(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 597 798 A1

(12) EUROPEAN PATENT APPLICATION

published in accordance with Art. 153(4) EPC

(43) Date of publication:
22.01.2020 Bulletin 2020/04

(21) Application number: **18724930.5**

(22) Date of filing: **21.02.2018**

(51) Int Cl.:
D01D 5/00 (2006.01)
D01D 5/098 (2006.01)
B32B 27/12 (2006.01)
B05D 1/06 (2006.01)
B82Y 30/00 (2011.01)
D06M 23/08 (2006.01)
B32B 5/02 (2006.01)

(86) International application number:
PCT/ES2018/070125

(87) International publication number:
WO 2018/167341 (20.09.2018 Gazette 2018/38)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
MA MD TN

(30) Priority: **13.03.2017 ES 201730327**

(71) Applicants:
- **Bioinicia, S.L.**
  46988 Paterna (Valencia) (ES)
- **Consejo Superior de Investigaciones Científicas (CSIC)**
  28006 Madrid (ES)

(72) Inventors:
- **LAGARÓN CABELLO, José María**
  46980 Paterna (Valencia) (ES)
- **CASTRO REINA, Sergio**
  46980 Paterna (Valencia) (ES)
- **GALAN NEVADO, David**
  46988 Paterna (Valencia) (ES)

(74) Representative: **Pons Ariño, Angel**
Pons Patentes y Marcas Internacional, S.L.
Glorieta Rubén Dario 4
28010 Madrid (ES)

(54) METHOD FOR THE ADHESION OF PARTICLES TO AN INERT SUBSTRATE

(57) The invention relates to a method for the adhesion of particles with exceptional functional properties, such as hydrophobicity, to an inert substrate. The invention pertains to the field of nanotechnology, specifically sectors in which the surface properties of a material or substance need to be modified, such as the food, pharmaceutical, biomedical or energy sectors.

Printed by Jouve, 75001 PARIS (FR)

Description

[0001] The present invention relates to a method for adhering particles with exceptional functional properties, such as hydrophobia, to an inert substrate.

[0002] The present invention falls within the area of nanotechnology, specifically in the sector where it is necessary to modify the surface properties of a material or substance, such as the food, pharmaceutical, biomedical or energy sector.

STATE OF THE ART

[0003] The development of nanoscience in recent decades has allowed for the development of nano and microparticles with exceptional functional properties, such as, for example, superhydrophobicity, superhydrophilicity, superoleophobicity, catalytic properties, self-cleaning properties, self-repairable properties, etc.

[0004] The deposition of nanoparticles on macroscopic surfaces is a necessary step to transmit said exceptional functional properties derived from the nanometric size of the particles to large surfaces. The adhesion of nanoparticles to surfaces mainly depends on the properties thereof, which may or may not offer different adhesive forces (chemical, electrostatic, Van der Waals, diffusive). There are costly techniques such as vacuum deposition, nanoimprinting, or multiple surface treatments that are mainly used with conventional substrates.

[0005] The adhesion of nanoparticles to plastic surfaces has the drawback that these nanoparticles are easily deformed, have low temperature resistance and have little adherence to inorganic particles, such as most nanoparticles. Furthermore, deposition on plastic materials is usually complicated due to the fact that these materials are usually chemically inert and do not have anchoring cores that allow for adhesion.

[0006] The adhesion of nanoparticles to inert plastics can be favored by means of corona treatment which activates the plastic surface, thus allowing for better adhesion, but which is generally insufficient since the nanoparticle has a very small contact surface. Mizoshita and Tanaka [ACS Appl. Mater. Interfaces 2016, 8, 31330-31338] propose an alternative method based applying an alcoholic solution of nanoparticles on the plastic surface, followed by a treatment in a reactive atmosphere of chloroform; this reactive atmosphere increases the adhesion of the nanoparticles to the plastic substrate. However, the difficulty of scaling due to the use of the reactive atmosphere is evident.

[0007] For example, the use of hydrophobic coatings is one of the most used strategies to prevent the deterioration of the materials under very humid conditions. Materials with hydrophobic properties offer significant advantages, such as: they prevent the corrosion and staining of the surfaces (i.e. they are self-cleaning), they increase barrier properties against water vapor and they prevent the attack of microorganisms, among others.

[0008] There are different alternatives for generating hydrophobic coatings, including chemical modification and coating with plasma, among others (Rahmawan, Y., Xu, L., & Yang, S. Journal of Materials Chemistry A, doi: 10.1039/C2TA00288D, 2013). In particular, the deposition of nanoparticles with hydrophobic properties on any type of substrate has created important advantages in this field due to the fact that the materials on the nanoscale have a greater surface to volume ratio. However, the adhesion between the hydrophobic nanoparticles and the surface is insufficient.

[0009] Therefore, it is necessary to develop new methods for improving the adhesion properties between the particles with, for example, hydrophobic properties, and the substrate.

DESCRIPTION OF THE INVENTION

[0010] The present invention relates to a method for adhering particles with exceptional functional properties to an inert substrate. The present invention is of special interest in various sectors, for example,

- in the food sector, where there is interest in highly slippery, hydrophobic, oleophobic, amphiphobic, amphiphilic also called amphipathic, superhydrophobic, superoleophobic, superamphiphobic, and superamphilic also called superamphipathic properties, or surfaces with an antioxidant and/or antimicrobial capacity;
- in the pharmaceutical or biomedical sector, where there is interest in antimicrobial surfaces; and
- in the energy sector, where there is interest in transparent, self-cleaning and/or non-reflecting surfaces.

[0011] In the present invention, a layer of adhesive fibers is used to join the inert substrate to particles that have exceptional functional properties, and a thermal treatment is then carried out which improves the adhesion of the particles deposited on said fibers, keeping the exceptional functional properties of the particles intact.

[0012] In the particular case of the invention, when plastic or biopolymer substrates are used, it has been observed that the system obtained with the method of the present invention is more transparent after the thermal treatment, keeping the intrinsic properties of the particles with excellent functional properties that are deposited on an inert substrate unaltered.

[0013] Therefore, in a first aspect, the present invention relates to a method for adhering particles to an inert substrate (hereinafter, "the method of the invention") characterized in that it comprises the following steps:

a) deposit adhesive fibers on an inert substrate by means of an electro-hydrodynamic or aero-hydrodynamic process or a combination of both processes;
b) optionally, thermally treat the deposit obtained in (a) at a temperature lower than the melting or degradation temperature of the adhesive fibers for a period of time between 0.1 s and 1 h;
c) homogeneously distribute particles of a size between 0.001 nm and 100 μm on the adhesive fibers obtained in step (a) or (b) by means of deposition; and
d) thermally treat the deposit obtained (c) at a temperature lower than the melting or degradation temperature of the adhesive fibers for a period of time between 0.1 s and 1 h.

[0014] In the present invention, "an inert substrate" is understood as a plastic, metal, ceramic or glass substrate with little or no capacity to adhere particles.

[0015] In a preferred embodiment, the substrate will be a thermoplastic, thermostable or elastomer plastic or a biopolymer.

[0016] Preferably, the inert substrate is selected from the list comprising polyolefins, polyesters, polyamides, polimides, polyketones, polyisocyanates, polysulphones, styrenic plastics, phenolic resins, amide resins, urea resins, melamine resins, polyester resins, epoxide resins, polycarbonates, polyvinylpyrrolidones, epoxy resins, polyacrylates, rubbers, polyurethanes, silicones, aramides, polybutadiene, polyisoprenes, polyacrylonitriles, polyvinylidene fluoride (PVDF), polyvinyl acetate (PVA), polyvinyl alcohol (PVOH), ethylene vinyl alcohol (EVOH) copolymer, ethylene-vinyl-alcohol (EVO), polyvinyl chloride (PVC), polyvinylidene chloride (PVDC) and a combination thereof.

[0017] Preferably, the substrate is a biopolymer selected from among proteins, polysaccharides, lipids, polyesters and a combination thereof.

[0018] The term "adhesive fibers" is understood in the present invention as the fibers that serve as an adhesive between the particles and the inert substrate.

[0019] In the method of the present invention, the adhesive fibers of step (a) are made up of any plastic whose melting temperature is typically lower than the softening temperature of the substrate.

[0020] Preferably, the adhesive fibers of the step (a) are comprised of

- polycaprolactone;
- polyamides, ethylene vinyl alcohol (EVOH) copolymers and derivatives thereof;
- or biopolymers.

[0021] Preferably, the biopolymers are selected from among peptides and natural or synthetic proteins obtained chemically or by genetic modification of microorganisms or plants and natural elements; synthetic polysaccharides obtained chemically or by genetic modification of microorganisms or plants; polypeptides, nucleic acids and synthetic nucleic acid polymers obtained chemically or by genetic modification of microorganisms or plants; biodegradable polyesters such as polylactic acid, polylactic-glycolic acid, adipic acid and derivatives thereof, and polyhydroxyalkanoates, polyhydroxybutyrate and its copolymers with valerate; and biomedical materials, such as hydroxyapatites, of the group of synthetic and natural (plant or animal) polysaccharides, such as cellulose and derivatives; carrageenans and derivatives; alginates, dextran, gum arabic and chitosan or any of the natural and synthetic derivatives thereof; and corn proteins (zein); gluten derivatives, such as gluten or the gliadin and glutenin fractions thereof; gelatin, casein and soy proteins and derivatives thereof; as well as natural or synthetic peptides preferably of the elastin type obtained chemically or by genetic modification of microorganisms or plants and mixtures thereof. More preferably, the biopolymers are biodegradable polyesters.

[0022] In another preferred embodiment of the method of the present invention, in addition to the polymers described in the previous paragraph, at least one additive that is selected from among plasticizers, emulsifiers, anti-flocculants, surfactants, process improvers, anti-static agents, cross-linking agents, foaming agents or any of the combinations thereof is added during the deposition of step (a). This additive can also be any additive used in the industry of the polymers known in the state of the art without size restrictions, in other words, including nano additives; and said additives can be used to provide better final properties to the final product or facilitate the processing thereof.

[0023] In the method of the present invention, the adhesive fibers of step (a) preferably have a diameter smaller than 5 μm.

[0024] As mentioned above, step (a) of the method of the invention relates to the deposition of adhesive fibers on an inert substrate. In a preferred embodiment, the deposit obtained after step (a) preferably has a thickness between 10 nm and 100 μm.

[0025] In step (a), the adhesive fibers are deposited by means of an electro-hydrodynamic or aero-hydrodynamic process or a combination of both. The solvents used in these deposition methods will be those that dissolve the polymer or adhering substance, which can be organic as well as polar, including water, ethanol, isopropanol, chloroform, dimethylformamide, acetone, acetic acid, TFA, etc.

[0026] Step (a) of the method of the invention relates to the deposition of adhesive fibers on an inert substrate; this is preferably carried out by means of an electro-hydrodynamic process with electrospinning.

[0027] Electrospinning is one of the most widely used methods for manufacturing meshes with micro- or nanometric fibers and with a high surface to volume ratio. This technique also enables obtaining fibers with high roughness on the surface and thick films by means of thermal and mechanical post-treatment. The electrospinning process consists of applying an electric field to a liquid droplet, generally a polymer solution. The electric force applied generates disturbances on the droplet, forming a geometric shape technically known as the "Taylor cone". When the electric field exceeds a critical value, a liquid stream or jet that moves toward a collector with an opposite charge is produced. Along the path of the stream, the solvent is evaporated, thus resulting in the formation of ultra-fine fibers.

[0028] In another preferred embodiment of step (a), the method is carried out by means of an aero-hydrodynamic process by means of blow spinning.

[0029] The method of the invention further comprises an optional step (b) for thermally treating the deposit obtained (a) at a temperature lower than the melting or degradation temperature of the adhesive fibers for a period of time between 0.1 s and 1 h.

[0030] In a preferred embodiment, step (b) is not optional, meaning that the method of the invention is characterized in that it comprises the followings steps:

a) deposit adhesive fibers on an inert substrate by means of an electro-hydrodynamic or aero-hydrodynamic process or a combination of both processes;
b) thermally treat the deposit obtained in (a) at a temperature lower than the melting or degradation temperature of the adhesive fibers for a period of time between 0.1 s and 1 h;
c) homogeneously distribute particles of a size between 0.001 nm and 100 μm on the adhesive fibers obtained in step (a) or (b) by means of deposition; and
d) thermally treat the deposit obtained (c) at a temperature lower than the melting or degradation temperature of the adhesive fibers for a period of time between 0.1 s and 1 h.

[0031] The thermal treatment of step (d) is preferably carried out by using a heating press even though this treatment is not exclusively limited to this technique, but rather any technique that can transmit heat in a controlled way.

[0032] In another preferred embodiment of the present invention, step (b) is carried out by applying pressure between 0.1 bar and 100 bar, preferably below 30 bar.

[0033] The method of the invention further comprises a step (c) for homogeneously distributing particles of a size between 0.001 nm and 100 μm on the adhesive fibers obtained in step (a) or (b) by means of deposition.

[0034] Preferably, the particles of step (c) have exceptional functional properties, such as hydrophobic, hydrophilic, oleophobic, oleophilic, amphiphobic, amphiphilic also called amphipathic, self-cleaning, antioxidant, antimicrobial, self-curing, UV-light absorbent or flame retardant properties, or serve as a barrier towards gases and vapors.

[0035] One application of great interest for the method of the present patent is the manufacture of hydrophobic surfaces. Hydrophobicity is defined as the property that the surface of some materials has to repel water. This property not only depends on the chemical composition of the surface, but also on the roughness thereof. The most commonly used parameter to measure hydrophobicity is the contact angle, defined as the angle that a liquid forms with respect to the surface of a solid substrate. When the contact angle is greater than 90°, it is said that the material is hydrophobic, while when this parameter is greater than 150°C, it is said that the material is superhydrophobic.

[0036] In a preferred embodiment of the method of the present invention, the particles of step (c) are selected from among cellulose nanocrystals, cellulose microfibers, kenaf nanofibers, keratin nanofibers, nanoclays, carbon nanotubes, carbon nanofibers, carbon nanosheets, metal oxides, metal hydroxides, nanosilica, silicon nanodioxide, metal nanoparticles, titanium nanodioxide with or without organic modification and a combination thereof. Preferably, the particles are selected from among nanosilica, silicon nanodioxide, titanium nanodioxide with or without organic modification and a combination thereof.

[0037] Silicon dioxide is obtained without limitation mainly by means of the extraction and purification of quartz. This product is suitable for many purposes; meanwhile for other purposes, chemical processing is necessary in order to make a product purer or, in another more suitable way, to make it more reactive or a fine-grained, for example.

[0038] Pyrogenic silica, sometimes called fumed silica, is a very fine form of silicon dioxide in the shape of colloidal particles. It is prepared by burning $SiCl_4$ in a flame of hydrocarbons rich in oxygen in order to produce a SiO_2 "fume".

[0039] The precipitated silica, also known as amorphous silica or silica gel, is produced by the acidification of sodium silicate solutions. The gelatinous precipitate is first washed and then dehydrated in order to produce colorless microporous silica.

[0040] Alternatively, fine sheets of silica spontaneously grow in silicon wafers by means of thermal oxidation. This route provides a layer that is very close to the surface (approximately 1 nm or 10 Å) of the so-called native oxides. Very high temperatures and alternative environments are used to make well-controlled layers of silicon dioxide grow on the silicon, for example, at temperatures between 600°C and 1200°C, using the so-called wet or dry oxidation with O_2.

[0041] Many routes to silicon dioxide begin with silicate esters, the most well-known being tetraethyl orthosilicate (TEOS). The dioxide is obtained by simply heating TEOS to 680°C - 730°C. By being highly stable, silicon dioxide results from many methods. Conceptually simple but with little practical value, the combustion of silane leads to silicon dioxide. This reaction is analogous to the combustion of methane.

[0042] In another preferred embodiment of the method of the present invention, the particles of step (c) are selected from among polytetrafluoroethylene (PTFE) and polystyrene.

[0043] Another preferred embodiment of the method of the present invention relates to when the particles of step (c) are selected from among hydroxyapatites and phosphates of organic salts, optionally modified preferably with quaternary ammonium salts and/or organosilanes.

[0044] The particles can be interspersed or modified with modifiers in order to ensure their compatibility with other materials. Therefore, they can be modified with quaternary ammonium salts and organosilanes, preferably substances allowed for the application, for example in the case of application in containers, which are allowed to come in contact with food (in other words, they are included in the lists of monomers and other starting substances authorized by law for their use in the manufacture of plastic materials and objects that are going to come in contact with foods, such as, but not limited to, hexadecyltrimethylammonium bromide, polyethylene glycol esters with aliphatic monocarboxylic acids (C6-C22) and ammonium and sodium sulphates thereof, perfluorooctanoic acid and ammonium salt thereof, N-methacryloyloxyethyl-N,N-dimethyl-N-carboxymethylammonium chloride, and bis(2-hydroxyethyl)-2-hydroxypropyl-3-(dodecyloxy)methylammonium chloride. Chitosan and derivatives thereof and/or combinations of the above can also be used. More preferably, quaternary ammonium salts such as hexadecyltrimethylammonium bromide and organosilanes will be used.

[0045] They can also be modified with metal salt particles, such as silver, copper, iron, nickel, and other particles or nanoparticles with microbial and oxygen absorbing properties, metal oxides, such as titanium oxide and zinc, non-metal oxides, such as chemically modified silicon oxides, and plastics, such as fluoropolymers (PTFA) or polystyrene, and/or combinations of the above.

[0046] Step (c) of the method of the invention is carried out by means of any technique for depositing the particles, preferably by means of electro-hydrodynamic deposition, aero-hydrodynamic deposition or a combination of both techniques. Alternatively, step (c) is carried out by means of electro-spraying, blow-spraying or gravimetric dusting. The blow-spraying technique is even more preferably selected from among pneumatic, piezo-electric or ultrasonic nebulization.

[0047] The final step of the method of the invention, step (d), relates to the thermal treatment of the deposit obtained in step (c) at a temperature lower than the melting or degradation temperature of the adhesive fibers used in step (a) for a period of time between 0.1 s and 1 h. Preferably, step (d) is carried out by applying pressure between 0.1 bar and 100 bar, more preferably below 30 bar.

[0048] In another preferred embodiment of the method of the present invention, step (d) is carried out by means of a heating press, a calender, an oven or an ultraviolet (UV) or infrared (IR) lamp.

[0049] Throughout the description and in the claims, the word "comprises" and its variants are not intended to exclude other technical characteristics, additives, components or steps. For those skilled in the art, other objects, advantages and characteristics of the invention may be deduced from both the description and the practical use of the invention. The following examples and drawings are provided by way of illustration, and are not meant to limit the present invention.

BRIEF DESCRIPTION OF THE FIGURES

[0050]

Figure 1 shows a diagram of the process of the present invention.

Figure 2 shows images of the measurement of the contact angle of the PET films coated with PLA nanofibers.

Figure 3 shows images of the measurement of the contact angle of the PET films coated with a layer of PLA nanofibers and another layer of organo-modified nanoparticles of SiO_2.

Figure 4 shows images of the measurement of the contact angle of the PE films coated with a layer of PCL nanofibers and another layer of organo-modified nanoparticles of SiO_2.

Figure 5 shows images of the measurement of the contact angle of the PE films coated with a layer of PCL nanofibers and another layer of PTFE nanoparticles.

Figure 6 shows images of the measurement of the contact angle with water (left) and olive oil (right) of the PE films coated with a layer of PCL nanofibers and another layer of PTFE nanoparticles.

Figure 7 shows images of the contact angle with water on the PET/PLA-NF/SiO_2 NPs and PET/PLA+TiO_2/SiO_2 NPs surfaces before (left column) and after (right column) the thermal treatment at 150°C for 3 s.

Figure 8 shows images of PET films: (A) PET without film; (B) PET/PLA processed at 50°C for 3 s; (C) PET/PLA processed at 50°C for 60 s; (D) PET/PLA processed at 60°C for 3 s; (E) PET/PLA processed at 60°C for 60 s and (F) PET/PLA processed at 70°C for 3 s.

EXAMPLES

[0051] The invention is illustrated below by means of assays carried out by the inventors which reveal the effectiveness of the product of the invention.

[0052] Fig. 1 shows the diagram of the method of the invention.

[0053] **Example 1.** Deposition of polylactic acid (PLA) nanofibers obtained by means of electrospinning on polyethylene terephthalate (PET).

[0054] A solution of PLA at 15% by weight was prepared in a mixture of dimethylformamide (DMF) and acetone (1:1). Said mixture was electrospun on a PET sheet under the following conditions:

- electrical voltage: 17 kV,
- rate of injection: 1 mL/h
- and distance to the collector: 15 cm.

[0055] The sheets coated with the nanofibers were placed between two plates at 50°C for 3 s to promote adhesion between the sheets.

[0056] The PET films coated with PLA nanofibers showed contact angles of around 120°, characteristic of hydrophobic surfaces (See Fig. 2). It is observed that the porous morphology created during electrospinning favors hydrophobicity.

[0057] **Example 2.** Deposition of modified silicon oxide nanoparticles (HDK H18 by Wacker) on the deposit obtained in Example 1.

[0058] PET films coated with PLA nanofibers were manufactured by using the method indicated in Example 1. A suspension of organo-modified silicon oxide particles (HDK H18 by Wacker) (1 % w/v in DMF) was deposited on these samples under the following conditions:

- electrical voltage: 10 kV,
- rate of injection: 0.3 mL/h and
- distance to the collector: 15 cm.

[0059] The coated PET films showed contact angles of around 130°, characteristic of hydrophobic surfaces (See Fig. 3). It is observed that the addition of the layer of organo-modified SiO_2 nanoparticles on the polymer layer improves the hydrophobic properties of the surface.

[0060] **Example 3.** Deposition of polycaprolactone (PCL) nanofibers obtained by means of electrospinning on polyethylene (PE).

[0061] PE films coated with PCL nanofibers were manufactured by using the method indicated in Example 1.

[0062] **Example 4.** Deposition of organo-modified silicon oxide nanoparticles on the deposit obtained in Example 3 and subsequent thermal treatment.

[0063] A suspension of organo-modified silicon oxide particles (HDK H18 by Wacker) (1 % w/v in butanol) was deposited on these samples under the following conditions:

- electrical voltage: 10 kV,
- rate of injection: 1 mL/h and
- distance to the collector: 15 cm.

[0064] Next, a thermal treatment was carried out at 50°C for 3 minutes. The coated PE films showed contact angles of around 160°, characteristic of superhydrophobic surfaces (See Fig. 4). It is observed that the addition of the layer of organo-modified SiO_2 nanoparticles (HDK H18 by Wacker) on the polymer layer improves the hydrophobic properties of the surface.

[0065] **Example 5.** Deposition of micronized polytetrafluoroethylene (PTFE) powder on the deposit obtained in Example 4 and subsequent thermal treatment.

[0066] PE films coated with PCL nanofibers were manufactured by using the method indicated in Example 1.

[0067] A micronized PTFE powder was deposited on these samples, followed by a thermal treatment at 50°C for 3 minutes. The coated PE films showed contact angles greater than 160°, characteristic of superhydrophobic surfaces (See Fig. 5). It is observed that the addition of the layer of PTFE microparticles on the polymer layer improves the hydrophobic properties of the surface.

[0068] Example 6. Deposition of polycaprolactone (PCL) nanofibers obtained by means of electrospinning on polyethylene (PE) and subsequent thermal treatment.

[0069] PE films coated with PCL nanofibers were manufactured by using the method indicated in Example 1.

[0070] Next, a thermal pre-treatment was applied at 50°C for 1 minute with the aim of generating a flat film and favoring the oleophobic nature of the film.

[0071] Example 7. Deposition of micronized PTFE powder on the deposit obtained in Example 6 and subsequent thermal treatment.

[0072] A micronized PTFE powder was deposited on these samples, followed by a thermal treatment at 50°C for 3 minutes.

[0073] The coated PE films showed contact angles with the water close to 160°, characteristic of superhydrophobic surfaces, and contact angles with oils close to 70° (See Fig. 6), characteristic of hydrophobic surfaces. This methodology enables amphiphobic or amphiphilic, also called amphipathic, films to be created according to that which is described.

[0074] Example 8. Deposition of SiO_2 and SiO_2/TiO_2 nanoparticles on the deposit obtained in Example **1** and subsequent thermal treatment.

[0075] Two PET sheets coated in PLA were manufactured according to Example 1. SiO_2 and SiO_2/TiO_2 nanoparticles were deposited, respectively. Thermal post-treatment was applied to these sheets at a temperature of 150°C for 3 s with the aim of transforming the morphology of PLA nanofibers into a flat film with few hydrophobic properties. Fig. 7 (right column) shows how the contact angle is reduced drastically after treatment at a high temperature.

[0076] Table 1 shows the effect of temperature and time on the final contact angle. It is observed how the thermal treatment improves the adhesion of the nanoparticles, keeping some properties intact, such as hydrophobicity.

Table 1. Effect of temperature and time on the contact angle of a water droplet.

Sample	Temperature (°C)	Time (s)	Contact angle (°)
A	50	3	122
B		60	90
C	60	3	134
D		60	114
E	70	3	133
F		60	nd

[0077] Another property of the film that is kept intact is transparency. Fig. 8 shows different films treated according to the different conditions defined in Table 1, covering printed letters on a paper. At first glance, it is observed how the different post-treatment conditions affect the the transparency of the film.

Claims

1. A method for adhering particles to an inert substrate, **characterized in that** it comprises the following steps:

   a) deposit adhesive fibers on an inert substrate by means of an electro-hydrodynamic or aero-hydrodynamic process or a combination of both processes;
   b) optionally, thermally treat the deposit obtained in (a) at a temperature lower than the melting or degradation temperature of the adhesive fibers for a period of time between 0.1 s and 1 h;
   c) homogeneously distribute particles of a size between 0.001 nm and 100 μm on the adhesive fibers obtained in step (a) or (b) by means of deposition; and
   d) thermally treat the deposit obtained in (c) at a temperature lower than the melting or degradation temperature of the adhesive fibers for a period of time between 0.1 s and 1 h.

2. The method according to claim 1, **characterized in that** it comprises the following steps:

   a) deposit adhesive fibers on an inert substrate by means of an electro-hydrodynamic or aero-hydrodynamic process or a combination of both processes;
   b) thermally treat the deposit obtained in (a) at a temperature lower than the melting or degradation temperature of the adhesive fibers for a period of time between 0.1 s and 1 h;

c) homogeneously distribute particles of a size between 0.001 nm and 100 μm on the adhesive fibers obtained in step (a) or (b) by means of deposition; and

d) thermally treat the deposit obtained in (c) at a temperature lower than the melting or degradation temperature of the adhesive fibers used in step (a) for a period of time between 0.1 s and 1 h.

3. The method according to any of claims 1 or 2, **characterized in that** the inert subsrtate is a thermoplastic, thermostable or elastomer plastic or a biopolymer.

4. The method according claim 3, **characterized in that** the inert substrate is selected from the list comprising polyolefins, polyesters, polyamides, polimides, polyketones, polyisocyanates, polysulphones, styrenic plastics, phenolic resins, amide resins, urea resins, melamine resins, polyester resins, epoxide resins, polycarbonates, polyvinylpyrrolidones, epoxy resins, polyacrylates, rubbers, polyurethanes, silicones, aramides, polybutadiene, polyisoprenes, polyacrylonitriles, polyvinylidene fluoride, polyvinyl acetate, polyvinyl alcohol, ethylene vinyl alcohol copolymer, ethylene-vinyl-alcohol, polyvinyl chloride, polyvinylidene chloride and a combination thereof.

5. The method according to claim 3, wherein the substrate is a biopolymer selected from among proteins, polysaccharides, lipids, polyesters and a combination thereof.

6. The method according to any of claims 1 to 5, **characterized in that** the adhesive fibers of step (a) are comprised of

- polycaprolactone;
- polyamides, ethylene vinyl alcohol (EVOH) copolymers and derivatives thereof;
- or biopolymers.

7. The method according to claim 6, **characterized in that** the biopolymers are selected from among peptides and natural or synthetic proteins obtained chemically or by genetic modification of microorganisms or plants and natural elements; synthetic polysaccharides obtained chemically or by genetic modification of microorganisms or plants; polypeptides, nucleic acids and synthetic nucleic acid polymers obtained chemically or by genetic modification of microorganisms or plants; biodegradable polyesters such as polylactic acid, polylactic-glycolic acid, adipic acid and derivatives thereof, and polyhydroxyalkanoates, polyhydroxybutyrate and its copolymers with valerate; and biomedical materials, such as hydroxyapatites, of the group of synthetic and natural (plant or animal) polysaccharides, such as cellulose and derivatives; carrageenans and derivatives; alginates, dextran, gum arabic and chitosan or any of the natural and synthetic derivatives thereof; and corn proteins (zein); gluten derivatives, such as gluten or the gliadin and glutenin fractions thereof;
gelatin, casein and soy proteins and derivatives thereof; as well as natural or synthetic peptides preferably of the elastin type obtained chemically or by genetic modification of microorganisms or plants and mixtures thereof.

8. The method according to claim 7, **characterized in that** the biopolymers are biodegradable polyesters.

9. The method according to any of claims 1 to 8, **characterized in that** the adhesive fibers of step (a) have a diameter smaller than 5 μm.

10. The method according to any of claims 1 to 9, **characterized in that** the deposit obtained after step (a) has a thickness between 10 nm and 100 μm.

11. The method according to any of claims 1 to 10, **characterized in that** step (a) is carried out by means of an electrohydrodynamic process with electrospinning.

12. The method according to any of claims 1 to 10, **characterized in that** step (a) is carried out by means of an aerohydrodynamic process with blow spinning.

13. The method according to any of claims 1 to 12, **characterized in that** step (b) is carried out by applying pressure between 0.1 bar and 100 bar.

14. The method according to claim 13, wherein step (b) is carried out by applying pressure below 30 bar.

15. The method according to any of claims 1 to 14, **characterized in that** the particles of step (c) have hydrophobic, hydrophilic, oleophobic, oleophilic, amphiphobic, amphiphilic or amphipathic, self-cleaning, antioxidant, antimicrobial, self-curing, UV light absorbent or flame retardant properties, or serve as a barrier towards gases and vapors.

16. The method according to any of claims 1 to 15, **characterized in that** the particles of step (c) are selected from among cellulose nanocrystals, cellulose microfibers, kenaf nanofibers, keratin nanofibers, nanoclays, carbon nanotubes, carbon nanofibers, carbon nanosheets, metal oxides, metal hydroxides, nanosilica, silicon nanodioxide, metal nanoparticles, titanium nanodioxide with or without organic modification and a combination thereof.

17. The method according to claim 16, **characterized in that** the particles of step (c) are selected from among nanosilica, silicon nanodioxide, titanium nanodioxide with or without organic modification and a combination thereof.

18. The method according to any of claims 1 to 15, **characterized in that** the particles of step (c) are selected from among polytetrafluoroethylene and polystyrene.

19. The method according to any of claims 1 to 15, **characterized in that** the particles of step (c) are selected from among hydroxyapatites and phosphates of organic salts, optionally modified with quaternary ammonium salts and/or organosilanes.

20. The method according to any of claims 1 to 19, **characterized in that** step (c) is carried out by means of electro-hydrodynamic deposition, aero-hydrodynamic deposition or a combination of both techniques.

21. The method according to any of claims 1 to 19, **characterized in that** step (c) is carried out by means of electro-spraying, blow-spraying or gravimetric dusting.

22. The method according to claim 21, **characterized in that** the blow-spraying technique is selected from among pneumatic, piezo-electric or ultrasonic nebulization.

23. The method according to any of claims 1 to 22, **characterized in that** step (d) is carried out by applying pressure between 0.1 bar and 100 bar.

24. The method according to claim 23, **characterized in that** step (d) is carried out by applying pressure below 30 bar.

25. The method according to any of claims 1 to 24, wherein step (d) is carried out by means of a heated press, a calender, an oven or an ultraviolet or infrared lamp.

Fig. 1

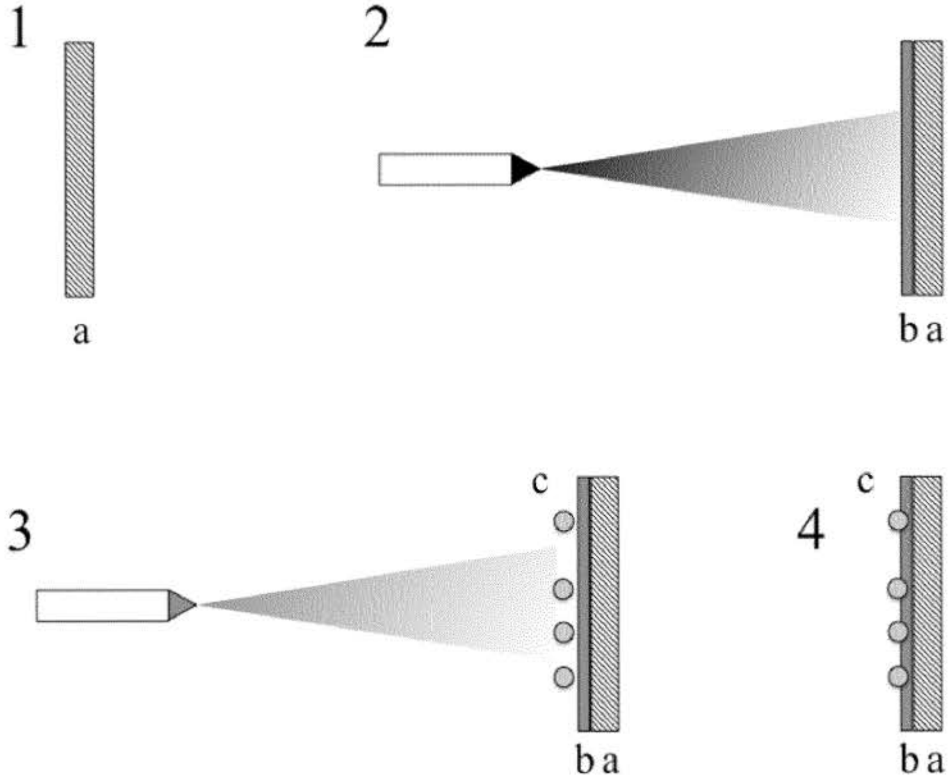


Fig. 2

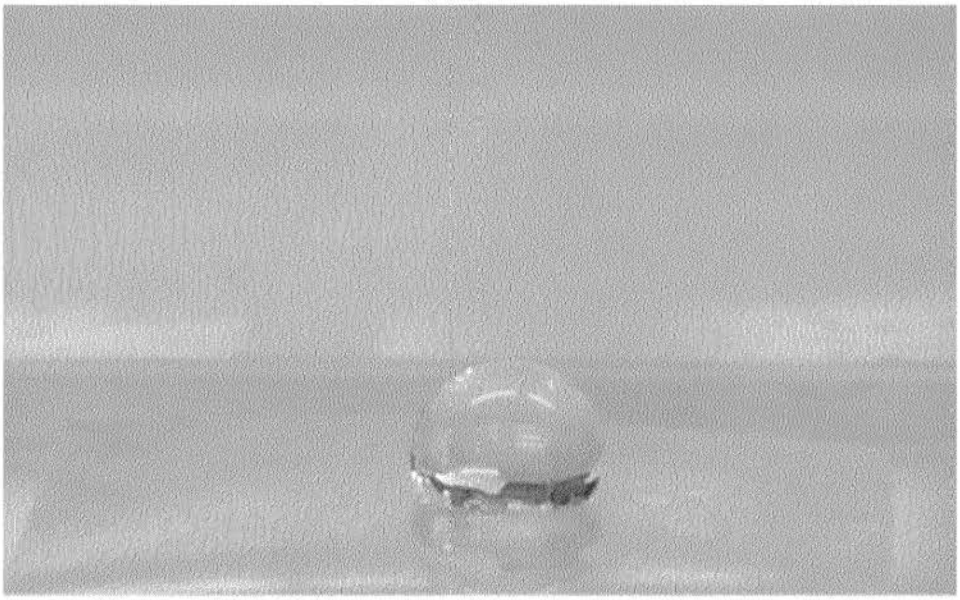


Fig. 3

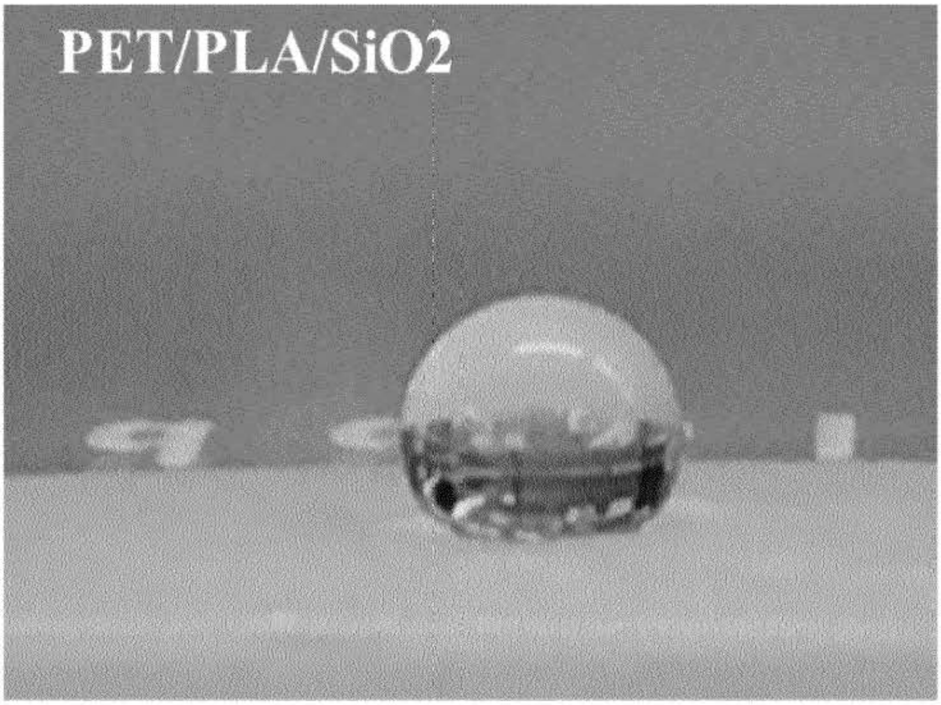


Fig. 4

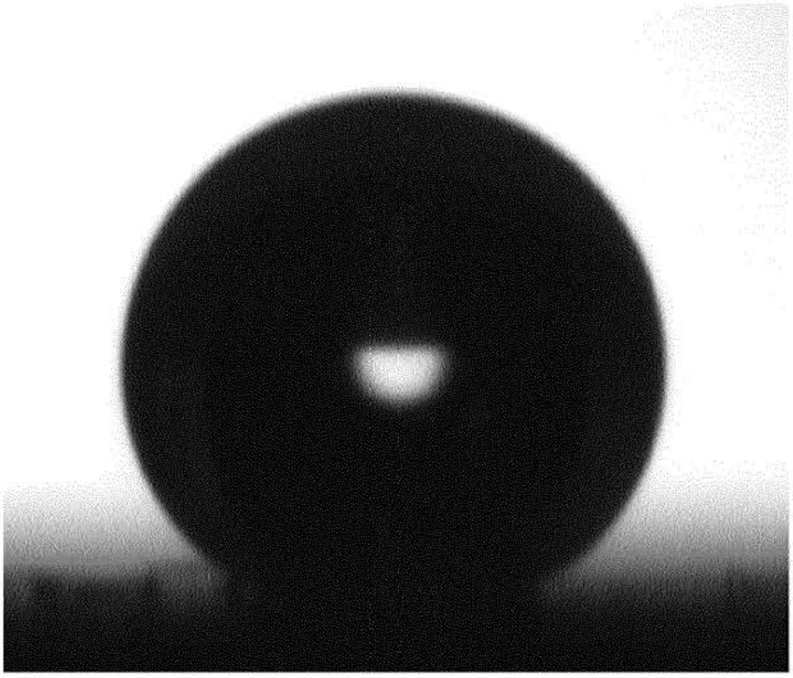


Fig. 5

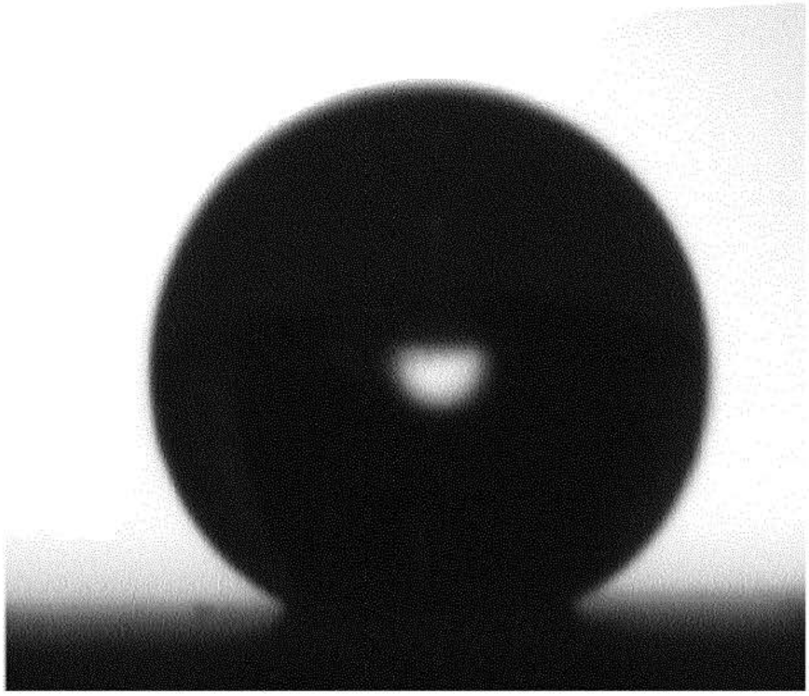


Fig. 6

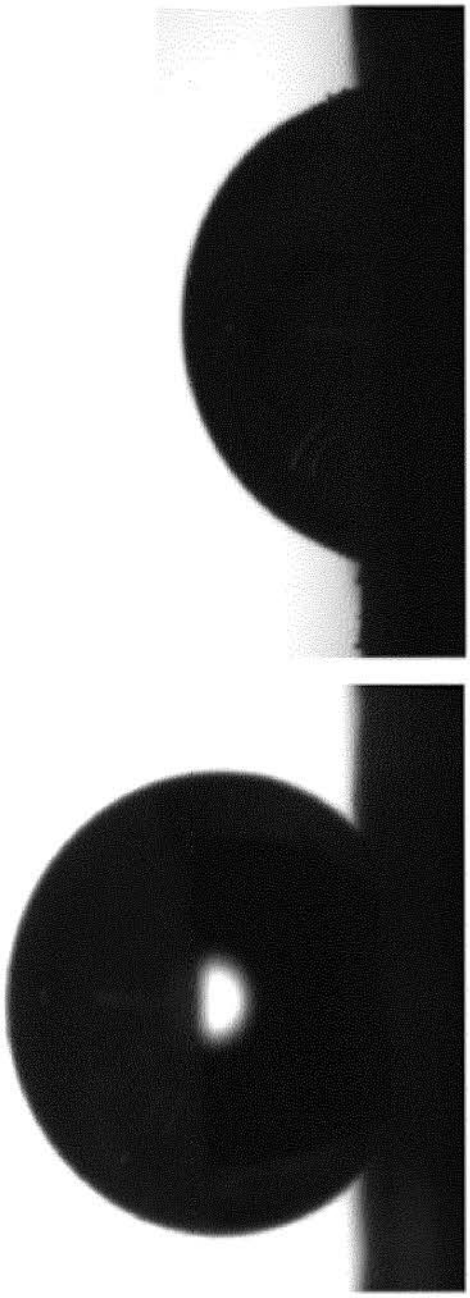


Fig. 7

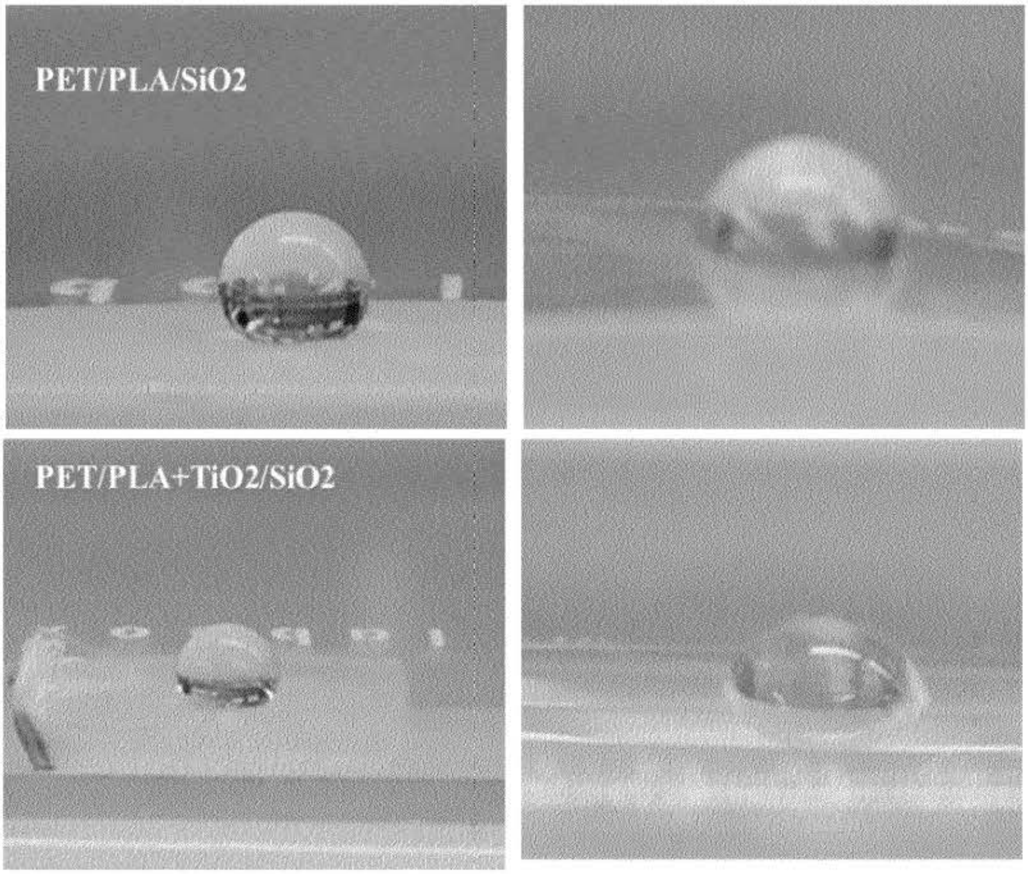
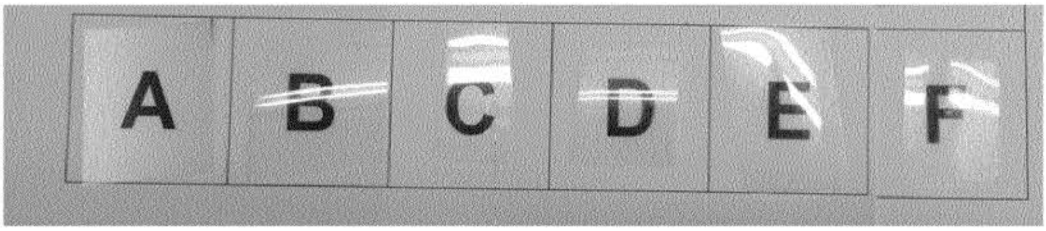


Fig. 8



INTERNATIONAL SEARCH REPORT

International application No
PCT/ES2018/070125

A. CLASSIFICATION OF SUBJECT MATTER
INV. D01D5/00 B82Y30/00 D01D5/098 D06M23/08 B32B27/12
B32B5/02 B05D1/06
ADD.

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)
D01D B82Y D06M B32B B05D C25D

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 6 054640 B2 (UNIV SHINSHU; TOPTEC CO LTD) 27 December 2016 (2016-12-27) abstract; claims 2-5; figures 2,4 paragraphs [0044] - [0049], [0061] - [0065], [0078], [0079] -----	1-25
X	US 2007/190319 A1 (KALAYCI VELI [US]) 16 August 2007 (2007-08-16) claims 1-3,9,10,43-50; examples 4,5 -----	1-6, 9-12,15, 16,21,25

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search
6 July 2018

Date of mailing of the international search report
17/07/2018

Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer
Malik, Jan

1

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/ES2018/070125

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 6054640 B2	27-12-2016	JP 6054640 B2	27-12-2016
		JP 2013251079 A	12-12-2013
		KR 20130134992 A	10-12-2013
US 2007190319 A1	16-08-2007	CN 101389793 A	18-03-2009
		DE 112007000361 T5	02-01-2009
		JP 4944133 B2	30-05-2012
		JP 2009526917 A	23-07-2009
		KR 20080094951 A	27-10-2008
		US 2007190319 A1	16-08-2007
		US 2011226690 A1	22-09-2011
		WO 2007095219 A2	23-08-2007

Form PCT/ISA/210 (patent family annex) (April 2005)

REFERENCES CITED IN THE DESCRIPTION

Non-patent literature cited in the description

- **MIZOSHITA ; TANAKA.** *ACS Appl. Mater. Interfaces,* 2016, vol. 8, 31330-31338 **[0006]**
- **RAHMAWAN, Y. ; XU, L. ; YANG, S.** *Journal of Materials Chemistry A,* 2013 **[0008]**