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(54) Title: HIGH-STRENGTH SUPERHYDROPHOBIC COATINGS ON NAPPED TEXTILE SURFACES

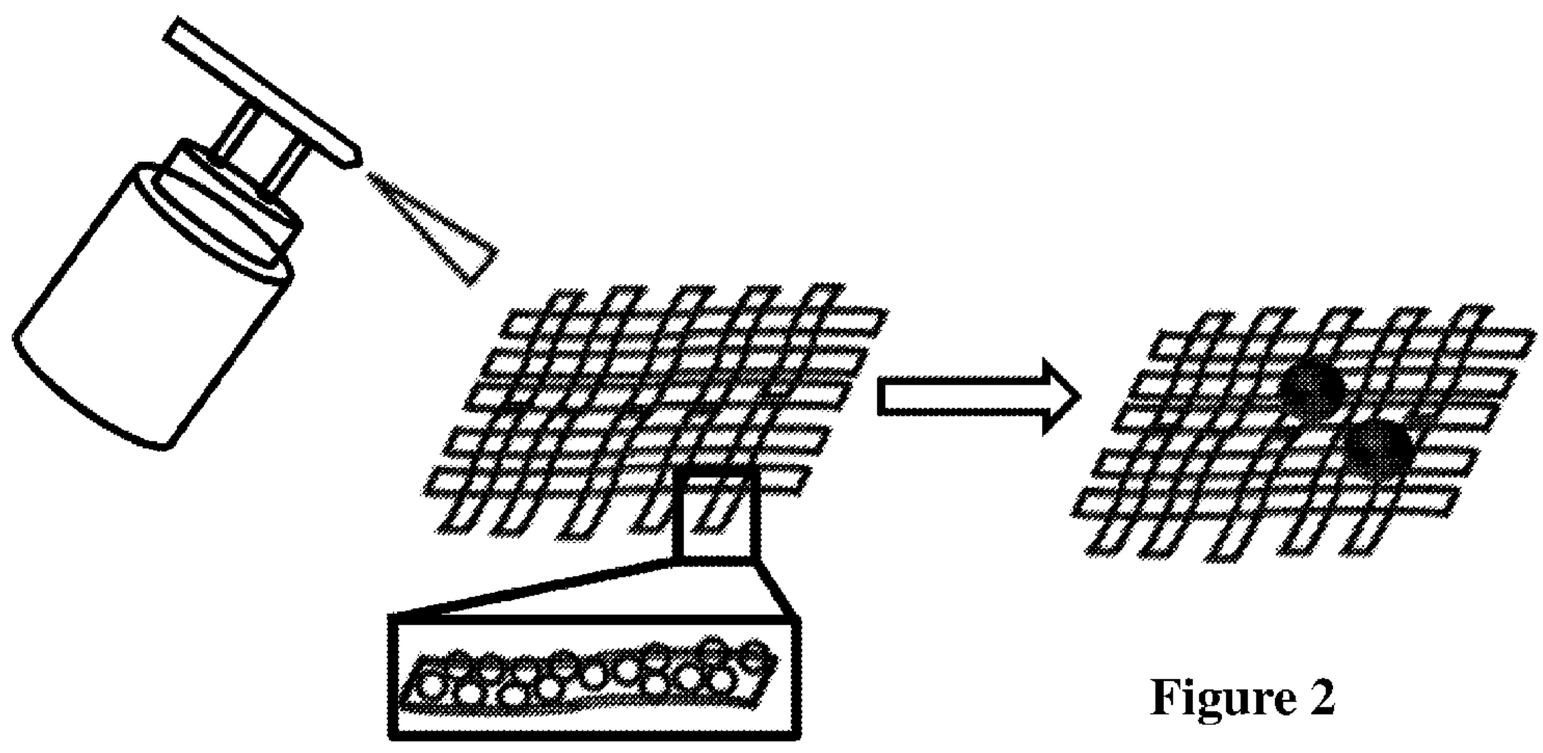

Figure 2

(57) **Abstract:** The invention is related to obtaining a structure consisting of free fibers on the fabric surface by means of a napping process and subsequently depositing nanoparticles modified with low energy molecules onto the fabric surface to obtain a superhydrophobic surface with high mechanical strength and water repellency.

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HIGH-STRENGTH SUPERHYDROPHOBIC COATINGS ON NAPPED TEXTILE SURFACES

Technical Field

The invention is related to the method of coating superhydrophobic textile surfaces by spraying hydrophobic inorganic nanoparticles coated with a self-assembled monolayer on the napped textile surface.

Known State of the Art (Prior Art)

Textile products are one of the basic requirements that people use to meet their basic needs. Day by day, its use increases and continues to increase due to the increase in population.

Textile products are obtained by using animal, vegetable and synthetic fibers. The main problem encountered during the use of textile products is, stain formation and the fact that they get dirty easily. In particular, stains that are difficult to remove can cause appearance problems, as well as aggressive cleaners used during cleaning can damage textile products.

Many studies are carried out in the prior art in order to eliminate such problems and to improve the function of textile products by giving them new features. One of these studies is related to the elimination of the main problems encountered in textile products, such as contamination and stain formation by giving textile products superhydrophobic properties.

Superhydrophobic coatings are coatings with a contact angle that is higher than 150 degrees and a sliding angle that is less than 10 degrees. Superhydrophobic coatings have properties such as anti-icing, anti-fogging, anti-corrosion and anti-contamination due to their low surface energy.

Like most technologies, superhydrophobic coatings have been developed by being inspired by nature. The first starting point of superhydrophobic coatings is the lotus plant. Although the lotus plant grows in the marsh area, the researchers were interested in how the plant kept its leaves clean. As a result of examinations, it has been observed that the leaves of the lotus plant have low surface energy and therefore with the falling rain, the dirt on the leaf surface is removed from the surface with the effect of rain drops. This effect can be easily applied to

textile surfaces with the developing technology. However, this technology cannot be used in textile products used in daily life due to some problems. These problems are that superhydrophobic coatings do not have the desired mechanical strength and they damage the texture (color) of the applied surface.

The textile industry includes many sub-fields such as furniture, clothing and accessories. Due to the high usage area, the manufacturing sector is among the important sectors. With the use of superhydrophobic coatings in this field, it is thought that it will contribute to the emergence of more useful and more comfortable products with higher added value.

In the prior art, superhydrophobic coatings can be applied by many techniques. These techniques are; immersion coating, spin coating and spray coating. However, the spray method is more preferred due to its advantages such as easy applicability, being cheap and easier to integrate into the industry. As mentioned, although superhydrophobic coatings have many advantages, superhydrophobic coatings cannot be used frequently in daily life due to their weak mechanical strength and as they damage the texture of the applied surface.

In the prior art, polymer materials are generally added to hydrophobic particles to increase the strength of superhydrophobic coatings. However, superhydrophobic coatings supplemented with polymer, disrupt the texture of the applied surface. When contacted, it creates a very distinct feeling, unlike the fabric texture. Therefore, a situation is encountered, where no user would prefer it.

In the field of superhydrophobic coatings, high strength superhydrophobic coatings are obtained by using double-layer coatings, besides the polymer additive, in the hydrophobic particles of products that are commercially sold. However, resin-based polymers are used as a base in double-layer coatings. These resin-based polymers create an undesirable situation from a decorative point of view as they disrupt the texture of the surfaces to be coated.

In patent document numbered CN105544221A, crosslinking polymers are used to increase the strength of the superhydrophobic coating. In said method, a homogeneous solution was obtained by mixing trimethoxy silane and ammonia, then polydimethylsiloxane was added to this solution and the mixing was continued. After the mixing process was completed, the fabric was covered by being immersed into this prepared solution. Thereby a superhydrophobic coating was obtained. The polymers used herein prevent the fabric from breathing and this situation causes excessive sweating of the fabric, and therefore it limits its usage area.

Hua Zhou et al. (Adv. Mater. 2010, 22, 5473-5477) prepared a hydrophobic solution by mixing polydimethylsiloxane (PDMS) and fluorine modified silica nanoparticles in a solvent in their studies. Then they immersed the fabric to be coated into this solution. After immersion, they carried out a heating process to cure the coating. As a result, they obtained a fabric with superhydrophobic property. PDMS used in their work disrupted the texture of the fabric. When touched, it created a feeling as if it is a very different material rather than the fabric.

The general approach in the prior art of applying superhydrophobic coatings on textile products is dispersing of nanoparticles in a polymer matrix. The major disadvantages of this approach are that there is an additional layer on the fabric in terms of feel and appearance and the repellency property is weakened due to the presence of superhydrophobic nanoparticles in the polymer. On the other hand, when nanoparticles providing superhydrophobic properties are deposited directly on the textile surface, the strength of the resulting coating is limited and these coatings can be easily removed from the surface with effects such as abrasion/impact. The basis of this situation is that, in applications, fabrics with a certain fiber arrangement (orientation) are generally preferred instead of fabrics with free fibers.

Brief description of the invention and its aims

The present invention relates to a method of superhydrophobic coating that meets the aforementioned requirements, eliminates the disadvantages and brings about some additional advantages.

The primary aim of the invention is to obtain superhydrophobic coatings with high mechanical strength by directly depositing nanoparticles on the fabric without the need for an external layer. This ensures that properties such as fabric feel are preserved.

Another aim of the invention is to obtain textile surfaces with high level of water repellency without using any molecules such as fluorocarbons that are harmful for human health.

With the invention method, since no matrix like a resin is used, superhydrophobic feature can be obtained easily and cheaply.

In the invention, free fiber structures required for mechanical strength can be obtained by napping, which is an existing process in the textile industry.

Since no crosslinking polymers are used in the method of the invention, there is no restriction regarding the flexibility of the fabric. Flexibility is very important both in terms of feel and comfort.

Since the fabrics are flexible, they are constantly exposed to wrinkling and marks are formed on the surface. Therefore they need to be ironed. In the method of the invention, even if ironing is performed at high temperature, the superhydrophobic coating is not disrupted. However, such situation is quite difficult with superhydrophobic coatings obtained with cross-linked polymers. Because crosslinking polymers harden even more at high temperatures, ironing further reduces the flexibility of fabrics.

The superhydrophobic coating developed with the invention exhibits high resistance to physical friction and impact tests.

With the method of the invention, very high contact angles such as 172 degrees can be obtained. In addition, no polymers such as cross-linkers that disrupt the texture of the surface are used. This situation does not affect the air permeability of the fabric. In other words, it does not cause sweating.

The spraying method is used in the superhydrophobic coating method of the invention.

Definitions of the Drawings Illustrating the Invention

Figure 1: Shows the napping of the fibers that are available in the structure of textile surface yarns to the surface of the textile by means of the napping process.

Figure 2: Shows that the superhydrophobic coating is obtained by coating the hydrophilic nanoparticle surface with a low surface energy molecule to provide hydrophobic properties and application of these nanoparticles to the surface of the textile surface with the spraying process.

Detailed Description of the Invention

The invention relates to obtaining a structure consisting of free fibers on the fabric surface by the napping process and subsequently depositing nanoparticles modified with low energy molecules on the fabric surface to obtain a superhydrophobic surface with high mechanical strength and water repellency.

The inventive method of textile surface coating includes the process steps of;

- Coating of inorganic nanoparticle surfaces with self-assembled monolayer molecules to provide hydrophobic properties,

- Napping the fibers that are available in the structure of textile surface yarns to the surface of the textile product using the napping process,

- Application of inorganic nanoparticles coated with self-assembled monolayer molecules to the surface of the textile product that has been subjected to a napping process by the spraying method in order to provide superhydrophobic properties.

In the invention, a method that can be used to obtain a structure with free fibers on the textile surface is napping (napping). Mechanical finishing processes are based on giving different properties and effects to fabrics with mechanical effects. Napping, which is one of these processes, is based on the principle of creating a napped surface by napping the fibers in the structure of the yarns of the woven fabric, to the surface of the fabric. Since the amount of air trapped in the pores increase as the product gains a more bulky structure as a result of the process, and the thermal insulation feature increases, the mechanical effect reduces the hardness of the product and provides a fuller and softer attitude. The napping process is a process used in the textile industry in order to make the fabric surface look better in terms of decoration and to provide thermal insulation. This process is carried out with a napping machine. The fabric can be processed according to the desired napping effect. With the invention, a structure consisting of free fibers on the fabric surface is obtained with the application of napping under certain conditions and this structure protects the nanoparticles that provide the surface with superhydrophobic properties, against mechanical effects. In the invention, in order to achieve the superhydrophobic effect, inorganic nanoparticles are coated with a self-assembled monolayer alkyl silane.

With the method of the invention, a superhydrophobic coating with very high impact and abrasion resistance was obtained. Free fibers obtained by the napping method are very important for the mechanical strength of superhydrophobic coatings. When the silica nanoparticles modified with alkyl silane are applied to fabrics that are not subjected to a napping technique and do not have free fiber structure, the obtained superhydrophobic coatings easily come off the surface.

In the method of the invention, superhydrophobic coating was obtained by depositing alkyl silane modified (with surface coated with alkyl silane) silica nanoparticles by spraying, on fabrics with free fibers on the surface, that were obtained by napping technique. The napping technique is basically the napping of the surface. In the napping method, fibers are pulled from the yarns used for weaving and are raised to the surface. As a result, a pile layer with

free fibers on the surface is formed. There are micron-sized gaps in fabrics with pile layer. Therefore, nanoparticles providing superhydrophobic property are not affected by the applied impacts. On the contrary, the applied impacts allow the particles to settle further into that pile layer. However, since such an effect is not observed in fabrics that do not have a pile structure, that is, fabrics that do not have a free fiber structure, nanoparticles move away from the surface as a result of impact. Therefore, the strength of superhydrophobic coatings is poor in fabrics that do not have a pile layer.

Preparation of Nanoparticles with Low Surface Energy:

Inorganic silica nanoparticles can be coated with self-assembled monolayer molecules in order for them to gain hydrophobic properties. Preferably, alkyl silane is used as a self-assembled monolayer in the invention. 2 grams of silica nanoparticles are added into 40 mL of toluene and mixed by means of a magnetic stirring bar at 600 rpm. After homogeneous mixing, 1 mL of alkyl silane is slowly added to the mixture of toluene silica nanoparticles. This solution is stirred for 3 hours. After mixing, this solution is centrifuged for 15 minutes in a centrifuge device. The hydrophobic silica nanoparticles obtained after centrifugation are dried in the oven at 80^0C. The drying process takes approximately 12 hours. In order to speed up the drying process, the drying process can be performed at higher temperatures. Silica nanoparticles are preferred in the invention. However, instead of silica nanoparticles, inorganic nanoparticles such as titanium dioxide, iron dioxide, zinc oxide can also be preferred. It is also possible to produce nanoparticles having low surface energy by using cheaper and readily available chemicals such as thinners instead of high purity chemicals such as toluene.

Application of the Napping Technique:

A layer consisting of free fibers is obtained by napping carried out on the surface of the fabric. For this purpose, by rubbing 2000 grit silicon carbide abrasive on the fabric surface, napping is formed on the surface of the fabric, in other words, free fibers are formed. In the method of the invention, the so called nubuck fabric is used. Nubuck fabric surface is a fabric that does not have free fibers that are pressed with the aid of a certain pressure or temperature. Due to this feature of the nubuck fabric, when superhydrophobic coating is applied to the nubuck fabric surface, the mechanical strength is poor. The napping process was applied to increase the strength of the superhydrophobic coating applied on the nubuck fabric surface. This process was carried out as follows: 2000 grit silicon carbide abrasive was bonded under

200 gram weights. This weight was moved over the nubuck fabric surface (5x5 cm^2). This process took approximately 5 minutes. At the end of this process, free fibers (pile layer) were formed on the nubuck fabric surface that did not have free fibers. As a result, a base material was prepared for the superhydrophobic coating (Figure 1).

Production of Superhydrophobic Coating;

Nanoparticles providing superhydrophobic property were deposited on the fabric that was napped by the napping technique. For this purpose, nanoparticles modified with low surface energy molecules were dispersed in ethanol (2% by weight). A magnetic stirrer was used to produce a homogeneous solution. The obtained alkyl silane solution was applied to the surface napped by the napping technique with a spray gun having a nozzle diameter of 0.35 mm at a pressure of 4 bars, from a distance of 10 cm (Figure 2).

In the method of the invention, the free fiber structure forming the pile layer on the surface of the fabric is important rather than the fabric type.

Some tests listed below were applied to determine the mechanical strength and water repellency of the superhydrophobic surface obtained by obtaining a structure consisting of free fibers on the fabric surface using the napping technique and then depositing the nanoparticles modified with low energy molecules on the fabric surface.

Abrasion Test with Weight;

The abrasion resistance of the superhydrophobic coating was characterized by bonding the superhydrophobic coated fabric with a surface area of $1cm^2$ under a weight of 200 grams and moving it over a 1000 grit silicon carbide abrasive surface. Although the superhydrophobic coating was moved about 200 cm over the abrasive, the static water contact angle is still 170° and still maintains high liquid repellency. There is no reduction in superhydrophobic coating as long as the fabric is not damaged. This process was repeated 20 times by measuring the static contact angle after every 10 cm movement of the superhydrophobic coated sample on the surface of silicon carbide. Despite the high abrasive feature of the silicon abrasive, the coating's superhydrophobic property shows that the developed method has a high mechanical strength.

Impact tests with water;

In the water jet impact test, it is seen that the static contact angle of the superhydrophobic coating that was applied with water impact under pressurized water for 10 minutes, is still

165°. Even though the pressurized water creates 32.0 kPa pressure on the superhydrophobic surface, the coating still maintains its static contact angle, which indicates that the coating has a high impact resistance.

In the spray test, another water impact test, the impact resistance of the coating is determined by spraying water onto the surface with the aid of a spray gun from a distance of 2.5 cm and by creating an impact on the surface. At the end of the 200 cycle process, it was observed that the static contact angle of the superhydrophobic coating was still (160°).

Washing test;

In the washing test, a water-detergent mixture was prepared by using 0.15% Mintax brand detergent. A homogeneous mixture was prepared using a stirrer, by spinning at 600 rpm. A washing test was carried out by putting the superhydrophobic coated fabric into the detergent-water mixture mixed at 600 rpm for 10 minutes. After 10 minutes, it was observed that it still maintained its superhydrophobic property and the contact angle was (163°).

In addition, one of the most important features of this method of invention is its high resistance to physical contact. Even if it is abraded by hand as strongly as desired, there is no loss of the repellency of the coating. As long as the superhydrophobic coated fabric is not torn, the repellency of the coating will remain.

CLAIMS

1. A method for coating a textile surface characterized by comprising the steps of;

a) Coating inorganic nanoparticle surfaces with a self-assembled monolayer molecule to provide hydrophobic properties,

b) Napping the fibers in the structure of textile surface yarns to the surface of the textile product, which is known as the napping process,

c) Application of inorganic nanoparticles coated with self-assembled monolayer obtained in the step a, to the surface of the textile product subjected to the napping process in the step b by the spraying method.

2. A method according to claim 1; characterized in that said inorganic nanoparticles are silica, titanium dioxide, iron dioxide or zinc oxide nanoparticles.

3. A method according to claim 1; characterized in that said self-assembled monolayer molecule is alkyl silane.

4. A method according to claim 1; characterized in that said textile product is a fabric.

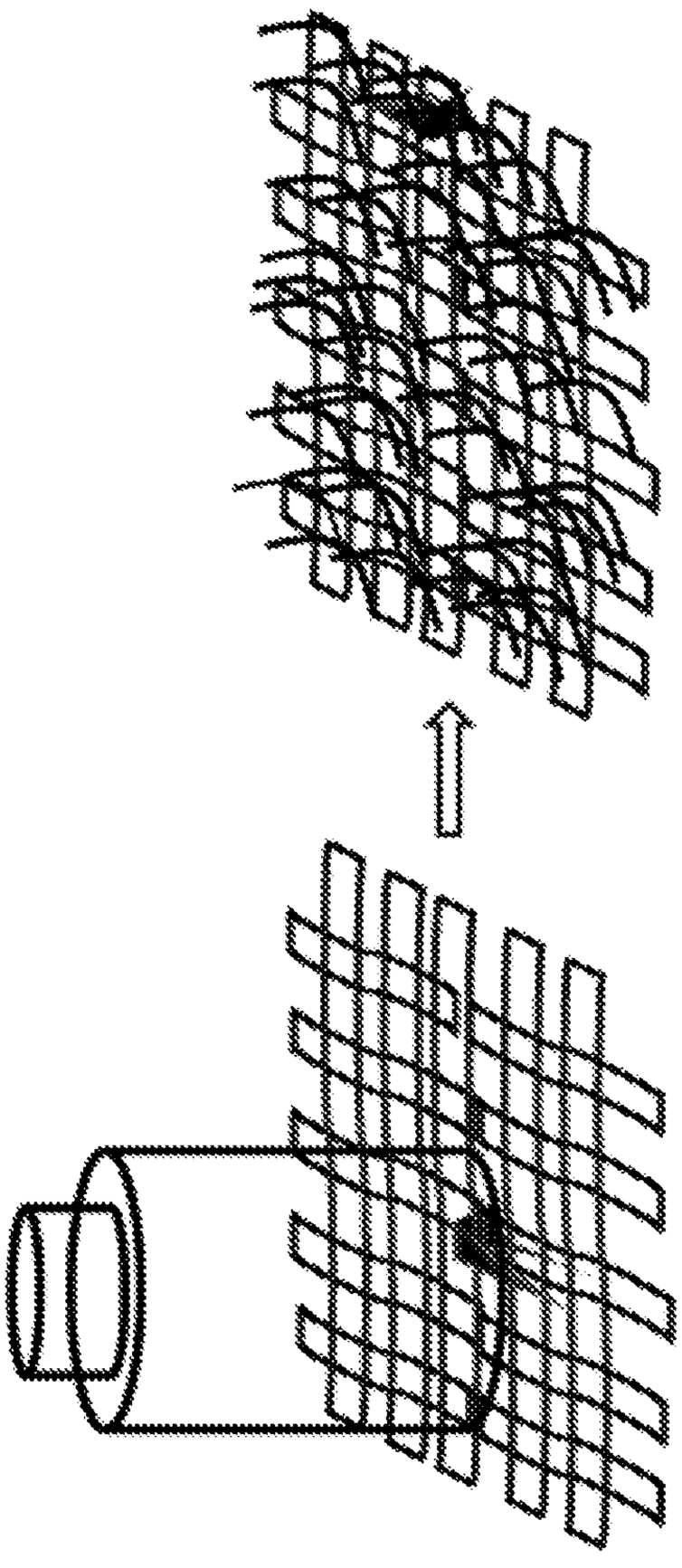

Figure 1

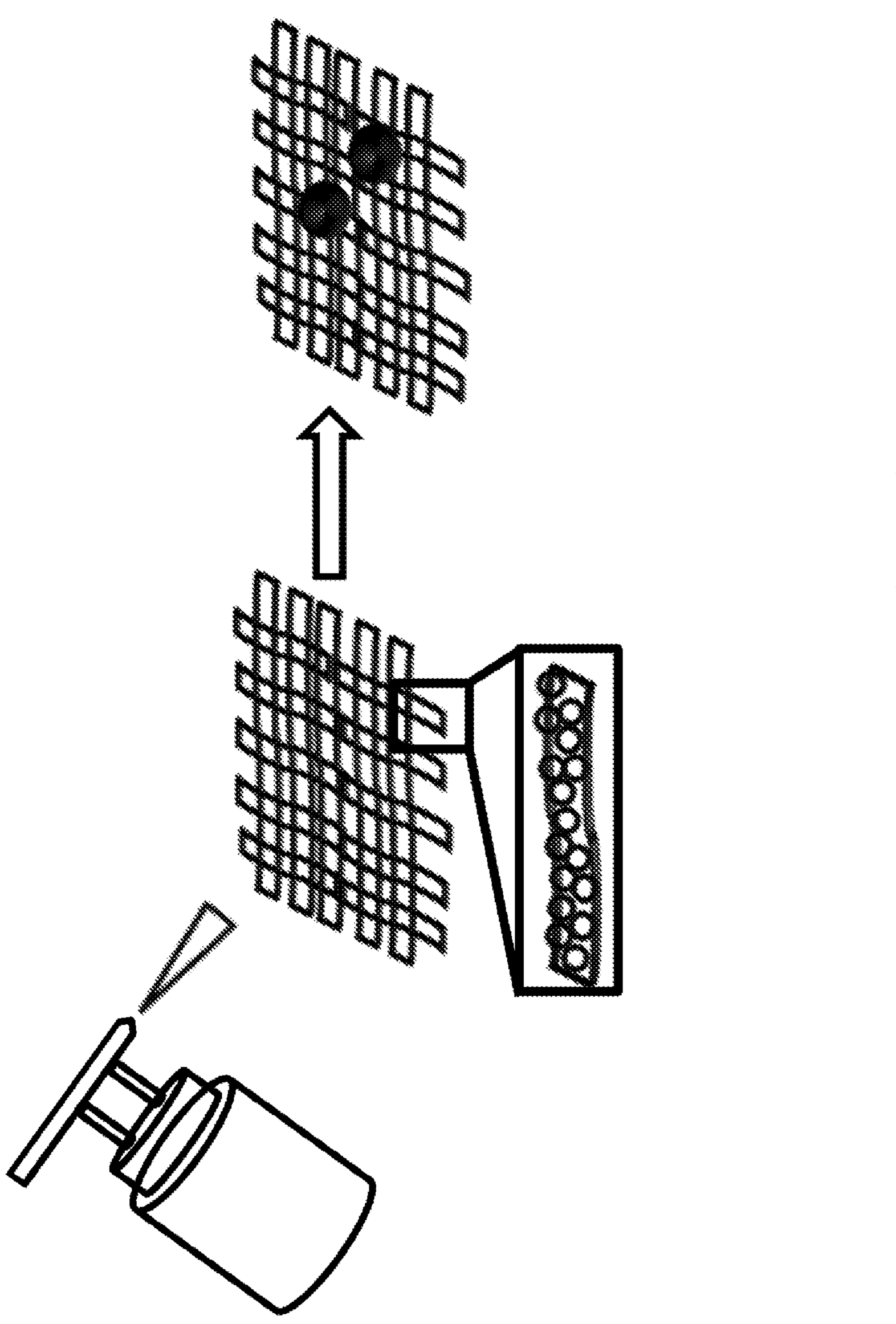

Figure 2

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

D06C 11/00 (2006.01)i; C09D 183/08 (2006.01)i; B82Y 30/00 (2011.01)i; D06M 11/79 (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)

D06C; C09D; B82Y; D06M

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

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

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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Y	US 2017298543 A1 (SHIUE HENG-HSING [TW]) 19 October 2017 (2017-10-19) Paragraph 20-26	1-4
A	AU 2005291822 A1 (NEWSOUTH INNOVATIONS PTY LTD) 13 April 2006 (2006-04-13) English translation of the document	1-4
A	CN 109400798 A (UNIV JIANGNAN) 01 March 2019 (2019-03-01) English translation of the document	1-4
A	WO 2005091755 A2 (UNIV FLORIDA STATE RES FOUND [US]) 06 October 2005 (2005-10-06) Paragraph 38	1-4

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

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Information on patent family members

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