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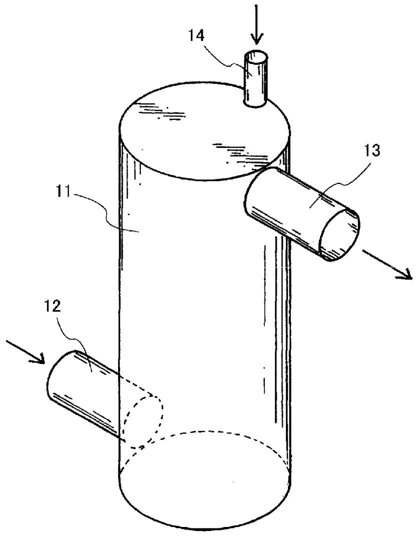
(54) METHOD FOR MANUFACTURING SURFACE-MODIFIED FIBER MATERIAL, AND SURFACE-MODIFIED FIBER MATERIAL

(57) The present invention provides a method of manufacturing a highly functional surface-modified fibrous material with high added value, to which a novel functionality is imparted while making use of the characteristics inherent in the fibrous material, by modifying the surface of a natural fibrous material derived from an animal or a plant, or of a synthetic fiber; and a surface-modified fibrous material thereby obtained. The method of manufacturing a surface-modified fibrous material according to the invention includes attaching an inorganic material on the surface of a fibrous material by a sol-gel reaction, while allowing the fibrous material to move via an air stream. Preferably, an atmospheric-pressure low-temperature plasma is further applied to the surface of the fibrous material on the surface of which the inorganic material has been attached, while allowing the fibrous material to move via an air stream.

FIG. 1



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Description

TECHNICAL FIELD

[0001] The present invention relates to a method of manufacturing a surface-modified fibrous material (hereinafter, also simply referred to as "manufacturing method") and a surface-modified fibrous material. More particularly, the present invention relates to a method of manufacturing a surface-modified fibrous material for obtaining a highly functional fibrous material, by enhancing the functionality of a natural fibrous material derived from an animal or a plant, or a synthetic fiber, by surface modification; and a surface-modified fibrous material thereby obtained.

BACKGROUND ART

[0002] In the field of fibrous materials and products, highly functional fibrous materials (so-called high-tech fibers) to which a novel functionality is added by modifying the fibrous materials themselves are actively developed in recent years, in addition to the development of novel synthetic fibrous materials. There have been proposed a variety of techniques which allow the functionalities which hitherto have been obtained by the improvement in the fibrous products, to be imparted to the fibrous materials themselves, which are the raw materials of the products. Such techniques serve to provide, for example, water absorbent fibers in which water absorbency of the fibrous materials themselves is enhanced, antibacterial fibers to which antibacterial properties are added, and super fibers having a strength capable of lifting an automobile having a weight of about 700 kg.

[0003] With the growing trend of preference for natural products in recent years, on the other hand, demand for natural fibers derived from animals and plants, such as silk and wool, is increasing, as for the fibrous materials as well. If various types of functionalities as described above can also be imparted to such natural fibers, it is possible to provide a fibrous material superior to conventional materials, while making use of the characteristics of the natural fibers which are absent in synthetic fibers.

[0004] However, the above described conventional techniques for enhancing the performance and functionality of the fibrous materials are developed for the improvement of the structure and the like of the synthetic fibers themselves, and are not applicable to natural fibers. In view of this, a surface modification technique for enhancing the functionality of a fibrous material has been proposed, which is applicable not only to a synthetic fiber, but also to a natural fiber.

[0005] For example, Patent Document 1 discloses a titanium oxide-containing natural fiber in which the surface of the fiber is plated with titanium oxide, and a method of manufacturing the same.

RELATED ART DOCUMENT

PATENT DOCUMENT

[0006] Patent Document 1: WO 98/053132

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0007] However, the technique disclosed in Patent Document 1 has not been sufficient, and realization of a surface-modified fibrous material with higher functionality has been demanded.

[0008] Accordingly, an object of the present invention is to provide a method of manufacturing a highly functional surface-modified fibrous material with high added value, to which a novel functionality is imparted while making use of the characteristics inherent in the fibrous material, by modifying the surface of a natural fibrous material derived from an animal or a plant, or of a synthetic fiber; and a surface-modified fibrous material thereby obtained.

MEANS FOR SOLVING THE PROBLEMS

[0009] The present inventors have found out, as a result of intensive studies, that the above mentioned problems can be solved by adopting the following constitution, thereby completing the present invention.

[0010] That is, the method of manufacturing a surface-modified fibrous material according to the present invention comprises attaching an inorganic material on the surface of a fibrous material by a sol-gel reaction, while allowing the fibrous material to move via an air stream.

[0011] In the manufacturing method according to the present invention, it is preferred that an atmospheric-pressure low-temperature plasma be applied to the surface of the fibrous material on the surface of which an inorganic material has been attached, while allowing the fibrous material to move via an air stream. In the manufacturing method according to the present invention, preferred examples of the inorganic material include titania, alumina, and ceramic. Further, in the manufacturing method according to the present invention, a natural fiber or a synthetic fiber can be used as the fibrous material. In particular, feathers, a powder or a microfiber made from cocoons, silk, wool, cotton, hemp, pulp, or a synthetic fiber, especially feathers, can be suitably used.

[0012] In addition, the surface-modified fibrous material according to the present invention is characterized by being manufactured by the above described manufacturing method according to the present invention.

EFFECTS OF THE INVENTION

[0013] According to the present invention, it is possible to impart a novel functionality not only to a synthetic fiber, but also to a natural fiber, while making use of the characteristics inherent in the fibrous material, and to obtain a highly functional surface-modified fibrous material with high added value.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014]

FIG. 1 is a schematic diagram showing a treatment apparatus used for applying a titania-attaching treatment to the surface of a fibrous material.
FIG. 2 is a schematic diagram showing a treatment apparatus used for applying a plasma irradiation treatment to a titania-attached fibrous material.
FIG. 3 is a schematic diagram showing a treatment apparatus used in Examples for applying the titania-attaching treatment to the surface of down.
FIG. 4(a) and FIG. 4(b) are photographs showing Ti gel.
FIG. 5(a) and FIG. 5(b) are photographs showing untreated down; and FIG. 5(c) and FIG. 5(d) are photographs showing a titania-attached down.
FIG. 6(a) and FIG. 6(b) are SEM photographs showing: (a) the untreated down; and (b) the titania-treated down.
FIG. 7(a) and FIG. 7(b) are spectral graphs showing the analysis results of EDX measurements of: (a) the untreated down; and (b) the titania-treated down.
FIG. 8 is a schematic diagram showing a treatment apparatus used in Examples for applying the plasma irradiation treatment to the titania-attached down.
FIG. 9 is a schematic diagram showing the configuration of a quadruple plasma torch system.
FIG. 10 is a partial sectional view showing the configuration of a plasma torch.
FIG. 11(a) and FIG. 11(b) are explanatory diagrams relating to a heat retention test of down.
FIG. 12(a) and FIG. 12(b) are graphs showing: (a) the temperature; and (b) the temperature change; in the heat retention test of down.
FIG. 13(a) and FIG. 13(b) are explanatory diagrams showing the state of temperature change at respective portions of comforters of: (a) Example 1; and (b) Comparative Example; 55 minutes after the start of heating.
FIG. 14(a) and FIG. 14(b) are graphs showing the changes in the internal temperature of the comforters with respect to: (a) the temperature; and (b) the temperature change.
FIG. 15 is a schematic diagram showing a treatment apparatus used for applying a blowing treatment to the treated down after washing.
FIG. 16 is an explanatory diagram showing the analysis results of the surface composition of each down, obtained by XPS.
FIG. 17 is a graph showing the C1s narrow spectra of the titania-treated down before and after the plasma treatment.
FIG. 18 is a graph showing the Ti2p narrow spectra of the titania-treated down before and after the plasma treatment.
FIG. 19 is an explanatory diagram showing the analysis results of the surface composition of a titania-attached and plasma-treated down after various times of washing, obtained by XPS.
FIG. 20 is a graph showing the changes in the concentration of Ti with respect to the number of times of washing.
FIG. 21 is an explanatory diagram showing the analysis results of the surface composition of a synthetic fiber, obtained by XPS.
FIG. 22 is an explanatory diagram showing the analysis results of the surface composition of silk, obtained by XPS.
FIG. 23 is an explanatory diagram showing the analysis results of the surface composition of wool, obtained by XPS.
FIG. 24(a) and FIG. 24(b) are explanatory diagrams showing a test apparatus used in a rigidity test of down.
FIG. 25 is an explanatory diagram showing the changes in the rigidity of the untreated down and the titania-attached and plasma-treated down, before and after the treatments.
FIG. 26 is an explanatory diagram showing the changes in the rigidity of the untreated down and the titania-attached

and plasma-treated down, before and after the washing.

FIG. 27 is an explanatory diagram showing the changes in the rigidity of the untreated down and the titania-attached and plasma-treated down, before and after the blowing treatment.

FIG. 28(a) and FIG. 28(b) are photographs showing an alumina-attached down.

FIG. 29 is an explanatory diagram showing the analysis results of the surface composition of the down before and after an alumina treatment, obtained by XPS.

FIG. 30 is a graph showing the XPS spectra of the down before and after the alumina treatment.

MODE FOR CARRYING OUT THE IVENTION

[0015] A preferred embodiment of the present invention will now be described in detail below, with reference to drawings.

[0016] In this embodiment, titania is used as an inorganic material to be attached on the surface of a fibrous material by sol-gel reaction. A specific description will be given below regarding the case in which titania is attached on the surface of a fibrous material by a sol-gel reaction of a titanium compound, while allowing the fibrous material to move via an air stream, in order to carry out a surface modification of the fibrous material.

[0017] In this embodiment, since titania is attached on the surface of a fibrous material while allowing the fibrous material to move via an air stream, a uniform treatment can be applied to the entire fibrous material. In addition, since the surface modification can be carried out while maintaining the shape and the characteristics inherent in the fibrous material, particularly in a natural fiber, it is possible to obtain a surface-modified fibrous material having a high quality. Therefore, by using the surface-modified fibrous material obtained according to this embodiment as a raw material, it is possible to realize a surface-modified fibrous product with high added value, in which the functionality of the fibrous material is utilized.

[0018] Specifically, a treatment for attaching titania (TiO_2, molecular weight: 79.87) to the surface of a fibrous material in this embodiment can be carried out, for example, by using titanium tetraisopropoxide (TTIP, molecular weight: 284.22) as the titanium compound, according to the following sol-gel reaction.

$$Ti\{OCH(CH_3)_2\}_4 + 2H_2O \text{ (water vapor)} \rightarrow TiO_2 + 4(CH_3)_2CHOH$$

[0019] FIG. 1 shows a schematic diagram of a treatment apparatus used for applying the titania-attaching treatment to the surface of a fibrous material, in the method of manufacturing a surface-modified fibrous material according to this embodiment. The treatment apparatus shown in FIG. 1 includes: an apparatus body 11 for carrying out the treatment; a feed inlet 12 for introducing the fibrous material into the apparatus body 11, a discharge outlet 13 for discharging the treated fibrous material from the apparatus body 11; and an introduction port 14 for introducing the titanium compound into the apparatus body 11.

[0020] In the treatment apparatus shown in FIG. 1, the introduction of the fibrous material into the apparatus body 11 and the discharging of the fibrous material from the apparatus body 11 are carried out via an air stream. Specifically, air is allowed to flow, for example at a speed of from 500 to 5,000 cm/s, particularly at about 2,000 cm/s, so that the fibrous material is allowed to move with the flowing air. Further, an opening may be provided at the upper portion or the like of the apparatus body 11, and the fibrous material may be directly fed into and retrieved from the apparatus body through the opening, and the method thereof is not particularly limited.

[0021] After introducing the fibrous material into the treatment apparatus 11, the titanium compound is introduced into the treatment apparatus 11 through the introduction port 14. When introducing the titanium compound, the compound can be introduced into the apparatus body 11 in the form of a mist, by spraying a solution of the titanium compound in an alcohol or the like via the introduction port 14. By injecting the solution of the titanium compound at a high pressure, at this time, it is possible to generate a transporting air stream rotating within the apparatus body 11 in the direction of height, and titania generated by the above described sol-gel reaction can be attached on the surface of the fibrous material filled in the apparatus body 11, while allowing the fibrous material to move via the transporting air stream.

[0022] In this embodiment, it is preferred that an atmospheric-pressure low-temperature plasma be further applied to the surface of the fibrous material on the surface of which titania has been attached. This allows titania attached on the surface of the fibrous material to be strongly fixed to the surface of the fibrous material, and thus it is possible to reliably prevent the peeling off of titania during the handling of the fibrous material after the surface modification, and to maintain the functionality imparted to a synthetic fiber or a natural fiber for a long period of time.

[0023] The atmospheric-pressure low-temperature plasma as used herein refers to a plasma which is generated under atmospheric pressure and at normal temperature of about 40°C or lower. By using the atmospheric-pressure low-temperature plasma for the treatment of the fibrous material, a pressure reduction is not required in the present invention, and thus the cost of facility and the treatment can be reduced. At the same time, since the treatment can be carried out at normal temperature, there is no risk of compromising the shape and the characteristics of the fibrous material to be treated. Such an atmospheric-pressure low-temperature plasma irradiation treatment can be carried out, for example using an atmospheric-pressure normal-temperature plasma jet generator, CAPPLAT, manufactured by Cresur Corporation. A gas for generating a plasma jet is not particularly limited, and any of various types of commonly used gases can be used. However, argon gas is preferred in terms of cost.

[0024] FIG. 2 shows a schematic diagram of a treatment apparatus used for applying a plasma irradiation treatment to the titania-attached fibrous material, in the method of manufacturing a surface-modified fibrous material according to the embodiment. The treatment apparatus shown in FIG. 2 includes: an apparatus body 21 for carrying out the treatment; a feed inlet 22 for introducing the titania-attached fibrous material into the apparatus body 21; a discharge outlet 23 for discharging the treated titania-attached fibrous material from the apparatus body 21; an irradiation device 24 for applying plasma to the fibrous material in the apparatus body 21; and a gas inflow port 25 for allowing air to flow into the apparatus body 21.

[0025] In the treatment apparatus shown in FIG. 2, the introduction of the titania-attached fibrous material into the apparatus body 21 and the discharging of the titania-attached fibrous material from the apparatus body 21 are carried out via an air stream. Specifically, air is allowed to flow, for example at a speed of from 500 to 5,000 cm/s, particularly at about 2,000 cm/s, so that the fibrous material is allowed to move with the flowing air.

[0026] In the apparatus shown in FIG. 2, as with the apparatus shown in FIG. 1, the introduction of air from the gas inflow port 25 allows for generation of a transporting air stream rotating within the apparatus body 21 in the direction of height. Therefore, in this embodiment, the plasma irradiation treatment can also be performed while allowing the titania-attached fibrous material to move via the transporting air stream, thereby allowing for a uniform application of the treatment to the entire titania-attached fibrous material.

[0027] Note that, in this embodiment, the treatment can be carried out while alternately switching between the introduction and discharge of the fibrous material into and out of the apparatus body, and between the introduction of the titanium compound and the introduction of air, in each of the apparatuses. Specifically, in each of the apparatuses, the fibrous material is first introduced into the apparatus body 11 or 21 through the feed inlet 12 or 22 via an air flow, with the introduction port 14 or the gas inflow port 25, and the discharge outlet 13 or 23 closed. Then the feed inlet 12 or 22 is closed, a titanium compound or air is introduced through the introduction port 14 or the gas inflow port 25, and the titania-attaching treatment or the plasma irradiation treatment is carried out. After the completion of the treatment, the introduction port 14 or the gas inflow port 25 is closed, and the treated fibrous material is retrieved from the discharge outlet 13 or 23. In this manner, the treatment of the fibrous material can be carried out in batches. It is needless to say, in this embodiment, that the positions of the feed inlet 12, the discharge outlet 13 and the introduction port 14 to be provided on the apparatus body 11, as well as the positions of the feed inlet 22, the discharge outlet 23, the irradiation device 24, and the gas inflow port 25 to be provided on the apparatus body 21, are not limited to those in the examples shown in FIG. 1 and FIG. 2, and the positions may be changed as desired and as appropriate.

[0028] Further, it is preferred that the interior of the apparatus, such as a nozzle and the like, be cleaned with an alcohol or the like after the titania-attaching treatment, to maintain the apparatus clean.

[0029] As the fibrous material to be used in this embodiment, any fibrous materials including natural fibers and synthetic fibers can be used. However, it is of particular significance that the invention enables the manufacture of a surface-modified fibrous material, using as a base material, a synthetic fiber for which functionality enhancement by a functional material has been barely performed, and especially, a natural fiber, namely, a natural fibrous material derived from an animal or a plant. Examples of the fibrous material derived from an animal or a plant include feathers, a powder or a microfiber made from cocoons, silk, wool, cotton, hemp, and pulp. As used herein, the powder made from cocoons refers to a powder of silk, so to speak, obtained by crushing the cocoons themselves, not by drawing a thread of raw silk from the cocoons; and the microfiber made from cocoons refers to minute fuzz attached on the surface of the cocoons. The silk as used herein includes both a single silk thread drawn from cocoons and a spun silk yarn, and also includes a silk thread obtained by a specialized method, such as SILKWAVE (trade name (registered trademark, manufactured by Mapepe Co. Ltd.), and the like. Further, fibrous materials obtained from fibrous raw materials which are used for paper products in general are also included in the present invention.

[0030] In the surface-modified fibrous material obtained according to this embodiment, the attachment of titania provides an effect of increasing the bulkiness of the fibrous material itself. In particular, the quality of feathers is represented by their bulkiness (filling power). Therefore, the application of the present invention to feathers provides an advantage of serving to provide high quality and low cost feathers, by enabling to significantly increase the bulkiness of the feathers, and thus to obtain a high quality feathers from low quality and low cost feathers.

[0031] In the manufacturing method according to the embodiment, when the titania-attaching treatment of 2 t of down using TTIP is carried out for 20 days per month (160 hs), the treatment can performed at a cost of 70,000 to 700,000 yen/month, to achieve the amount of titania supported on the down of from 0.1 to 1% by mass. Further, an additional cost in the case of using the atmospheric-pressure low-temperature plasma in combination is about 60,000 yen/month. Thus, an advantage of low manufacturing cost can be provided.

[0032] Another embodiment of the present invention may be, for example, one in which alumina is used as the inorganic material to be attached on the surface of the fibrous material by the sol-gel reaction.

[0033] In the another embodiment, the same operation as in the above described embodiment can be carried out except for using an aluminum compound, preferably aluminum isopropoxide, instead of the titanium compound in the above embodiment.

[0034] The effect of increasing the bulkiness of the fibrous material itself can be obtained by the attachment of alumina, in the surface-modified fibrous material obtained according to the another embodiment as well. In particular, the attachment of alumina to feathers provides an advantage of serving to provide high quality and low cost feathers, by enabling to significantly increase the bulkiness of the feathers, and thus to obtain a high quality feathers from low quality and low cost feathers.

[0035] Still another embodiment of the present invention may be, for example, one in which a ceramic is used as the inorganic material to be attached on the surface of the fibrous material by the sol-gel reaction.

[0036] In the still another embodiment, the same operation as in the above described embodiment can be carried out, except for using a ceramic compound instead of the titanium compound in the above described embodiment. Further, the effect of increasing the bulkiness of the fibrous material itself can be obtained by the attachment of a ceramic, in the resulting surface-modified fibrous material as well. Accordingly, as with the case of attaching titania or alumina, the attachment of a ceramic to feathers enables to significantly increase the bulkiness of the feathers, and thus to obtain a high quality feathers from low quality and low cost feathers.

EXMAPLES

[0037] The present invention will now be described in further detail, with reference to Examples.

Example 1

(Preparation of Ti Sol)

[0038] A quantity of 100 ml of titanium tetraisopropoxide (TTIP) was dissolved in 900 ml of methanol dehydrated by a molecular sieve. To the resultant, 10 ml of a 1.5M HCl aqueous solution was added, followed by stirring, to prepare a Ti sol.

[0039] The weights of methanol and the Ti sol before and after spraying for 1 minute were measured 3 times at an N_2 pressure of about 0.07 MPa, and the measured values were averaged to obtain a mean value, thereby confirming the liquid spray velocity of the nozzle. As a result, the liquid spray velocity was 11.4 g/min in the case of methanol. In contrast, the liquid spray velocity of the Ti sol was 8.5 g/min, which was slightly decreased probably due to high viscosity, but not significantly different, as compared to that of methanol. As shown in Table 1, when the period of time required for carrying out the titania-attaching treatment to down as a fibrous material was calculated from the liquid spray velocity obtained above and the concentration of the Ti sol, the time required to add 1% by mass of TiO_2 to 5 g of down was about 11 seconds. Therefore, in the following Example 1, the treatment time was set to 15 seconds.

[Table 1]

Amount of drown (g)	TiO_2 ratio (%)	Amount of TiO_2 (g)	Spray velocity of Ti sol (g/min)	Ti sol concentration (wt%)	Spray velocity of TTIP (g/min)	In terms of TiO_2 (g/min)	Spray velocity of TiO_2 (g/s)	Required time (s)
5	1	0.05	8.5	11.8	1.0	0.3	4.7×10^{-3}	10.6

(Titania-Attaching Treatment Apparatus)

[0040] The titania-attaching treatment was applied to down as a fibrous material, using a treatment apparatus having the configuration shown in FIG. 3. The treatment apparatus shown in FIG. 3 includes an apparatus body 31 for carrying out the attachment of titania to down; an injection inlet 32 for injecting air; a discharge outlet 33 for discharging the treated down from the apparatus body 31; and an introduction port 34 for introducing TTIP into the apparatus body 31.

[0041] To the injection inlet 32 for injecting air, a blower 36 is connected through a valve 35. A nozzle 37 for spraying a titanium compound is disposed to the introduction port 34, and a flow passage 39a connected to the nozzle 37 is configured to be able to communicate with a flow passage 39b on the side of the atmosphere, or with a flow passage 39c on the side of the titanium compound, by switching a three-way cock 38. The flow passage 39c is further configured to be able to communicate with a flow passage 39d on the side of the Ti sol or a flow passage 39e on the side of methanol, by switching a three-way cock 40, and an N_2 balloon 43 is connected to a Ti sol container 41 and a methanol container 42. Further, the discharge outlet 33 is connected to a storage container 44 for storing the treated down. Still further, an opening 45 for feeding down is provided on the upper portion of the apparatus body 31, and mesh portions M for discharging gas are each provided on the upper portion of the apparatus body 31, and on the upper portion of the storage container 44.

(Titania-Attaching Treatment)

[0042] First, 5 g of down was introduced into the apparatus body 31 through the opening 45 of the apparatus body 31, with the valve 35 provided in the injection inlet 32 and the discharge outlet 33 closed. Then the opening 45 was closed, the three-way cock 38 was switched so as to allow communication between the flow passage 39a on the side of the nozzle 37 and the flow passage 39b on the side of the atmosphere, and N_2 gas was allowed flow through the nozzle 37. The pressure of N_2 gas during the treatment was set to about 0.07 MPa.

[0043] Subsequently, the three-way cock 40 was switched so as to allow communication between the flow passage 39c on the side of three-way cock 38 and the flow passage 39d on the side of the Ti sol. Then the three-way cock 38 was switched so as to allow communication between the flow passage 39a connected to the nozzle 37 and the flow passage 39c, and a mist of the Ti sol was sprayed into the apparatus body 31 for 15 seconds. In this manner, the titania-attaching treatment was applied to the surface of the down, while allowing the down to move rotationally within the apparatus body 31 in the direction of height.

[0044] After the completion of the treatment, the three-way cock 40 was switched so as to allow communication between the flow passage 39c on the side of the three-way cock 38, and the flow passage 39e on the side of methanol, to wash the nozzle 37 with methanol. Then the three-way cock 38 was switched so as to allow communication between the flow passage 39a connected to the nozzle 37 and the flow passage 39b on the side of the atmosphere, to discharge methanol remaining in the nozzle 37. Further, the flow of N_2 gas was terminated, the opening 45 and the mesh portion M provided on the upper portion of the apparatus body 31 were closed, and the blower 36 was activated with the valve 35 open, to transfer the treated down to the storage container 44.

[0045] FIG. 4(a) and FIG. 4(b) show the photographs of the Ti gel, FIG. 5(a) and FIG. 5(b) show the photographs of untreated down, and FIG. 5(c) and FIG. 5(d) show the photographs of titania-attached down, all obtained by a digital microscope (VHX-600; manufactured by KEYENCE CORPORATION). As shown in the figures, when the untreated down and the titania-attached down are compared, no change in the feather structure is observed in the titania-attached down after the treatment, and it can be seen that the feather structure is maintained. Further, the observation by the digital microscope revealed that the Ti gel is in the form of a film. Since no powder-like deposit is observed in the titania-treated down as well, it is thought that titania is covering the surface of the down in the form of a thin film. Further, the SEM (scanning electron microscope) photographs of (a) the untreated down and (b) the titania-treated down, are shown in FIG. 6(a) and FIG. 6(b), respectively. It is observed from the photographs that, the surface of the untreated down is smooth and nothing is attached thereon, while on the other hand, fissures and a minute amount of particle-like deposits are present on the surface of the titania-treated down, even though the surface thereof is smooth. In addition, the spectral graphs showing the analysis results of EDX (energy dispersive X-ray spectroscopy) measurements of (a) the untreated down, and (b) the titania-treated down, are shown in FIG. 7 (a) and FIG. 7 (b), respectively. It can be seen from the results that, no titanium is detected in the untreated down in the EDX measurement as well, while on the other hand, titanium is detected in the deposited portion of the titania-attached down. These results confirmed that there is hardly any difference in the shape between the titania-treated down and the untreated down, and that titania is covering the down as a uniform film.

(Plasma Irradiation Treatment Apparatus)

[0046] The plasma irradiation treatment to the titania-attached down was carried out using a treatment apparatus having the configuration shown in FIG. 8. The treatment apparatus shown in FIG. 8 includes an apparatus body 51 for carrying out the plasma irradiation treatment to down; an injection inlet 52 for injecting air; a discharge outlet 53 for discharging the treated down from the apparatus body 51; an irradiation device 54 for applying plasma to the down in the apparatus body 51; and a gas inflow port 55 for allowing air to flow into the apparatus body 51.

[0047] A blower 56 is connected to the injection inlet 52 for injecting air. The discharge outlet 53 is connected to a storage container 58 for storing the treated down, through a valve 57. A bag made of fabric is used as the storage container 58. Further, an opening 59 for feeding down and a mesh portion M for discharging gas are provided on the upper portion of the apparatus body 51. Still further, the irradiation device 54 is connected to a high voltage power supply HV As the irradiation device 54, an atmospheric-pressure normal-temperature plasma jet generator, CAPPLAT, (manufactured by Cresur Corporation) equipped with a quadruple plasma torch system as shown in FIG. 9 was used.

[0048] The quadruple plasma torch system shown in FIG. 9 includes four plasma torches 61 which are disposed in parallel at intervals of 40 mm. In FIG. 9, reference numeral 62 denotes an acrylic plate, reference numeral 63 denotes a connector, and reference numeral 64 denotes a vinyl chloride tube. Further, FIG. 10 shows a partial sectional view of the configuration of the plasma torch 61. As shown in FIG. 10, the plasma torch 61 includes a glass capillary 65; a Cu pipe (outer diameter: 8 mm, inner diameter: 7 mm, high voltage electrode) 66 covering the outer periphery of the glass capillary 65; a double-layered silicone tube (outer diameter: 12 mm, inner diameter: 8 mm; and outer diameter: 16 mm, inner diameter: 12 mm) 67 covering one end of the Cu pipe 66; and a silicone tube 68 covering the glass capillary 65 at the other end side of the Cu pipe 66. Further, a pinch cock 69 is attached to the silicone tube 68, and a Cu tape (width: 20 mm, earth electrode) 70 and a metal mesh (150 mesh) 71 are disposed on the side of the double-layered silicone tube 67 of the plasma torch 61.

[0049] The plasma irradiation was carried out by applying a voltage of ± 8kV in the form of pulses, at 20 kHz, and using Ar gas as the plasma gas at 20 LPM (l/min).

(Plasma Irradiation Treatment)

[0050] First, 5 g of the titania-treated down was introduced into the apparatus body 51 through the opening 59 of the apparatus body 51, with the valve 57 closed. Then the opening 59 was closed, and air was allowed to flow into the apparatus body through the gas inflow port 55. In cases where the down is not disentangled, air is blown through the injection inlet 52, using the blower 56.

[0051] Next, under the conditions of atmospheric pressure and room temperature, Ar gas was supplied to the plasma torches of the irradiation device 54 and a high voltage was applied thereto, and then plasma was applied to the down for 30 seconds, while allowing the down to move rotationally within the apparatus body 51 by air in the direction of height. Subsequently, the supply of Ar gas and air was terminated, the mesh portion M was closed, and the blower 56 was activated with the valve 57 open, to transfer the treated down to the storage container 58.

[0052] Further, according to the method as described above, a synthetic fiber (polyester), silk, and wool were treated in the same manner.

(Heat Retention Test of Down)

[0053] A quantity of 20 g of down subjected to the titania-attaching treatment and the plasma irradiation treatment, and 20 g of untreated down were used to prepare the comforter samples of Example 1 and Comparative Example, respectively, each having a size of 500 mm × 380 mm. The evaluation of these comforter samples was carried out as follows.

[0054] First, a ribbon heater (diameter: 80 mm, height: 40 mm) was adjusted to about 40°C by a variable transformer. After measuring the temperature of each of the comforters before heating, a ribbon heater 82 adjusted to 40°C was placed under a comforter 81 so that the ribbon heater 82 was positioned at the central portion of the comforter 81, as shown in FIG. 11(a), and the ribbon heater 82 was left to stand on a mat 83. Then a paper guide 84 as shown in FIG. 11(b) was placed on the comforter 81, and the temperature of the top surface (outer side) of the comforter 81 was measured by a radiation thermometer 55 minutes after the start of the heating, at each of the numbered-locations of the paper guide 84 in the order of the numbers. The measurement of the temperature at location 1 of the paper guide 84 alone was carried out every 10 minutes after the start of the heating.

[0055] FIG. 12(a) and FIG. 12(b) are graphs showing the measurement results of the temperature of the top surface of the comforters at location 1 of the paper guide, with respect to: (a) the temperature; and (b) the temperature change. FIG. 13(a) and FIG. 13(b) are explanatory diagrams showing the state of temperature change at respective portions of the comforters of: (a) Example 1; and (b) Comparative Example; 55 minutes after the start of the heating. Further, FIG. 14(a) and FIG. 14(b) are graphs showing the changes in the internal temperature of the comforters, with respect to: (a) the temperature; and (b) the temperature change.

[0056] As a result, in the comforter sample of Comparative Example in which the untreated down was used, the increase in the surface temperature almost reached 4°C over time, whereas in the comforter sample of Example 1 in which the treated down was used, the increase in the surface temperature did not exceed 2°C. It can be seen from the results that the treated down has a higher heat retention as compared to the untreated down, thereby preventing the escape of heat to the exterior of the comforter.

[0057] Further, the temperature of the ribbon heater 82, which had been set at about 40°C, started to increase after placing the heater inside the comforter 81. In the treated down, the increase in the temperature was higher as compared to that in the untreated down, perhaps because heat is less likely to escape to the exterior of the comforter.

(Washing Resistance Test of Treated Down)

[0058] First, a cotton fabric having a size of 450 mm × 100 mm was folded in half. After sewing two sides of the fabric, 3 g of down was placed therein, and then the remaining side was sewn to prepare a washing sample. i) A quantity of 5 ml of neutral detergent was dissolved in 2 L of water (about 25°C). The washing sample was placed into the resultant, and washed 40 times with pressing, followed by draining. ii) Next, the washing sample was washed 40 times with pressing in water to carry out rinsing and draining. This step was repeated twice. The above described i) and ii) were repeated 10 times, and the sample was then dried in a dryer controlled at 60°C overnight.

(Blowing Treatment of Treated Down After Washing)

[0059] A blowing treatment of the washed down was carried out using the blowing treatment apparatus shown in FIG. 15. The apparatus shown in FIG. 15 includes an apparatus body 91 for carrying out the blowing treatment of down; a blower 92 for blowing air into the apparatus body 91; and a valve 93. An opening 94 for feeding down into the apparatus body 91 and a mesh portion M for discharging the air inside the apparatus body 91 are provided at the upper portion of the apparatus body 91.

[0060] First, the down was retrieved from the washed cotton fabric, the retrieved down was fed into the apparatus body 91 through the opening 94 with a funnel, and the opening 94 was closed. Then the valve 93 was closed, the blower 92 was activated, and the down inside the treatment apparatus 91 was subjected to the blowing treatment (air flow velocity: 1600 cm/s) for 10 minutes. Thereafter, the down was retrieved from the treatment apparatus 91.

(XPS Measurement of Down)

[0061] The surface composition of the untreated down, the titania-attached down, and the down subjected to the plasma treatment after attaching titania thereto, were analyzed by XPS (X-ray photoelectron spectroscopy). As the measurement apparatus, ESCA 5600 manufactured by PerkinElmer Inc. was used, and the measurement was carried out under the conditions of X-ray source: Mg Kα, 14 kV, 400 W, and TOA: 45°. FIG. 16 shows the analysis results of the surface composition of each down, obtained by XPS. Further, FIG. 17 and FIG. 18 show the C1s and Ti2p narrow spectra, respectively, of the titania-treated down before and after the plasma treatment.

[0062] It can be seen from the results shown in FIG. 16 that the surface of the down is coated with titanium, by carrying out the titania treatment. Further, the results shown in FIG. 17 and FIG. 18 indicate that the application of the plasma treatment to the titania-treated down does not cause the alteration of the feathers, while on the other hand, it is assumed that the amount of impurities is decreased, since the peak position of Ti shows a shift to the higher energy side, nearing to 459 eV of TiO_2.

[0063] FIG. 19 shows a graph illustrating the analysis results of the surface composition, obtained by XPS, of the titania-attached and plasma-treated down, after 1 to 10 times of washings; and FIG. 20 shows a graph illustrating the changes in the concentration of Ti, with respect to the number of times of washing. These results show that there is only a little difference in the Ti concentration between the titania-attached and plasma-treated down before the washing, and the titania-attached and plasma-treated down after the washing, and thus, it is assumed that washing does not cause the exfoliation of titanium.

[0064] At the same time, the surface compositions of the synthetic fiber, silk and wool which had been treated in the same manner as the down were also analyzed by XPS. FIG. 21 to FIG. 23 show the analysis results of the surface compositions obtained by XPS of the synthetic fiber, silk and wool, respectively. It can be seen from the results shown in FIG. 21 to FIG. 23 that each of the surfaces of the synthetic fiber, silk and wool is coated with titanium, by carrying out the titania treatment.

(Rigidity Test of Down)

[0065] The changes in the rigidity before and after the treatments, the changes in the rigidity before and after the washing, and the changes in the rigidity before and after the blowing treatment, of the untreated down, and the titania-attached and plasma-treated down were evaluated. Specifically, i) as shown in FIG. 24(a), 1.5 g of down D was fed into an acrylic pipe 101 having a size of an outer diameter of 49 mm, an inner diameter of 45 mm, and a height of 500 mm, and a height h_1 of the down D was measured, with a lid (2.5 g, made of expanded polystyrene) 102 and a weight (50 g) 103 placed on the down D. Subsequently, ii) as shown in FIG. 24(b), the weight 103 and the lid 102 were removed, and a height h_2 of the down D was measured again. After puffing up the squeezed down, the above described steps i) and ii) were repeated about 10 times. The results are shown in FIG. 25 to FIG. 27.

[0066] It can be seen from the results shown in FIG. 25 to FIG. 27 that the decrease in the height of the titania-attached and plasma-treated down was smaller when the weight was placed thereon, and thus the treated down has a higher rigidity, as compared to the untreated down. Further, although the recovery of the height occurred immediately after the removal of the weight, the degree of the recovery was not so high. When the elastic modulus of the down is calculated from the strain, the weight of the weight 103, and the cross-sectional area, the titania-attached and plasma-treated down has a higher elastic modulus as compared to the untreated down, revealing that the treated down has a higher quality.

[0067] Further, it can be seen that the titania-attached and plasma-treated down has a higher rigidity as compared to the untreated down, even after the washing. The titania-attached and plasma-treated down also has a higher elastic modulus as compared to the untreated down, revealing that the effect of the treatment is retained even after the washing. Although the difference between the untreated down and the titania-attached and plasma-treated down was reduced after the washing, the difference between the untreated down and the titania-attached and plasma-treated down was increased again, by subjecting the washed down to the blowing treatment.

Example 2

[0068] The same procedure as in Example 1 was repeated except that aluminum isopropoxide was used instead of titanium tetraisopropoxide, to prepare an Al sol. Then an alumina-attaching treatment was carried out in the same manner as in Example 1.

[0069] FIG. 28(a) and FIG. 28(b) show the photographs of the alumina-attached down, obtained by a digital microscope (VHX-600; manufactured by KEYENCE CORPORATION). As shown in FIG. 28(a) and FIG. 28(b), no change in the feather structure is observed when the untreated down and the alumina-attached down are compared, and it can be seen that the feather structure is maintained.

[0070] The analysis results of the surface compositions of the untreated down and the alumina-attached down obtained by XPS in the same manner as in Example 1 are shown in FIG. 29. Further, FIG. 30 shows the XPS spectra of the down before and after the alumina treatment.

[0071] It can be seen from the results shown in FIG. 29 and FIG. 30 that the surface of the down is coated with alumina, by carrying out the alumina treatment. This reveals that the down having the same quality as those obtained by the titania treatment carried out in Example 1 can also be obtained by the alumina treatment. Further, it was also confirmed that the same effect can be obtained by a ceramic treatment.

DESCRIPTION OF SYMBOLS

[0072]

11, 21, 31, 51, 91	apparatus body
12,22	feed inlet
13, 23, 33, 53	discharge outlet
14, 34	introduction port
24, 54	irradiation device
25, 55	gas inflow port
32, 52	injection inlet
35, 57, 93	valve
36, 56, 92	blower
37	nozzle
38, 40	three-way cock
39a to 39e	flow passage
41	Ti sol container
42	methanol container
43	N_2 balloon
44, 58	storage container
45, 59, 94	opening
61	plasma torch
62	acrylic plate
63	connector
64	vinyl chloride tube
65	glass capillary
66	Cu pipe
67	silicone tube
68	silicone tube
69	pinch cock
70	Cu tape
71	metal mesh
81	comforter

82 ribbon heater
83 mat
84 paper guide
101 acrylic pipe
102 lid
103 weight
M mesh portion
D down

Claims

1. A method of manufacturing a surface-modified fibrous material, the method comprising attaching an inorganic material on a surface of a fibrous material by a sol-gel reaction, while allowing the fibrous material to move via an air stream.

2. The method of manufacturing a surface-modified fibrous material according to claim 1, wherein titania is attached on the surface of the fibrous material by a sol-gel reaction of a titanium compound, while allowing the fibrous material to move via an air stream.

3. The method of manufacturing a surface-modified fibrous material according to claim 2, wherein an atmospheric-pressure low-temperature plasma is applied to the surface of the fibrous material on the surface of which titania has been attached, while allowing the fibrous material to move via an air stream.

4. The method of manufacturing a surface-modified fibrous material according to claim 2 or 3, wherein titanium tetraisopropoxide is used as the titanium compound.

5. The method of manufacturing a surface-modified fibrous material according to claim 1, wherein alumina is attached on the surface of the fibrous material by a sol-gel reaction of an aluminum compound, while allowing the fibrous material to move via an air stream.

6. The method of manufacturing a surface-modified fibrous material according to claim 5, wherein an atmospheric-pressure low-temperature plasma is applied to the surface of the fibrous material on the surface of which alumina has been attached, while allowing the fibrous material to move via an air stream.

7. The method of manufacturing a surface-modified fibrous material according to claim 5 or 6, wherein aluminum isopropoxide is used as the aluminum compound.

8. The method of manufacturing a surface-modified fibrous material according to claim 1, wherein a ceramic is attached on the surface of the fibrous material by a sol-gel reaction of a ceramic compound, while allowing the fibrous material to move via an air stream.

9. The method of manufacturing a surface-modified fibrous material according to claim 8, wherein an atmospheric-pressure low-temperature plasma is applied to the surface of the fibrous material on the surface of which the ceramic has been attached, while allowing the fibrous material to move via an air stream.

10. The method of manufacturing a surface-modified fibrous material according to any one of claims 1 to 9, wherein a natural fiber or a synthetic fiber is used as the fibrous material.

11. The method of manufacturing a surface-modified fibrous material according to claim 10, wherein feathers, a powder or a micro fiber made from cocoons, silk, wool, cotton, hemp, pulp, or the synthetic fiber are/is used as the fibrous material.

12. The method of manufacturing a surface-modified fibrous material according to claim 11, wherein the feathers are used as the fibrous material.

13. A surface-modified fibrous material manufactured by the method of manufacturing a surface-modified fibrous material according to any one of claims 1 to 12.

FIG. 1

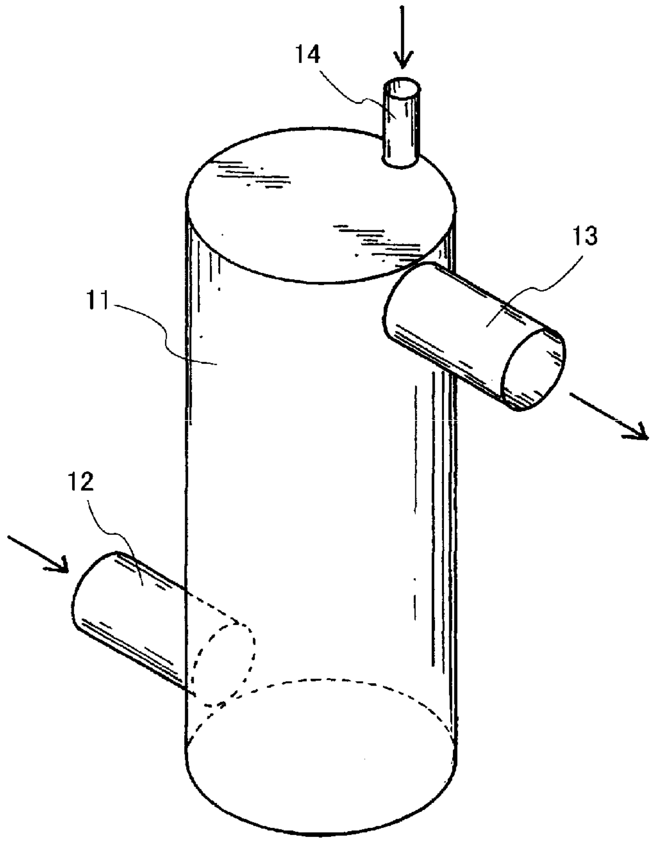


FIG. 2

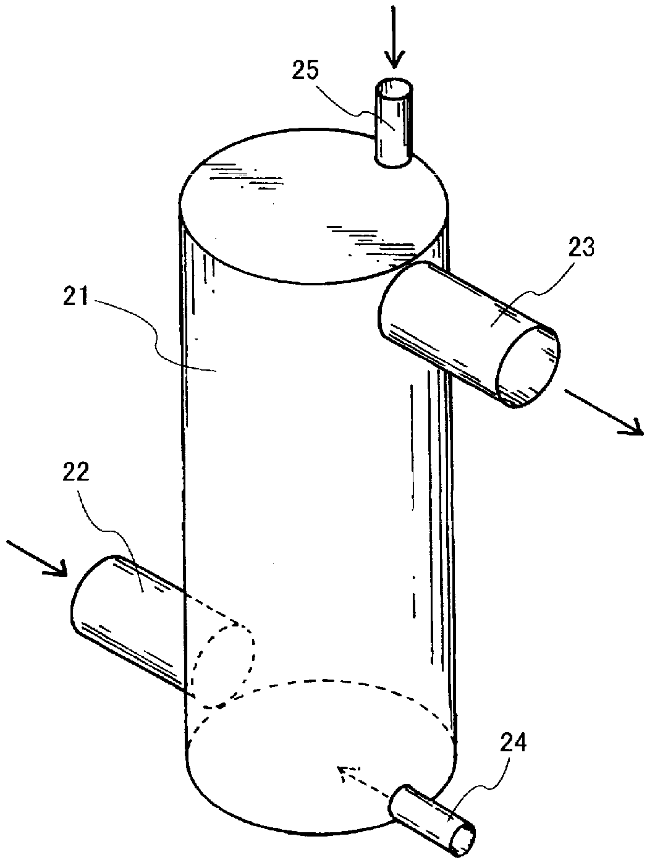

25
23
21
22
24

FIG. 3

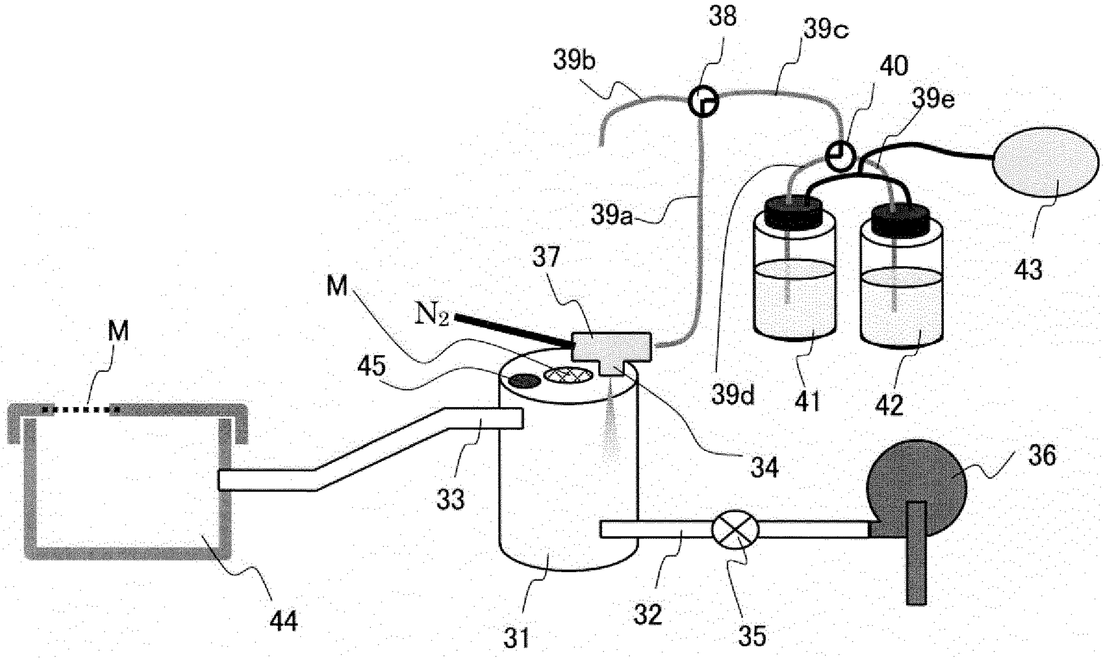

38
39c
39b
40
39e
39a
37
43
M
N_2
M
45
39d
41
42
34
36
33
44
31
32
35

FIG. 4

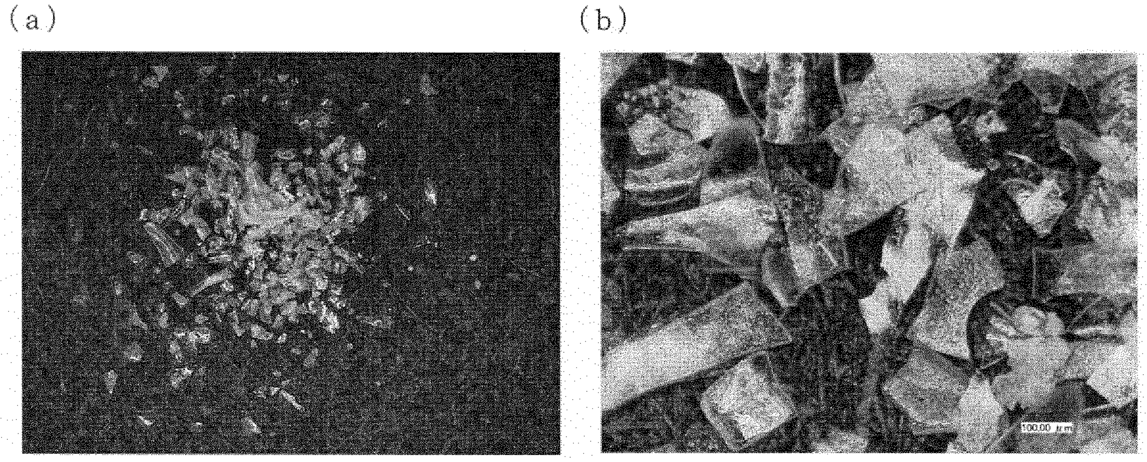


FIG. 5

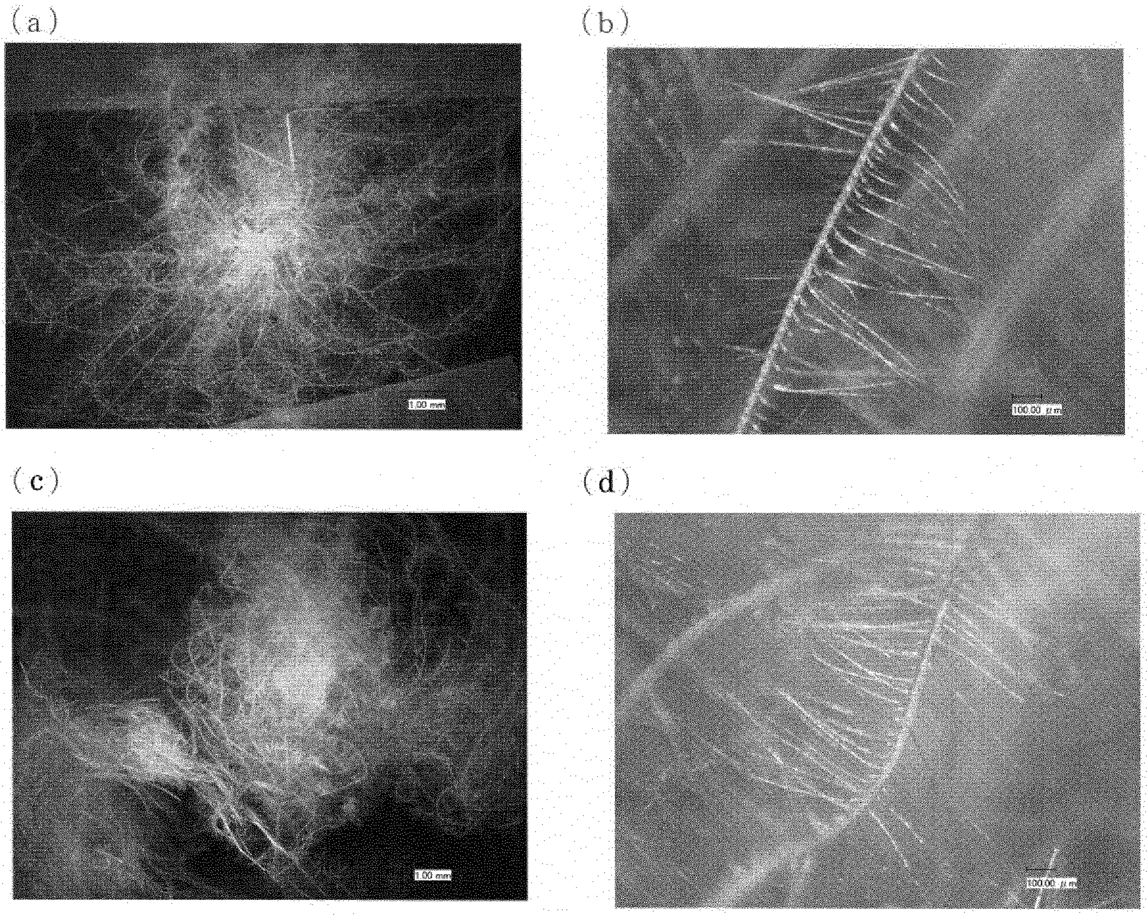


FIG. 6

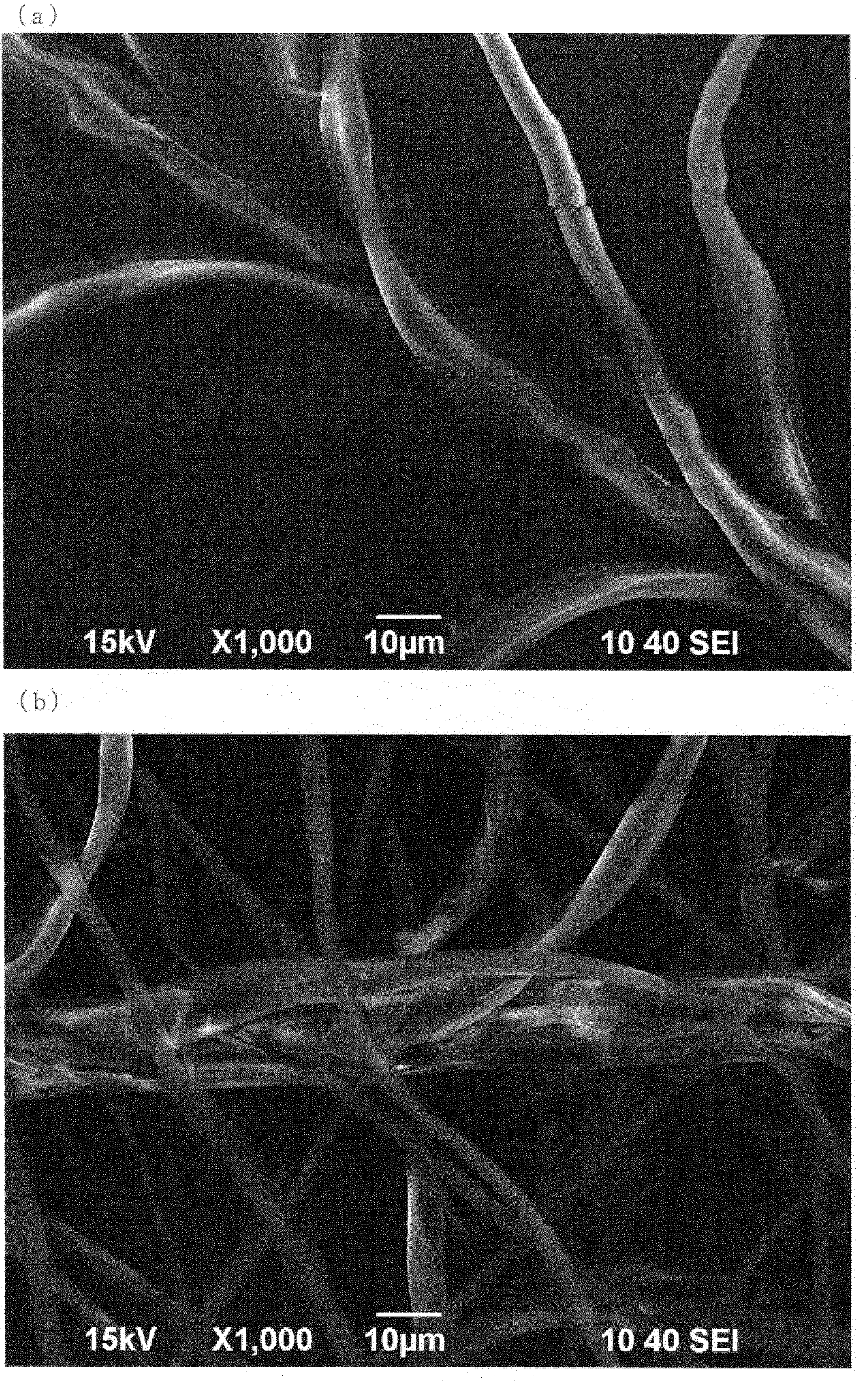


FIG. 7

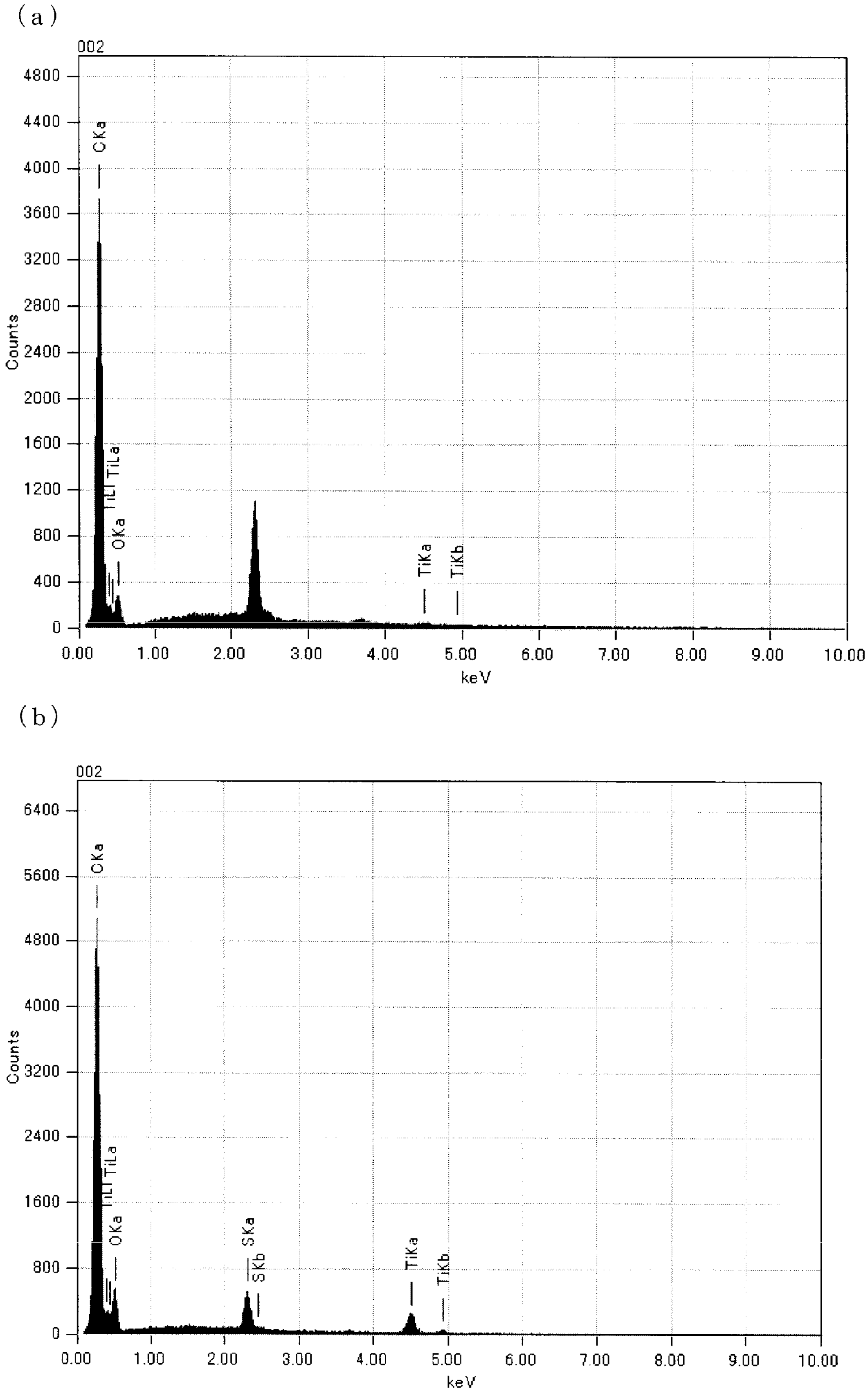

(a)
002
Counts
4800
4400
4000
3600
3200
2800
2400
2000
1600
1200
800
400
0
CKa
TiLl
TiLa
OKa
TiKa
TiKb
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.00
keV
(b)
002
Counts
6400
5600
4800
4000
3200
2400
1600
800
0
CKa
TiLl
TiLa
OKa
SKa
SKb
TiKa
TiKb
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.00
keV

FIG. 8

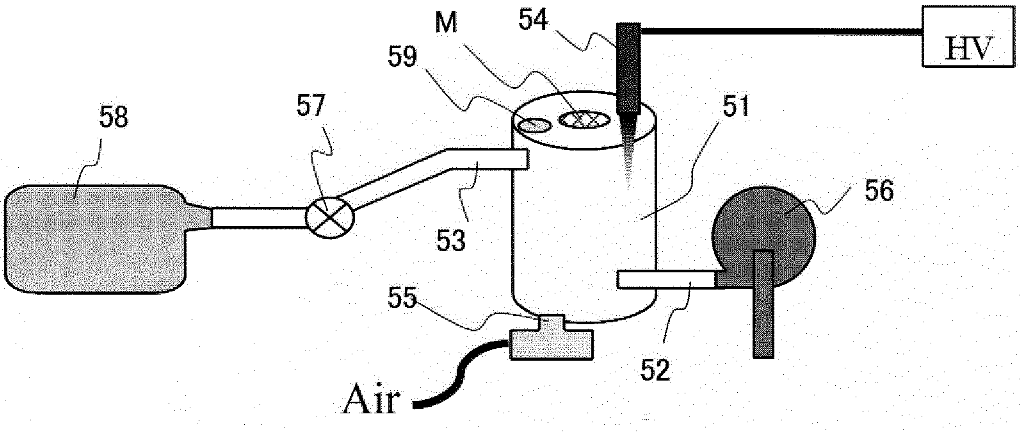


FIG. 9

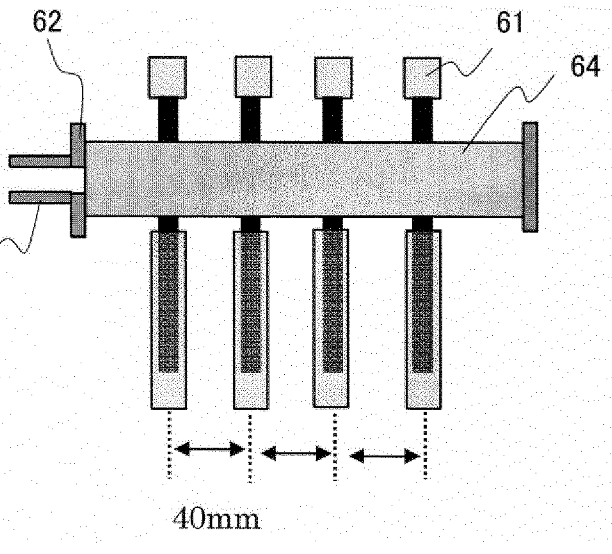


FIG. 10

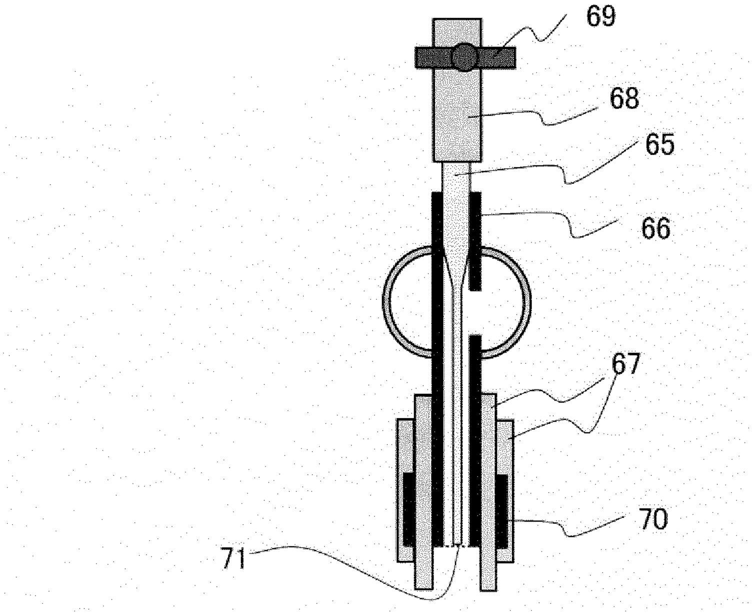


FIG. 11

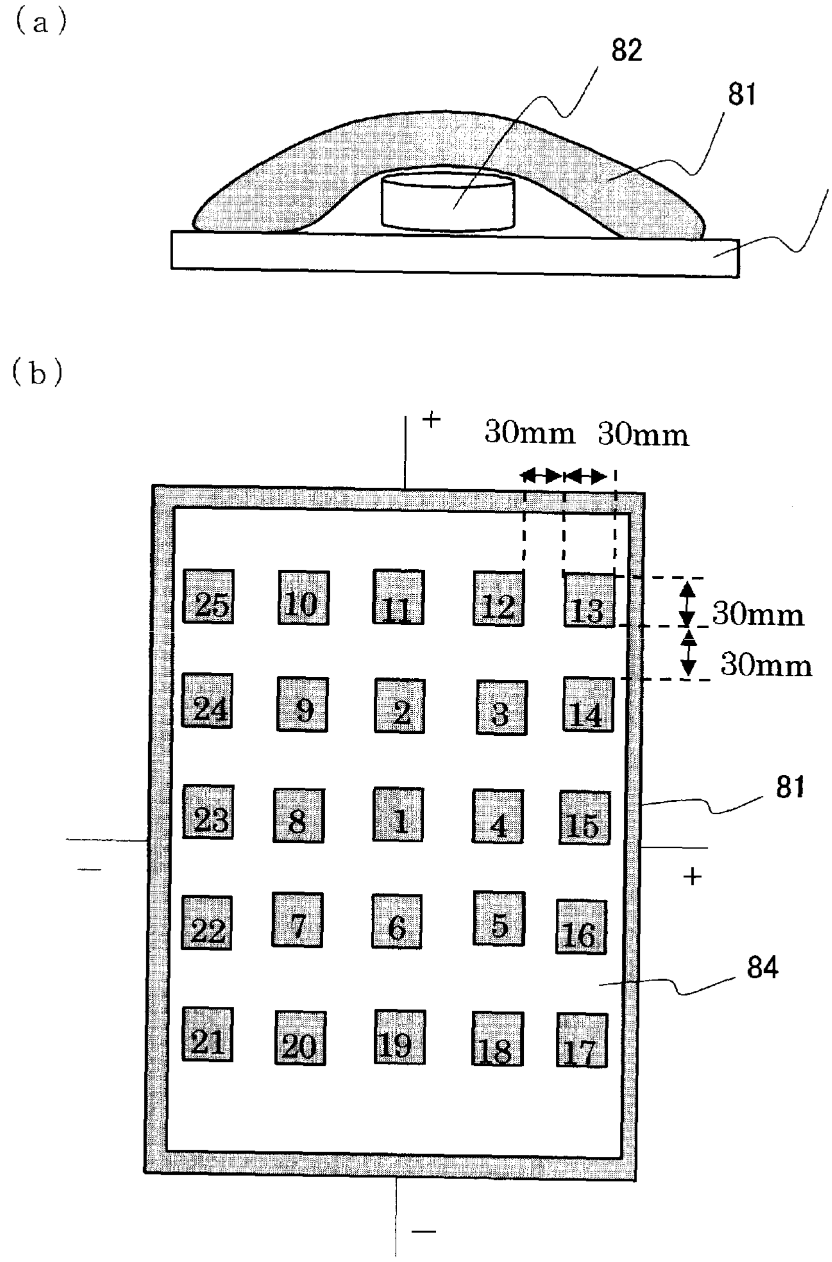
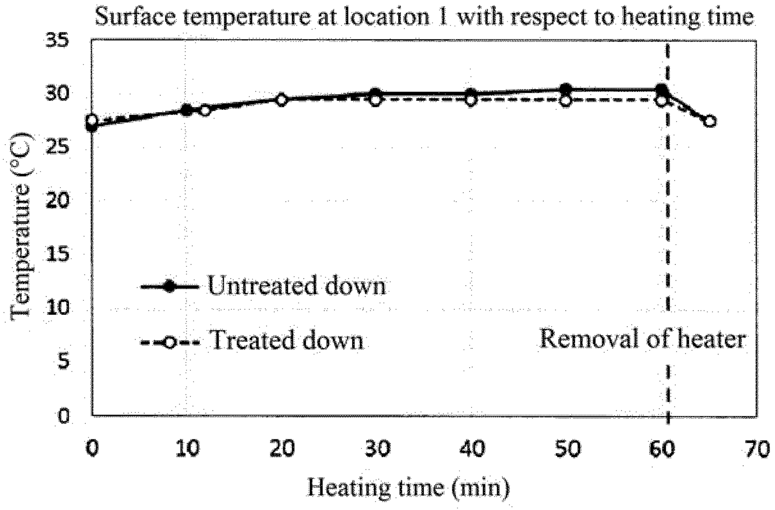

(a)
82
81
83
(b)
+
30mm
30mm
25
10
11
12
13
30mm
30mm
24
9
2
3
14
23
8
1
4
15
81
−
+
22
7
6
5
16
84
21
20
19
18
17
−

FIG. 12

(a)


Surface temperature at location 1 with respect to heating time
Temperature (°C)
35
30
25
20
15
10
5
0
Untreated down
Treated down
Removal of heater
0
10
20
30
40
50
60
70
Heating time (min)

(b)

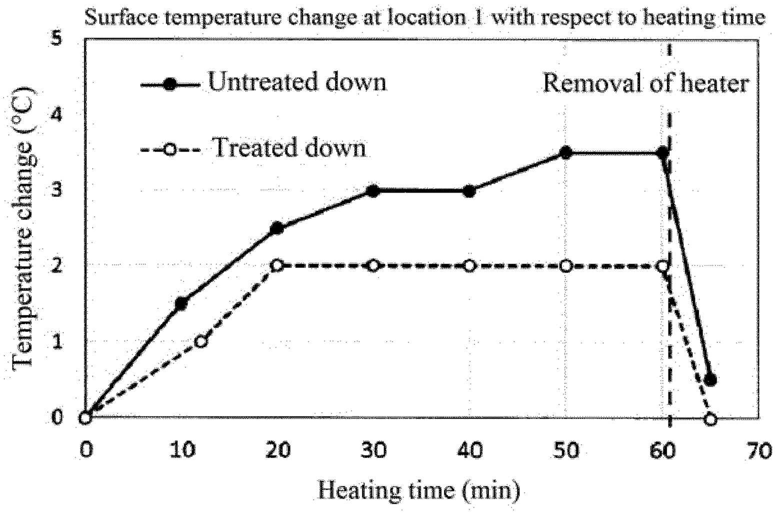

Surface temperature change at location 1 with respect to heating time
Temperature change (°C)
5
4
3
2
1
0
Untreated down
Treated down
Removal of heater
0
10
20
30
40
50
60
70
Heating time (min)

FIG. 13

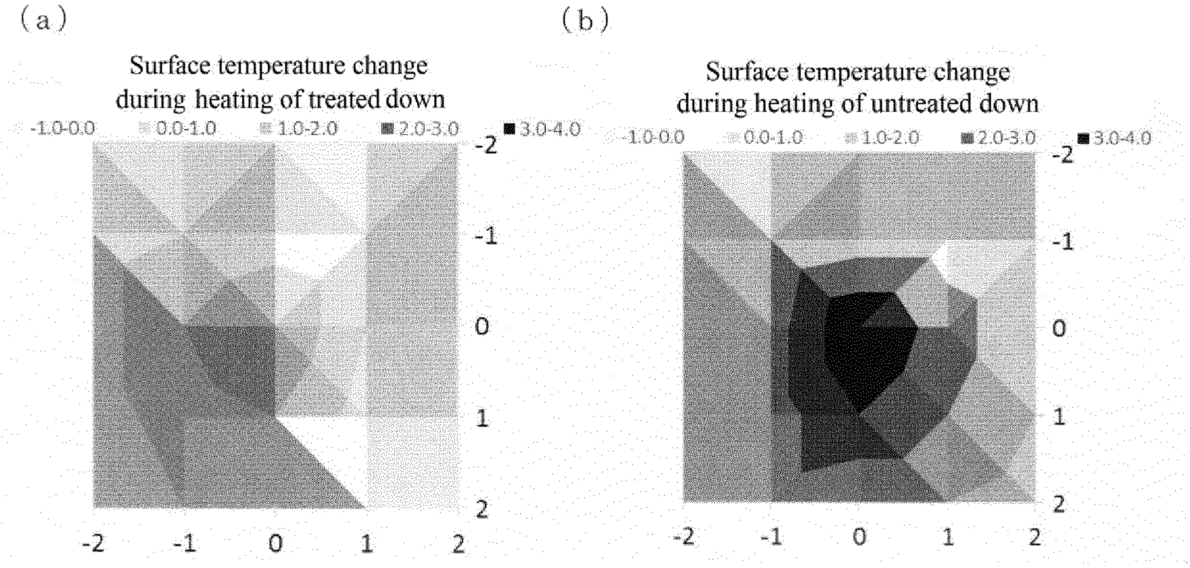

(a)
Surface temperature change during heating of treated down
-1.0-0.0
0.0-1.0
1.0-2.0
2.0-3.0
3.0-4.0
-2
-1
0
1
2
-2
-1
0
1
2
(b)
Surface temperature change during heating of untreated down
-1.0-0.0
0.0-1.0
1.0-2.0
2.0-3.0
3.0-4.0
-2
-1
0
1
2
-2
-1
0
1
2

FIG. 14

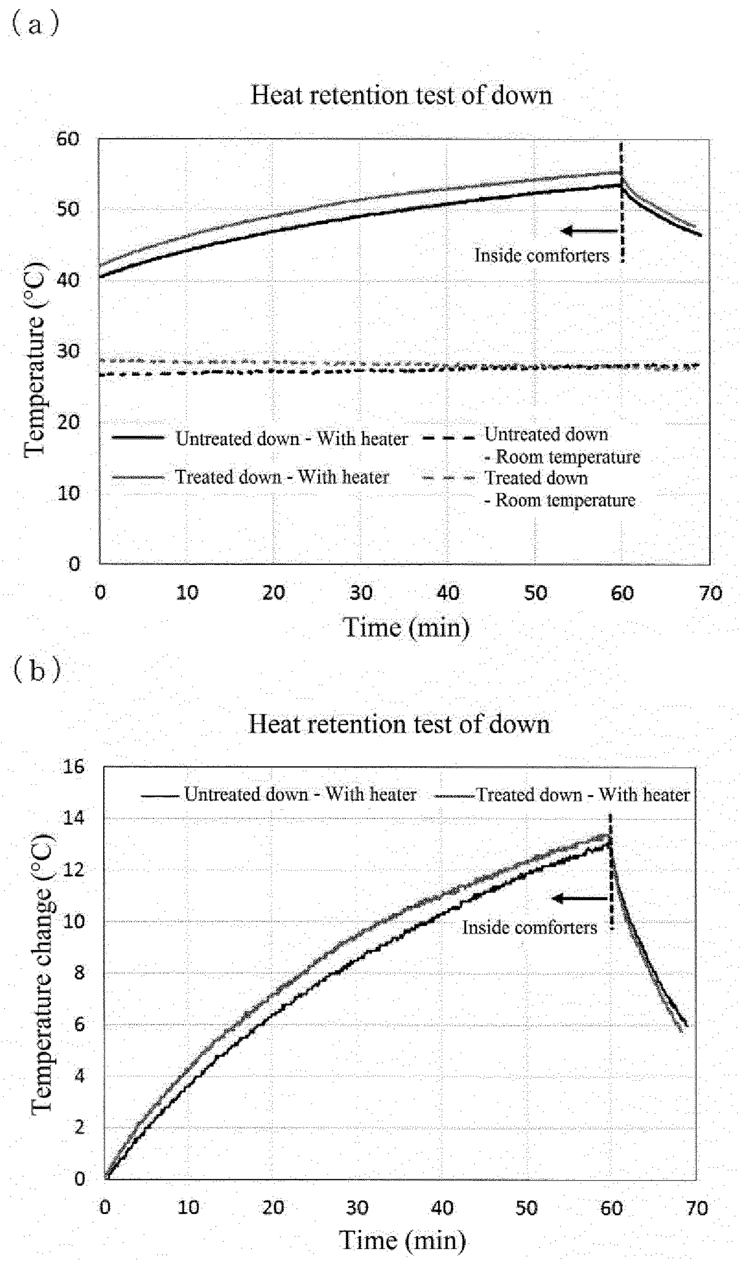

(a)
Heat retention test of down
Temperature (°C)
60
50
40
30
20
10
0
Time (min)
0
10
20
30
40
50
60
70
Inside comforters
Untreated down - With heater
Treated down - With heater
Untreated down - Room temperature
Treated down - Room temperature
(b)
Heat retention test of down
Temperature change (°C)
16
14
12
10
8
6
4
2
0
Time (min)
0
10
20
30
40
50
60
70
Untreated down - With heater
Treated down - With heater
Inside comforters

FIG. 15

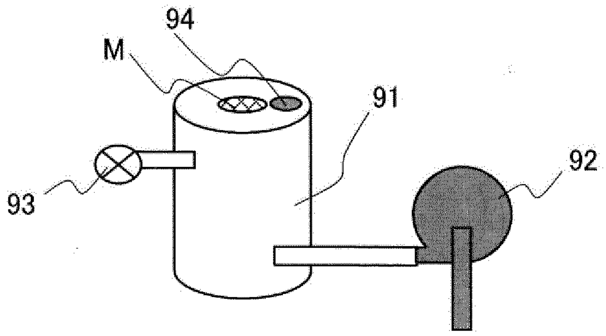
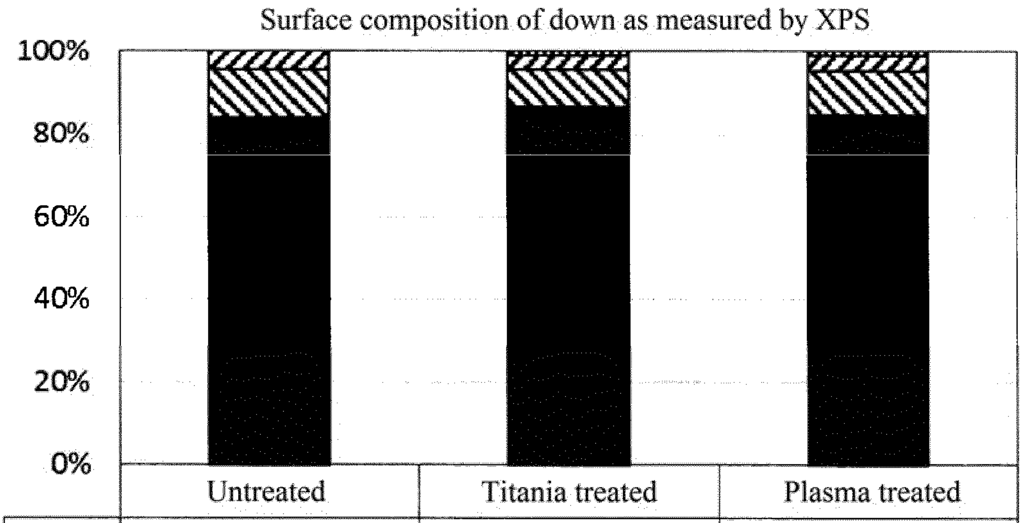

94
M
91
92
93

FIG. 16



	Untreated	Titania treated	Plasma treated
▥ Ti2p	0.0	1.1	1.1
▨ N1s	4.3	3.4	3.8
▧ O1s	11.6	8.8	10.5
■ C1s	84.2	86.7	84.6

FIG. 17

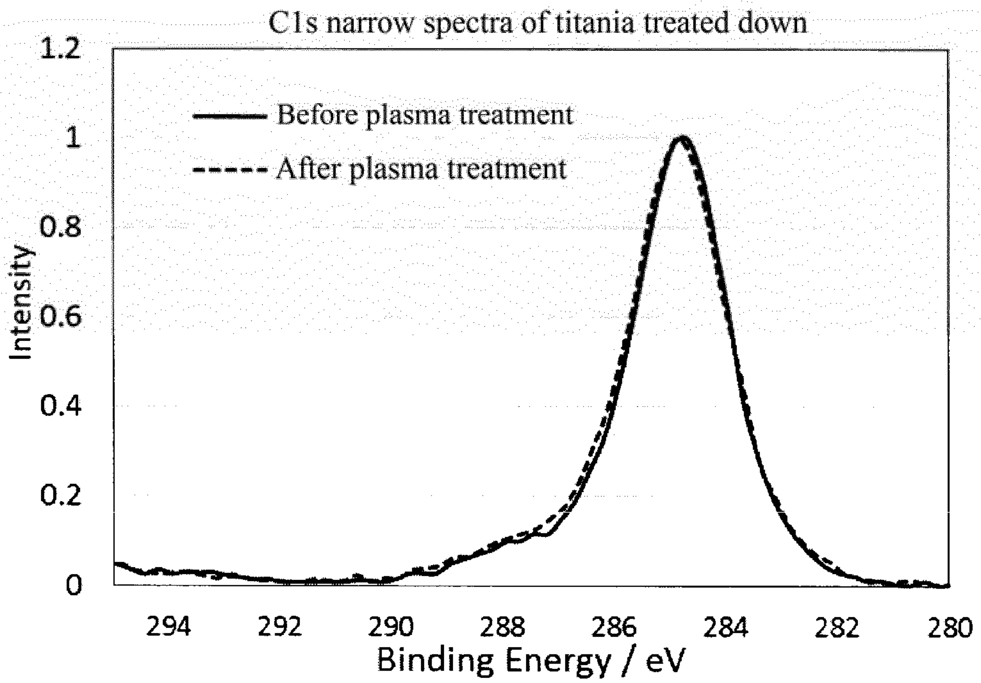


FIG. 18

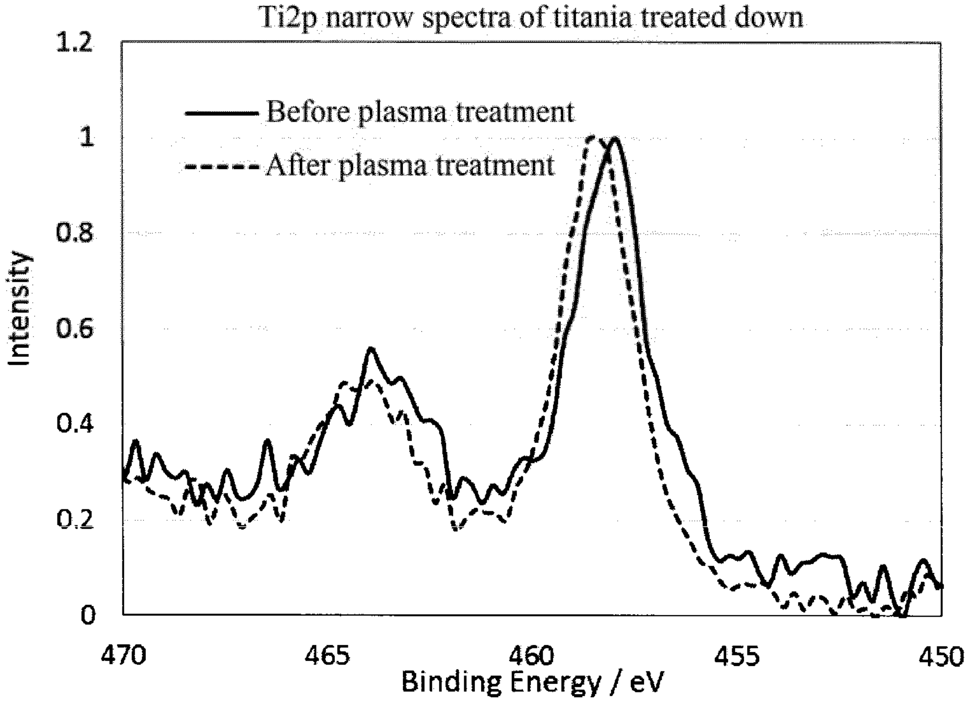
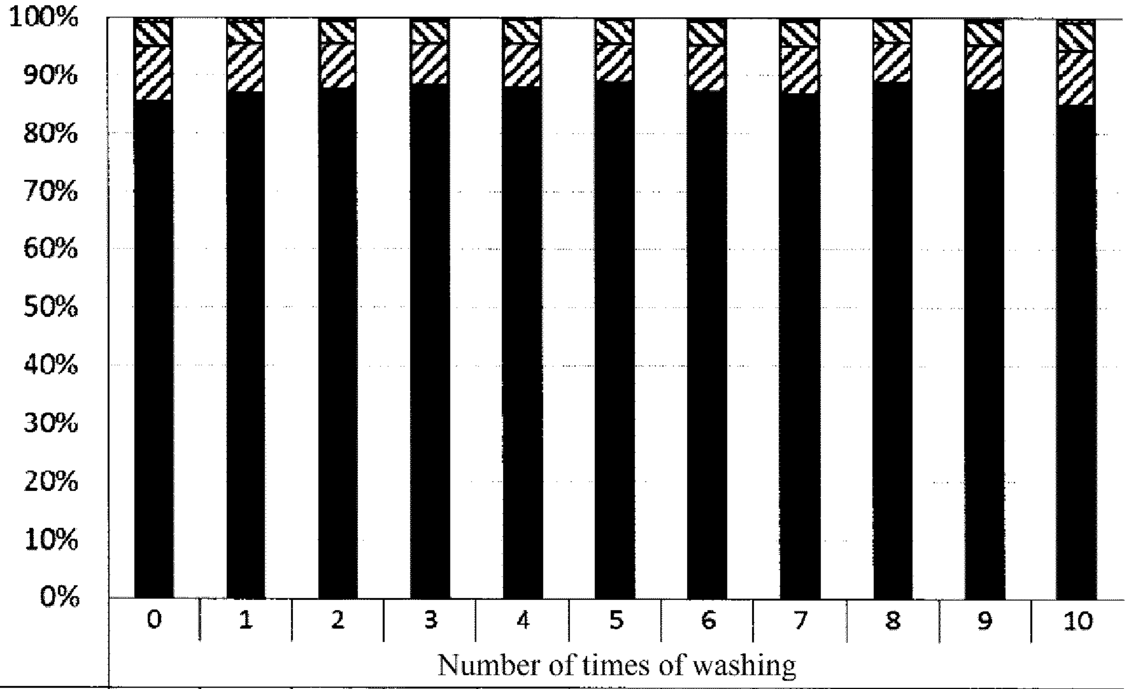


FIG. 19



	0	1	2	3	4	5	6	7	8	9	10
▥ Ti2p	0.71	0.75	0.49	0.49	0.23	0.20	0.49	0.60	0.34	0.52	0.75
▧ N1s	4.19	3.90	4.13	4.12	4.22	4.25	4.34	4.35	3.95	4.18	4.85
▨ O1s	9.79	8.38	7.72	7.18	7.77	6.82	7.92	8.33	6.88	7.81	9.42
■ C1s	85.32	86.98	87.67	88.22	87.79	88.74	87.26	86.73	88.83	87.51	84.99

FIG. 20

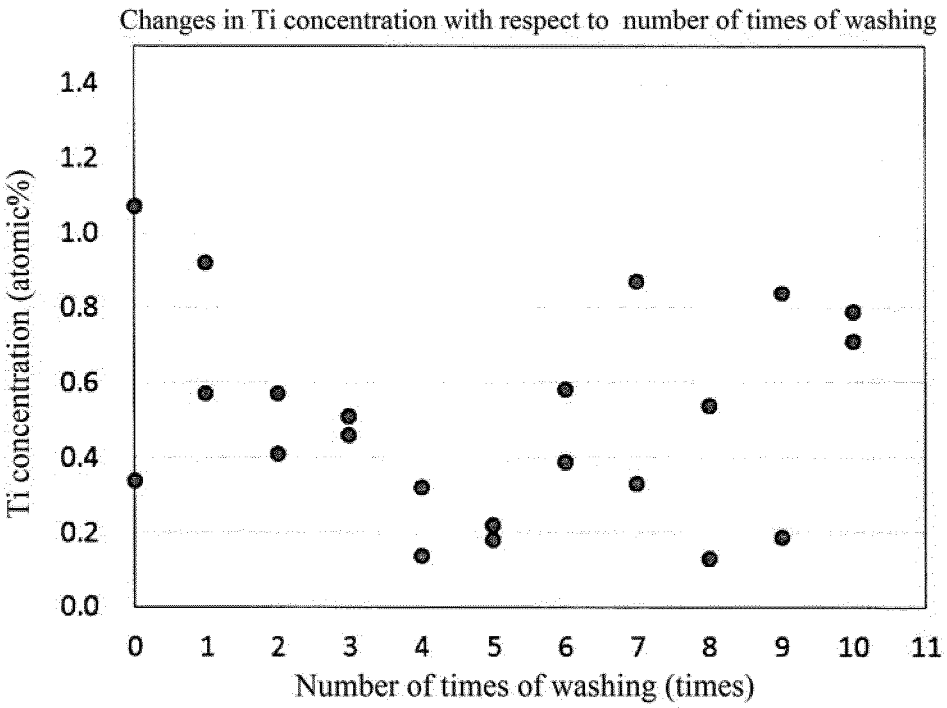
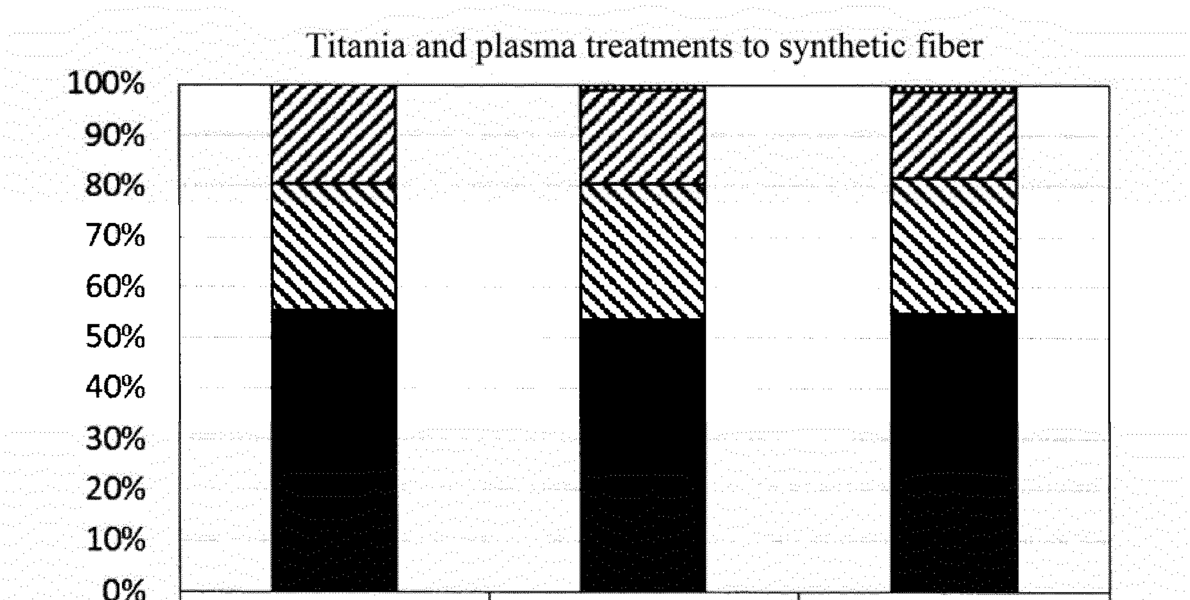
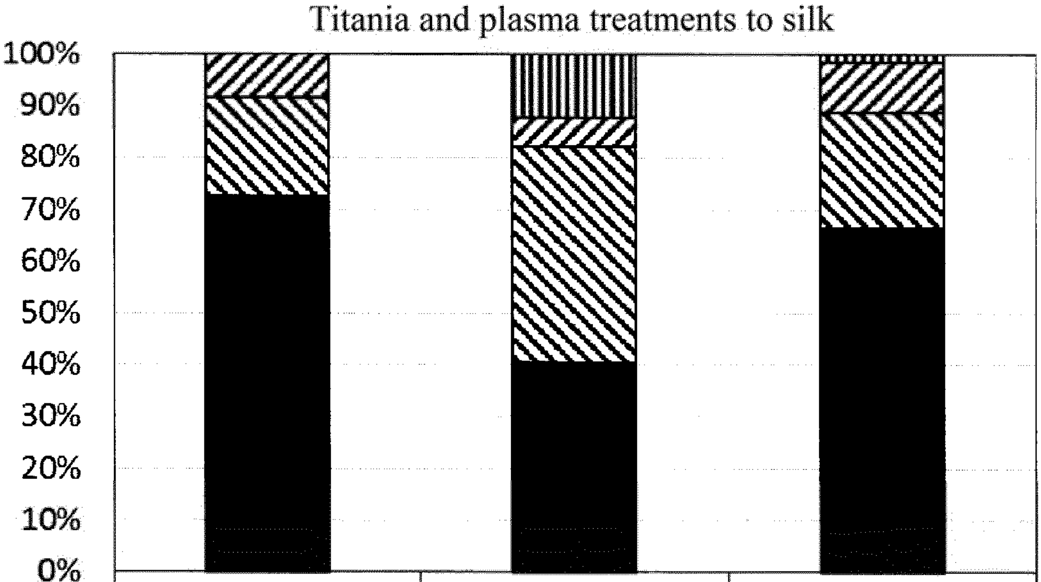


FIG. 21



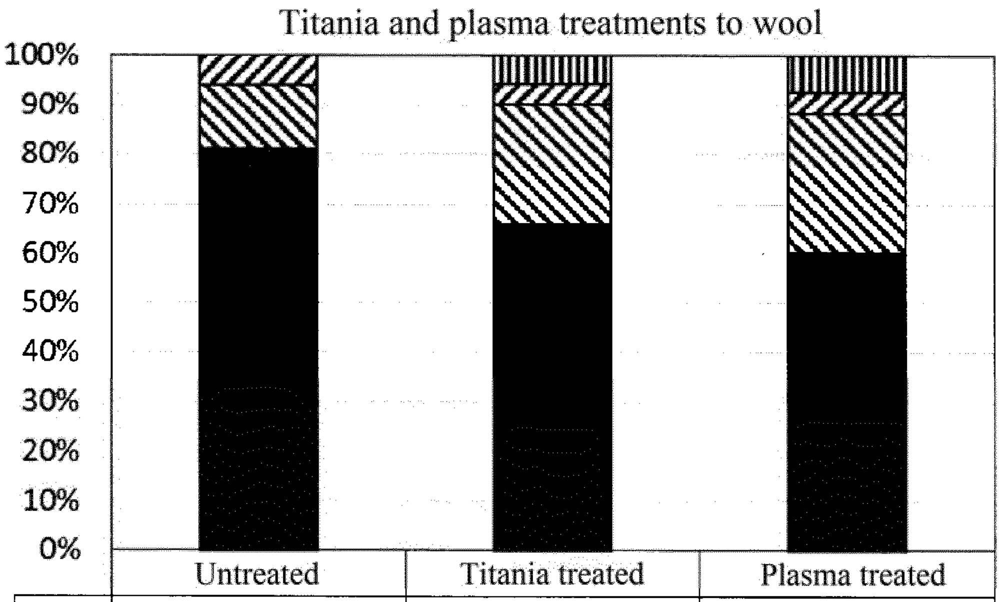
	Untreated	Titania treated	Plasma treated
□ Ti2p	0.00	1.03	1.44
▨ Si2p	19.47	18.48	17.01
▧ O1s	25.19	26.87	26.88
■ C1s	55.35	53.62	54.69

FIG. 22



	Untreated	Titania treated	Plasma treated
▥ Ti2p	0.00	12.26	1.60
▨ N1s	8.36	5.54	9.53
▧ O1s	19.05	41.76	22.33
■ C1s	72.60	40.44	66.55

FIG. 23



	Untreated	Titania treated	Plasma treated
▥ Ti2p	0.00	5.62	7.44
▨ N1s	6.07	4.19	4.31
▧ O1s	12.74	24.27	28.09
■ C1s	81.20	65.95	60.17

FIG. 24

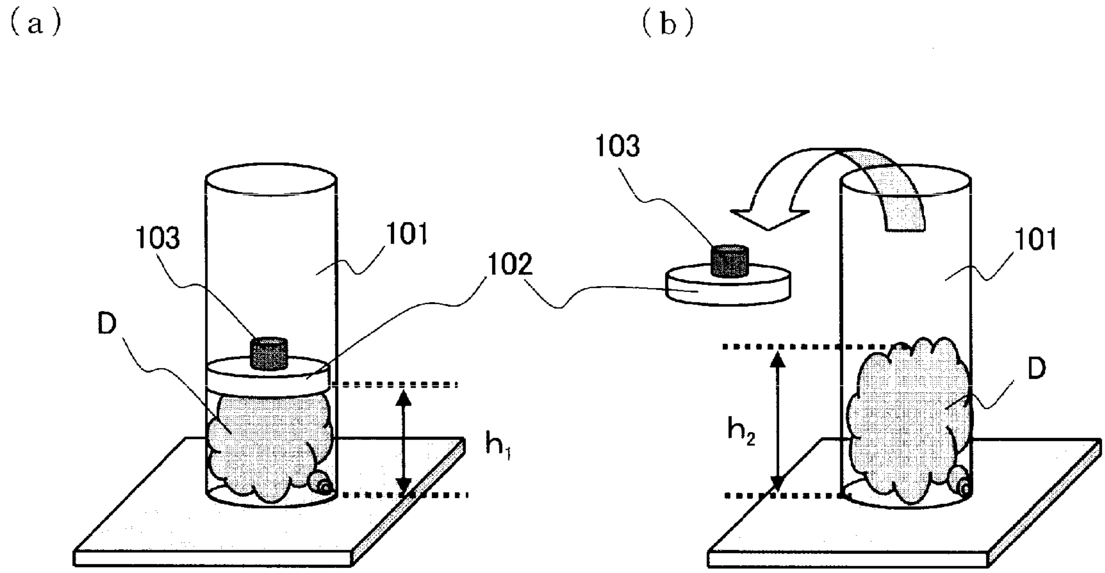
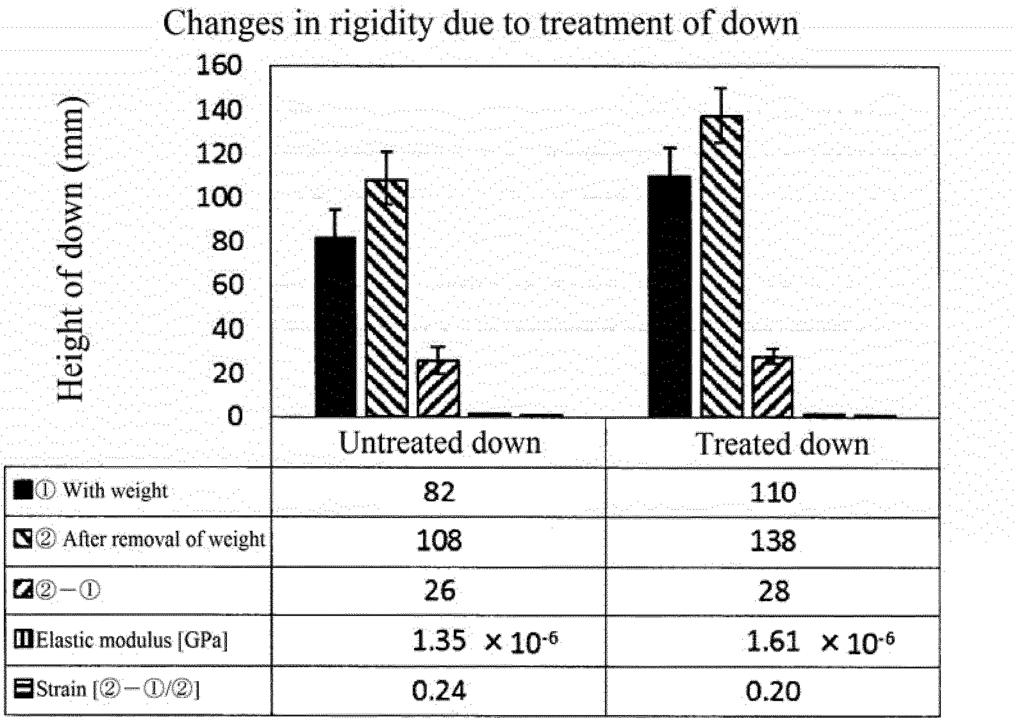
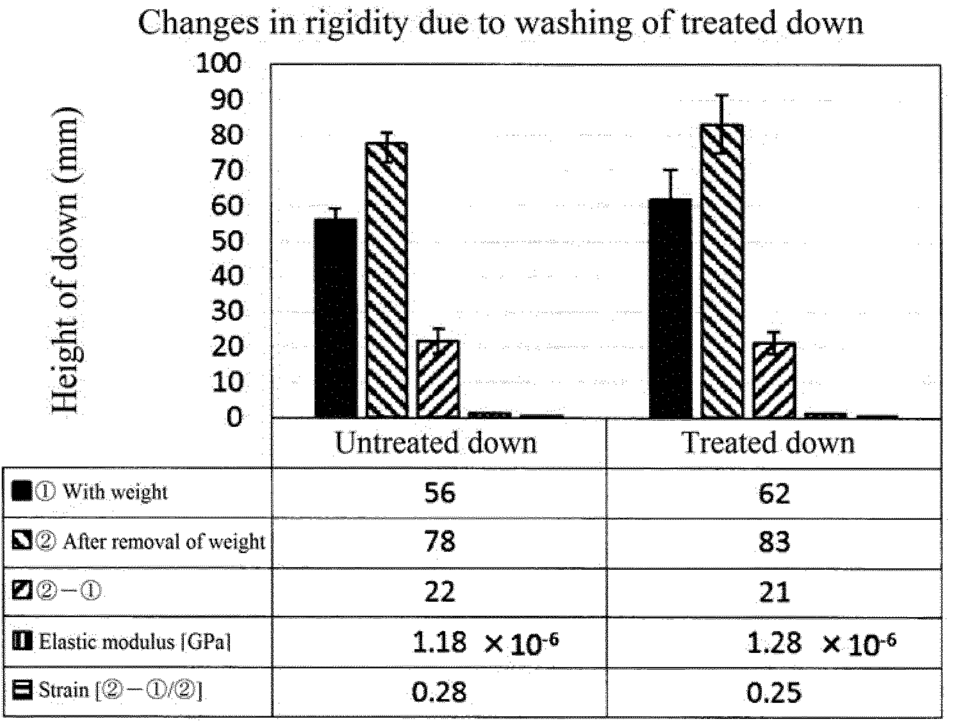


FIG. 25



	Untreated down	Treated down
■① With weight	82	110
▧② After removal of weight	108	138
▨②−①	26	28
▥Elastic modulus [GPa]	1.35 $\times 10^{-6}$	1.61 $\times 10^{-6}$
▤Strain [②−①/②]	0.24	0.20

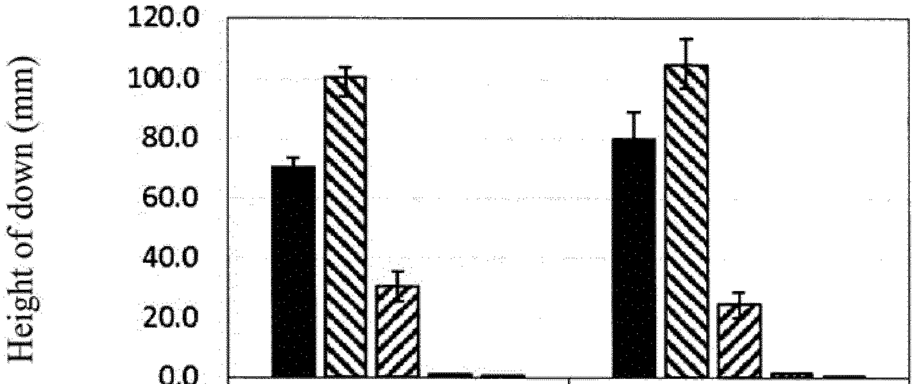
FIG. 26



	Untreated down	Treated down
■① With weight	56	62
▧② After removal of weight	78	83
▨②−①	22	21
▥ Elastic modulus [GPa]	1.18 $\times 10^{-6}$	1.28 $\times 10^{-6}$
▤ Strain [②−①/②]	0.28	0.25

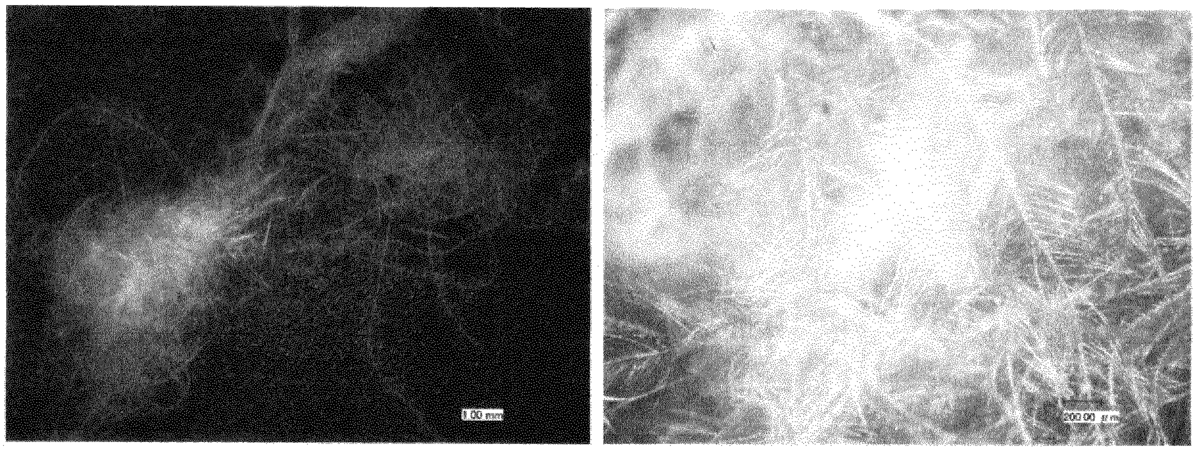
FIG. 27

Changes in rigidity due to washing of treated down (blowing treatment)



	Untreated down	Treated down
■ ① With weight	70.0	80.0
▧ ② After removal of weight	100.5	104.5
▨ ②−①	30.5	24.5
▥ Elastic modulus [GPa]	1.08×10^{-6}	1.39×10^{-6}
⊟ Strain [②−①/②]	0.30	0.23

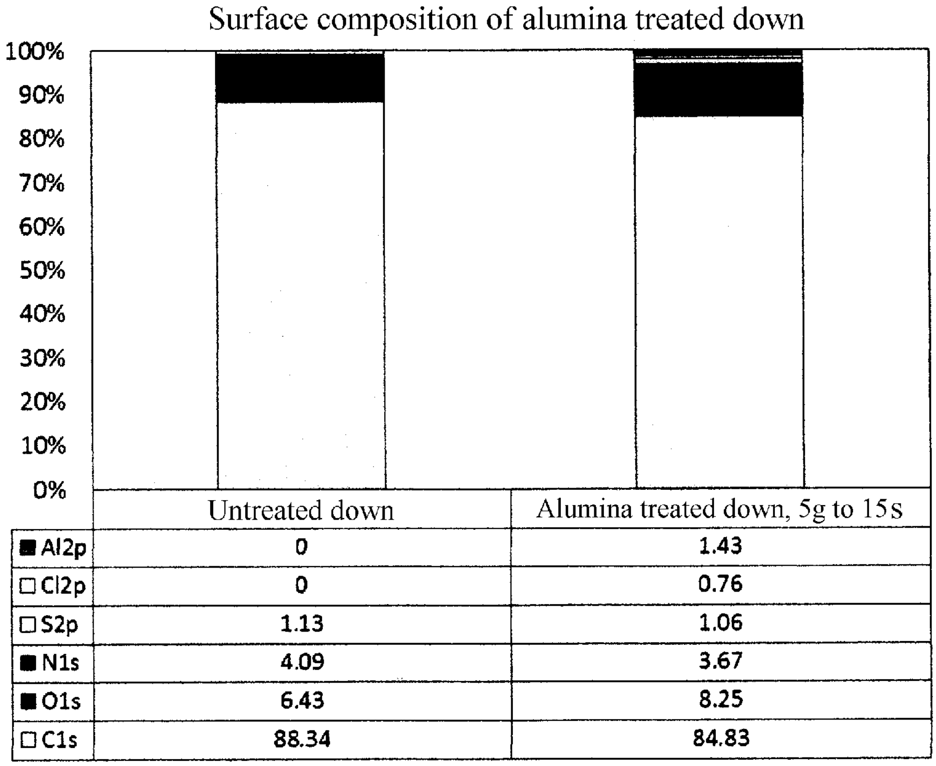
FIG. 28



(a)

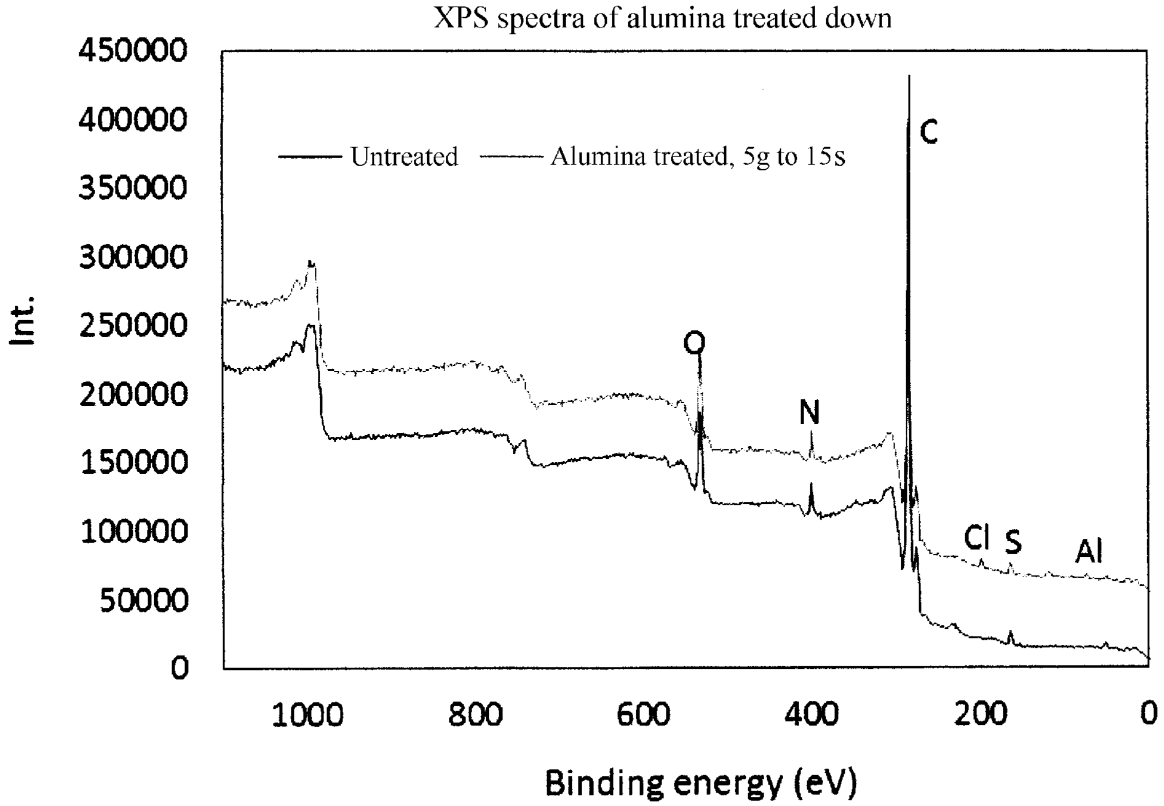
(b)

FIG. 29



	Untreated down	Alumina treated down, 5g to 15s
■ Al2p	0	1.43
□ Cl2p	0	0.76
□ S2p	1.13	1.06
■ N1s	4.09	3.67
■ O1s	6.43	8.25
□ C1s	88.34	84.83

FIG. 30



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/070404

A. CLASSIFICATION OF SUBJECT MATTER
D06M11/46(2006.01)i, *D06M10/02*(2006.01)i, *D06M11/45*(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)
D06M10/00-16/00, D06M19/00-23/18

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2015
Kokai Jitsuyo Shinan Koho	1971-2015	Toroku Jitsuyo Shinan Koho	1994-2015

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
JSTPlus/JMEDPlus/JST7580(JDreamIII)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X Y	JP 59-216977 A (Kuraray Co., Ltd.), 07 December 1984 (07.12.1984), claims; page 2, upper left column, line 9 to upper right column, line 20; page 2, lower right column, lines 7 to 18; page 3, lower right column, lines 4 to 10; examples 3, 4 (Family: none)	13 2,4

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search 31 August 2015 (31.08.15)	Date of mailing of the international search report 08 September 2015 (08.09.15)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/070404

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	WO 1998/53132 A1 (Kyorasha Co., Ltd.), 26 November 1998 (26.11.1998), claims; page 7, lines 1 to 6 & US 6265064 B1 & EP 997575 A1 & CN 1257560 A & KR 10-0483935 B1	13
Y	JP 2013-530316 A (Pavlos, Christopher, M.), 25 July 2013 (25.07.2013), claims; paragraphs [0019], [0020], [0034] & US 2014/0141179 A1 & WO 2011/143488 A2 & EP 2569474 A2 & CA 2799043 A & AU 2011252996 A	1,2,4,5,7,8, 10-12
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A	JP 2007-530265 A (Vlaamse Instelling voor Technologisch Onderzoek (VITO), Fraunhofer Gesellschaft), 01 November 2007 (01.11.2007), claims; paragraphs [0022], [0046] & US 2007/0202270 A1 & WO 2005/095007 A1 & EP 1582270 A1 & EP 1729892 A1	1-13

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