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(54) CONDUCTIVE FIBER SPINNING

(57) The present disclosure relates to a method for producing a conductive cellulosic fibre. The method comprises providing an ionic liquid comprising an anion and dissolving cellulose in the ionic liquid, thereby providing a solution of cellulose and ionic liquid. From this solution, a cellulosic fibre comprising the ionic liquid is formed. The method further comprises applying PEDOT:PSS to the surface of the cellulosic fibre comprising said ionic liquid and allowing substitution of the anion for PSS, thereby forming a coating on the cellulosic fibre, which coating comprises PEDOT. The present disclosure further relates to a conductive fibre.

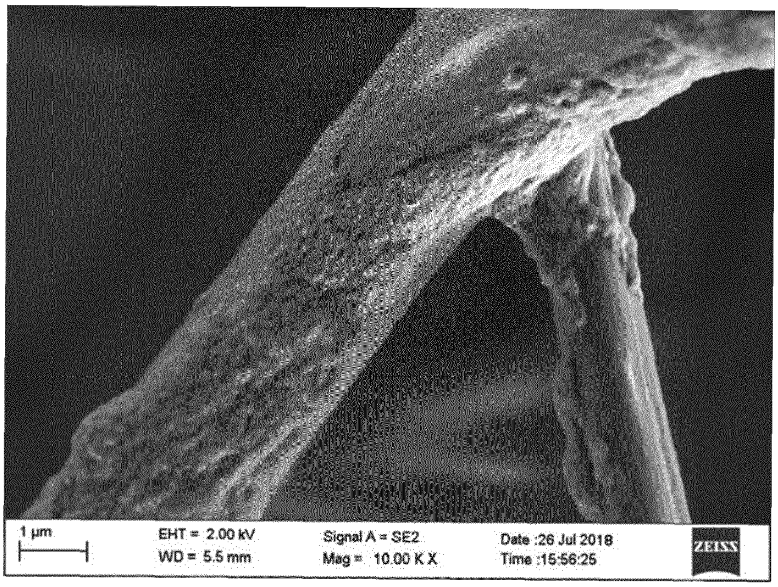

Fig. 2

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Description

Technical field

[0001] The present disclosure relates to a method for producing a conductive cellulosic fibre, comprising the polymeric material PEDOT. The present disclosure furthermore relates to a cellulosic fibre comprising a coating, which coating comprises PEDOT.

Background

[0002] Cellulose is one of the most bioredundant resources of the planet and displays many advantageous properties. For example, it is biodegradable, displays high crystallinity and has superior stability. These are some of the reasons to the growing attention to this polysaccharide as a prefered choice of starting material in production in various technical fields. One such field is the field of conductive fibres. A cellulose fibre may be made conductive by the provision of a conductive entity, such as a conductive polymer. There are many examples of conductive polymers, of which the polymer mixture of the two ionomeres poly(3,4-ethylenedioxythiophene) and poly(4-styrenesulfonate) is well known. PEDOT and PSS forms a complex, referred to as PEDOT:PSS. The complex is recognized for sucessfully combining optical and electrical properties of PEDOT with water solubility of PSS.

[0003] From WO 2012/041714 it is known that cellulosic fibres may be provided with an impregnation of electrically conductive polymers, wherein the impregation may comprise PEDOT:PSS.

[0004] WO 2012/120006 discloses a conductive fibre material with nanoparticles deposited on its surface. A conductive polymer layer, such as PEDOT:PSS may further be deposited on the surface.

[0005] The field of conductive fibres has indeed emerged over the last couple of years. However, due to the high demand of these types of materials there is a need in the art for more effective methods both for their production and for improved products with high conductivity. In other words, there is a call for new, efficient methods for producing highly conductive cellulosic fibres.

Disclosure of the invention

[0006] It is an object of the present invention to at least partly reduce or overcome challenges in the prior art, and provide for production of a cellulosic fibre with a conductive coating. It is another object of the present invention to provide for an efficient production method of a conductive cellulosic fibre, in which the conductive coating is applied in close connection to the fibre spinning process. Finally, an object of the present invention is to provide for production of a conductive cellulosic fibre, suitable as a nonwoven.

[0007] These and other objects, which will be apparent to a person of skill in the art from the present disclosure, are achieved by the different aspects of the disclosure as defined in the appended claims and as generally disclosed herein.

[0008] In a first aspect of the present invention, there is provided a method for producing a conductive cellulosic fibre. The method comprises providing an ionic liquid comprising an anion and dissolving cellulose in the ionic liquid, thereby providing a solution of cellulose and ionic liquid. From this solution, a cellulosic fibre comprising the ionic liquid is formed. The method further comprises applying PEDOT:PSS to the surface of the cellulosic fibre comprising said ionic liquid and allowing substitution of the anion for PSS, thereby forming a coating on the cellulosic fibre, which coating comprises PEDOT.

[0009] As used herein, the term "cellulosic fibre" is defined as a fibre comprising cellulose. The fibre may be a textile fibre. The fibre may also comprise other materials, for example chemicals or additives, such as solvents, ions and/or carbon or metal based compounds.

[0010] A conductive fibre may be obtained by first forming a fibre by any fibre production technique, and subsequently coating the formed fibre with a conductive material. According to the present disclosure, a cellulosic fibre is typically obtained by first dissolving cellulose in an ionic liquid. A fibre is thereafter produced by spinning means, followed by contacting of the formed fibre with PEDOT:PSS. Thereby, a cellulosic fibre comprising PEDOT is formed.

[0011] By the addition of the conductive material, PEDOT:PSS and the ionic liquid present in the cellulosic fibre are brought into contact. The provided contact between PEDOT, PSS and the anion of the ionic liquid allows an ion exchange between PSS and the anion. Thereby, substitution of the anion for PSS is enabled. Beneficially, upon applying PEDOT:PSS to a cellulosic fibre comprising ionic liquid, PSS at least partly decouples from PEDOT, and an anion of the ionic liquid replaces at least part of the PSS in the PEDOT:PSS. Thereby, a coating on the fibre is formed. The coating may at least partially comprise both PEDOT and an anion A (PEDOT:A). An at least partial segregation of PEDOT and PSS is possibly a consequence of allowing substitution of the anion for PSS. The substitution of the anion for PSS may allow for precipitation of PEDOT on the cellulosic fibres.

[0012] An advantage of the present invention is that the method as disclosed herein provides for efficient production of a conductive cellulosic fibre. For example, the conductive material is applied in close connection to the fibre spinning process. PEDOT:PSS may be applied to the cellulose while the cellulose is in an at least partly dissolved state, e.g, after the fibre is formed but before the fibre is introduced to a coagulation bath. Thereby, the process may allow instant formation of an conductive coating.

[0013] Another advantage is that the method as disclosed herein provides for a cellulosic fibre with good mechanical properties. The process avoids long time immersion of the cellulose fibre in PEDOT :PSS solution, thereby avoiding cellulose degradation of the acidic solution (pH =2.3).

[0014] PEDOT:PSS films may show unsatisfactory electrical transport properties. This is possibly a result of that, for example, PSS is an insulating ionomer that may inhibit the formation of a well-aligned PEDOT conducting network. An advantage of the present disclosure is that by the replacement of at least part of the PSS with an anion of an ionic liquid provides for an ability to obtain a coating with different characteristics compared to a PEDOT:PSS coating. While not wishing to be bound by this theory, it can be contemplated that upon applying PEDOT:PSS onto the cellulosic fibres, another anion may induce a conformational change of the PEDOT, in which the PEDOT transforms towards an extended coil structure. Such conformational change may result in an improved conductivity and/or charge carrier mobility. Yet another advantage is that the provision of a smaller anion, as compared to PSS, may further provide for a large specific surface area of the conductive portion of the PEDOT-comprising cellulosic fibres.

[0015] As described elsewhere herein, the method further comprises applying PEDOT:PSS to the cellulose fibres comprising an ionic liquid. PEDOT:PSS may be applied to the cellulosic fibres by spraying, by chemical vapour deposition or by dip coating. Preferably, PEDOT:PSS is applied by spraying.

[0016] Due to its stability in water, PEDOT:PSS is generally known to be water processable. As such, PEDOT:PSS may be applied as an aqueous composition. In water, a PEDOT:PSS composition may be in the form of dispersed micelles. According to the disclosure, PEDOT:PSS is present in a concentration of from 0.3 to 1.3 % by volume in the aqueous composition, preferably of from 0.4 to 0.5 % by volume.

[0017] An aqueous composition comprising PEDOT:PSS may be applied onto the cellulosic fibre by spraying. The aqueous composition comprising PEDOT:PSS may further comprise one or more organic solvents to improve the conductivity of the resulting fibre according to the present disclosure. Non-limiting examples of organic solvents that may be added are dimethyl sulfoxide, ethylene glycol, dimethyl formamide, tetrahydrofuran, glycerol, sorbitol, methoxyethanol, diethylene glycol, dimethyl sulfate, meso-erythritol, and xylitol. The addition of other solvents is also possible, as acknowledged by persons skilled in the art.

[0018] The aqueous composition comprising PEDOT:PSS may further comprise one or more carbon based conductive materials, which may improve the conductivity of the resulting fibre. Non-limiting examples of carbon based conductive materials that may be added are graphene nanoplatelets and carbon nanotubes. Other carbon or metal based conductive materials, as apparent to persons skilled in the art, are also plausible.

[0019] The method disclosed herein provides for a cellulosic fibre with a coating comprising PEDOT. However, the coating may further comprise PSS and an anion A. As apparent to persons of skill in the art, the ratio of PEDOT:PSS and PEDOT:A is possibly dependent on parameters such as the choice of the ionic liquid, such as the anion the choice of the ionic liquid, and the specific reaction conditions, such as time, temperature and concentration of the species in the aqueous composition. Other parameters can also influence the resulting ratio.

[0020] The conductivity of the fibre according to the present invention may be dependent on how evenly PEDOT is distributed on the fibre surface, as well as the thickness of the coating. For applications in the area of electrodes, the ideal case would be a cellulose fibre that is as thin as possible, while the conductive coating on the fibre would be as thick as possible. The diameter of the fibre according to the present disclosure may be between 1.5 μm and 2.5 μm, such as 1.8-2.2 μm. The coating comprising PEDOT may have a thickness of from 100 to 300 nm, preferably of from 150 to 250 nm, such as 180-220 nm.

[0021] According to the present disclosure, the produced conductive cellulosic fibre may be a hydrophobic fibre. A hydrophobic fibre may be any fibre that does not absorb water, or does absorb water only partly.

[0022] As described above, the method according to the present invention includes dissolving cellulose in an ionic liquid. Non-limiting examples of ionic liquids that may be used are 1,3-dimethylimidazolium dimethyl phosphate, 1-butyl-3-methylimidazolium hexafluorophosphate, 1-ethyl-3-methylimidazolium ethyl sulfate, 1-ethyl-3-methylimidazolium hydrogen sulfate, 1-ethyl-3-methylimidazolium methane sulfonate, 1-ethyl-3-methylimidazolium trifluoromethane sulfonate, 1-ethyl-3-methylimidazolium tetracyanoborate, 1-butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium chloride, 1-hexyl-3-methylimidazolium chloride, 1-methyl-3-n-octylimidazolium chloride, 1-methyl-3-propylimidazolium iodide, 1-ethyl-3-methylpyridinium ethyl sulfate, 1-dodecyl-3-methylimidazolium bromide, N,N-diethyl-N-methyl-N-(2-methoxyethyl) ammonium tetrafluoroborate, hexadecyl trimethylammonium bromide, and 1-ethyl-3-methylimidazolium acetate. Furthermore, a mixture of 1H,1H,2H,2H-perfluoro-1-decyl-3-methylimidazolium iodide/1-dodecyl-3-methylimidazolium bromide may be used in an cellulose solution which may improve the conductivity of the PEDOT:PSS coating of the cellulose fibre. However, as persons of skill in the art would understand, any ionic liquid can be used provided that it at least partly dissolves cellulose. The ionic liquid may be 1-ethyl-3-methylimidazolium acetate.

[0023] According to the present disclosure, the anion of the ionic liquid may be any anion which is able to be part of an ionic liquid. It may be advantageous with low binding energy between cation and anion, as this provides for an easier ion exchange, i.e. that the substitution of the anion for PSS is facilitated. Non-limiting examples of possible anions to use in the method disclosed herein are acetate, tetrafluoroborate, hexafluorophosphate, bis[(trifluoromethyl)sulfonyl] imide, chloride, bromide, iodide, nitrate, tetracyanoborate, methylsulfate, triflate, tricyanomethanide, ethylene sulfate and heptaxyanocyclopentenide. The anion may be selected from the group of acetate, tosylate and triflate. Any combination thereof is also possible. An advantage of using an acetate, tosylate or triflate is that this may provide for a satisfactory conductivity in the PEODT coating, where the coating may comprise both PEDOT:PSS and PEDOT:A. Preferably, the anion A is acetate.

[0024] According to the present disclosure, the cation of the ionic liquid may be any cation which is able to be part of an ionic liquid. Non-limiting examples of ionic liquid cations are imidazolium, ammonium, pyrrolidinium, pyridinium, tetraalkylammonium and tetraalkylphosphonium, and any derivative thereof. As acknowledged by persons skilled in the art, the term "any derivative" is to be defined as "any functionalization by any group attached to any position" in the above listed cations. The ionic liquid comprises a cation, the cation may comprise an imidazole moiety. The cation may be 1-ethyl-3-methylimidazole.

[0025] According to the present disclosure, a solution comprising cellulose and ionic liquid is formed. The solution may comprise of from 75 % to 97 % by volume of ionic liquid, preferably from 94 to 96 %. The cellulose may be in the form of dissolving pulp. Other cellulose materials or forms of cellulose are also possible to use in the method disclosed herein, as appreciated by persons of skill in the art.

[0026] As apparent for persons of skill in the art, the cellulosic fibres comprising ionic liquid according to the present disclosure may be formed by any conventional technique producing cellulosic fibres. For example, the cellulosic fibres comprising ionic liquid may be formed by fibre spinning, such as electrospinning, melt spinning, dry spinning or wet spinning, preferably by solution blow spinning. Solution blow spinning, also known as solution blowing or solution blown, is a fibre fabrication process in which a polymer is dissolved in a volatile solvent and a pressurized gas flows around the polymer solution when forced out of openings in a nozzle, thereby creating fibres in the direction of the gas flow.

[0027] The method of the present disclosure may further comprise washing of the formed cellulosic fibres having a coating comprising PEDOT, thereby removing excess ion of the ionic liquid, PEDOT and/or PSS. Washing may be performed in a coagulation bath, which may also be referred to as a spin bath. The coagulation bath may comprise a nonsolvent, i.e. a solvent in which the formed fibre is not dissolved. Non-limited examples of nonsolvents are methanol, ethanol, isopropanol and isobutanol, as appreciated by persons of skill in the art.

[0028] In order to improve the conductivity of the resulting fibre salts may be added to the coagulation bath, such as salts comprising a metal, such as salts comprising Cu, Ag, and/or In. Other salts are also possible to add to the bath, as apparent to persons of skill in the art.

[0029] In order to improve the conductivity of the resulting fibre acid may be added to the coagulation bath. Non-limiting examples of acids that may be added are hydrochloric acid and/or sulphuric acid. Other acids are also possible to add to the bath, as apparent to persons of skill in the art.

[0030] Coagulation of the cellulosic fibres and regeneration of crystalline cellulose may occur during the step of washing the formed cellulosic fibres having a coating comprising PEDOT. In one embodiment, coagulation of the cellulosic fibre and regeneration of the crystalline cellulose occurs in the coagulation bath.

[0031] After the step of washing, the PEDOT-coated cellulosic fibre may be dried at for example at 150-250 °C for 5-15 minutes, such as at 200 °C for 10 minutes. Drying the PEDOT-coated cellulosic fibre may improve the conductivity of the resulting fibre. The obtained cellulosic fibres may be used as a nonwoven material.

[0032] In a second aspect of the present invention there is provided a conductive cellulosic fibre comprising a cellulosic fibre and a coating that is at least partly covering the cellulosic fibre. The coating comprises PEDOT and an anion. The anion may be selected from acetate or triflate. Any combination of the two is also possible. Preferably, the anion is acetate.

[0033] The diameter of the fibre may be between 1.5 μm and 2.5 μm, such as 2 μm. The coating comprising PEDOT may have a thickness of from 100 to 300 nm, preferably of from 150 to 250 nm, such as 200 nm. Furthermore, PEDOT may be present in 12-22 % by volume in said cellulosic fibre.

[0034] It should be understood that the embodiments disclosed in connection with the method aspects are equally relevant, if applicable, to the product aspect as disclosed herein. The cellulosic fibre may further be defined as laid out in connection to any one of the above mentioned method features. The invention will be further illustrated by the following non-limiting drawings and example.

Brief description of the drawings

[0035]

Fig. 1 is a optical microscopy image of a nonwoven fibre resulting from the metod according to the present disclosure.

Fig. 2 is a SEM image of the surface of a PEDOT-coated cellulosic fibre.

Fig. 3 is a SEM image of a cross section of the PEDOT-coated cellulosic fibre. The fibre as well as the coating is seen, and the coating is indicated by an arrow.

Example

Materials

[0036] Dissolving pulp (Södra purple, alpha cellulose 96 %, moisture content 4 %) was supplied from Södra AB. Clevios PH 1000 (poly(3,4-ethelenedioxythiophene polystyrene sulfonate (PEDOT:PSS), 1-1.3 % in aqueous solution, PEDOT:PSS ratio 1:2.5, D50=30 nm) was purchased from Heraeus. 1-ethyl-3-methylimidazolium acetate (EmimAc, 97 %) and dimethyl sulfoxide (DMSO) were purchased from Sigma-Aldrich. All materials were used as received.

Methods

Dissolution of cellulose

[0037] 4.7 g dissolving pulp was dissolved in 70 g EmimAc at 80 °C, and left for 1 hour in a closed reactor with overhead stirring at 70 rpm, to prepare a 6.3 % cellulose solution. Complete dissolution was confirmed by lack of illumination of cellulose crystals under visible polarized light in light microscopy (Nikon Eclipse Ci-POL, Nikon Instruments, Japan). The solution was centrifuged for 5 min at room temperature at 3000 rpm for deaeration prior to solution blow spinning. The solution was used without filtering.

Preparation of PEDOT:PSS solution

[0038] 50 ml PH 1000 was added to 2.5 ml DMSO (5 vol % to PH 1000) and 50 ml distilled water to prepare 100 ml 0.5 % PEDOT:PSS aqueous solution.

Solution blow spinning (solution blown) of conductive cellulosic fibre (nonwoven)

[0039] The conductive cellulosic fibre was produced using a lab-scale solution blow spinning spin nozzle with 9 capillaries (diameter = 220 μm, Biax Fibrefilm, USA). During the solution blow spinning process, the cellulose-containing solution was extruded by a cylinder pump at 70 °C, with the solution flow rate set to 1.8 ml/min and the air pressure set to 1.2 bar, at room temperature. The PEDOT:PSS solution was sprayed, substantially perpendicular to the fibre spinning direction, onto the cellulosic fibre formed. The solution blown fibres with PEDOT:PSS were collected in a coagulation bath comprising ethanol, and thereafter washed in distilled water for 1 hour, to coagulate the fibres and to remove excess EmimAc and PEDOT:PSS from the fibres. The conductive nonwoven fibre was collected for further analyses after air drying in room temperature for 24 hours.

Characterization of solution blown conductive fibre

[0040] Optical microscopy was used to examine the macrostructure of the solution blown nonwoven fibres. The solution blown nonwoven fibres were placed between two glass slides and analysed using a Nikon Eclipse Ci-POL optical microscope (Nikon Instruments Co., Ltd., Japan) equipped with a Nikon TV-lens (C-0.38x) digital camera and a Berek compensator (No. 11055, Nichika Inc., Japan). An example of the resulting picture is shown in Fig. 1.

[0041] Scanning electron microscopy images of the solution blown fibres were obtained by a field emission scanning electron microscope JSM 7800F (JEOL, Tokyo, Japan) coupled with an energy dispersive X ray spectroscopy analyzer XFlash 5010 (Bruker AXS Microanalysis, Germany). A sample of solution blown nonwoven was mounted on carbon conductive tabs and sputtered with a 1.5 nm platinum coating. An example of the resulting picture is shown in Fig. 2.

[0042] A cross section of nonwoven fibres was prepared by casting the nonwoven in an epoxy matrix and mounting the matrix on the sample holder. The sample surface for cross section was subsequently polished by broad ion beam at 5 keV and cooled with liquid nitrogen to avoid heating by a Precision Ion Polish System (GATAN, Pleasanton, CA). The solution blown nonwoven sample was mounted on carbon conductive tabs and sputtered with a 1.5 nm platinum coating. A PEDOT coating thickness of around 1-2 μm on a fibre with a diameter of 5-10 μm can be seen on the resulting cross-section images of the fibres in Fig. 3.

[0043] Sheet resistance was measured by the Ossila Four-Point Probe System (Ossila Ltd., UK) with a probe spacing of 1.27 mm. The conductive nonwoven sample was placed under the probes and measured at several places on the sample, the value of the sheet resistance was recorded from Ossila Sheet Resistance software (Ossila Ltd., UK). The thickness of the nonwoven fibre was measured by a digital micrometer (Buchel B.V., Holland). The sheet resistance of the PEDOT-coated cellulosic nonwoven was surface density deepened, because of the bulky fibre structure, in order to obtain more fibre contacts. Thereby, more electron transmission paths may be created, providing for higher conductivity. At 25 g/m^2 surface density, the sheet resistance was 476 Ω/sq.

Claims

1. A method for producing a conductive cellulosic fibre, the method comprising:

- providing an ionic liquid comprising an anion;
- dissolving cellulose in said ionic liquid, thereby providing a solution;
- forming, from said solution, a cellulosic fibre comprising said ionic liquid;
- applying PEDOT:PSS to the surface of said cellulosic fibre comprising said ionic liquid; and
- allowing substitution of the anion for PSS,

thereby forming a coating on said cellulosic fibre, said coating comprising PEDOT.

2. The method according to any of the preceding claims, wherein A designates the anion and said coating at least partially comprises PEDOT:A.

3. The method according to any of the preceding claims, wherein said substitution of the anion for PSS allows for precipitation of PEDOT on said cellulosic fibres.

4. The method according to any of the preceding claims, wherein PEDOT:PSS is applied to said cellulosic fibres by spraying.

5. The method according to any of the preceding claims, wherein the PEDOT:PSS is applied as an aqueous composition.

6. The method according to claim 5, wherein the PEDOT:PSS is present in a concentration of from 0.3 to 1.3 % by volume in said aqueous composition, preferably of from 0.4 to 0.5 % by volume.

7. The method according to any of the preceding claims, wherein said coating has a thickness of from 100 to 300 nm, preferably of from 150 to 250 nm.

8. The method according to any of the preceding claims, wherein said anion is selected from the group consisting of acetate, tosylate, triflate, and combinations thereof, preferably acetate.

9. The method according to any of the preceding claims, wherein said ionic liquid is 1-ethyl-3-methylimidazolium acetate.

10. The method according to any of the preceding claims, wherein said solution comprises from 75 % to 97 % by volume of ionic liquid, preferably from 94 % to 96 %.

11. The method according to any of the preceding claims, wherein said cellulosic fibres comprising ionic liquid are formed by fibre spinning, such as by electrospinning, melt spinning, dry spinning, wet spinning or solution blow spinning, preferably by solution blow spinning.

12. The method according to any of the preceding claims, the method further comprising:

    - washing the formed cellulosic fibres having a coating comprising PEDOT, thereby removing excess ions of the ionic liquid, PEDOT and/or PSS.

13. A conductive cellulosic fibre comprising:

    a cellulosic fibre, and
    a coating at least partly covering said cellulose fibre, said coating comprising PEDOT and an anion, wherein said anion is selected from acetate, triflate or any combination thereof, preferably acetate.

14. The cellulosic fibre according to claims 13, wherein PEDOT is present in 12-22 % by volume in said cellulosic fibre.

15. The cellulosic fibre according to claims 13-14, further defined as in any one of claims 1 to 12.

Fig. 1

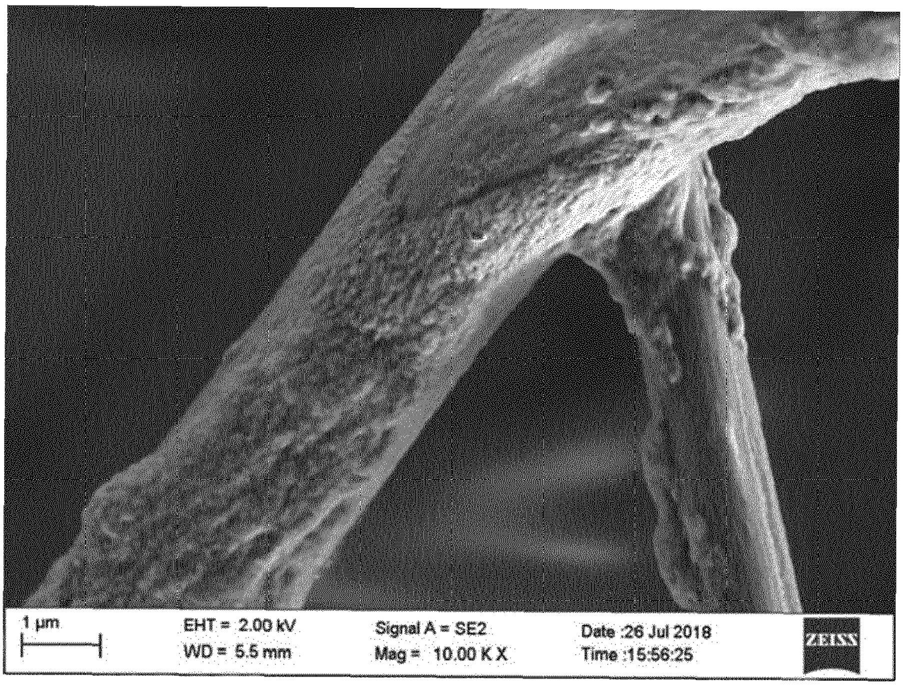
1 μm
EHT = 2.00 kV
WD = 5.5 mm
Signal A = SE2
Mag = 10.00 K X
Date :26 Jul 2018
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Fig. 2

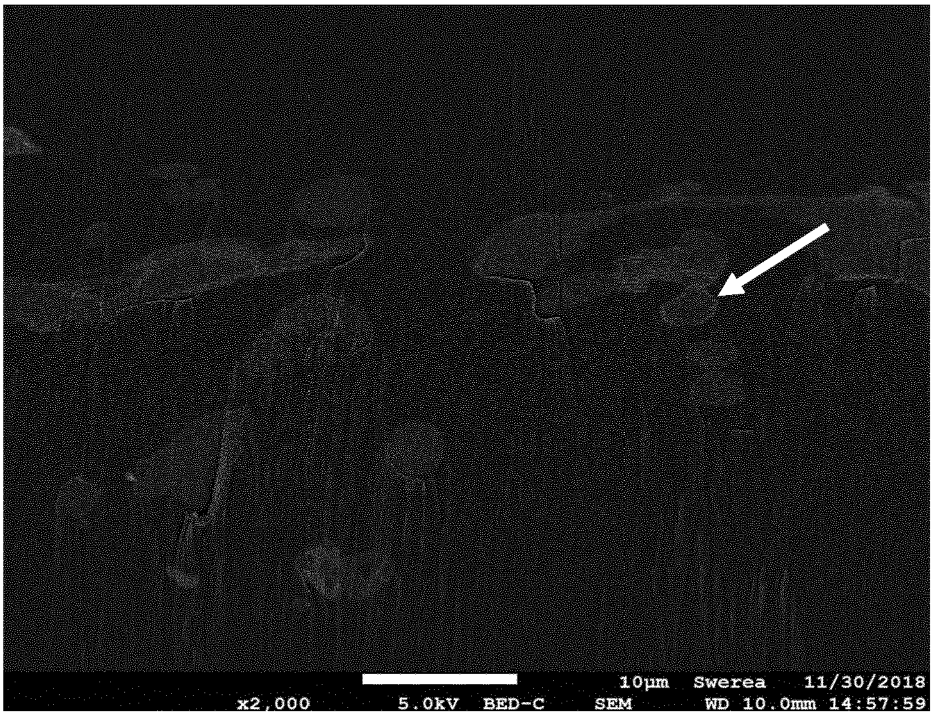

Fig. 3

EUROPEAN SEARCH REPORT

Application Number
EP 20 15 2431

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	WO 2009/101985 A1 (UNIV TOKYO [JP]; SOMEYA TAKAO [JP]; SEKITANI TSUYOSHI [JP]) 20 August 2009 (2009-08-20) * paragraphs [0091] - [0096]; figure 5 *	1-15	INV. D01F2/00 D06M15/356 D06M23/10
X	US 2016/258110 A1 (ALAMER FAHAD ABDULLAH ALHASHMI [SA]) 8 September 2016 (2016-09-08)	13-15	
A	* abstract; claims 1-8,17; figure 2 *	1-12	
A	ELSON MONTIBON ET AL: "Characterization of poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT:PSS) adsorption on cellulosic materials", CELLULOSE, KLUWER ACADEMIC PUBLISHERS (DORDRECHT), NL, vol. 16, no. 5, 21 May 2009 (2009-05-21), pages 807-815, XP019728353, ISSN: 1572-882X, DOI: 10.1007/S10570-009-9303-3 * abstract; figures 2-6 *	1-15	
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A	DAWEI ZHAO ET AL: "Highly Flexible and Conductive Cellulose-Mediated PEDOT:PSS/MWCNT Composite Films for Supercapacitor Electrodes", ACS APPLIED MATERIALS & INTERFACES, vol. 9, no. 15, 5 April 2017 (2017-04-05), pages 13213-13222, XP055705701, US ISSN: 1944-8244, DOI: 10.1021/acsami.7b01852 * abstract * * Part 2.2; page 13214, column 2 *	1-15	D01F D06Q D06M

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	17 June 2020	Malik, Jan

CATEGORY OF CITED DOCUMENTS

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EP 20 15 2431

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17-06-2020

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EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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- WO 2012120006 A **[0004]**