A method for fabricating a three-dimensional carbon structure

Mohanty, Soumyaranjan; Emnéus, Jenny; Wolff, Anders; Heiskanen, Arto

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(71) Applicant: **DANMARKS TEKNISKE UNIVERSITET** [DK/DK]; Anker Engelunds Vej 101 A, 2800 Kgs. Lyngby (DK).

(72) Inventors: **MOHANTY, Soumyaranjan**; Værebrovej 68, 2-4, 2880 Bagsværd (DK). **EMNÉUS, Jenny**; Hantverkaregatan 17a, 211 55 Malmö (SE). **WOLFF, Anders**; Abildgaardgade 35, 2100 Copenhagen Ø (DK). **HEISKANEN, Arto**; Vikingavägen 7 B 1002, 22476 Lund (SE).

(74) Agents: **THEIL, Christa** et al.; Inspicos P/S, Kogle Allé 2, 2970 Hørsholm (DK).

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(54) Title: A METHOD FOR FABRICATING A THREE-DIMENSIONAL CARBON STRUCTURE

(57) Abstract: A method for fabricating a three-dimensional carbon structure (4) is disclosed. A mould (1) defining a three-dimensional shape is provided, and natural protein containing fibres are packed in the mould (1) at a predetermined packing density. The packed natural protein containing fibre structure (3) undergoes pyrolysis, either while still in the mould (1) or after having been removed from the mould (1). Thereby a three-dimensional porous and electrically conducting carbon structure (4) having a three-dimensional shape defined by the three-dimensional shape of the mould (1) and a porosity defined by the packing density of the packed natural protein containing fibre structure (3) is obtained. The carbon structure (4) is well suited for use as a scaffold for tissue engineering, or for material for batteries, fuel cells, supercapacitors, sorbents for separation processes, gas storage, supports for many important catalysts, etc.

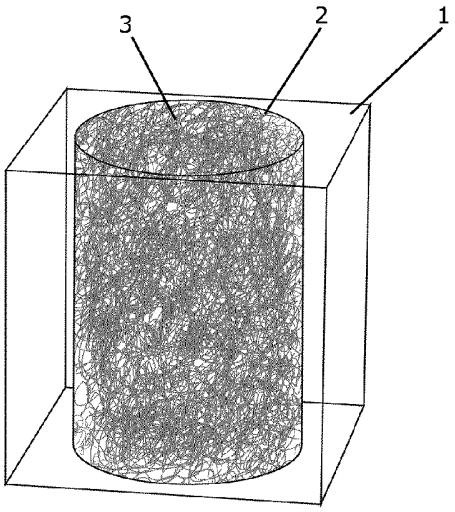

Fig. 2

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A METHOD FOR FABRICATING A THREE-DIMENSIONAL CARBON STRUCTURE

FIELD OF THE INVENTION

The present invention relates to a method for fabricating a three-dimensional carbon structure, e.g. for use as a scaffold for tissue engineering, as electrode materials for batteries, fuel cells and supercapacitors, as sorbents for separation processes and gas storage, as supporters for many important catalysts, etc. When applying the method of the invention the micro-porosity of the resulting three-dimensional carbon structure can be controlled, and any desired three-dimensional shape of the structure can be obtained. Furthermore, the carbon fibres of the three-dimensional carbon structure fabricated by means of the method of the invention contain nitrogen, thereby making the structure suitable for a wide range of applications.

BACKGROUND OF THE INVENTION

For some purposes, such as tissue engineering, electrode materials for batteries, fuel cells and supercapacitors, sorbents for separation processes and gas storage, supports for many important catalysts, etc., there is a need for conductive porous scaffolds, made from a biocompatible material. It is, furthermore, desirable to be able to provide such scaffolds in various sizes and shapes, and with a scalable porosity. Finally, it is desirable to be able to provide such scaffolds in an easy and cost effective manner.

US 2008/0085648 A1 discloses a method of producing an electric conductive material by spirally winding a yarn composed of organic fibres on a core member. The core member is removed, and the yarn is carbonized. In the method disclosed in US 2008/0085648 A1 the packing density of the spirally wound yarn is not controlled, and neither is the porosity of the carbonized yarn.

US 2012/0125071 A1 discloses carbon moulds for use in the fabrication of bulk metallic glass parts and moulds. A master shape is patterned into a pyrolyzable material, and the master shape is pyrolyzed into a carbon mould.

DESCRIPTION OF THE INVENTION

It is an object of embodiments of the invention to provide a method for fabricating a three-dimensional carbon structure in an easy and cost effective manner.

It is a further object of embodiments of the invention to provide a method for fabricating a three-dimensional carbon structure in which the porosity of the structure can be controlled.

The invention provides a method for fabricating a three-dimensional carbon structure, the method comprising the steps of:

- providing a mould defining a three-dimensional shape,
- packing natural protein containing fibres in the mould at a predetermined packing density, thereby obtaining a packed natural protein containing fibre structure,
- performing pyrolysis on the packed natural protein containing fibre structure, thereby obtaining a three-dimensional porous and electrically conducting carbon structure having a three-dimensional shape defined by the three-dimensional shape of the mould and a porosity defined by the packing density of the packed natural protein containing fibre structure.

In the present context the term 'three-dimensional carbon structure' should be interpreted to mean a structure which has a three-dimensional shape, and which contains carbon material.

According to the method of the invention, a mould defining a three-dimensional shape is initially provided. The three-dimensional shape of the mould corresponds to a desired three-dimensional shape of the carbon structure, which is fabricated by means of the method. Thus, any desired shape or size of the resulting three-dimensional carbon structure can be obtained, simply by providing an appropriate mould, defining a corresponding three-dimensional shape.

Next, natural protein containing fibres are packed into the mould at a predetermined packing density. Thereby a structure is obtained, which comprises or consist of packed natural protein containing fibres, i.e. a packed natural protein containing fibre structure. Since the packed natural protein containing fibre structure has been obtained by packing protein containing fibres into the mould, the packed natural protein containing fibre structure has a size and a shape which corresponds to the size and shape of the mould. Furthermore, the packing density of the packed natural fibre containing structure can be controlled by controlling the packing process to obtain a predetermined packing density.

In the present context the term 'packing density' should be interpreted to mean a density at which the fibres are packed. Thus, a high packing density indicates that the fibres are packed closely, while a lower packing density indicates that the fibres are packed somewhat looser.

Accordingly, the packing density of the packed natural protein containing fibre structure is closely linked to the porosity of this structure.

Finally, pyrolysis is performed on the packed natural protein containing fibre structure. Since the structure comprises protein containing fibres, the structure also comprises carbon. Accordingly, as a result of the pyrolysis, a porous and electrically conducting carbon structure is obtained. Furthermore, since the carbon structure is formed by performing pyrolysis on the packed natural protein containing fibre structure, the carbon structure has a three-dimensional shape which corresponds to the three-dimensional shape of the packed natural protein containing fibre structure, and thereby to the three-dimensional shape defined by the mould. Furthermore, since the natural protein containing fibres also contain nitrogen, the pyrolysis process produces nitrogen-doped carbon. This is an advantage, because this has turned out to be important for catalysing hydrogen evolution and for cell adhesion for, e.g., tissue engineering and microbial biofilm formation.

The size of the three-dimensional porous and electrically conducting carbon structure may be identical to the size of the packed natural protein containing fibre structure. However, the pyrolysis may cause the structure to shrink by up to 50%, depending on the material of the fibres. Thus, the three-dimensional porous and electrically conducting carbon structure may be smaller than the packed natural protein containing fibre structure by up to 50%.

Furthermore, the porosity of the carbon structure is defined by the packing density of the packed natural protein containing fibre structure. Since the packing density of the packed natural protein containing fibre structure is controlled during the packing process, as described above, a desired porosity of the resulting porous and electrically conducting carbon structure can be obtained by carefully selecting a predetermined packing density of the packed natural protein containing fibres, and controlling the packing process to obtain the predetermined packing density. Furthermore, the surface area of the resulting carbon structure depends on the porosity of the structure. Accordingly, the surface area of the resulting carbon structure is controllable and scalable, and, for instance, a structure with a very high surface area can be obtained.

Thus, the method according to the invention results in the fabrication of a three-dimensional porous and electrically conducting carbon structure, having a desired and appropriate three-dimensional shape, and having a desired and appropriate porosity. The three-dimensional shape and the porosity of the carbon structure can be designed to meet any specific requirement, simply by designing the mould in an appropriate manner, and by controlling the packing process in an appropriate manner. Accordingly, the method of the invention provides an easy and cost effective manner of fabricating a three-dimensional carbon structure having

a desired three-dimensional shape and porosity. This makes the resulting carbon structure suitable for use as a porous carbon scaffold for tissue engineering, or as a porous carbon material for batteries, fuel cells, supercapacitors, sorbents for separation processes or gas storage, supports for many important catalysts, etc.

The natural protein containing fibres may be silk fibres, and the method may further comprise the step of extracting the silk fibres from raw silk cocoons. Raw silk cocoons are readily available at reasonable costs. Therefore this embodiment provides suitable natural protein containing fibres in an easy and cost effective manner. Furthermore, pyrolysed single silk fibres have nanoporous structure, which increases the surface area of the bulk material. Thus, the method according to this embodiment of the invention makes it possible to control the macroporosity of structures composed of multiple pyrolysed silk fibres.

As an alternative, the natural protein containing fibres may be of any other suitable kind, including, but not limited to, spider silk, fibrin and sericine.

The packed natural protein containing fibre structure may be removed from the mould prior to the step of performing pyrolysis on the packed natural protein containing fibre structure. In this case, the removed structure maintains its size, shape and packing density, but is no longer contained in the mould, and is therefore ready for undergoing pyrolysis. The size, shape and packing density of the structure may, e.g., be maintained by wetting the fibres before packing them into the mould, and drying the fibres after the packing step, but before removing the packed natural protein containing fibre structure from the mould.

As an alternative, the packed natural protein containing fibre structure may remain in the mould during the pyrolysis step. In this case, the mould may be made from a material which is capable of withstanding the temperatures prevailing during the pyrolysis. Examples of such materials are ceramics, quartz, and metals, such as stainless steel or titanium. As an alternative, the mould may be made from a material which is removed by volatilisation or burning during the pyrolysis. Examples of such materials are polyvinyl alcohol (PVA), polylactic acid (PLA), acrylonitrile butadiene styrene (PLC) and polycaprolactone (PLC). As another alternative, the mould may be made from a material which forms a partial solid cover around the structure during pyrolysis and after the pyrolysis. Such material may, e.g., be the negative photoresist SU8 that, when pyrolysed, will facilitate electrical connection to the three-dimensional porous, electrically conducting carbon structure after the pyrolysis.

The step of packing natural protein containing fibres may further comprise packing the natural protein containing fibres in the mould in a predetermined pattern, and the porosity of

the three-dimensional porous, electrically conducting carbon structure may further be defined by the pattern of the packed natural protein containing fibre structure.

According to this embodiment, porosity of the resulting three-dimensional porous, electrically conducting carbon structure depends on the packing density as well as on the pattern, with which the natural protein containing fibres are packed.

According to this embodiment, a three-dimensional, conductive structure, with a high surface area and with macro-, micro- and nanoporosity is provided. Furthermore, clean room facilities are not required in order to perform the method, thereby providing a very cost effective process. Finally, the use of protein containing fibres inherently provides the possibility of tuning the nitrogen content of the resulting carbon structure.

The method may further comprise the step of using the three-dimensional porous, electrically conducting carbon structure as a scaffold for tissue engineering. For instance, the three-dimensional porous, electrically conducting carbon structure may be used for forming a brain implant. As an alternative, the three-dimensional porous, electrically conducting carbon structure may be used for other purposes, such as for electrode materials for batteries, fuel cells and supercapacitors, sorbents for separation processes and gas storage, supports for many important catalysts, etc.

Since the three-dimensional carbon structure resulting from the method of the invention is produced on the basis of natural protein containing fibres, it is biocompatible. This makes the three-dimensional carbon structure suitable for use for tissue engineering purposes. Furthermore, since the three-dimensional structure is a carbon structure, the structure is electrically conducting, making it further suitable for tissue engineering purposes, such as neuronal and cardiac tissue engineering purposes. Finally, the controllable size, shape and porosity of the three-dimensional structure allows the three-dimensional structure to be designed to exactly match a required application, such as to exactly match a part which it is desired to provide by means of tissue engineering, thereby making the three-dimensional structure even further suitable for tissue engineering purposes. In summary, according to this embodiment of the invention, a suitable scaffold for tissue engineering is provided in an easy and cost effective manner.

Using the structure for other purposes than tissue engineering, the method of the invention provides suitable porous carbon structures which can be produced in an easy and cost effective manner, e.g. for applications such as batteries, fuel cells, supercapacitors, sorbents for separation processes and gas storage, supports for catalysts, etc.

The method may further comprise the step of using the three-dimensional porous, electrically conducting carbon structure as an actuator and/or as a sensor during the tissue engineering. This is possible due to the electrical conductivity of the three-dimensional carbon structure. This is further relevant for applications within the field of microbial electrosynthesis or bioremediation.

According to this embodiment, the structure facilitates direct monitoring of cellular behaviour in the tissue engineering scaffold, using electrical sensing. Furthermore, the structure facilitates electrical stimulation of cells that can differentiate into different tissue specific lineages, e.g. neurons, cardiac cells and osteoblasts. Furthermore, the structure provides electrical stimulation of microbes to intensify biofilm formation in the porous carbon structure and production of chemicals. The conductive porous carbon can be directly used as electrode material in biofuel cells. Finally, the inherent nitrogen content additionally improves cell adhesion in microbial biofilm formation and tissue engineering.

The step of performing pyrolysis on the packed natural protein containing fibre structure may comprise positioning the packed natural carbon containing fibres in a furnace and reducing an oxygen level inside the furnace, such as minimising the oxygen content inside the furnace. This may, e.g., be obtained by supplying an inert gas, such as nitrogen, into the furnace.

The step of performing pyrolysis may comprise increasing the temperature inside the furnace to between 600°C and 1000°C, or to approximately 1000°C or above, depending on the required conductivity.

The step of packing natural protein containing fibres may comprise the steps of:

- determining a desired weight of natural protein containing fibres to be contained in the resulting packed natural protein containing fibre structure,

- providing an amount of natural protein containing fibres corresponding to said desired weight, and

- packing the provided amount of natural protein containing fibres into the mould in such a manner that a volume defined by the mould is filled.

According to this embodiment, the packing density of the packed natural protein containing fibre structure, and thereby the porosity of the resulting three-dimensional porous and electrically conducting carbon structure, is controlled by determining a desired weight of

natural protein containing fibres to be arranged in the mould during the step of packing the natural protein containing fibres. The bulk density of the natural protein containing fibres is known for a given kind of fibres, and since the size and shape of the mould are known, the volume defined by the mould is also known, and thereby the total weight of the natural protein containing fibres being packed into the mould defines the packing density of the packed fibres. Accordingly, the desired weight of natural protein containing fibres is selected in such a way that the predetermined packing density is obtained.

Next, an amount of natural protein containing fibres is provided, which corresponds to the determined desired weight, and the provided amount of natural protein containing fibres is packed into the mould, in such a manner that the volume defined by the mould is exactly filled by the fibres. Thereby it is ensured that the natural protein containing fibres are packed with exactly the predetermined packing density.

Thus, according to this embodiment, the packing density of the packed natural protein containing fibres is controlled by controlling the total weight of the fibres being packed. This is very simple, and thereby it is easy to perform the method and obtain a desirable porosity of the resulting three-dimensional porous and electrically conducting carbon structure. Accordingly, this is a very suitable and reproducible way of controlling the packing density of the packed natural protein containing fibre structure.

As an alternative, the packing density of the packed natural protein containing fibre structure may be controlled by correlating to optical transmission and/or light scattering, or by ultrasound transmission measurements.

The step of packing the natural protein containing fibres may further comprise the step of wetting the natural protein containing fibres prior to packing the natural protein containing fibres into the mould. Wetting the natural protein containing fibres will squeeze the fibres together, thereby allowing the fibres to fit more easily into the mould. The step of wetting the fibres may, e.g., be performed using water. The amount of liquid used for wetting the fibres depends on the amount of fibres to be packed. According to this embodiment, the method may further comprise the step of drying the packed fibres before performing pyrolysis on the packed natural protein containing fibre structure, e.g. by means of air drying or freeze drying.

Alternatively or additionally, the method may further comprise the step of cutting the natural protein containing fibres before packing the fibres into the mould. The cutting may be performed using mechanical or chemical methods. According to this embodiment, the size of

the natural protein containing fibres is controlled, and the smaller, cut fibres fit more easily into the mould.

The method may further comprise the step of suspending the natural protein containing fibres into solution, after cutting the fibres and before packing the fibres into the mould. The fibres solution may further be dried, e.g. by means of air drying or freeze drying, before performing the pyrolysis step.

The method may further comprise the steps of:

- obtaining the porosity of the three-dimensional porous, electrically conducting carbon structure, and

- adjusting a predetermined packing density to be applied for the step of packing natural protein containing fibres in a mould during fabrication of an additional three-dimensional carbon structure, based on the obtained porosity.

According to this embodiment, the actual porosity of the resulting three-dimensional porous, electrically conducting carbon structure is obtained and used as a feedback to the process, in the sense that it is investigated whether or not the predetermined packing density of the packed natural protein containing fibre structure results in a desired porosity of the three-dimensional porous, electrically conducting carbon structure. If this turns out not to be the case, the predetermined packing density is adjusted in accordance with the actual, obtained porosity of the three-dimensional porous, electrically conducting carbon structure. Thereby the porosity of the next three-dimensional porous, electrically conducting carbon structure being fabricated by means of the method will have a porosity which is closer to the desired porosity. Thus, according to this embodiment of the invention, it is possible to improve and optimize the fabrication process.

The step of obtaining the porosity of the three-dimensional porous, electrically conducting carbon structure may comprise measuring the weight of the three-dimensional porous, electrically conducting carbon structure, e.g. in the manner described above, or by measuring an impedance of the three-dimensional porous, electrically conducting carbon structure and deriving the porosity from the measured impedance. The impedance of the three-dimensional porous, electrically conducting carbon structure may, e.g., be measured by using the three-dimensional porous, electrically conducting carbon structure as an electrode together with another electrode, both immersed in an electrolyte solution.

As an alternative, the porosity of the three-dimensional porous, electrically conducting carbon structure could be measured directly, e.g., by BET (Brunauer, Emmett and Teller) analysis, i.e. by physical adsorption of a gas on the surface of the solid and by calculating the amount of adsorbate gas corresponding to a monomolecular layer on the surface. The determination is usually carried out at the temperature of liquid nitrogen. The amount of gas adsorbed can be measured by a volumetric or continuous flow procedure.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will now be described in further detail with reference to the accompanying drawings in which

Figs. 1-4 illustrate a method according to a first embodiment of the invention, and

Figs. 5-7 illustrate a method according to a second embodiment of the invention.

DETAILED DESCRIPTION OF THE DRAWINGS

Figs. 1-4 illustrate a method according to a first embodiment of the invention. Fig. 1 is a perspective view of a mould 1 defining a volume 2 having a substantially cylindrical shape.

In Fig. 2 natural protein containing fibres, e.g. in the form of silk fibres, have been packed into the volume 2 of the mould 1. The fibres form a packed natural protein containing fibre structure 3. The fibres have been packed in such a manner that the packed natural protein containing fibre structure 3 has a predetermined and desired packing density. This may, e.g., be obtained by providing a weighed amount of fibres which will result in the desired packing density when the weighed amount of fibres exactly fills the volume 2 defined by the mould 1, and then packing these fibres into the volume 2 defined by the mould 1.

In Fig. 3 the packed natural protein containing fibre structure 3 has been removed from the mould 1. It can be seen that the packed natural protein containing fibre structure 3 maintains the size and shape defined by the mould 1, i.e. the structure 3 is cylindrical. Accordingly, the packing density of the packed natural protein containing fibre structure 3 is also maintained, even though the structure 3 is removed from the mould 1.

In Fig. 4 pyrolysis has been performed on the packed natural protein containing fibre structure 3, and thereby a three-dimensional porous and electrically conducting carbon structure 4 has been obtained. The carbon structure 4 has the same shape as the packed

natural protein containing fibre structure 3, i.e. the shape of the carbon structure 4 is determined by the shape of the volume 2 defined by the mould 1. Furthermore, the size of the carbon structure 4 may be the same as the size of the packed natural protein containing fibre structure 3. However, the pyrolysis may cause the structure to shrink by up to 50%, depending the material of the fibres. In this case the carbon structure 4 will have a size which is smaller than the size of the packed natural protein containing fibre structure 3, by up to 50%. Furthermore, the porosity of the carbon structure 4 is defined by the packing density of the packed natural protein containing fibre structure 3.

Accordingly, performing the method illustrated in Figs. 1-4 results in a porous and electrically conducting carbon structure 4 with a porosity which can be adjusted by adjusting the packing density of the packed fibres. Furthermore, the carbon structure 4 can be given any desired size or shape, simply by providing a suitable mould 1 which defines a volume 2 having the desired shape, and a size providing the desired size, possibly after an expected shrinking of the structure. Thus, an electrically conducting carbon structure 4 with a desired size, shape and porosity can be provided in a simple and cost effective manner. Such a carbon structure 4 is well suited for use as a carbon scaffold for tissue engineering, or for material for batteries, fuel cells, supercapacitors, sorbents for separation processes, gas storage, or supports for many important catalysts.

It should be noted that, even though the mould 1 used when performing the method illustrated in Figs. 1-4 has a simple cylindrical shape, the method described above could be performed using a mould 1 defining a volume 2 having any desired size or shape.

Figs. 5-7 illustrate a method according to a second embodiment of the invention. Fig. 5 shows a mould 1 having eight through-going rods 5 arranged therein. The mould 1 further defines a substantially box-shaped volume 2, which is traversed by the through-going rods 5.

In Fig. 6 natural protein containing fibres have been packed in the mould, thereby obtaining a packed natural protein containing fibre structure 3, essentially in the manner described above with reference to Figs. 1-4. Since the through-going rods 5 are arranged inside and extend through the volume 2 defined by the mould 1, the fibres are packed around the through-going rods 5. As a consequence, the through-going rods 5 are embedded in the resulting packed natural protein containing fibre structure 3.

Furthermore, in Fig. 6, the packed natural protein containing fibre structure 3 and the through-going rods 5 have been removed from the mould 1.

In Fig. 7 the through-going rods 5 have been removed from the packed natural protein containing fibre structure 3, thereby leaving eight through-going channels 6 in the packed natural protein containing fibre structure 3. This may, e.g., be obtained by removing the through-going rods 6 in a mechanical manner, or by dissolving the through-going rods 5.

Furthermore, in Fig. 7, pyrolysis has been performed on the packed natural protein containing fibre structure 3, and thereby a three-dimensional porous and electrically conducting carbon structure 4 has been obtained. As described above with reference to Figs. 1-4, the carbon structure 4 has a size and shape which is determined by the size and shape of the volume 2 defined by the mould 1, including the sizes, shapes and positions of the through-going rods 5, and a porosity which is defined by the packing density of the packed natural protein fibres.

CLAIMS

1. A method for fabricating a three-dimensional carbon structure, the method comprising the steps of:

- providing a mould defining a three-dimensional shape,
- packing natural protein containing fibres in the mould at a predetermined packing density, thereby obtaining a packed natural protein containing fibre structure,
- performing pyrolysis on the packed natural protein containing fibre structure, thereby obtaining a three-dimensional porous and electrically conducting carbon structure having a three-dimensional shape defined by the three-dimensional shape of the mould and a porosity defined by the packing density of the packed natural protein containing fibre structure.

2. A method according to claim 1, wherein the natural protein containing fibres are silk fibres, and wherein the method further comprises the step of extracting the silk fibres from raw silk cocoons.

3. A method according to claim 1 or 2, further comprising the step of removing the packed natural protein containing fibre structure from the mould prior to the step of performing pyrolysis on the packed natural protein containing fibre structure.

4. A method according to any of the preceding claims, wherein the step of packing natural protein containing fibres further comprises packing the natural protein containing fibres in the mould in a predetermined pattern, and wherein the porosity of the three-dimensional porous, electrically conducting carbon structure is further defined by the pattern of the packed natural protein containing fibre structure.

5. A method according to any of the preceding claims, further comprising the step of using the three-dimensional porous, electrically conducting carbon structure as a scaffold for tissue engineering.

6. A method according to claim 5, further comprising the step of using the three-dimensional porous, electrically conducting carbon structure as an actuator and/or as a sensor for tissue engineering applications and microbial electrosynthesis or bioremediation.

7. A method according to any of the preceding claims, wherein the step of performing pyrolysis on the packed natural protein containing fibre structure comprises positioning the packed natural carbon containing fibres in a furnace and reducing an oxygen level inside the furnace.

8. A method according to any of the preceding claims, wherein the step of packing natural protein containing fibres comprises the steps of:

- determining a desired weight of natural protein containing fibres to be contained in the resulting packed natural protein containing fibre structure,
- providing an amount of natural protein containing fibres corresponding to said desired weight, and
- packing the provided amount of natural protein containing fibres into the mould in such a manner that a volume defined by the mould is filled.

9. A method according to claim 8, wherein the step of packing the natural protein containing fibres further comprises the step of wetting the natural protein containing fibres prior to packing the natural protein containing fibres into the mould.

10. A method according to any of the preceding claims, further comprising the step of cutting the natural protein containing fibres before packing the fibres into the mould.

11. A method according to claim 10, further comprising the step of suspending the natural protein containing fibres into solution, after cutting the fibres and before packing the fibres into the mould.

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

- obtaining the porosity of the three-dimensional porous, electrically conducting carbon structure, and
- adjusting a predetermined packing density to be applied for the step of packing natural protein containing fibres in a mould during fabrication of an additional three-dimensional carbon structure, based on the obtained porosity.

13. A method according to claim 12, wherein the step of obtaining the porosity of the three-dimensional porous, electrically conducting carbon structure comprises measuring an impedance of the three-dimensional porous, electrically conducting carbon structure and deriving the porosity from the measured impedance.

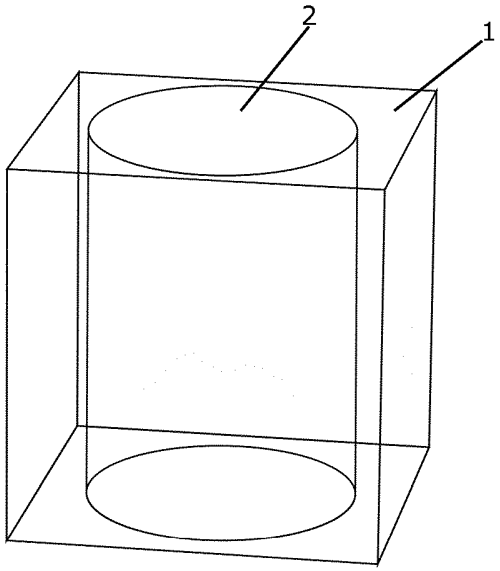

Fig. 1

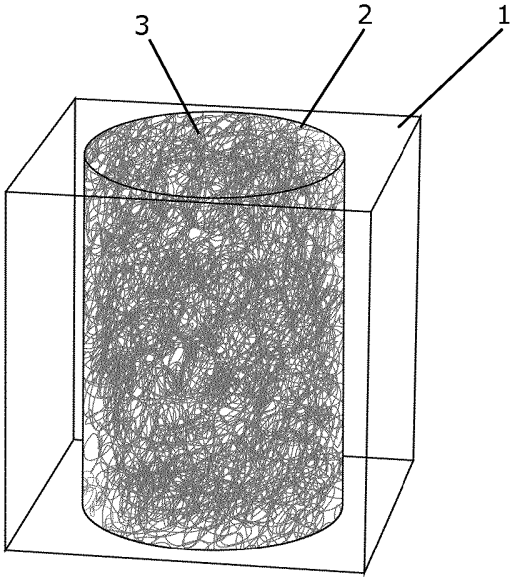

Fig. 2

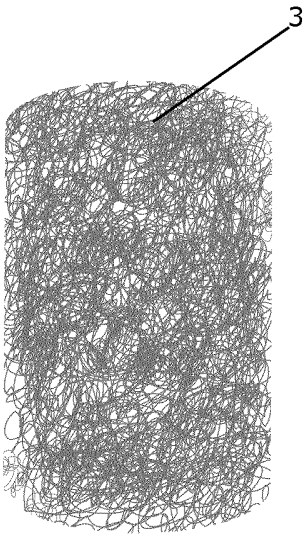

Fig. 3

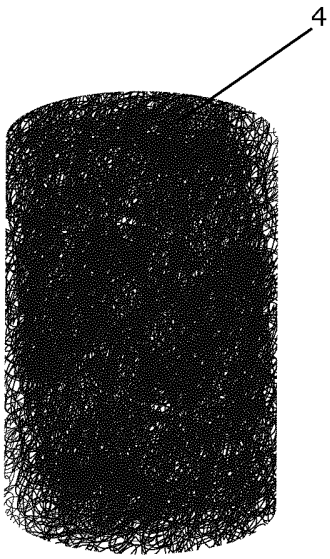

Fig. 4

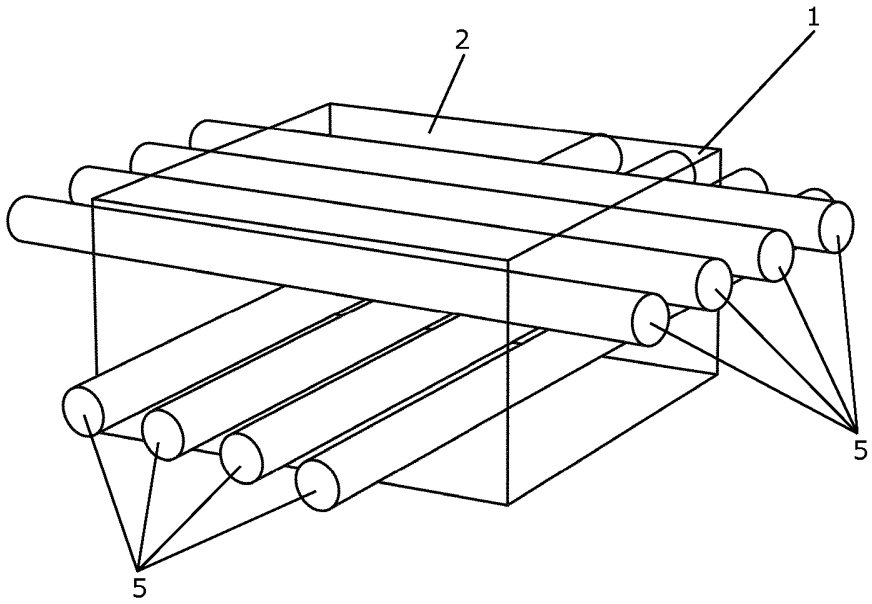

Fig. 5

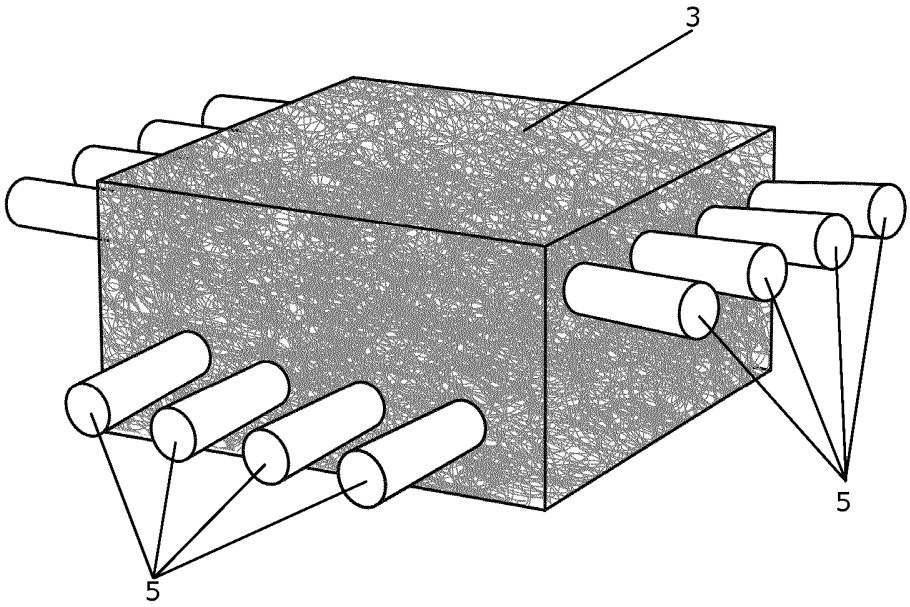

Fig. 6

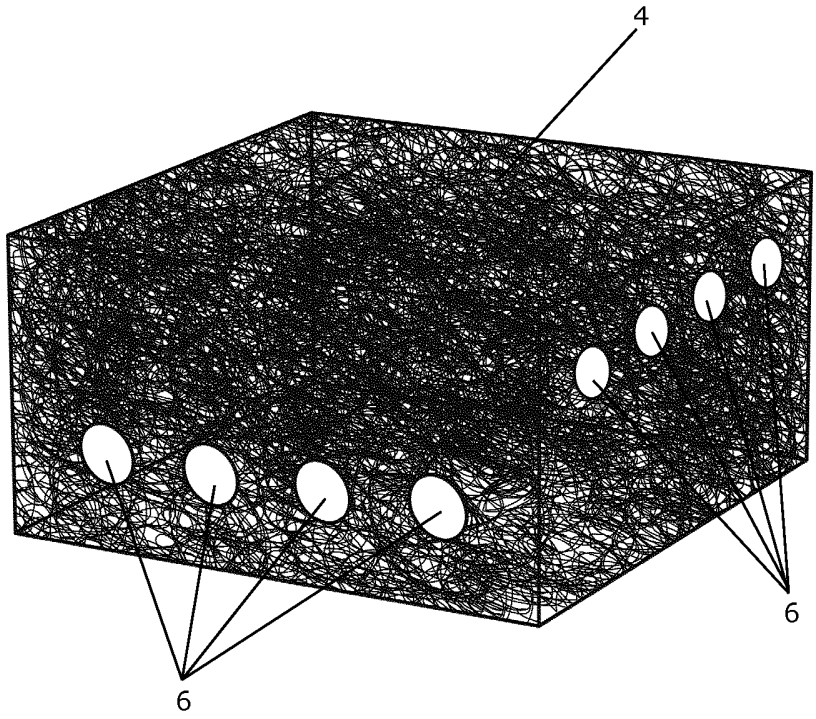

Fig. 7

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/070088

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B31/02
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)
C01B A61L D01F

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	US 2008/085648 A1 (HIROSUE SHINSUKE [JP] ET AL) 10 April 2008 (2008-04-10) cited in the application examples 3-4	1-13
A	US 2004/258729 A1 (CZERNUSZKA JAN TADEUSZ [GB] ET AL) 23 December 2004 (2004-12-23) the whole document	1-13
A	WO 99/33641 A1 (MOLECULAR GEODESICS INC [US]; INGBER DONALD E [US]; MEUSE ARTHUR J [US]) 8 July 1999 (1999-07-08) claim 43	1-13

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

☒ See patent family annex.

* Special categories of cited documents :

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 September 2016	22/09/2016

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

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2016/070088

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2008085648 A1	10-04-2008	JP 2008112720 A	15-05-2008
		US 2008085648 A1	10-04-2008
US 2004258729 A1	23-12-2004	CA 2498589 A1	20-03-2003
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		JP 2005501662 A	20-01-2005
		US 2004258729 A1	23-12-2004
		WO 03022319 A1	20-03-2003
WO 9933641 A1	08-07-1999	NONE	