pores having a greater size than the porous pattern formed on the graphene layer **10**. Such a structure may be formed of a polymer. However, the present invention is not limited thereto and any material, which may support the graphene layer **10** without lowering the function of the graphene layer **10** having the above-described porous pattern, may be employed.

[0056] Such a supporter **20** may continuously support the graphene layer **10**, as exemplarily shown in FIG. **1**. That is, the supporter **20** may be continuously provided so as not to expose the lower surface of the graphene layer **10** to the outside.

[0057] FIG. **2** is a cross-sectional view illustrating a graphene membrane in accordance with another embodiment of the present invention.

[0058] As exemplarily shown in FIG. 2, a bonding layer 30 may be further provided between a supporter 20 and a graphene layer 10. That is, such a bonding layer 30 may effectively fix the supporter 20 and the graphene layer 10.

[0059] The bonding layer **30** may have a lower molecular weight than a general polymer. Further, the bonding layer **20** may have a pattern of pores **31** having a size which is equal to or greater than a pattern of pores **11** of the graphene layer **10**. That is, any material, which may bond the graphene layer **10** and the supporter **20** to each other without lowering the function of the graphene layer **10** having the porous pattern, may be applied to the bonding layer **30**.

[0060] However, the bonding layer **30** may be omitted, as exemplarily shown in FIG. **1**. That is, according to a specific

treatment method, for example, according to surface treatment of the graphene layer 10 and/or the supporter 20, the graphene layer 10 may be directly bonded to the supporter 20.

[0061] FIG. **3** is a cross-sectional view illustrating a graphene membrane in accordance with yet another embodiment of the present invention.

[0062] As exemplarily shown in FIG. **3**, a supporter **21** may discontinuously support a porous graphene layer **10** having a pattern of pores **11**.

[0063] That is, the supporter 21 may have a structure to expose at least a part of the graphene layer 10 contacting the supporter 21. Here, the supporter 21 may be bonded to the lower surface of the graphene layer 10 under the condition that areas of the supporter 21 are separated by designated intervals.

[0064] As the supporter **21** of a discontinuous type, a silicon substrate having holes may be used. In addition, ceramic, a dielectric, a metal and a polymer may be used as the supporter **21**.

[0065] The membrane including such a graphene layer **10** may effectively act as a filter.

[0066] Material separation using such a membrane is carried out by an action in which a material to be removed does not permeate open pores of the membrane and a fluid to be purified (water, air and the like) permeates the pores.

[0067] Here, as the thickness of the membrane decreases, the amount of the fluid permeating the membrane may increase and, as the sizes of pores of the membrane become more uniform, a removal rate may increase and material removal may be stable.

[0068] As described above, since the graphene layer **10** in which a single atomic layer is formed or several atomic layers are stacked may be used as the membrane and the graphene layer **10** may have the pattern of the uniform pores **11**, the effect of the graphene layer **10** as the membrane may be maximized.

[0069] That is, since the graphene layer **10** may include a monolayer and have high strength, the membrane including the graphene layer **10** having the pattern of the pores **11** may be implemented as an ideal membrane having high permeability.

[0070] FIGS. **4** to **13** are schematic cross-sectional views illustrating a process for manufacturing a graphene membrane in accordance with one embodiment of the present invention and FIG. is a flowchart illustrating a process for manufacturing a graphene membrane in accordance with one embodiment of the present invention.

[0071] Hereinafter, with reference to FIGS. **4** to **14**, a process for manufacturing a graphene membrane will be described in detail. When the respective figures of FIGS. **4** to **13** are referred to, the flowchart of FIG. **14** will be simultaneously referred to.

[0072] In order to manufacture the graphene membrane, first, as exemplarily shown in FIG. **4**, a graphene layer **10** is formed on a substrate **40** (Operation S**10**).

[0073] The substrate **40** may be formed of a catalytic metal. Ni, Co, Fe, Pt, Au, Al, Cr, Cu, Mg, Mn, Mo, Rh, Si, Ta, Ti, W, U, V, Zr and the like may be used as the catalytic metal, and the graphene layer **10** may be formed using chemical vapor deposition (CVD) on the catalytic metal. Hereinafter, the substrate **40** formed of a catalytic metal will be exemplarily described. **[0074]** However, various other methods, such as rapid thermal annealing (RTA), atomic layer deposition (ALD) and physical vapor deposition (PVD), may be used to form the graphene layer **10**.

[0075] Among these methods, in CVD, a catalytic metal **40** is located in a chamber, a carbon source is injected into the chamber and proper growth conditions are provided, thereby growing a graphene layer.

[0076] For example, as the carbon source, a gas, such as methane (CH_4) or acetylene (C_2H_2) , a solid, such as a powder or polymer, and a liquid, such as bubbling alcohol, may be supplied.

[0077] In addition, various carbon sources, such as ethane, ethylene, ethanol, acetylene, propane, butane, butadiene, pentane, pentene, cyclopentadiene, nucleic acid, cyclonucleic acid, benzene, toluene and the like, may be used.

[0078] For example, copper (Cu) may be used as the catalytic metal 40 and methane (CH_4) may be used as the carbon source.

[0079] When methane gas is injected into the chamber in the hydrogen atmosphere while maintaining a proper temperature on the catalytic metal **40**, methane and hydrogen react and thus, the graphene layer **10** is formed on the catalytic metal **40**. Formation of such a graphene layer **10** may be carried out at a temperature of about 300 to 1,500° C.

[0080] Copper (Cu) used as the catalytic metal **40** has low solubility to carbon and may thus be advantageous in terms of formation of a graphene monolayer.

[0081] As circumstances require, the graphene layer **10** may be formed while a chemical vapor deposition apparatus continuously supplies the catalytic metal **40** through a roller.

[0082] Thereafter, as exemplarily shown in FIG. **5**, the graphene layer **10** formed on the catalytic metal **40** may be transcribed into a supporter **20** (Operation S**20**).

[0083] Transcription of the graphene layer 10 into the supporter 20 may be carried out by a general process. For example, transcription of the graphene layer 10 into the supporter 20 may be carried out by bonding the supporter 20 to the graphene layer 10 and then removing the catalytic metal 40.

[0084] Such a supporter **20** may have the above-described structure and characteristics. That is, the supporter **20** may include a material having a net structure, for example, a non-woven fabric. Further, the supporter **20** may include a structure with a pattern of pores having a greater size than a porous pattern, which will be subsequently formed on the graphene layer **10**.

[0085] Thereafter, in order to form the pattern of pores on the graphene layer **10**, a porous block copolymer pattern may be formed on the graphene layer (Operation S**30**).

[0086] Formation of such a porous block copolymer pattern may include forming a block copolymer **60** in which a first polymer and a second polymer are covalently bonded to each other on the graphene layer **10**, as exemplarily shown in FIG. **6**, and self-assembling the block copolymer **60**, as exemplarily shown in FIG. **7**.

[0087] The block copolymer **60** means a form in which polymers having different characteristics are covalently bonded to each other. According to compositions between blocks forming the block copolymer **60**, the lengths of chains and mutual attraction coefficients, basic structures, such as lamellas, cylinders, and spheres, or various other three-dimensional nano-structures may be formed.

[0088] The block copolymer **60** formed in a thin film on the graphene layer **10** has fluidity at more than a glass transition temperature, and nano-structures (particularly, lamellas or cylinders) formed by self assembly may be arranged in a specific pattern on the graphene layer **10** so a to minimize free energy due to interfacial and surface attraction between the block copolymer **60** and the graphene layer **10**.

[0089] FIG. 8 illustrates one example of the self-assembled block copolymer 60 located on the supporter 20. Here, the graphene layer 10 is omitted.

[0090] As exemplarily shown in this figure, the block copolymer **60** may have a pattern of nano-structures of a cylinder type.

[0091] Here, a first polymer 61 and a second polymer 62 are self-assembled so as to form a nano-pattern. The first polymer and the second polymer 62 may be used in a regular ratio according to the size of a pore pattern which will be formed on the graphene layer 10 and the surface porosity of the graphene layer 10.

[0092] For example, in order to form the pattern shown in FIG. 8, the first polymer 61 and the second polymer 62 may be used in a mass ratio of 85:15.

[0093] Here, for example, the first polymer **61** may be polystyrene and the second polymer **62** may be PMMA.

[0094] Hereinafter, a process for forming a pattern of the porous block copolymer **60** to form the pore pattern on the graphene layer **10** will be described in detail.

[0095] First, the first polymer **61** and the second polymer **62** in a mass ratio of 85:15 which dissolve in toluene are spin-coated on the graphene layer **10** to a thickness of about 40 nm.

[0096] Thereafter, the first polymer 61 and the second polymer 62 are self-assembled through heat treatment at a temperature of 180° C. for 24 hours, thus forming a nano-pattern in which the first polymer 61 and the second polymer 62 are arranged in a cylinder shape, as exemplarily shown in FIGS. 7 and 8.

[0097] Thereafter, such a nano-pattern is developed, thus forming a porous pattern shown in FIG. **10**. A process for forming such a porous pattern may be carried out as described below.

[0098] First, ultraviolet (UV) light is radiated and thus breaks covalent bonds between the first polymer **61** and the second polymer **62**.

[0099] Thereafter, the second polymer (PMMA) **62** is developed through acid treatment and thus forms a porous block copolymer pattern having the structure shown in FIG. **10**.

[0100] The process for forming the porous pattern may be formed through ion beam etching, as exemplarily shown in FIG. **9**, and such ion beam etching may be executed together with the above-described process.

[0101] When such a nano-pattern is formed in such a manner, the second polymer **62** is removed and the porous block copolymer pattern having a plurality of pores **63** within the first polymer **61** may be formed, as exemplarily shown in FIGS. **10** and **11**.

[0102] FIG. 11 is a photograph illustrating the pattern of the porous block copolymer 60. From the photograph, it may be understood that a pattern having a plurality of pores 63 is formed within the first polymer 61.

[0103] Such a porous block copolymer pattern is a porous pattern having a high porosity and may have a pore size of 5 to 100 nm according to material ratios of the copolymer **60**.

[0104] The mean size of the pores 63 may be 5 to 50 nm, and more properly, be 10 to 30 nm. Further, the surface porosity of the block copolymer 60 may be 5 to 70%. Here, a surface porosity means a ratio of an area occupied by the pores 63 to the unit area of the block copolymer 60.

[0105] As described above, the block copolymer **60** may have the porous pattern including a plurality of pores **63** having a size of 5 to 100 nm while simultaneously having the above-described surface porosity.

[0106] That is, the block copolymer **60** may have the porous pattern having a pore size of 5 to 100 nm and a surface porosity of 5 to 70%.

[0107] Thereafter, a porous pore pattern is formed on the graphene layer **10** using the above-described pattern of the block copolymer **60** (Operation S**40**).

[0108] Formation of the porous pore pattern may include executing ion beam etching using oxygen, as exemplarily shown in FIG. **12**.

[0109] As exemplarily shown in FIG. 13, a pattern of pores 11 which is the same as the pattern of the block copolymer 60 may be formed on the graphene layer 10 through the above process. That is, since the pattern of the pores 11 is formed on the graphene layer 10 in a state in which the block copolymer 60 serving as a mask is attached closely to the graphene layer 10, the pattern of the pores 11 having a high porosity may be formed.

[0110] That is, as described above, the graphene layer **10** may have a pore size of 5 to 100 nm.

[0111] The mean size of the pores **11** of the graphene layer **10** may be 5 to 50 nm, and more properly, be 10 to 30 nm. Further, the surface porosity of the graphene layer **10** may be 5 to 70%.

[0112] As described above, the graphene layer **10** may have the porous pattern including a plurality of pores **11** having a size of 5 to 100 nm while simultaneously having the above-described surface porosity.

[0113] Thereafter, removal of the block copolymer 60 (Operation S50) may be performed. When the block copolymer 60 is removed, the above-described graphene membrane shown in FIGS. 1 to 3 may be formed.

[0114] Removal of the block copolymer **60** may be carried out by dissolving the block copolymer **60** in a proper solvent or burning the block copolymer **60** at a high temperature.

[0115] As circumstances require, the pattern of the block copolymer **60** may not be removed.

[0116] As apparent from the above description, the present invention provides a membrane designed to have a desired porosity, thus realizing a sufficient porosity and a uniform pore size and distribution.

[0117] Further, a high efficiency membrane having a monomer thickness which may not be implemented using conventional materials, such as polymers, ceramics and metals, may be acquired.

[0118] Further, since a block copolymer pattern is used and may thus be attached closely to a graphene layer, a method for manufacturing a graphene membrane having high precision without damage to the graphene layer may be provided.

[0119] Moreover, a method for manufacturing a graphene membrane which is mass-produced may be provided.

[0120] It will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the spirit or scope of the invention. Thus, it is intended that the present invention

covers the modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.

What is claimed is:

- 1. A graphene membrane comprising:
- a graphene layer having a porous pattern including a plurality of pores having a size of 5 to 100 nm; and
- a supporter configured to support the graphene layer and including a plurality of pores having a greater size than the pores of the graphene layer.

2. The graphene membrane according to claim 1, wherein the surface porosity of the graphene layer indicating a ratio of an area occupied by the pores to the unit area of the graphene layer is 5 to 70%.

3. The graphene membrane according to claim **1**, wherein the supporter includes a non-woven fabric or a polymer configured to continuously support the graphene layer.

4. The graphene membrane according to claim **1**, wherein the supporter is configured to discontinuously support the graphene layer.

5. The graphene membrane according to claim **4**, wherein the supporter configured to discontinuously support the graphene layer includes at least one of silicon, ceramic, a dielectric, a metal, or a polymer provided with holes.

6. The graphene membrane according to claim 1, further comprising a bonding layer disposed between the graphene layer and the supporter.

7. The graphene membrane according to claim **6**, wherein the bonding layer includes a pattern including a plurality of pores having a size which is equal to or greater than the pores of the graphene layer.

8. The graphene membrane according to claim 1, wherein the mean size of the pores of the graphene layer is 5 to 50 nm.

9. A method for manufacturing a graphene membrane comprising:

preparing a graphene layer located on a supporter;

- forming a porous block copolymer pattern on the graphene layer; and
- forming a porous pattern on the graphene layer using the porous block copolymer pattern.

10. The method according to claim **9**, wherein the formation of the porous block copolymer pattern includes:

- self-assembling a block copolymer, in which a first polymer and a second polymer are covalently bonded to each other, on the graphene layer; and
- developing the block copolymer so as to form the porous pattern.

11. The method according to claim 10, wherein the selfassembly of the block copolymer, in which the first polymer and the second polymer are covalently bonded to each other, on the graphene layer includes:

- spin-coating the first polymer and the second polymer in a dissolving state on the graphene layer; and
- executing heat treatment on the spin-coated first and second polymers.

12. The method according to claim **10**, wherein the development of the block copolymer includes:

radiating ultraviolet light to the block copolymer; and

executing acid treatment on the block copolymer.

13. The method according to claim **12**, wherein the development of the block copolymer includes executing ion beam etching on the block copolymer.

14. The method according to claim 10, wherein the first polymer is polystyrene and the second polymer is PMMA.

15. The method according to claim **9**, wherein the porous pattern includes a plurality of pores having a size of 5 to 100 nm.

16. The method according to claim **9**, wherein the formation of the porous pattern on the graphene layer includes executing ion beam etching.

17. The method according to claim 9, wherein the surface porosity of the graphene layer indicating a ratio of an area occupied by the pores to the unit area of the graphene layer is 5 to 70%.

18. The method according to claim 9, wherein the block copolymer has a pattern of cylinder-shaped nano-structures.

19. The method according to claim **9**, wherein the mean size of the pores of the graphene layer is 5 to 50 nm.

20. The method according to claim **9**, further comprising removing the porous block copolymer pattern.

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