

METHOD FOR MAKING FUNCTIONALLY GRADIENT COATINGS BY 3D PRINTING BASED ON ELECTROSTATIC SPINNING AND ELECTROSTATIC SPRAYING

FIELD

The present invention relates to tissue engineering technology and, more specifically, to a method for making functionally gradient coatings by 3D printing based on electrostatic spinning and electrostatic spraying.

BACKGROUND

Traditional 3D printers are developed based on the working principle of an inkjet printer, which use a nozzle for continuous inkjet to selectively spray and deposit liquid-containing binder on a powdered material layer for bonding powder, so that orderly printed two-dimensional powder layers can be piled up to form a three-dimensional structure. 3D printing has been widely applied to the manufacture of minute structures, especially in biomedical tissue engineering fields, due to its low manufacturing cost and flexible manufacturing process in the manufacture of complicated micro three-dimensional microstructures. The 3D printing has distinctly unique advantages in implementing forming of individualized structures.

In the tissue engineering technology, how to repair or replace articular cartilage is a hot point of recent researching. The material used in cartilaginous bionic scaffolds is a function material of a gradient structure, and each of different structural layers has its particular functions according to its characteristics. For example, a porous superficial layer is low in intensity, but it can absorb and release synovial fluid to decrease the wear; an intermediate layer has certain toughness, and can withstand impact and absorb shock; a lower layer is calcified to form a strong physical connection with a bone.

The muscle tendon is a carrier for connecting a muscle with a bone as a cartilage, which can implement the transmission of motion and force. The connecting portion (tendon-to-bone interface) between the muscle tendon and the bone is a complicated gradient structure, which may be divided into four layers (for example, including muscle

tendon, non-calcified cartilage, calcified cartilage and bone) gradually from a soft tissue to a hard tissue, and belongs to functionally gradient tissue structures in biology. Such tissue structure plays a crucial role in the connection between the muscle tendon and the bone, which can transmit forces from the muscle tendon to the bone, reduce stress concentration and support biotic links between different kinds of cells. Therefore, many scholars are devoted to the replaceable functionally gradient bionic structure.

At present, there are many bionic designs and manufacture methods for the tendon-to-bone interface. For example, Xiaoran Li et al. has presented a permeation method was in which calcium phosphate may permeate into a nanofiber membrane surface layer and a nanofiber membrane lower layer in a nanofiber structure to form coatings of gradient structure, but this method is quite time consuming in forming process and it only has gradient structures in the surface layer and the lower layer; Cevat Erisken et al. has presented a method to use twin screw extrusion mechanism to make a functionally gradient coating, in which β -tricalcium phosphate (β -TCP) is distributed in polycaprolactone (PCL) by the twin screw extrusion mechanism to form a functionally gradient structure, but such twin screw extrusion mechanism is complex and difficult to operate; and Satyavrata Samavedi et al. has presented a method use electrostatic spinning to make a gradient structure with a simple manufacture technology, in which the gradient structure made has good biocompatibility, but this method can only generate a gradient structure of three layers, which is far from meeting the requirement of multiple layers of functional gradient coatings.

SUMMARY

Based on the above, it is necessary to provide a method for making functionally gradient coatings by 3D printing based on electrostatic spinning and electrostatic spraying, to over the defects of the prior art.

According to an aspect of the present invention, a method for making functionally gradient coatings by 3D printing based on electrostatic spinning and electrostatic spraying is provided. The method uses a hybrid 3D printing system based on electrostatic spinning and electrostatic spraying, and the hybrid 3D printing system including:

a first injection pump, a second injection pump, a first nozzle, a second nozzle, a high voltage power supply, a core rod collector, a controller, a motor and a speed-adjusting unit; the first injection pump, the first nozzle, the high voltage power supply, the core rod collector and the controller constitute an electrostatic spinning subsystem which uses the high voltage power supply to apply a first high-voltage electrostatic field so that first material sprayed from the first nozzle forms filaments under the applied first high-voltage electrostatic field, and the core rod collector is adapted to collect the filaments to form a first material coating; the second injection pump, the second nozzle, the high voltage power supply, the core rod collector and the controller constitute an electrostatic spraying subsystem which uses the high voltage power supply to apply a second high-voltage electrostatic field so that second material sprayed from the second nozzle move in a definite direction under the applied second high-voltage electrostatic field, and the core rod collector is adapted to collect the second material to form a second material coating.

The method includes the following steps:

step A, controlling the electrostatic spinning subsystem, by the controller, to generate the first material coating; and

step B, controlling the electrostatic spraying subsystem, by the controller, to generate the second material coating.

In one embodiment, the method further includes repeating the step A two or more times and/or repeating the step B two or more times.

In one embodiment, the step A and the step B are conducted simultaneously or successively.

In one embodiment, the step A includes:

preparing the first material;

putting the prepared first material into the first injection pump;

inputting, into the controller, initial values of a first set of control parameters used in electrostatic spinning process, wherein the first set of control parameters includes one or more selected from the group consisting of feed rate of the first material, time for spinning, voltage of the first nozzle, distance between the first nozzle and the core rod collector, and

rotational speed of the core rod collector;

adjusting, by the controller, the first set of control parameters according to the initial values of the first set of control parameters; and

conducting spinning between the first nozzle and the core rod collector to generate
5 the first material coating on the core rod collector.

In one embodiment, the step B includes:

preparing the second material;

putting the prepared second material into the second injection pump;

inputting, into the controller, initial values of a second set of control parameters used
10 in electrostatic spraying process, wherein the second set of control parameters includes one or more selected from the group consisting of feed rate of the second material, time for spinning, voltage of the second nozzle, distance between the second nozzle and the core rod collector, and rotational speed of the core rod collector;

adjusting, by the controller, the second set of control parameters according to the
15 initial values of the second set of control parameters; and

conducting spraying on the core rod collector to generate the second material coating.

In one embodiment, the method further includes changing, by the controller, values of the first set of control parameters and/or values of the second set of control parameters dynamically and in real time when the electrostatic spinning subsystem and/or the
20 electrostatic spraying subsystem is working, during manufacturing process of the functionally gradient coatings.

In one embodiment, the first material is polymer, and the electrostatic spinning subsystem is adapted to form a polymer coating from the first material.

In one embodiment, the second material is inorganic salt, and the electrostatic
25 spraying subsystem is adapted to form an inorganic coating from the second material.

In one embodiment, the electrostatic spinning subsystem and the electrostatic spraying subsystem are configured to work separately, alternatively or simultaneously.

In one embodiment, the method further includes:

configuring the electrostatic spinning subsystem and the electrostatic spraying
30 subsystem to work simultaneously, and combining the generated first material coating and

the generated second material coating into a mixed material coating;

changing, by the controller, values of the first set of control parameters and values of the second set of control parameters dynamically and in real time when the electrostatic spraying subsystem and the electrostatic spinning subsystem are working, to form a plurality of mixed material coatings; and

stacking and combining the plurality of mixed material coatings to form functionally gradient coatings.

The above method for making functionally gradient coatings by 3D printing based on electrostatic spinning and electrostatic spraying can both implement spraying printing for inorganic salt, such as hydroxylapatite (HA), and implement electrostatic spinning for polymer, such as polycaprolactone (PCL), to achieve the manufacture of the preparing functionally gradient coatings. The present invention is simple in structure and easy to operate, simplifies technological process of making the functionally gradient coatings, and can make multiple layers of functional gradient coatings according to individual needs.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings illustrate one or more embodiments of the present invention and together with the written description, serve to explain the principles of the present invention. Wherever possible, the same reference numbers are used throughout the drawings to refer to the same or like elements of an embodiment.

FIG. 1 is a schematic diagram illustrating a hybrid 3D printing system based on electrostatic spinning and electrostatic spraying in accordance with one embodiment of the present invention.

FIG. 2 is a schematic diagram illustrating a process of electrostatic spinning.

FIG. 3 is a schematic diagram illustrating a process of electrostatic spraying.

FIGS. 4a-4e are SEM images showing functionally gradient coatings of different physicochemical properties generated by a hybrid 3D printing system based on electrostatic spinning and electrostatic spraying according to different printing parameters in accordance with one embodiment of the present invention.

FIG. 5 is an analysis diagram showing the calcium content of the functionally gradient

coatings shown in FIGS 4a-4e respectively.

FIG. 6 is a schematic diagram showing layers of a functionally gradient structure formed by the functionally gradient coatings shown in FIGS 4a-4e.

ETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the following description of embodiments, reference is made to the accompanying drawings which form a part hereof, and in which it is shown by way of illustration specific embodiments of the present invention that can be practiced. It is to be understood that other embodiments can be used and structural changes can be made without departing from the scope of the disclosed embodiments.

FIG. 1 is a schematic diagram illustrating a hybrid 3D printing system based on electrostatic spinning and electrostatic spraying in accordance with one embodiment of the present invention. The hybrid 3D printing system may include: a first injection pump 21, a second injection pump 22, a first nozzle 31, a second nozzle 32, a high voltage power supply 4, a core rod collector 5, a controller 1, a motor 6 and a speed-adjusting unit 7. The first injection pump 21, the first nozzle 31, the high voltage power supply 4, the core rod collector 5 and the controller 1 constitute an electrostatic spinning subsystem; and the second injection pump 22, the second nozzle 32, the high voltage power supply 4, the core rod collector 5 and the controller 1 constitute an electrostatic spraying subsystem

The process to make a material coating by the electrostatic spinning subsystem is described as below.

Preparing the first material, i.e., polymer solution, such as polycaprolactone or acetic acid solution;

putting the prepared first material into the first injection pump 21;

inputting, into the controller 1, initial values of a set of control parameters used in electrostatic spinning process;

adjusting, by the controller, feed rate of the first material, time for spinning, voltage of the first nozzle 31, distance between the first nozzle 31 and the core rod collector 5, and rotational speed of the core rod collector 5 according to the initial values of the set of control parameters; and

conducting spinning between the first nozzle 31 and the core rod collector 5 to generate the first material coating on the core rod collector 5.

FIG. 2 shows the operating principle of electrostatic spinning.

The electrostatic spinning subsystem may use the high voltage power supply 4 to
5 apply a first high-voltage electrostatic field; the high voltage power supply 4 may charge the droplets of the polymer solution, the droplets on the surface of the polymer solution may overcome surface tension to develop and lengthen because of electrostatic repulsion in the first high-voltage electrostatic field, and the droplets that overcome surface tension may be sprayed from the first nozzle 31 at a critical force point to form polymer filaments;
10 and the core rod collector 5 may collect the filaments to form a polymer coating. The continuous working of the high voltage power supply 4 may cause a continuous polymer coating formed on the core rod collector 5.

The process to make a material coating by the electrostatic spraying subsystem is described as below.

15 preparing the second material, i.e., inorganic salt solution, such as hydroxyapatite or ethanol solution;

putting the prepared second material into the second injection pump 22;

inputting, into the controller, initial values of a set of control parameters used in electrostatic spraying process;

20 adjusting, by the controller, feed rate of the second material, time for spinning, voltage of the second nozzle 32, distance between the second nozzle 32 and the core rod collector 5, and rotational speed of the core rod collector according to the initial values of the set of control parameters; and

conducting spraying on the core rod collector 5 to generate the second material
25 coating.

FIG. 3 shows the operating principle of electrostatic spraying.

The electrostatic spraying subsystem may use the high voltage power supply 4 to apply a second high-voltage electrostatic field; the hydroxyapatite solution may overcome surface tension to be sprayed from the second nozzle 32 under the high voltage power
30 supply 4; and the material the surface of which is positively charged may be received by

the grounded core rod collector 5 to form a hydroxyapatite coating. The continuous working of the high voltage power supply 4 may cause a continuous hydroxyapatite coating formed on the core rod collector 5.

In the embodiment, the electrostatic spinning subsystem and the electrostatic spraying subsystem are configured to work simultaneously, so that the generated polymer coating and the generated hydroxyapatite coating may be combined to form a mixed material coating. In addition, the electrostatic spinning subsystem and the electrostatic spraying subsystem may be configured to work separately, to form a first material coating and a second material coating respectively.

The hybrid 3D printing system based on electrostatic spinning and electrostatic spraying may dynamically change the two sets of control parameters used in the two subsystems during the printing process based on the actual requirements of design, to produce a mixed material coating of given physicochemical properties which meets the actual needs.

FIGS. 4a-4e are SEM images showing functionally gradient coatings of different physicochemical properties generated by a hybrid 3D printing system based on electrostatic spinning and electrostatic spraying according to different printing parameters (a first set of control parameters used in the electrostatic spinning subsystem and a second set of control parameters used in the electrostatic spraying subsystem) in accordance with one embodiment of the present invention. FIGS. 4a-4e with number from 1 to 5 show five coatings arranged from 1 to 5. FIG. 5 is an analysis diagram showing the calcium content of the functionally gradient coatings shown in FIGS 4a-4e respectively. It shows that the first coating has the lowest calcium content, and the calcium content of the second, third, fourth and fifth coating increases gradually. Changes in the calcium content of the five functionally gradient coatings may meet the requirement of functional gradient. The different functionally gradient coatings may be generated by changing printing parameters dynamically and in real time, and these functionally gradient coatings can be stacked and combined to form a functionally gradient bionic structure with gradiently distributed calcium content, as shown in FIG. 6.

The above preferred embodiments of the present invention are described in detail,

and should not be deemed as limitations to the scope of the present invention. It should be noted that variations and improvements will become apparent to those skilled in the art to which the present invention pertains without departing from its spirit and scope. Therefore, the scope of the present disclosure is defined by the appended claims.

CLAIMS

1. A method for making functionally gradient coatings by 3D printing based on electrostatic spinning and electrostatic spraying, using a hybrid 3D printing system based on electrostatic spinning and electrostatic spraying, wherein the hybrid 3D printing system
5 comprises:

a first injection pump, a second injection pump, a first nozzle, a second nozzle, a high voltage power supply, a core rod collector, a controller, a motor and a speed-adjusting unit; the first injection pump, the first nozzle, the high voltage power supply, the core rod collector and the controller constitute an electrostatic spinning
10 subsystem which uses the high voltage power supply to apply a first high-voltage electrostatic field so that first material sprayed from the first nozzle forms filaments under the applied first high-voltage electrostatic field, and the core rod collector is adapted to collect the filaments to form a first material coating; the second injection pump, the second nozzle, the high voltage power supply, the core rod collector and the controller
15 constitute an electrostatic spraying subsystem which uses the high voltage power supply to apply a second high-voltage electrostatic field so that second material sprayed from the second nozzle move in a definite direction under the applied second high-voltage electrostatic field, and the core rod collector is adapted to collect the second material to form a second material coating; and

20 the method comprise:

step A, controlling the electrostatic spinning subsystem, by the controller, to generate the first material coating; and

step B, controlling the electrostatic spraying subsystem, by the controller, to generate the second material coating.

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2. The method of claim 1, further comprises: repeating the step A for two or more times and/or repeating the step B for two or more times.

3. The method of claim 1 or 2, wherein the step A and the step B are conducted
30 simultaneously or successively.

4. The method of claim 1, wherein the step A comprises:

preparing the first material;

putting the prepared first material into the first injection pump;

5 inputting, into the controller, initial values of a first set of control parameters used in electrostatic spinning process, wherein the first set of control parameters comprises one or more selected from the group consisting of feed rate of the first material, time for spinning, voltage of the first nozzle, distance between the first nozzle and the core rod collector, and rotational speed of the core rod collector;

10 adjusting, by the controller, the first set of control parameters according to the initial values of the first set of control parameters; and

conducting spinning between the first nozzle and the core rod collector to generate the first material coating on the core rod collector.

15 5. The method of claim 1, wherein the step B comprises:

preparing the second material;

putting the prepared second material into the second injection pump;

inputting, into the controller, initial values of a second set of control parameters used in electrostatic spraying process, wherein the second set of control parameters comprises
20 one or more selected from the group consisting of feed rate of the second material, time for spinning, voltage of the second nozzle, distance between the second nozzle and the core rod collector, and rotational speed of the core rod collector;

adjusting, by the controller, the second set of control parameters according to the initial values of the second set of control parameters; and

25 conducting spraying on the core rod collector to generate the second material coating.

6. The method of claim 4 or 5, further comprises: changing, by the controller, values of the first set of control parameters dynamically and in real time when the electrostatic spinning subsystem is working and/or values of the second set of control parameters
30 dynamically and in real time when the electrostatic spraying subsystem is working, during

manufacturing process of the functionally gradient coatings.

7. The method of claim 1, wherein the first material is polymer and the electrostatic spinning subsystem is adapted to form a polymer coating from the first material.

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8. The method of claim 1, wherein the second material is inorganic salt and the electrostatic spraying subsystem is adapted to form an inorganic coating from the second material.

10 9. The method of claim 1, wherein the electrostatic spinning subsystem and the electrostatic spraying subsystem are configured to work separately, alternatively or simultaneously.

15 10. The method of claim 9, further comprises: configuring the electrostatic spinning subsystem and the electrostatic spraying subsystem to work simultaneously, and combining the generated first material coating and the generated second material coating into a mixed material coating.

20 11. The method of claim 10, further comprises: changing, by the controller, values of the first set of control parameters and values of the second set of control parameters dynamically and in real time when electrostatic spinning subsystem and the electrostatic spraying subsystem are working, to form a plurality of mixed material coatings; and stacking and combining the plurality of mixed material coatings to form functionally gradient coatings.

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