CLAIMS

1. A method for making ~~functionally gradient coatings~~ a tendon-to-bone interface 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 ~~comprises~~ 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, and a motor, ~~and a speed-adjusting unit;~~ wherein 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~~ that uses the high voltage power supply to apply a first high-voltage electrostatic field so that a 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; and 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~~ that uses the high voltage power supply to apply a second high-voltage electrostatic field so that a second material ~~prayed~~ is sprayed from the second nozzle ~~move~~ that moves 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~~

the method ~~comprise~~ comprising:

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~~.~~ that has a calcium content, in which the second material coating is formed from the second material sprayed from the second nozzle with the second nozzle moving in a definite direction under the second high-voltage electrostatic field used by the electrostatic spraying subsystem;

step C) combining the first material coating and the second material coating to form a mixed material coating, which has a calcium content from the second material coating;

step D) repeating steps A) to C) to form a plurality of mixed material coatings by

operating the electrostatic spinning subsystem and the electrostatic spraying subsystem, respectively, by changing values of a first set of control parameters and a second set of control parameters dynamically and in real time to gradually increase the calcium content of each mixed material coating from that of the firstly formed mixed material coating to that of the lastly formed mixed material coating; and finally,

step E) stacking and combining the plurality of mixed material coatings to form multiple layers of a tendon-to-bone interface;

wherein the first material is polycaprolactone; the second material is hydroxyapatite; the first set of control parameters include 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; and the second set of control parameters include 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.

2. The method of claim 1, further ~~comprises:~~ comprising 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~~ performed 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;

inputting, into the controller, initial values of ~~a~~ the 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;

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.

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~~ the second set of control parameters used in electrostatic spraying process, wherein the second set of control parameters comprises 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

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

6. The method of claim 4 ~~or 5~~, further ~~comprises:~~ comprising 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 dynamically and in real time when the electrostatic spraying subsystem is working, during manufacturing process of the ~~functionally gradient coatings~~ tendon-to-bone interface.

~~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.~~

~~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.~~

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

7. The method of claim 2, wherein step A and step B are performed simultaneously or successively.

8. The method of claim 5, further comprising 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 dynamically and in real time when the electrostatic spraying subsystem is working, during manufacturing process of the tendon-to-bone interface.

9. A method for making a tendon-to-bone interface 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 electrostatic spinning subsystem and the electrostatic spraying subsystem are configured to work separately, alternatively, or simultaneously, 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, and a motor, wherein the first injection pump, the first nozzle, the high voltage power supply, the core rod collector, and the controller constitute an electrostatic spinning subsystem that uses the high voltage power supply to apply a first high-voltage electrostatic field so that a 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; and the second injection pump, the second nozzle, the high voltage power supply, the core rod collector, and the controller constitute an electrostatic spraying subsystem that uses the high voltage power supply to apply a second high-voltage electrostatic field so that a second material is sprayed from the second nozzle that moves 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 comprising:

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

controlling the electrostatic spraying subsystem, by the controller, to generate the second material coating that has a calcium content, in which the second material coating is formed from the second material sprayed from the second nozzle with the second nozzle moving in a definite direction under the second high-voltage electrostatic field used by the electrostatic spraying subsystem;

combining the first material coating and the second material coating to form a mixed material coating, which has a calcium content from the second material coating;

repeating the controlling and combining steps above to form a plurality of mixed material coatings by operating the electrostatic spinning subsystem and the electrostatic spraying subsystem, respectively, by changing values of a first set of control parameters and a second set of control parameters dynamically and in real time to gradually increase the calcium content of each mixed material coating from that of the firstly formed mixed material coating to that of the lastly formed mixed material coating; and finally

stacking and combining the plurality of mixed material coatings to form multiple layers of a tendon-to-bone interface;

wherein the first material is polycaprolactone; the second material is hydroxyapatite; the first set of control parameters include 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; and the second set of control parameters include 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.

10. The method of claim 9, further ~~comprises:~~ comprising 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.

11. The method of claim 10, further comprises: wherein step D is performed by changing, by the controller, values of the a first set of control parameters and values of the a second set of control parameters dynamically and in real time when the 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.