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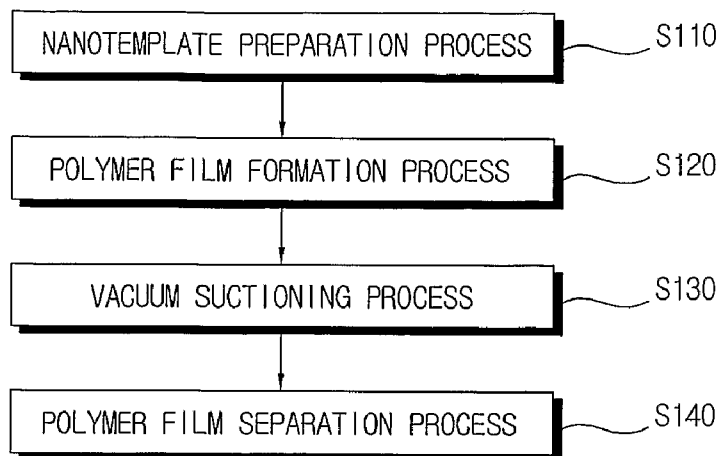
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(54) Title: METHOD OF FORMING NANOSTRUCTURE ON SURFACE OF A POLYMER FILM

[Fig. 1]



(57) Abstract: Provided is a method of forming nanostructures on a surface of a polymer film. The method includes: (a) preparing a porous nanotemplate having a plurality of nanoholes on one surface of template substance in a vacuum state; (b) preparing a polymer film on the surface of the nanotemplate and heating a surface of the polymer film contacting the nanotemplate; (c) vacuum suctioning the surface of a polymer film in contact with the nanotemplate inward the nanoholes, thereby forming a plurality of nanostructures on the surface of the polymer film; and (d) separating the surface-modified polymer film from the nanotemplate. According to the present invention, nanodots, nanobrushes, or nanofibers are easily formed on the surface of the polymer film and thus, the surface-modified polymer film can be used as various functional substances.



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## Description

# METHOD OF FORMING NANOSTRUCTURE ON SURFACE OF A POLYMER FILM

### Technical Field

- [1] The present invention relates to a method of forming nanostructures on a surface of a polymer film, and in particular, to a method of forming various nanostructures on a surface of a polymer film that can be used as a novel functional polymer film or a fiber substance in various industries in order to obtain a surface- modified polymer film.

### Background Art

- [2] When synthesized polymer substances, that is, plastic, were initially developed, they were used as an alternative to metal, wood, glass, ceramics, or leathers. Recently, however, they are no more alternatives and used as a necessary material for a novel substance in various industries, such as an electrical industry, an electronic industry, a mechanics industry, or a construction industry, because synthesized polymer substances are lightweight, strong, resistant to corrosion, and they can be colored, mass-produced, and easily processed.
- [3] In order to be used in various industries, polymer substances should have specific properties required by the corresponding industry.
- [4] Conventionally, synthetic polymers are prepared by polymerizing various monomers, but each polymer may have a limitation to be used as a specific application that may require very special properties.
- [5] As for a polymer film used as a novel substance having super water-repellent properties and a large surface area, research is performed in a direction in which a surface of the polymer film is modified to obtain desirable functions. That is, there is an increasing need to develop a method of forming nanostructures on a surface of a polymer film used as a novel substance requiring special surface properties such as super water-repellent property, good optical properties, novel electrical properties, etc.
- [6] According to a conventional method of processing a surface of a polymer film with a nanotemplate, a liquid polymer material obtained either by heating a thermoplastic polymer material or by dissolving a polymer into a solvent is attached to a porous nanoplate. Then, nanofiber structures can be formed on the polymer film by capillary force or surface wetting phenomenon.
- [7] That is, the liquid polymer material flows into nanoholes formed in the nanotemplate and then the resultant structure can be hardened to form a polymer film with

a nanofiber structure on it. Then, the polymer film is separated from the nanotemplate, thereby completing the manufacture of a polymer film having nanostructures on its surface.

[8] The polymer film prepared with the method described above may have, various special properties such as super water-repellent, good optical characteristics, desirable electrical properties due to the nanostructures formed on its surface, and thus can be used as a functional substance for a novel film or fiber substance.

[9] However, the conventional method of forming nanostructures on the surface of a polymer film described above has many disadvantages. For example, it is difficult to uniformly control the amount of the liquid polymer material flowing into nanoholes because the liquid polymer material is prepared and then the prepared liquid polymer material is poured onto a nanotemplate to form a polymer film. In addition, when the viscosity of the liquid polymer material is too high, the processing time may be prolonged, on the other hand, when the viscosity of the liquid polymer material is too low, a length of a nanostructure brush cannot be easily controlled.

[10] Accordingly, there is a need to develop a method of efficiently modifying a surface of a polymer film.

## **Disclosure of Invention**

### **Technical Problem**

[11] The present invention provides a method of efficiently and easily forming various nanostructures, such as nanodots, nanobrushes, or nanofibers, on a surface of a polymer film in order to produce a surface-modified polymer film that can be used as a novel substance.

### **Technical Solution**

[12] According to an aspect of the present invention, provided is a method of quickly and easily forming various nanostructures, such as nanodots, nanobrushes, or nanofibers, on a surface of a polymer film by vacuum suctioning, wherein the nanostructures formed on the surface of the polymer film may be controlled by changing at least one parameter selected from the group consisting of vacuum level inside the nanoholes, degree of external pressure, the temperature of nanotemplates, the temperature of a polymer, and a vacuum suctioning time.

### **Advantageous Effects**

[13] The method of forming nanostructures on a surface of a polymer film according to the present invention has following advantages:

- [14] First, various nanostructures, such as nanodots, nanobrushes, or nanofibers, can be quickly and easily formed on a surface of a polymer film, and thus, the surface-modified polymer film having various special properties such as super water-repellent properties, good optical and electrical properties, a large surface area, and stain resistance properties can be used as a novel polymer substance;
- [15] Second, various nanostructures, such as nanodots, nanobrushes, or nanofibers, can be formed by easily controlling the length of nanostructures formed on a surface of a polymer film, and various thermoplastic polymer materials can be used;
- [16] Third, the processing time is short and thus, producibility can be increased at low costs; and
- [17] Fourth, the method can be used in various industries to produce high functional and valued substances.

### **Brief Description of the Drawings**

- [18] FIG 1 shows a block flow chart illustrating a method of forming nanostructures on a surface of a polymer film by vacuum suctioning according to an embodiment of the present invention.
- [19] FIGS. 2-5 are schematic views illustrating the method of FIG 1.
- [20] FIGS. 6-9 are scanning electron microscopic (SEM) images of surface-modified polymer films prepared according to a method of forming nanostructures on a surface of a polymer film by vacuum suctioning.

### **Best Mode for Carrying Out the Invention**

- [21] According to an aspect of the present invention, provided is a method of forming nanostructures on a surface of a polymer film, the method including: (a) preparing a porous nanotemplate having a plurality of nanoholes on one side of the template substance in a vacuum state ; (b) preparing a polymer film on the surface of the nanotemplate and heating a surface of the polymer film in contact with the nanotemplate; (c) vacuum suctioning the surface of a polymer film contacting the nanotemplate inward the nanoholes, thereby forming a plurality of nanostructures on the surface of the polymer film ; and (d) separating the surface-modified polymer film from the nanotemplate.
- [22] The nanoholes may have a depth of 0.1 to 1000  $\mu\text{m}$  and a diameter of 10 to 2000 nm.
- [23] The thickness of the polymer film may be in a range of 0.1 to 1000  $\mu\text{m}$
- [24] In process (b), the surface of the polymer film is heated at a temperature ranging

from a glass transition temperature of a polymer used to form the polymer film to a temperature about 150°C higher than a melting point of the polymer.

- [25] In process (c), a length of the nanostructures is controlled by changing at least one parameter selected from the group consisting of vacuum level inside the nanoholes, degree of the external pressure, the temperature of nanotemplate, the temperature of a polymer, and a vacuum suctioning time.
- [26] Vacuum level inside the nanoholes may be in a range of 0.0001 to 0.9 bar, and the degree of the external pressure may be in a range of 0.1 to 3 bar.
- [27] The vacuum suctioning time is in a range of 1 to 3600 seconds.
- [28] The nanotemplate is formed of aluminium oxide or silicon, or other materials. The nanotemplate can be used as it is or it may be coated with a surfactant or subjected to a chemical reaction.
- [29] The polymer film that is surface-modified according to a method of forming nanostructures on a surface of a polymer film of the present invention can be used in one element selected from the group consisting of an optical film, an electronic display film, a solar cell, a biosensor, and a functional films for clothing fabrics.
- [30] However, use of the surface-modified polymer film is not limited to the applications described above. That is, the surface-modified polymer film can be used in any industry requiring a novel substance having various functions due to formation of nanostructures on a surface of the polymer film.
- [31] According to another aspect of the present invention, provided is a solar cell including: a bottom electrode on a plane substrate; a energy transforming bilayer; a transparent electrode; and an anti-reflective layer, which are sequentially formed in this order, wherein the energy transforming bilayer comprises a donor and acceptor layers having nanostructures prepared according to the method described above. Furthermore the anti-reflective layer can be used with the polymer film having nanostructures prepared according to the the method described above.
- [32] That is, the polymer film is surface-modified according to a method of forming nanostructures on a surface of a polymer film, wherein the method includes: (a) preparing a porous nanotemplate having a plurality of nanoholes on one side of the template substance in a vacuum state; (b) preparing a polymer film on the surface of the nanotemplate and heating a surface of the polymer film in contact with the nanotemplate; (c) vacuum suctioning the surface of a polymer film contacting the nanotemplate inward the nanoholes, thereby forming a plurality of nanostructures on the surface of the polymer film ; and (d) separating the surface-modified polymer film

from the nanotemplate.

[33] The present invention will now be described more fully with reference to the accompanying drawings, in which exemplary embodiments of the invention are shown. Terminologies used in the present specification and the claims thereof should not be construed based on conventional understandings or definitions in dictionaries, and should be understood in consideration of technical spirits of the present invention based on a principle that inventors may appropriately define their terminologies to describe the invention with the optimal method.

[34] Therefore, embodiments and drawings of the present specification are preferred embodiments of the present invention and do not completely, fully convey the spirits of the present invention. Therefore, it would be obvious that there could be various equivalent, different forms of the present invention on the filing date of the present application.

[35] Hereinafter, a method of forming nanostructures on a surface of a polymer film according to an embodiment of the present invention will be described with reference to FIGS. 1- 5.

[36] FIG 1 shows a block flow chart illustrating a method of forming nanostructures on a surface of a polymer film by vacuum suctioning according to an embodiment of the present invention. FIGS. 2-5 are schematic views illustrating the method of FIG 1.

[37] Referring to FIG 1, the method of forming nanostructures on a surface of a polymer film according to the current embodiment of the present invention includes: a nanotemplate preparation process (S110), a polymer film formation process (S120), a vacuum suctioning process (S130) and a polymer film separation process (S140).

[38] Referring to FIG 2, a porous nanotemplate 100 having a plurality of nanoholes 110 on one surface of the template substance is prepared in a vacuum state (S110).

[39] The nanoholes 110 shall determine the shape and number of nanostructures 210 to be formed on a surface of a polymer film 200 that will be described later.

[40] The nanoholes may have a depth of 0.1 to 500  $\mu\text{m}$  and a diameter of 10 to 2000 nm. Since the size of the nanostructures 210 to be formed on the polymer film 200 is dependent upon the depth and diameter of the nanoholes 110, the size of the nanostructures 210 to be formed on the polymer film 200 may be within the ranges described above.

[41] Likewise, the number of the nanostructures 210 to be formed on the surface of the polymer film 200 is determined by the number of the nanoholes 110.

[42] Referring to FIG 3, the polymer film 200 is formed on one surface of the nan-

otemplate 100 and a surface of the polymer film 200 in contact with the nanotemplate 100 is heated (S120).

[43] The thickness of the polymer film 200 formed on the surface of the nanotemplate 100 may be in a range of 0.1 to 1000  $\mu\text{m}$

[44] When the thickness of the polymer film 200 is less than 0.1  $\mu\text{m}$ , a difference between the thickness of the polymer film 200 and the size of the nanostructures 210 formed on the surface of a polymer film 200 may be too small, and therefore, the opposite surface of the polymer film 200 corresponding to the surface on which the nanostructures 210 are formed may be partially processed. On the other hand, when the thickness of the polymer film 200 is greater than 1000  $\mu\text{m}$ , the polymer film 200 is too thick and thus its use as a polymer film is limited.

[45] The surface of the polymer film 200 may be heated at a temperature ranging from a glass transition temperature of a polymer that is used to form the polymer film 200 to a temperature about 150°C higher than a melting point of the polymer.

[46] The polymer that is used to form the polymer film 200 may be any thermoplastic resin. For example, the polymer may be a thermoplastic resin having a low melting point or a thermoplastic resin having a high melting point.

[47] When the surface of the polymer film 200 is heated and the vacuum around the template is released, the nanostructures 210, such as nanodots, nanobrushes, or nanofibers, can be formed on the surface of the polymer film 200 by vacuum suctioning while the polymer film 200 retains its original structure.

[48] Referring to FIG 4, when the surface of the polymer film 200 is softened by heating and the vacuum around the template is released, the surface of a polymer film 200 contacting the nanotemplate 100 is vacuum suctioned toward the nanoholes 110, thereby forming a plurality of nanostructures 210 on the surface of the polymer film 200 (S130).

[49] The length of the nanostructures 210 may be controlled by changing at least one parameters out of various process parameters such as vacuum level inside the nanoholes 110, degree of the external pressure, the temperature of nanotemplate, the temperature of the polymer, and the vacuum suctioning time.

[50] That is, the vacuum pressure of the nanoholes 110 is adjusted to be in a range of 0.0001 to 0.9 bar and an external pressure outside the vacuum nanoholes 110 is adjusted to be in a range of 0.1 to 3 bar, thereby generating a pressure difference. Due to the pressure difference, the surface of the polymer film 200 is vacuum suctioned inward the nanoholes 110. The vacuum suctioning process is performed for 1 to 3600

seconds, and therefore, nanostructures 210 are formed on the surface of the polymer film 200.

[51] When the external pressure is less than 0.1 bar, the pressure difference is too small and the vacuum suctioning time may be prolonged. On the other hand, when the external pressure is more than 3 bar, the vacuum suctioning occurs too quickly and the length of nanostructures 210 may be difficult to controll.

[52] When the vacuum suctioning time is less than one second, the length of nanostructures 210 cannot be controlled. On the other hand, when the vacuum suctioning time is longer than 1 hour, productivity and efficiency may be decreased.

[53] Nanostructures 210 formed on the modified polymer film 200 may be in a form of a dot, a brush, or a fiber, according to the length of the nanostructures 210.

[54] Referring to FIG 5, after nanostructures 210 are formed on the polymer film 200 by vacuum suctioning, the polymer film 200 is separated from the nanotemplate 100 (S140).

[55] The nanotemplate 100 may be formed with aluminium oxide or silicon, but can also be formed with other materials. For example, the nanotemplate 100 may be formed with any metal or inorganic material that allows the polymer film 200 attached to the surface of the nanotemplate 100 and the nanoholes 110 to be easily separated from the nanotemplate 100 according to the principles of the present invention.

[56] The surface of the nanotemplate 100 may be coated with a surfactant or subjected to a chemical reaction in order to control surface properties.

[57] The surfactant may allow the polymer film 200 attached to the surface of the nanotemplate 100 and the nanoholes 110 to be easily separated from the nanotemplate 100. The surfactant may be a silicon-based surfactant, specifically polysiloxane-based surfactant or short chain hydrocarbons, fluorinated hydrocarbons. The silicon-based surfactant is a specific surfactant that is used in a coating process, such as a parting agent.

[58] The polysiloxane-based surfactant may be polydimethylsiloxane (PDMS).

[59] As described above, a high-quality surface-modified polymer film can be efficiently and easily prepared according to the method of forming nanostructures on a surface of a polymer film according to the current embodiment of the present invention.

[60] The modified polymer film can be used as a novel substance in many applications that requires a polymer film having nanostructures such as nanodots, a nanobrush, or nanofibers. For example, the surface-modified polymer film can be used as an optical film, a film for an electronic display, a solar cell, a biosensor, or a functional film for

clothing fabrics

[61] Specifically, the surface-modified polymer film can be used to produce a functional fabric as described above. For example, nanodots, a nanobrush, or nanofibers are formed on a polymer film and then the resultant polymer film can be laminated to a fabric to prepare a functional fabric.

[62] Unlike a nanofiber web prepared by electrospinning, the surface-modified polymer film can be directly laminated to a surface of a fabric, and thus, the obtained functional fabric may exhibit various special surface properties. Since the functional fabric prepared as described above includes a film having nanostructures on its surface, the functional fabric may exhibit additional excellent surface properties, in addition to water-repellent properties. Thus, the functional fabric can be used in various specialty clothing, such as relieving clothing, or sportswear for mountain climbing, skiing, swimming, or training.

[63] In addition, since, like toe pads of gecko, small sized lizard, nanostructures can be formed on the surface of a polymer film, the film having nanostructures on its surface can be used as a functional film substance to which a novel adhering property is required.

[64] Furthermore, when the surface-modified polymer film is used in a solar cell, energy conversion efficiency of the solar cell can be substantially improved. Recently, as techniques for solar cells are being quickly developed, researches to improve energy conversion efficiency are being extensively performed. In this background, use of the surface-modified polymer film may contribute to the solar cell technology by enhancing the energy conversion efficiency.

[65] Currently, among solar cells, silicon-based solar cells are widely available and show the highest energy efficiency. However, the silicon-based solar cells are expensive. Therefore, research into alternatives to the silicon-based solar cells has continued.

[66] That is, to solve the disadvantage of the silicon-based solar cell, relatively inexpensive solar cells such as multi-layered stack-type solar cells, organic solar cells, or dye-sensitized solar cells have been developed.

[67] When a functional polymer film having a nanostructure on its surface prepared according to the present invention is used in the solar cells described above, the energy conversion efficiency of a solar cell can be substantially improved.

[68] A solar cell including a interface-modified organic bilayer film according to the present invention consists of a plane substrate, a bottom electrode, a energy generating

bilayer (donor and acceptor layers), a transparent electrode, and an anti-reflective layer which are sequentially stacked in this order, and generates electric energy when light is absorbed from the sun and a free electron flows between the bilayer and the transparent electrode. The surface-modified film can be used also as an anti-reflective layer to reduce reflection loss of an incoming solar energy. The surface-modified film structure can also be used to form the interface structure of the bilayer converting the light energy into the electrical energy, and thus more electrical energy can be generated due to nanostructures at the interface of the bilayer and energy conversion efficiency of a solar cell can be improved.

[69] A method of preparing the surface-modified polymer film may include: a) preparing a porous nanotemplate having a plurality of nanoholes on one side of the template substance in a vacuum state; b) preparing a polymer film on the surface of the nanotemplate and heating a surface of the polymer film in contact with the nanotemplate; c) vacuum suctioning the surface of a polymer film contacting the nanotemplate inward the nanoholes, thereby forming a plurality of nanostructures on the surface of the polymer film; and d) separating the surface-modified polymer film from the nanotemplate.

[70] The method of preparing the surface-modified polymer film is the same as the method of forming nanostructures on a surface of a polymer film according to the previous embodiment, and thus, will not be described herein.

[71] Hereinafter, among various solar cells described above, an organic solar cell including an interface-modified organic bilayer prepared according to the present invention will be described in detail.

[72] The organic solar cell is an example of a solar cell including an interface-modified organic bilayer prepared according to the present invention. That is, a solar cell including an interface-modified organic bilayer prepared according to the present invention can be any type of organic solar cell that has better energy conversion efficiency by using an interface-modified bilayer structure in an energy transforming layer or using a surface-modified polymer film as an anti-reflective layer.

[73] Organic solar cells are developed to solve the disadvantages of silicon-based inorganic solar cells. Unlike silicon-based solar cells, organic solar cells do not require a clean room and can be easily produced at low costs. Due to these advantages, organic solar cells have been extensively studied as an alternative of a silicon-based solar cell.

[74] An organic solar cell can be easily mass-produced at low costs by using various methods of forming a polymer film.

- [75] However, the organic solar cell shows energy conversion efficiency lower than the inorganic solar cell. Such low energy conversion efficiency, though, may be overcome by using a interface-modified bilayer film prepared by using a method of forming nanostructures on a surface of a polymer film according to the present invention. The organic solar cell prepared described above may have high energy conversion efficiency while retaining its advantages.
- [76] The organic solar cell includes a 200 nm-thick bilayer of which the interface is modified to have nanostructure according to the present invention acting as a energy transforming layer interposed between a multi-layered bottom transparent electrode and a top electrode. The interface-modified bilayer absorbs photons when exposed to the sun and electrons and holes within a doner layer are activated to generate an effective current flowing to an electrode. Since the electrons and holes (exciton) has to move to the interface of the bilyer and electron has to cross the interface of the bilayer, the increased interface area of the interface-modified bilayer according to the present convention can contribute significantly to enhance the energy conversion efficiency.
- [77] To further improve a energy conversion efficiency of a solar cell, amount of the photons arriving at the bilayer should be increased. Therefore, when a polymer film that is surface-modified by using a method of forming nanostructures on a surface of a polymer film according to the present invention is used as an anti-reflective layer, loss due to the light reflection at the surface of a solar cell can be reduced and the absorbed light energy can be increased. Accordingly, low energy conversion efficiency of a conventional organic solar cell can be improved and an organic solar cell may show higher energy conversion efficiency.
- [78] In general, a solar cell includes a substrate, a bottom electrode, a energy transforming bilayer, a transparent electrode, and an anti-reflective layer, which are sequentially stacked, and are formed of different materials in different compositions from each other.
- [79] The substrate may be formed of glass. Also, the substrate can be a ceramic substrate formed of alumina, a metal substrate formed of stainless steel or copper tape, or a polymer substrate. The bottom electrode may be formed of a substance that has low specific resistance and excellent adhesive properties with respect to the substrate to prevent an exfoliation phenomenon caused by a thermal expansion coefficient difference.
- [80] The energy transforming layer consist of a p-type semiconducting doner layer and an n-type acceptor semiconducting layer. Therefore, a p-n junction is formed at the

interface between the donor and acceptor layers. If the bilayer is exposed to the sun light, free electrons and holes are generated at the p-n junction of the bilayer and the electrons move to n-type layer and holes move to p-type layer, thus, generating the direct current.

- [81]        Herein, to form the efficient p-n junction, the surface of the donor layer can be modified by forming the nanostructure with the present invention. Since the acceptor layer is formed on top of the donor layer, the structure of the acceptor layer will resemble the nanostructure of the donor layer. The increased interface area between the donor and acceptor layer will facilitate the formation of the free electron and holes, thus, enhancing the generated direct current.
- [82]        In addition, an anti-reflective layer can be formed on the transparent electrode to reduce sunlight reflection loss. When a polymer film that is surface-modified by using a method of forming nanostructures on a surface of a polymer film according to the present invention is used as the anti-reflective layer, the anti-reflective layer can reduce the reflection loss effectively due to the nanostructures of the modified polymer film, and therefore, reflection loss of absorbed sunlight can be reduced and the efficiency of a solar cell can be further improved.
- [83]        As described above, the size of a solar cell is limited and thus, to increase a energy conversion efficiency of the solar cell having the limited size, a interface-modified bilayer structure can be used in a energy transforming layer to maximize the interface area between an donor and an acceptor layer as well as in an anti-reflective layer by reduing the reflection loss at the surface of a solar cell.
- [84]        Accordingly, when the interface-modified bilayer is used in a energy transforming layer of a solar cell or used as an anti-reflective layer of a solar cell, a interface area of the energy transforming bilayer can be maximized and the reflection loss can be minimized by the anti-reflective layer. Therefore, an energy conversion efficiency of a solar cell can be greatly improved.
- [85]        In addition, the surface-modified polymer film has excellent super water-repellent properties, and can be used as an optic film or an anti-reflective film for various electronic display media.
- [86]        Furthermore, the surface-modified polymer film can be used as a nano-structured biosensor by selectively coating the tip of the nanostructures with Au, Ag, or other metals and then chemically combining with a functional organic material thereon.
- [87]        For example, as for a DNA hybridization biosensor, hybridization hardly occurs because Target DNA has a hard access to Probe DNA. However, if only the tip of the

nanostructures of the surface-modified polymer film are selectively coated with metal and then an organic substance is combined thereto, an interval between Probe DNAs is widened and therefore, Target DNA can be easily hybridized with Probe DNAs.

- [88] As described above, a polymer film that is surface-modified by using a method of forming nanostructures on a surface of a polymer film according to the present invention can be used as a useful functional substance in various industries. Due to various functions described above, the surface-modified polymer film can be used in, in addition to the applications described above, other industries.

### **Mode for the Invention**

- [89] Polymer films that are surface-modified by using a method of forming nanostructures on a surface of a polymer film according to the present invention were prepared according to Examples 1-4.
- [90] FIGS. 6-9 are scanning electron microscopic (SEM) images of polymer films that are surface-modified according to Examples 1-4.
- [91] Example 1: Preparation of polymer film having nanodots at its surface
- [92] Nanotemplate having nanoholes of a diameter of 45 nm and a depth of 20  $\mu\text{m}$  and polystyrene as a polymer film were prepared. The number of nanoholes was about 120 per 1  $\mu\text{m}^2$ .
- [93] Polystyrene film of a thickness of 500  $\mu\text{m}$  was prepared on the nanotemplate in a chamber at a pressure of 0.5 bar, and then the resultant polymer film was heated at 180°C for 120 seconds.
- [94] Then, the external pressure was adjusted to 1 bar and one surface of the polymer film was vacuum suctioned for 10 seconds to form nanodots having a length of about 0.1  $\mu\text{m}$  on the surface of the polymer film.
- [95] Then, the polymer film having nanodots was taken out from the chamber and cooled. The resultant polymer film was separated from the nanotemplate to obtain a surface-modified polymer film. The SEM image of the surface-modified polymer film is shown in FIG 6.
- [96] Example 2: Preparation of polymer film having nanobrushes at its surface
- [97] Nanotemplate having nanoholes of a diameter of 45 nm and a depth of 20  $\mu\text{m}$  and polystyrene film were prepared. The number of nanoholes was 120 per 1  $\mu\text{m}^2$ .
- [98] Polystyrene film of a thickness of 500  $\mu\text{m}$  was prepared on the nanotemplate in a chamber at a pressure of 0.001 bar, and then the resultant polymer film was heated at 200°C for 120 seconds.
- [99] Then, the external pressure was adjusted to 1 bar and one surface of the polymer

film was vacuum suctioned for 60 seconds to form nanobrushes having a length of about  $0.5\ \mu\text{m}$  on the surface of the polymer film.

[100] Then, the polymer film having nanobrushes was taken out from the chamber and cooled. The resultant polymer film was separated from the nanotemplate to obtain a surface-modified polymer film. The SEM image of the surface-modified polymer film is shown in FIG 7.

[101] Example 3: Preparation of polymer film having nanofibers at its surface

[102] Nanotemplate having nanoholes of a diameter of 45 nm and a depth of  $20\ \mu\text{m}$  and polyvinylfluoride (PVDF) polymer film were prepared. The number of nanoholes was 120 per  $1\ \mu\text{m}^2$ .

[103] PVDF film of a thickness of  $500\ \mu\text{m}$  was prepared on the nanotemplate in a chamber at a pressure of 0.001 bar, and then the resultant polymer film was heated at  $220^\circ\text{C}$  for 120 seconds.

[104] Then, the external pressure was adjusted to 1 bar and one surface of the polymer film was vacuum suctioned for 40 seconds to form nanofibers having a length of about  $10\text{-}20\ \mu\text{m}$  on the surface of the polymer film.

[105] Then, the polymer film having nanofibers was taken out from the chamber and cooled. The resultant polymer film was separated from the nanotemplate to obtain a non-aligned nanofibers on the surface of polymer film. The SEM image of the surface-modified polymer film is shown in FIG 8.

[106] Example 4: Preparation of polymer film having an aligned nanofibers structure at its surface

[107] Nanotemplate having nanoholes of a diameter of 100 nm and a depth of  $60\ \mu\text{m}$  and polyethylene (PE) polymer film were prepared. The number of nanoholes was 120 per  $1\ \mu\text{m}^2$ .

[108] PE film of a thickness of  $500\ \mu\text{m}$  was prepared on the nanotemplate in a chamber at a pressure of 0.001 bar, and then the resultant polymer film was heated at  $170^\circ\text{C}$  for 120 seconds.

[109] Then, the external pressure was adjusted to 1 bar and one surface of the polymer film was vacuum suctioned for 120 seconds to form aligned nanofibers having a length of about  $40\ \mu\text{m}$  on the surface of the polymer film.

[110] Then, the polymer film having nanofibers was taken out from the chamber and cooled. The resultant polymer film and nanotemplate was dipped in a 5 wt% sodium hydroxide solution to obtain a surface-modified polymer film. The SEM image of the surface-modified polymer film is shown in FIG 9.

[111] While the present invention has been particularly shown and described with reference to exemplary embodiments thereof, it will be understood by those of ordinary skill in the art that various changes in form and details may be made therein without departing from the spirit and scope of the present invention as defined by the following claims.

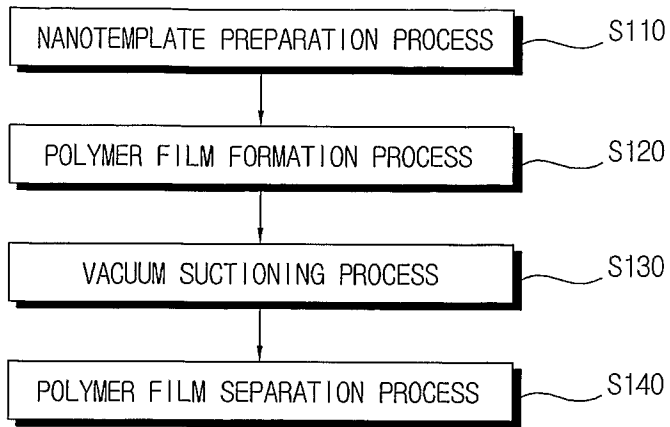
## Claims

- [1] A method of forming nanostructures on a surface of a polymer film, the method comprising:
- (a) preparing a nanotemplate having a plurality of nanoholes in a vacuum state in one surface;
  - (b) forming a polymer film on the surface of the nanotemplate and heating a surface of the polymer film in contact with the nanotemplate;
  - (c) releasing the vacuum state at the outside of the nanoholes and vacuum suctioning the surface of a polymer film contacting the nanotemplate inward the nanoholes, thereby forming a plurality of nanostructures on the surface of the polymer film ; and
  - (d) separating the polymer film from the nanotemplate.
- [2] The method of claim 1, wherein the nanoholes has a depth of 0.1 to 1000  $\mu\text{m}$  and a diameter of 10 to 2000 nm.
- [3] The method of claim 1, wherein a thickness of the polymer film is in a range of 0.1 to 1000  $\mu\text{m}$
- [4] The method of claim 1, wherein, in process (b) , the surface of the polymer film is heated at a temperature ranging from a glass transition temperature of a polymer used to a temperature 150°C higher than a melting point of the polymer.
- [5] The method of claim 1, wherein, in process (c), a length of the nanostructures is controlled by changing at least one parameter selected from the group consisting of vacuum level inside the nanoholes, degree of external pressure, the temperature of nanotemplate, the temperature of a polymer used to form the polymer film, and a vacuum suctioning time.
- [6] The method of claim 5, wherein vacuum level inside the nanoholes is in a range of 0.0001 to 0.9 bar, and the degree of external pressure is in a range of 0.1 to 3 bar.
- [7] The method of claim 6, wherein the vacuum suctioning time is in a range of 1 to 3600 seconds.
- [8] The method of claim 1, wherein the nanotemplate is formed of aluminium oxide or silicon, or the nanotemplate is coated with a surfactant or subjected to a chemical reaction.
- [9] The method of any one of claims 1-8, wherein the polymer film is used in one element selected from the group consisting of an optical film, an electronic

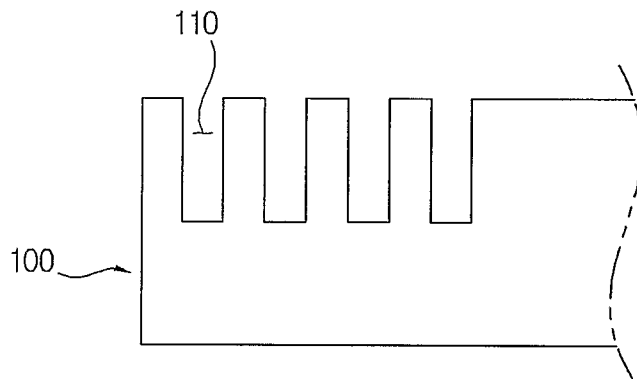
display film, a solar cell, a biosensor, and a functional clothing fabrics.

- [10] A solar cell comprising: a bottom electrode on a plane substrate; a energy transforming bilayer ; a transparent electrode; and an anti-reflective layer, which are sequentially formed in this order, wherein the energy transforming bilayer comprises a donor and acceptor layers having nanostructures prepared according to the method of any one of claims 1-8, or the anti-reflective layer is used with the polymer film having nanostructures prepared according to the method of any one of claims 1-8.

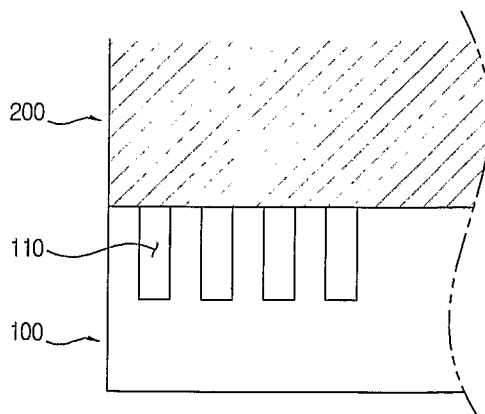
[Fig. 1]



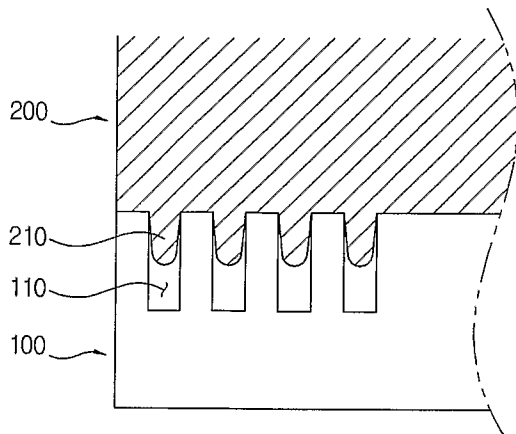
[Fig. 2]



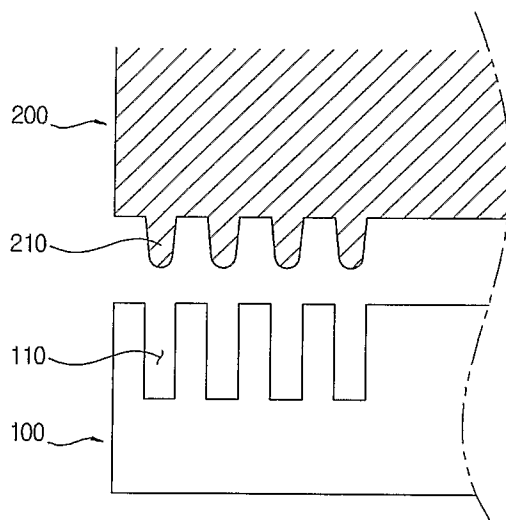
[Fig. 3]



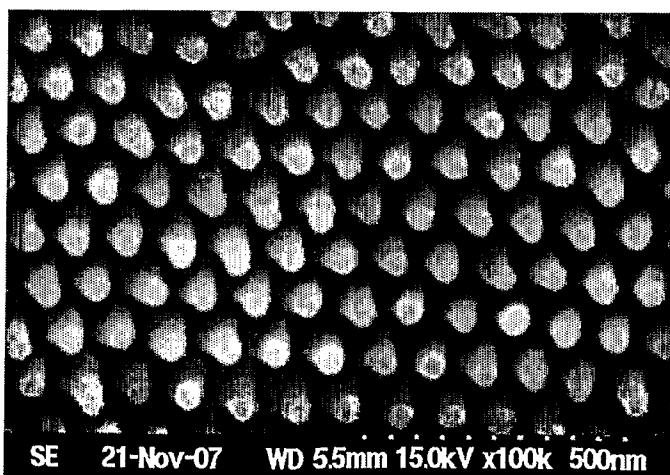
[Fig. 4]



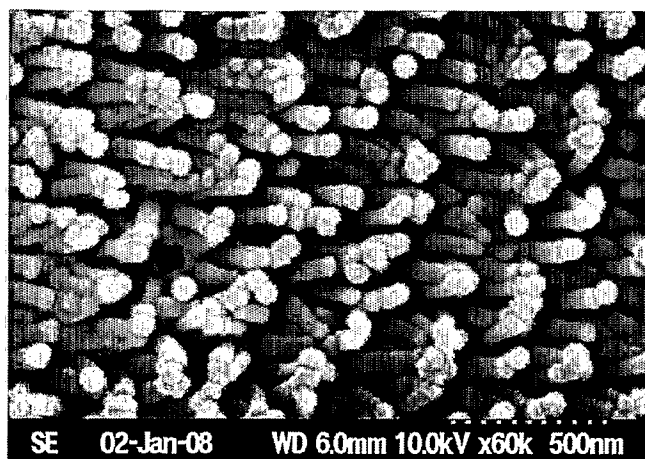
[Fig. 5]



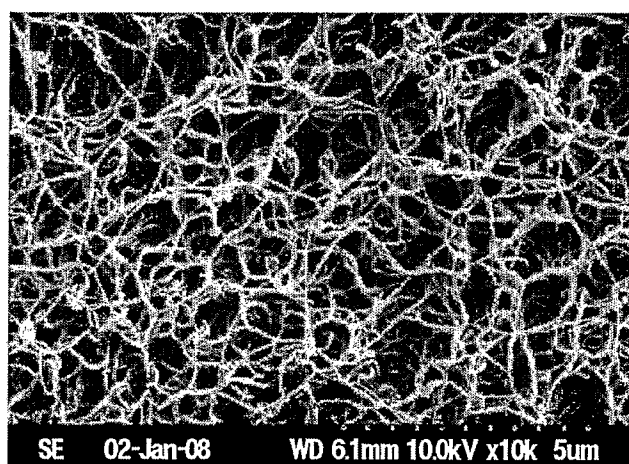
[Fig. 6]



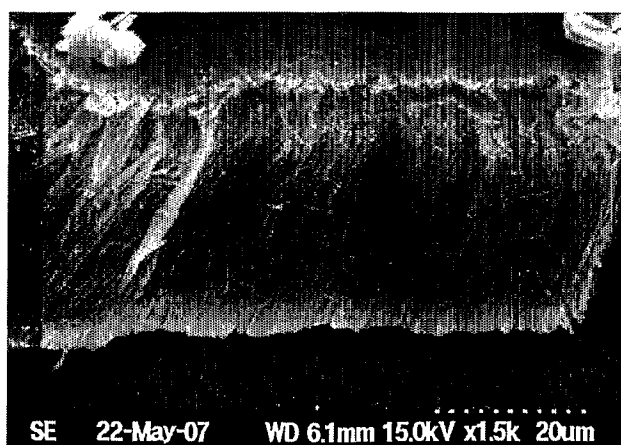
[Fig. 7]



[Fig. 8]



[Fig. 9]



**A. CLASSIFICATION OF SUBJECT MATTER****B82B 3/00(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)

IPC B82B 3/00

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 since 1975

Japanese Utility models and applications for Utility models since 1975

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

eKIPASS (KIPO internal) &amp; Keywords: nano, polymer, film, vacuum, template

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                | Relevant to claim No. |
|-----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| A         | KR 10-2003-0084279 A (FAR EAST ASIA CORPORATION et al.) 01 November 2003<br>See claims 1-9 & Figure 1                                                                                                                                                             | 1-10                  |
| A         | KR 10-2007-0015260 A (SAMSUNG ELECTRONICS CO., LTD.) 02 February 2007<br>See abstract and claims 1-51                                                                                                                                                             | 1-10                  |
| A         | KIM, DONG SUNG et al., Replication of high-aspect-ratio nanopillar array for biomimetic gecko foot-hair prototype by UV nano embossing with anodic aluminum oxide mold, Microsystem Technologies, March 2007, Vol. 13, No. 5-6, pp. 601-606<br>See 2 Experimental | 1-10                  |
| A         | KR 10-0747074 B1 (KUMOH NATIONAL INSTITUTE OF TECHNOLOGY) 07 August 2007<br>See claims 1-10                                                                                                                                                                       | 1-10                  |



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents:

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

25 FEBRUARY 2009 (25.02.2009)

Date of mailing of the international search report

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Authorized officer

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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/KR2008/004626**Patent document  
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