

DESCRIPTION

TITLE OF INVENTION: [GLASSY CARBON MICRONEEDLE, PREPARATION METHOD THEREFOR AND USE THEREOF]

REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the priority to Chinese patent application No. [CN2023117246296], filed [December 14, 2023], the contents of which are incorporated herein by reference.

TECHNICAL FIELD

[0002] The present disclosure relates generally to the field of glassy carbon preparation, and specifically to a glassy carbon microneedle, preparation method therefore and use thereof.

BACKGROUND

[0003] Microneedle products, such as microneedle patches, are composed of a plurality of fine needle tips connected to a base in an array, and have wide applications in disease prevention, diagnosis, rehabilitation, medical aesthetics, and other fields.

[0004] Glassy carbon (also referred to as glassy carbon) is a type of amorphous carbon having good weight-loss-rate fluctuation temperature performance, electrical conductivity, biocompatibility, and chemical stability. Compared with commonly used materials for preparing microneedle patches, such as polymers, metals, and ceramics, glassy carbon has some unique properties. Microneedle patches based on glassy carbon have unique applications in medicine, electronics, chemical industry, and other fields, and the development of glassy carbon microneedle patches and other products is of great significance.

[0005] Glassy carbon is usually prepared by gradient pyrolysis of a polymer precursor. The process is complex, and a large volume shrinkage occurs during the pyrolysis process, causing significant product defects such as denaturation, foaming, cracking, and breakage, making the development of high-quality glassy carbon microneedle patches quite difficult. For example, CN109627003A discloses a method for preparing a novel glassy carbon material using furfural-furfuryl alcohol modified resin. As another example, CN105819859A discloses a method for preparing a glassy carbon material based on a polymer prepolymer precursor. However, on the one hand, such processes involve a relatively complicated heating procedure, particularly requiring relatively frequent heat-preservation treatments at multiple temperature points (which

also involve multi-stage temperature control, resulting in relatively high process implementation costs and monitoring difficulty), and the process takes a relatively long time; on the other hand, when preparing minute glassy carbon microneedle products, it is extremely difficult to avoid significant product defects, which severely affects the morphology and performance of the glassy carbon.

[0006] Currently, studies have achieved the preparation of glassy carbon microneedles; however, microneedles often need to be made into microneedle patches for convenient use and efficacy, and in particular, the efficacy of glassy carbon microneedles, such as electrical conductivity, heavily depends on the performance of the microneedle base. However, due to the fine and complex structure of microneedle patches, the pyrolysis process in glassy carbon preparation leads to severe deformation defects in conventional microneedle patches, and the development of high-quality glassy carbon microneedle patches faces enormous challenges.

[0007] Therefore, the development of novel glassy carbon microneedle patches and efficient preparation methods has important scientific significance and great application value. There is an urgent need for a preparation method that can improve the morphology and performance of glassy carbon microneedle patch products while controlling implementation costs.

SUMMARY

[0008] An object of the present invention is to provide a method for preparing a glassy carbon microneedle, which partially solves or alleviates the above-mentioned deficiencies of the prior art, improves the preparation quality of microneedles, and reduces preparation costs. In order to solve the above-mentioned technical problems, the present invention specifically adopts the following technical solutions: In one aspect, the present invention provides a method for preparing a glassy carbon microneedle, the method comprising the steps of:

[0009] preparing a precursor using a carbon-based polymer raw material, wherein the precursor has a microneedle or microneedle-like structure;

[0010] placing the precursor in a heating chamber and starting a centralized heat-preservation method, wherein starting the centralized heat-preservation method comprises: in a first heating stage, selecting a stress-relief temperature to perform a heat-preservation treatment on the precursor, so as to relieve stress in the precursor; wherein the stress-relief temperature is selected according to a first selection rule; wherein the first selection rule is: selecting the stress-relief temperature from a weight-loss-rate fluctuation temperature; and wherein the weight-loss-rate fluctuation temperature corresponds to a temperature value of a data point, in a derivative

thermogravimetry curve, having a greatest curvature change in an interval less than a pyrolytic carbonization temperature;

[0011] raising temperature to enter a second heating stage, and in the second heating stage, selecting the pyrolytic carbonization temperature to perform another heat-preservation treatment on the precursor, so as to cause the precursor to undergo pyrolytic carbonization, wherein the microneedle or the microneedle-like structure shrinks during the pyrolytic carbonization; wherein the pyrolytic carbonization temperature is selected according to a second selection rule; wherein the second selection rule is: selecting the pyrolytic carbonization temperature from a weight-loss fluctuation temperature; wherein the weight-loss fluctuation temperature corresponds to a temperature value of a curve segment, in a thermogravimetric analysis curve, having a greatest curvature change in an interval in which a slope gradually decreases;

[0012] in a subsequent third heating stage, continuously raising temperature from the pyrolytic carbonization temperature to a target heating temperature, so that the precursor prepared from the carbon-based polymer is finally converted into the glassy carbon microneedle.

[0013] Further, the present invention provides a glassy carbon microneedle patch, comprising: a body, and a hollow region optionally provided in the body; wherein the body comprises: a mesh substrate having a plurality of mesh holes arranged on the mesh substrate at intervals, and a plurality of microneedles or microneedle-like structures provided at edges of the mesh holes; wherein the glassy carbon microneedle patch is prepared by subjecting a mesh precursor to a centralized heat-preservation pyrolysis treatment, and the mesh precursor is prepared from a carbon-based polymer.

[0014] In some embodiments, a line width L1 of the mesh holes in the mesh precursor is less than or equal to 2 mm, and a radius L2 of the body of the precursor is less than or equal to 100 mm. In some embodiments, the body may have one or more of the following shapes: circular, annular, elliptical, rounded rectangular, or regular polygonal. In some embodiments, a base of the microneedle-like structure may have one or more of the following shapes: circular, rectangular, cross-shaped, and asterisk-shaped.

[0015] The present invention also provides a method for preparing a glassy carbon microneedle patch, wherein the centralized heat-preservation step comprises: S20 placing the mesh precursor in a heating chamber and starting a centralized heat-preservation method; and S20 comprises:

[0016] S21 in a first heating stage, selecting a stress-relief temperature to perform a heat-preservation treatment on the mesh precursor, so as to relieve stress in the mesh precursor;

wherein the stress-relief temperature is selected according to a first selection rule; and the first selection rule is: selecting the stress-relief temperature from a weight-loss-rate fluctuation temperature; and the weight-loss-rate fluctuation temperature corresponds to a temperature value of a data point, in a derivative thermogravimetry curve, having a greatest curvature change in an interval less than a pyrolytic carbonization temperature.

[0017] In some embodiments, S20 further comprises: S22 raising temperature to enter a second heating stage, and in the second heating stage, selecting the pyrolytic carbonization temperature to perform another heat-preservation treatment on the mesh precursor, so as to cause the mesh precursor to undergo pyrolytic carbonization, wherein the microneedle or the microneedle-like structure to be formed on the mesh precursor and the mesh holes shrink proportionally during the pyrolytic carbonization, and impurities generated during the process can be uniformly discharged outward by utilizing the mesh arrangement; wherein the pyrolytic carbonization temperature is selected according to a second selection rule; the second selection rule is: selecting the pyrolytic carbonization temperature from a weight-loss fluctuation temperature; wherein the weight-loss fluctuation temperature corresponds to a temperature value of a curve segment, in a thermogravimetric analysis curve, having a greatest curvature change in an interval in which a slope gradually decreases.

[0018] That is to say, in some embodiments of the present invention, only one heat-preservation treatment can be used for the low temperature range, for example, only one pyrolytic carbonization treatment is performed. Moreover, experimental verification has shown that performing only one low-temperature heat-preservation treatment still results in microneedles with good morphology. For instance, in some embodiments, the method for preparing a glassy carbon microneedle provided by the present invention comprises: raising temperature to enter a second heating stage, and in the second heating stage, selecting the pyrolytic carbonization temperature to perform another heat-preservation treatment on the precursor, so as to cause the precursor to undergo pyrolytic carbonization, wherein the microneedle or microneedle-like structure to be formed shrinks proportionally during the pyrolytic carbonization, and impurities generated during the process are uniformly discharged outward; wherein the pyrolytic carbonization temperature is selected according to a second selection rule; the second selection rule is: selecting the pyrolytic carbonization temperature from a weight-loss fluctuation temperature; wherein the weight-loss fluctuation temperature corresponds to a temperature value of a curve segment, in a thermogravimetric analysis curve, having a greatest curvature change in an interval in which a slope gradually decreases.

[0019] In some embodiments, the method further comprises: S30 in a subsequent third heating stage, continuously raising temperature from the pyrolytic carbonization temperature to a

target heating temperature; finally converting the precursor prepared from the carbon-based polymer into the glassy carbon microneedle (e.g., converting a mesh precursor into a microneedle patch).

[0020] In some embodiments, the method further comprises: in the third heating stage, selecting the target heating temperature to perform another heat-preservation treatment on the precursor.

[0021] In some embodiments, the method further comprises: during the heating stage of the (mesh) precursor, introducing an inert gas into the heating chamber to protect the precursor and discharge impurities generated during the heating stage; and collecting a concentration indicator of the impurities by a gas monitoring device.

[0022] In some embodiments, the method further comprises: in the third heating stage, when the concentration indicator of the impurities is monitored to be lower than a preset concentration range, selecting a switching time according to a current time, wherein a difference between the switching time and the current time is less than a preset difference range; at the switching time, increasing a current first heating rate to a second heating rate, and continuing to raise temperature to the target heating temperature.

[0023] In some embodiments, the carbon-based polymer comprises: a carbon-rich polymer, wherein the carbon-rich polymer comprises one or more of: polyurethane, epoxy resin, phenolic resin, polyacrylonitrile, polyimide, polystyrene, polytetrafluoroethylene, polyethylene, polyaniline, or a product obtained by further modifying or modifying the carbon-rich polymer; and/or the method for preparing the mesh precursor comprises mold forming and/or 3D printing.

[0024] In another aspect, the present invention further provides a method for preparing a glassy carbon microneedle, wherein the glassy carbon is prepared by a centralized heat-preservation method based on a mesh precursor. Accordingly, the method comprises the steps of: S10 preparing a precursor using a carbon-based polymer raw material, for example, the precursor may be a mesh precursor, wherein the mesh precursor comprises a plurality of mesh holes arranged at intervals, the mesh holes intersect with each other to form a mesh arrangement, and a microneedle or microneedle-like structure to be formed is provided at edges of the mesh holes; S20 placing the mesh precursor in a heating chamber and starting a centralized heat-preservation method, S20 comprising:

[0025] S21 in a first heating stage, selecting a stress-relief temperature to perform a heat-preservation treatment on the mesh precursor, so as to relieve stress in the mesh precursor; wherein the stress-relief temperature is selected according to a first selection rule; S22 raising

temperature to enter a second heating stage, and in the second heating stage, selecting the pyrolytic carbonization temperature to perform another heat-preservation treatment on the mesh precursor, so as to cause the mesh precursor to undergo pyrolytic carbonization, wherein the target to be formed on the mesh precursor and the mesh holes shrink proportionally during the pyrolytic carbonization, and impurities generated during the process can be uniformly discharged outward by utilizing the mesh arrangement; wherein the pyrolytic carbonization temperature is selected according to a second selection rule; S30 in a subsequent third heating stage, continuously raising temperature from the pyrolytic carbonization temperature to a target heating temperature; finally converting the carbon-based polymer into glassy carbon; wherein the first selection rule is: selecting the stress-relief temperature from a weight-loss-rate fluctuation temperature; and the weight-loss-rate fluctuation temperature corresponds to a temperature value of a data point, in a derivative thermogravimetry curve, having a greatest curvature change in an interval less than a pyrolytic carbonization temperature; and the second selection rule is: selecting the pyrolytic carbonization temperature from a weight-loss fluctuation temperature; wherein the weight-loss fluctuation temperature corresponds to a temperature value of a curve segment, in a thermogravimetric analysis curve, having a greatest curvature change in an interval in which a slope gradually decreases.

[0026] In some embodiments, when there is a first quantity of weight-loss-rate fluctuation temperatures, and the first quantity is greater than or equal to 2, S21 comprises:

[0027] selecting a second quantity of weight-loss-rate fluctuation temperatures from the first quantity of weight-loss-rate fluctuation temperatures at intervals, and correspondingly obtaining a second quantity of stress-relief temperatures, wherein the second quantity is less than or equal to the first quantity, and the stress-relief temperatures at least comprise: a first stress-relief temperature and a second stress-relief temperature; in the first heating stage, using the first stress-relief temperature to perform a heat-preservation treatment, so as to perform a first stress relief on the mesh precursor; continuously raising temperature from the first stress-relief temperature to the second stress-relief temperature to perform a heat-preservation treatment, so as to perform a second stress relief on the mesh precursor.

[0028] In some embodiments, the method further comprises the step of: during the heating stage of the mesh precursor, introducing an inert gas into the heating chamber to discharge the impurities out of the heating chamber through an exhaust pipe; and collecting a concentration indicator of the impurities by a gas monitoring device connected to the exhaust pipe.

[0029] In some embodiments, the method further comprises the step of: in the third heating stage, when the concentration indicator of the impurities is monitored to be lower than a preset concentration range, selecting a switching time according to a current time, wherein a difference

between the switching time and the current time is less than a preset difference range; at the switching time, increasing a current first heating rate to a second heating rate, and continuing to raise temperature to the target heating temperature.

[0030] Further, in some embodiments, S10 comprises: providing a carbon-rich photopolymerizable material as a raw material, and obtaining process parameters for preparing the mesh precursor from the photopolymerizable material, wherein the process parameters comprise one or more of: a line width of the mesh holes, a radius of the body, a size of the target to be formed, and a thickness of the mesh precursor; inputting the process parameters into a photopolymerization-based 3D printing system, and discretely stacking the photopolymerizable material through the 3D printing system to prepare the corresponding mesh precursor.

[0031] In some embodiments, the carbon-based polymer comprises: (1) a carbon-rich polymer, wherein the carbon-rich polymer comprises one or more of: furan resin, furfuryl alcohol resin, furfuryl ketone resin, phenolic resin, epoxy resin, polyurethane, polyimide, polyethylene glycol, acrylic resin, polylactic acid, polycaprolactone, polyethylene, polyether ether ketone, nylon, polycarbonate, polymethyl methacrylate, polyvinyl butyral, polyethylene terephthalate, polyacrylonitrile, polyvinylidene fluoride, polyvinylidene chloride, polystyrene, polytetrafluoroethylene, polybutadiene, polyphenylene ether, polyphenylene sulfide, polybutene-1, polybenzimidazole, polyaryletherketone, polyarylsulfone, polyethylene naphthalate, polyaniline, polyacetylene, poly(p-phenylene), polyphthalimide, poly(phenylene ethynylene), polylactide, polychloroprene, polycyanoacrylate, poly(naphthylene ethynylene), poly(p-xylylene), polymethylphenylsiloxane, liquid crystal polymer, polythiophene, polyvinylacetylene, polyoxadiazole, poly(bisphenol A), acrylonitrile-butadiene-styrene copolymer, polychlorotrifluoroethylene, epoxy resin-acrylate copolymer, polyquinone, poly(p-phenylene sulfone), polyphenylene, polybenzoxazole, polypiperidine, polyvinyl acetal, polybenzothiazole, and polyvinylpyrrolidone; or (2) a product obtained by further and/or modifying the carbon-rich polymer.

[0032] In some embodiments, the method for preparing the precursor comprises mold forming and/or 3D printing. In some embodiments, the 3D printing is performed by laser stereolithography, two-photon polymerization, digital light processing, liquid crystal display polymerization, continuous liquid interface production, fused deposition modeling, selective laser sintering, computed axial lithography, powder binder jetting, electric-field direct writing, inkjet direct writing, or static optical projection lithography. In some embodiments, a base of the microneedle or the microneedle-like structure is capable of having one or more of the following shapes: circular, rectangular, cross-shaped, asterisk-shaped, or a hollow structure. In some embodiments, the precursor has a substrate, and a plurality of microneedles or microneedle-like

structures are arranged on the substrate at intervals; or the precursor is a microneedle particle. In some embodiments, the substrate comprises a plurality of mesh holes arranged at intervals, the mesh holes intersect with each other to form a mesh arrangement, and the microneedle or the microneedle-like structure to be formed is provided at edges of the mesh holes.

[0033] In some embodiments, the substrate comprises: a body, wherein a hollow region is provided in the body; the plurality of mesh holes are arranged on the body at intervals, and the body is capable of having one or more of the following shapes: circular, annular, elliptical, or rounded rectangular. In some embodiments, a line width L1 of the mesh holes is less than or equal to 2 mm, and a radius L2 of the body of the precursor is less than or equal to 100 mm. The present invention also provides a glassy carbon microneedle, wherein the glassy carbon microneedle is prepared by the method according to any one of the embodiments of the present invention.

[0034] Beneficial Technical Effects: Glassy carbon materials are typically prepared using a full-range gradient heat-preservation high-temperature sintering process (for example, not only is repeated heat-preservation treatment required in a low temperature range to reduce the heating rate, but also the temperature often needs to be raised to around 1000°C for heat preservation). In contrast, the present invention provides a centralized heat-preservation treatment process that can complete the preparation of complex carbon microneedles (e.g., microneedle particles or microneedle patches) through only a limited number of low-temperature heat-preservation treatments. Moreover, in the centralized treatment process, the heat-preservation treatment is directly oriented toward technical outcomes. That is, the heat-preservation treatment is specifically aimed at stress relief or pyrolytic carbonization, so as to directly achieve the purposes of stress relief or pyrolytic carbonization. This reduces the influence of the heating rate on precursor deformation in subsequent heating stages, so that the subsequent heating stages (e.g., the third heating stage) can rapidly raise the temperature to the target heating temperature without relying on heat-preservation treatments, thereby simplifying the heating process.

BRIEF DESCRIPTION OF THE DRAWINGS

[0035] In order to more clearly illustrate the technical solutions in the embodiments of the present invention or the prior art, the accompanying drawings required for description of the embodiments or the prior art will be briefly introduced below. In all the drawings, similar elements or portions are generally denoted by similar reference numerals. In the drawings, elements or portions are not necessarily drawn to scale. Obviously, the drawings described below are some embodiments of the present invention, and for a person of ordinary skill in the art, other drawings may be obtained based on these drawings without creative efforts.

[0036] **[Fig. 1]:** is a schematic flowchart of a centralized heat-preservation method according

to an exemplary embodiment of the present invention;

[0037] **[Fig. 2a]:** a schematic diagram of temperature design of the centralized heat-preservation method according to an exemplary embodiment of the present invention;

[0038] **[Fig. 2b]:** a schematic diagram of temperature design of the centralized heat-preservation method according to another exemplary embodiment of the present invention;

[0039] **[Fig. 3]:** a schematic diagram of a thermogravimetric curve of a precursor according to an exemplary embodiment of the present invention;

[0040] **[Fig. 4]:** a schematic structural diagram of a mesh microneedle according to an exemplary embodiment of the present invention;

[0041] **[Fig. 5]:** a schematic diagram of a surface morphology of a mesh precursor after pyrolysis treatment by the centralized heat-preservation method according to an exemplary embodiment of the present invention;

[0042] **[Fig. 6]:** a schematic structural diagram of a mesh precursor according to an exemplary embodiment of the present invention;

[0043] **[Fig. 7]:** is a schematic diagram showing the influence of different heating temperatures on the electrical conductivity of mesh microneedles;

[0044] **[Fig. 8]:** a schematic diagram of a failed product;

[0045] **[Fig. 9]:** a schematic block diagram of a monitoring system according to an exemplary embodiment of the present invention;

[0046] **[Fig. 10]:** a schematic structural diagram of a microneedle according to an exemplary embodiment of the present invention;

[0047] **[Fig. 11]:** a first physical photograph of the microneedle shown in Fig. 10 after sintering;

[0048] **[Fig. 12]:** a second physical photograph of the microneedle shown in Fig. 10 after sintering;

[0049] **[Fig. 13]:** a schematic diagram of temperature design of a heat-preservation method applicable to the microneedle shown in Fig. 10;

[0050] **[Fig. 14]:** a schematic structural diagram of a roller microneedle precursor according

to an exemplary embodiment of the present invention;

[0051] [Fig. 15]: a side view of the precursor shown in Fig. 14;

[0052] Reference Numerals: 01 body, 011 microneedle, 012 mesh hole, 02 hollow region.

DETAILED DESCRIPTION

[0053] In order to make the objectives, technical solutions, and advantages of the embodiments of the present invention clearer, the technical solutions in the embodiments of the present invention will be described clearly and completely below with reference to the accompanying drawings in the embodiments of the present invention. Obviously, the described embodiments are some, but not all, of the embodiments of the present invention. Based on the embodiments of the present invention, all other embodiments obtained by a person of ordinary skill in the art without creative efforts shall fall within the protection scope of the present invention. Throughout this document, suffixes used to denote elements such as "module", "component", or "unit" are only used to facilitate the description of the present invention and have no specific meaning by themselves. Therefore, "module", "component", or "unit" may be used interchangeably. Throughout this document, terms such as "upper", "lower", "inner", "outer", "front", "rear", "one end", "the other end", etc., indicating orientation or positional relationships are based on the orientation or positional relationships shown in the accompanying drawings, and are only for the convenience of describing the present invention and simplifying the description. They do not indicate or imply that the device or element referred to must have a specific orientation, be constructed and operate in a specific orientation, and therefore cannot be construed as limiting the present invention. In addition, the terms "first", "second", etc., are used for descriptive purposes only and cannot be understood as indicating or implying relative importance.

[0054] Throughout this document, unless otherwise clearly specified and limited, the terms "installed", "provided with", "connected", etc., should be understood in a broad sense. For example, "connected" may be a fixed connection, a detachable connection, or an integral connection; it may be a mechanical connection, a direct connection, or an indirect connection through an intermediate medium; it may be a communication between the interiors of two elements. For a person of ordinary skill in the art, the specific meanings of the above terms in the present invention can be understood on a case-by-case basis. Throughout this document, "and/or" includes any and all combinations of one or more of the associated listed items. Throughout this document, "a plurality of" means two or more, i.e., includes two, three, four, five, etc. It should be noted that, throughout this document, the terms "comprising", "including", or any other variation thereof are intended to cover non-exclusive inclusion, such that a process, method,

article, or device that includes a series of elements includes not only those elements but also other elements not expressly listed, or also includes elements inherent to such process, method, article, or device. Without further limitation, an element defined by the phrase "comprising a ..." does not exclude the presence of additional identical elements in the process, method, article, or device that includes the element.

[0055] As used in this specification, the term "about" typically means $\pm 5\%$ of the stated value, more typically $\pm 4\%$ of the stated value, more typically $\pm 3\%$ of the stated value, more typically $\pm 2\%$ of the stated value, even more typically $\pm 1\%$ of the stated value, and even more typically $\pm 0.5\%$ of the stated value. In this specification, certain embodiments may be disclosed in a format that is within a certain range. It should be understood that such description of "being within a certain range" is only for convenience and brevity and should not be construed as an inflexible limitation on the disclosed range. Accordingly, the description of a range should be considered to have specifically disclosed all possible subranges as well as individual numerical values within that range. For example, the description of a range of 1 to 6 should be considered to have specifically disclosed subranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6, etc., as well as individual numbers within that range, such as 1, 2, 3, 4, 5, and 6. This rule applies regardless of the breadth of the range. Throughout this document, "data point" may refer to a piece of data corresponding to one or more temperature points.

[0056] Throughout this document, the term "carbon-based polymer" generally refers to a carbon-rich polymer. For example, it may be a photocurable polymer material such as polyurethane or epoxy resin, or a polymer such as acrylonitrile resin, phenolic resin, or polyimide. For example, the carbon-rich polymer in the present invention may include one or more of the following polymers: furan resin, furfuryl alcohol resin, furfuryl ketone resin, phenolic resin, epoxy resin, polyurethane, polyimide, polyethylene glycol, acrylic resin, polylactic acid, polycaprolactone, polyethylene, polyether ether ketone, nylon, polycarbonate, polymethyl methacrylate, polyvinyl butyral, polyethylene terephthalate, polyacrylonitrile, polyvinylidene fluoride, polyvinylidene chloride, polystyrene, polytetrafluoroethylene, polybutadiene, polyphenylene ether, polyphenylene sulfide, polybutene-1, polybenzimidazole, polyaryletherketone, polyarylsulfone, polyethylene naphthalate, polyaniline, polyacetylene, poly(p-phenylene), polyphthalimide, poly(phenylene ethynylene), polylactide, polychloroprene, polycyanoacrylate, poly(naphthylene ethynylene), poly(p-xylylene), polymethylphenylsiloxane, liquid crystal polymer, polythiophene, polyvinylacetylene, polyoxadiazole, poly(bisphenol A), acrylonitrile-butadiene-styrene copolymer, polychlorotrifluoroethylene, epoxy resin-acrylate copolymer, polyquinone, poly(p-phenylene sulfone), polyphenylene, polybenzoxazole, polypiperidine, polyvinyl acetal, polybenzothiazole, and polyvinylpyrrolidone. Alternatively, the carbon-rich polymer may also refer to a product obtained by further modifying one or more of the above polymers. For example, the modification

method may be one or more of: blending modification, filling modification, reinforcing modification, physical/chemical crosslinking modification, graft copolymerization modification, nanocomposite modification, enzyme-catalyzed modification, or chemical modification. The precursor, or the glassy carbon microneedle prepared from the precursor, may also be modified, and the modification methods used may include one or more of: chemical modification, physical vapor deposition, laser surface modification, chemical vapor deposition, spraying, sputtering, etching, surface roughening treatment, electrochemical treatment, or plasma treatment. Such modification methods can also be used to modify the glassy carbon microneedle.

[0057] Throughout this document, the term "concentration indicator" refers to an indicator that can be used to characterize the amount/concentration of a substance (e.g., impurities). For example, in some embodiments, the concentration indicator may be characterized by the flow rate of impurities per unit time; alternatively, in other embodiments, the concentration indicator may be characterized by the amount of impurities discharged per unit time; or in still other embodiments, the concentration indicator may be characterized by the concentration of impurities per unit volume of gas.

[0058] Throughout this document, the term "mesh material" is also referred to as a "mesh precursor", and refers to a material having a plurality of mesh holes (or openings) distributed on a material plane, with targets to be formed (e.g., microneedles) provided at edges of the mesh holes. Such mesh holes can be arranged on the material plane to form a regular mesh distribution. The preparation method that enables the formation of mesh holes on the precursor is referred to as a mesh preparation method, and in the present document, the mesh preparation method is preferably a 3D printing method.

[0059] Glassy carbon materials are typically prepared using a full-range gradient heat-preservation high-temperature sintering process (for example, the temperature often needs to be raised to around 1000°C for heat preservation). Throughout this document, the term "centralized heat-preservation method", also referred to as a low-temperature gradient heat-preservation method, refers to a heat-preservation treatment that is relatively concentrated on key processes of the microneedle structure (e.g., the mesh precursor), such as stress relief and pyrolytic carbonization. Moreover, in the centralized treatment process, the heat-preservation treatment is directly oriented toward technical outcomes. That is, the heat-preservation treatment is specifically aimed at stress relief or pyrolytic carbonization, so as to directly achieve the purposes of stress relief or pyrolytic carbonization. This reduces the influence of the heating rate on precursor deformation in subsequent heating stages, so that the subsequent heating stages (e.g., the third heating stage) can rapidly raise the temperature to the target heating temperature without relying on heat-preservation treatments, thereby simplifying the heating process.

[0060] In other words, unlike the procedures that set heat-preservation treatments dispersedly in both low and high temperature ranges, the centralized heat-preservation method for microneedle structures provided by the present invention is directly aimed at stress relief or pyrolytic carbonization, and achieves the processing requirements of the low-temperature range through a limited number (even as few as one, two, or three heat-preservation treatments) of heat-preservation treatments. Moreover, this centralized heat-preservation treatment design in the low-temperature range unexpectedly allows the preparation of glassy carbon to break away from dependence on high-temperature heat-preservation treatments. For example, when preparing a simpler microneedle particle structure, the microneedle particles can be prepared with a limited number (e.g., one low-temperature heat-preservation treatment) of low-temperature heat-preservation treatments, thereby reducing dependence on high-temperature heat-preservation treatments, as shown in Fig. 11-13, where even only one low-temperature heat-preservation treatment still yields microneedles with good morphology.

[0061] It should be understood that the centralized heat-preservation method in the present invention has the following advantages: 1) it can reduce dependence on high-temperature heat-preservation treatments (for example, it can lower the temperature of high-temperature heat-preservation treatment, or shorten the duration of high-temperature heat-preservation treatment), but it does not limit the user from performing high-temperature heat-preservation treatment. For example, depending on the morphology of different microneedle products, such as microneedle particles, the user can still freely choose whether to add a high-temperature heat-preservation treatment process. 2) It can reduce the necessary number of low-temperature heat-preservation treatments, but it should be understood that depending on the process requirements of different microneedle products (e.g., strength requirements), the user can still freely choose to use more times, such as two or three low-temperature heat-preservation treatments, to complete the preparation of the microneedle product.

[0062] Moreover, experimental verification has shown that the glassy carbon products (e.g., microneedles or microneedle patches) obtained by the centralized heat-preservation method still achieve good quality (i.e., defects such as foaming, cracking, and deformation are effectively controlled).

[0063] Throughout this document, the term "heat-preservation treatment" refers to placing an object (e.g., a precursor) in an environment with a set heat-preservation temperature and maintaining that heat-preservation temperature for at least a period of time. For example, the heat-preservation time may be at least about 5 min, at least about 10 min, at least about 30 min, at least about 60 min, or at least about 90 min. "Maintaining" means that the degree of temperature fluctuation is less than a set proportional threshold, for example, the proportional

threshold may be set to about 1%, about 2%, about 3%, about 4%, about 5%, etc. For example, the degree of fluctuation may be characterized by a fluctuation ratio (fluctuation ratio = (actual temperature - set heat-preservation temperature)/set heat-preservation temperature). Of course, it should be understood that the actual heat-preservation time and the set proportional threshold can be adaptively adjusted according to the type of material and the morphology of the precursor.

[0064] Throughout this document, as shown in Fig. 2b, the term "rapid temperature increase process" refers to a continuous and rapid temperature increase method (for example, without the need to perform heat-preservation treatments again in multiple high-temperature ranges such as 600°C and 1000°C) that can be used after the pyrolytic carbonization heat-preservation treatment (i.e., the third heating stage) to complete the final transformation of material properties and prepare high-purity glassy carbon. For example, the rapid temperature increase rate may be greater than or equal to about 0.5°C/min, and may even reach about 2°C/min after a speed change.

[0065] Microneedles (MN) are a novel physical permeation-enhancing technology. For example, they may be composed of a plurality of micron-scale fine needle tips connected to a base in an array, or as another example, as shown in Fig. 10, they may be independent microneedle particles. Specifically, the "microneedles" on a microneedle patch typically have a tapered shape, with the tip of the taper being the needle tip, and are capable of penetrating the skin to a certain extent (e.g., penetrating the stratum corneum). The term "microneedle-like structure" refers to other similar morphological designs that also have a needle tip capable of penetrating the skin, for example, the base of the microneedle-like structure may be circular, rectangular, cross-shaped, asterisk-shaped, or a hollow structure, with the needle tip formed at its top. The microneedles may be nanoscale microneedles or microscale microneedles.

[0066] Throughout this document, a glassy carbon microneedle patch is provided, comprising: a body, and a hollow region optionally provided in the body; wherein the body comprises: a mesh substrate having a plurality of mesh holes arranged on the mesh substrate at intervals, and a plurality of microneedles or microneedle-like structures provided at edges of the mesh holes; wherein the glassy carbon microneedle patch is prepared by subjecting a mesh precursor to a centralized heat-preservation pyrolysis treatment, and the mesh precursor is prepared from a carbon-based polymer.

[0067] Embodiment 1

[0068] Referring to Fig. 1-7, to reduce defects such as foaming caused by the sintering process of glassy carbon products (e.g., microneedle structures, such as microneedle particles shown in Fig. 10, or microneedle patches shown in Fig. 6), the present invention

provides a method for preparing glassy carbon, comprising:

[0069] preparing a precursor using a carbon-based polymer raw material, wherein the precursor has a microneedle or microneedle-like structure;

[0070] placing the precursor in a heating chamber and starting a centralized heat-preservation method, wherein starting the centralized heat-preservation method comprises: in a first heating stage, selecting a stress-relief temperature to perform a heat-preservation treatment on the precursor, so as to relieve stress in the precursor; wherein the stress-relief temperature is selected according to a first selection rule; and the first selection rule is: selecting the stress-relief temperature from a weight-loss-rate fluctuation temperature; and the weight-loss-rate fluctuation temperature corresponds to a temperature value of a data point, in a derivative thermogravimetry curve, having a greatest curvature change in an interval less than a pyrolytic carbonization temperature;

[0071] raising temperature to enter a second heating stage, and in the second heating stage, selecting the pyrolytic carbonization temperature to perform another heat-preservation treatment on the precursor, so as to cause the precursor to undergo pyrolytic carbonization, wherein the microneedle or the microneedle-like structure shrinks during the pyrolytic carbonization; wherein the pyrolytic carbonization temperature is selected according to a second selection rule; the second selection rule is: selecting the pyrolytic carbonization temperature from a weight-loss fluctuation temperature; wherein the weight-loss fluctuation temperature corresponds to a temperature value of a curve segment, in a thermogravimetric analysis curve, having a greatest curvature change in an interval in which a slope gradually decreases;

[0072] in a subsequent third heating stage, continuously raising temperature from the pyrolytic carbonization temperature to a target heating temperature, so that the precursor prepared from the carbon-based polymer is finally converted into the glassy carbon microneedle.

[0073] The following is an exemplary description of the preparation method using a mesh precursor: the glassy carbon is prepared by a centralized heat-preservation method based on a mesh precursor, and accordingly, the method comprises the steps of:

[0074] S10: preparing a mesh precursor using a carbon-based polymer raw material, wherein the mesh precursor comprises a plurality of mesh holes arranged at intervals, the mesh holes forming a mesh arrangement, wherein a plurality of targets to be formed are provided at edges of the mesh holes.

[0075] For example, in some embodiments, the targets to be formed are provided at intersections of the mesh holes.

[0076] As another example, in some embodiments, the targets to be formed may also be arranged at intervals along the edges of the mesh holes.

[0077] S20: placing the mesh precursor in a heating chamber and starting the centralized heat-preservation method, wherein S20 comprises:

[0078] S21: in a first heating stage, selecting a stress-relief temperature to perform a heat-preservation treatment on the mesh precursor, so as to relieve stress in the mesh precursor; wherein the stress-relief temperature is selected according to a first selection rule;

[0079] S22: raising temperature to enter a second heating stage, and in the second heating stage, selecting the pyrolytic carbonization temperature to perform another heat-preservation treatment on the mesh precursor, so as to cause the mesh precursor to undergo pyrolytic carbonization, wherein the targets to be formed on the mesh precursor and the mesh holes undergo shrinkage deformation during the pyrolytic carbonization, and impurities generated during the process can be uniformly discharged outward by utilizing the mesh arrangement; the temperature of the second heating stage is higher than the temperature of the first heating stage; wherein the pyrolytic carbonization temperature is selected according to a second selection rule;

[0080] S30: in a subsequent third heating stage, continuously raising temperature from the pyrolytic carbonization temperature to a target heating temperature; finally converting the carbon polymer into glassy carbon.

[0081] In some embodiments, the first selection rule is: selecting the stress-relief temperature from a weight-loss-rate fluctuation temperature (equivalent to a recommended temperature); wherein the weight-loss-rate fluctuation temperature corresponds to one or more temperature values of at least one curve segment (or data point) having a greatest curvature change in a derivative thermogravimetry curve (e.g., DTG curve, as shown in the second curve in Fig. 3); and the weight-loss-rate fluctuation temperature is typically less than the pyrolytic carbonization temperature. Herein, the derivative thermogravimetry curve is a curve representing the rate of weight change as a function of temperature.

[0082] For example, using the DTG curve as an illustration, an exemplary selection rule for the stress-relief temperature is described as follows:

[0083] A DTG curve of the precursor is obtained, wherein the DTG curve is considered to be composed of a plurality of curve segments. Then, the curvature change value of each curve segment before the pyrolytic carbonization temperature (e.g., in this example, before about 350°C) can be calculated (for example, when a curve segment involves a plurality of data points, the average of the curvature change values of the data points in that curve segment can be

calculated), and then the temperature value corresponding to the curve segment having the greatest curvature change is selected as the weight-loss-rate fluctuation temperature.

[0084] Alternatively, in some other embodiments, a screening threshold may be preset by the user, a limited number (e.g., 1, 2, etc.) of curve segments may be selected, and a limited number of selectable weight-loss-rate fluctuation temperatures may be correspondingly provided, wherein the curvature change values of the selected curve segments fall within the screening threshold.

[0085] In some embodiments, when multiple weight-loss-rate fluctuation temperatures are present, two heat-preservation treatments may be preferably used for stress relief. For example, if multiple weight-loss-rate fluctuation temperatures exist, two (or more) stress-relief temperatures may be selected at intervals from the multiple weight-loss-rate fluctuation temperatures, so as to avoid frequently performing heat-preservation treatments within a single temperature range.

[0086] The second selection rule for selecting the pyrolytic carbonization temperature is: selecting the pyrolytic carbonization temperature from a weight-loss fluctuation temperature (equivalent to a recommended temperature); wherein the weight-loss fluctuation temperature corresponds to one or more temperature values of a curve segment having a greatest curvature change in a thermogravimetric analysis curve (e.g., TGA curve) in an interval in which a slope gradually decreases. The thermogravimetric analysis curve is a curve representing the relationship of weight change as a function of temperature, and is also referred to as a thermogravimetric curve.

[0087] For example, taking the TGA curve (as shown in the first curve) as an example, an exemplary illustration of the selection of the pyrolytic carbonization temperature is described as follows:

[0088] The TGA curve can also be considered to be composed of several curve segments. In an interval in which the slope gradually decreases (for example, in an interval before about 425°C), the curve segment having the greatest slope change value is selected, and the temperature corresponding thereto is the weight-loss fluctuation temperature, whereby the selected pyrolytic carbonization temperature is about 350°C.

[0089] As another example, in some embodiments, the temperature corresponding to a data point having the greatest curvature change in the thermogravimetric analysis curve (i.e., the data point where the slope difference between the current data point and the previous data point is the greatest, as compared to the slope difference between any two adjacent data points in the curve) may also be selected as the weight-loss fluctuation temperature.

[0090] In this embodiment, only one heat-preservation treatment for stress relief and one

heat-preservation treatment for pyrolytic carbonization may be used in combination, so that the precursor can undergo relatively concentrated deformation at a relatively low pyrolytic carbonization temperature (for example, in Verification Example 1, the heat-preservation treatment is performed only within 350°C), thereby reducing the influence of the heating rate on precursor deformation in the third heating stage.

[0091] Of course, in other embodiments, in order to achieve more uniform stress relief and avoid improper deformation during stress relief, when there is a first quantity of weight-loss-rate fluctuation temperatures, and the first quantity is greater than or equal to 2, S21 comprises the steps of:

[0092] selecting a second quantity of weight-loss-rate fluctuation temperatures from the first quantity of weight-loss-rate fluctuation temperatures at intervals, and correspondingly obtaining a second quantity of stress-relief temperatures (for example, providing one stress-relief temperature corresponding to each weight-loss-rate fluctuation temperature), wherein the second quantity is less than or equal to the first quantity, and the stress-relief temperatures at least comprise: a first stress-relief temperature and a second stress-relief temperature; in the first heating stage, performing a heat-preservation treatment using the first stress-relief temperature, so as to perform a first stress relief on the mesh precursor; continuously raising temperature from the first stress-relief temperature to the second stress-relief temperature and performing a heat-preservation treatment, so as to perform a second stress relief on the mesh precursor.

[0093] Thus, in this embodiment, for situations where stress relief is difficult, multiple heat-preservation treatments may also be used for stress relief.

[0094] Moreover, it should be understood that the stress-relief temperature (or the pyrolytic carbonization temperature) of the material is not a single temperature value. As the material type changes or the external processing conditions vary, a person skilled in the art can flexibly adjust the actual stress-relief temperature or the pyrolytic carbonization temperature according to the actual situation based on the weight-loss-rate fluctuation temperature or the weight-loss fluctuation temperature.

[0095] For example, in some embodiments, the stress-relief temperature may deviate from the given weight-loss-rate fluctuation temperature (e.g., deviations of $\pm 1^{\circ}\text{C}$, $\pm 5^{\circ}\text{C}$, $\pm 10^{\circ}\text{C}$, $\pm 15^{\circ}\text{C}$, etc.).

[0096] Of course, in practical applications, the weight-loss-rate fluctuation temperature or the weight-loss fluctuation temperature may also be obtained from existing thermogravimetric analysis data, as long as the purposes of stress relief and pyrolytic carbonization are achieved.

[0097] For example, in some embodiments, after heating to the target heating temperature, no further heat-preservation treatment may be performed, so that the microneedles can be naturally cooled in the heating chamber.

[0098] Alternatively, in other embodiments, after heating to the target temperature, the user may also selectively perform a heat-preservation treatment according to the actual product morphology or the strength requirements of the product, and the present invention does not impose limitations in this regard.

[0099] In some embodiments, the precursor has a substrate, and a plurality of microneedles or microneedle-like structures are arranged on the substrate at intervals. For example, when the precursor is a mesh precursor, it comprises a plurality of mesh holes arranged at intervals on the substrate (which may also be referred to as a body), the mesh holes intersect with each other to form a mesh arrangement, and the microneedle or the microneedle-like structure to be formed is provided at edges of the mesh holes. Alternatively, the precursor may also be a microneedle particle.

[0100] In some embodiments, S30 comprises the steps of: S31 obtaining conversion information for switching the heating rate, wherein the conversion information comprises: a conversion temperature C4, and/or a conversion time; S32 when heating from the pyrolytic carbonization temperature C2 to the conversion temperature C4 at a first set sub-rate VIII-1, or when the heating time reaches the conversion time, switching the heating rate from the first set sub-rate VIII-1 to a second set sub-rate VIII-2; S33 heating to the target heating temperature C5 at the second set sub-rate VIII-2; wherein the second set sub-rate VIII-2 is greater than the first set sub-rate VIII-1.

[0101] In some embodiments, the first set sub-rate VIII-1 is set in a range of approximately 0.1-1°C/min, and the second set sub-rate VIII-2 is set in a range of approximately 1-3°C/min.

[0102] In order to improve the quality of glassy carbon (e.g., reduce defect area and increase strength), the present invention provides a centralized heat-preservation method based on a mesh precursor. Unlike the existing full-range gradient heat-preservation processes, the present invention designs the following preparation stages for glassy carbon preparation: (1) a mesh preparation stage; (2) a technical-outcome-oriented stage, directly performing centralized stress relief and pyrolytic carbonization in a low temperature range; and (3) a stage directly using a continuous temperature increase method to raise the temperature to the target heating temperature.

[0103] In the present invention, the cooperation of stages (1)-(3) can effectively improve the uniformity of the stress relief process of the precursor during the heating stage (avoiding cracks or unfavorable deformations caused by stress), while also alleviating possible surface damage caused by major deformation processes such as pyrolytic carbonization and continuous temperature increase.

[0104] Moreover, the present invention, through the cooperation of the mesh design and the centralized heat-preservation method, reduces to a certain extent the deformation effect of the heating mode (e.g., heating rate) on the precursor during the high temperature stage, thereby eliminating dependence on high-temperature heat-preservation treatments and reducing process costs. Experimental verification has shown that, for example, as shown in Fig. 5, defects such as foaming, deformation, or breakage on the surface of the microneedle patch are very few.

[0105] Furthermore, to facilitate industrial application of the centralized heat-preservation method, the temperature of each heat-preservation treatment for low-temperature heat preservation of the mesh precursor can be directly obtained from relevant thermogravimetric analysis data, so as to assist users in quickly exploring the preparation conditions for low-temperature gradient heat preservation. It should be understood that, in order to improve the accuracy and reliability of temperature selection, the head portion of the pyrolysis curve (e.g., TGA or DTG) is usually discarded (for example, depending on the type of material or the difference in pyrolysis analysis instruments, the curve segment with a temperature below about 50°C may be discarded), and then the effective interval of the curve is analyzed.

[0106] In some embodiments, the set curve segment may be a length of one data point or a plurality of data points.

[0107] The following provides Verification Example 1 to illustrate exemplary preparation steps of the glassy carbon microneedle patch of the present invention:

[0108] Using a photosensitive resin as a raw material, a mesh precursor was prepared and printed by 3D printing technology based on the principle of photopolymerization. The line width L1 of the mesh holes of the mesh precursor (i.e., the edge width of the mesh holes, or the width of the edge sidewall of the mesh holes) was 0.6 mm, the size of the mesh holes (corresponding to the line spacing) was 1 mm, and the radius L2 of the body (i.e., the radius dimension of the edge of the precursor) was 10 mm.

[0109] The mesh precursor was subjected to a heat treatment using a heating chamber (e.g., a high-temperature furnace) to convert the photosensitive resin into glassy carbon. The heat treatment mainly comprised the following three stages:

[0110] First heating stage: Step 1) heating to a first stress-relief temperature C1 at a first set speed V I (1.5°C/min), and performing a heat-preservation treatment at the first stress-relief temperature C1 for a first duration T1 (30 min), wherein the first stress-relief temperature obtained by the first selection rule was 150°C;

[0111] Second heating stage: Step 2) heating to a pyrolytic carbonization temperature C2 at a second set speed V II (1°C/min), and performing a heat-preservation treatment at the pyrolytic carbonization temperature C2 for a second duration T2 (120 min), wherein the pyrolytic carbonization temperature obtained by the second selection rule was 350°C; during this process, the mesh precursor was capable of undergoing relatively uniform shrinkage deformation;

[0112] Third heating stage: Step 3) after the two heat-preservation treatments in the low temperature range were completed, entering the third heating stage of continuous temperature increase; specifically, directly heating to a target heating temperature C5 (1000°C) at a third set speed VIII (0.5°C/min), thereby converting the mesh precursor from the carbon polymer into a glassy carbon material.

[0113] In this Verification Example 1, a mesh design was adopted for the precursor, and only two key heat-preservation treatments were performed in the low temperature range to specifically achieve the purposes of stress relief and pyrolytic carbonization, omitting high-temperature heat-preservation treatment. Moreover, the defect area (or defect generation rate) of the prepared mesh microneedles was effectively controlled within 1% (product quality being excellent). That is, the surface of the mesh microneedles had good continuity, with no defects such as foaming, cracking, or deformation, and thus also had high strength, making them suitable for practical industrial application requirements.

[0114] It should be noted that in this experiment, the defect area (i.e., the percentage of defect area to the total surface area of the mesh microneedles) was used to evaluate the product quality of the mesh microneedles. When the defect area was between 0% and 5%, the product quality was rated as excellent; when the defect area was between 5% and 15%, the product quality was rated as good; and when the defect area exceeded 15%, the product quality was rated as poor.

[0115] As another example, in some embodiments, since the present invention reduces the dependence of the third heating stage on the heating rate, a variable heating rate treatment can also be performed in the third heating stage.

[0116] The recommended speed change point (equivalent to a recommended temperature) for switching the heating rate may be the temperature corresponding to a data point on the thermogravimetric analysis curve where the slope is zero or approximately zero (e.g., within about

±0.001) during the process of gradually increasing slope, as shown in Fig. 3, where the obtained recommended speed change point is about 600°C. Moreover, the actually selected speed change point is preferably not lower than the recommended speed change point (or generally only lower than the recommended speed change point by within 1°C, within 5°C, within 10°C, etc.).

[0117] The effect of variable heating rate was verified by Verification Example 2 and Comparative Example 1:

[0118] In Verification Example 2, the same mesh precursor as in Verification Example 1 was selected for the centralized heat-preservation treatment, which comprised:

[0119] First heating stage: heating to a first stress-relief temperature C1 (150°C) at a first set speed V I (1.5°C/min) and performing a heat-preservation treatment at the first stress-relief temperature for 30 min; then heating to a second stress-relief temperature C3 (250°C) at a fourth set speed VIV (1°C/min) and performing a heat-preservation treatment at the second stress-relief temperature for 60 min;

[0120] Second heating stage: heating from 250°C to 350°C at a heating rate of 1°C/min, and performing a heat-preservation treatment for 120 min;

[0121] Third heating stage: heating from 350°C at a rate of 0.5°C/min, and then at 600°C, further heating to 1000°C at a rate of 2°C/min.

[0122] The surface morphology of the product prepared in Verification Example 2 can also be seen in Fig. 5. It can be seen that the mesh microneedles prepared by the present invention still have a good surface morphology even from a microscopic perspective.

[0123] Comparative Example 1

[0124] The differences in preparation process between Comparative Example 1 and Verification Example 2 are shown in Table 1:

[0125] Table 1

Verification Example	First heating rate in the third heating stage (°C/min)	Temperature change point (°C)	Second heating rate in the third heating stage (°C/min)	Defect area
Verification Example 2	0.5	600	2.0	Excellent

Comparative Example 1	0.5	450	2.0	Poor
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[0126] Further, the present invention also provides Verification Example 3 to demonstrate that the temperature selection method based on the pyrolytic carbonization can also meet the preparation requirements when applied to relatively simple microneedle structures (e.g., microneedle particles). For example, a precursor of microneedle particles was prepared using polyurethane acrylate as a raw material, and was heated using the simplified centralized heat-preservation method shown in Fig. 13. Specifically, the first heat-preservation temperature was about 350°C (which is the pyrolytic carbonization temperature) with a heat-preservation duration of about 60 min, and the second heat-preservation temperature was about 800°C with a heat-preservation duration of about 30 min.

[0127] The actual morphology of the obtained product is shown in Fig. 11 and Fig. 12. Apparently, it can be demonstrated that the centralized heat-preservation method reduces the dependence on complex gradient heat preservation, i.e., defect formation can also be avoided by a simpler heat-preservation treatment.

[0128] In some embodiments, the method further comprises the steps of:

[0129] S200: when the glassy carbon preparation enters the centralized heat-preservation method stage (preferably the second heating stage or the third heating stage), monitoring a concentration indicator of impurities discharged through an exhaust pipe of the heating chamber; wherein the impurities comprise a first type of impurities, and the first type of impurities comprise one or more of: carbon monoxide, carbon dioxide, nitric oxide, nitrogen dioxide, and nitrogen;
S201: automatically adjusting the centralized heat-preservation method according to the concentration indicator and a current state of the centralized heat-preservation method; wherein the concentration indicator comprises a first concentration indicator for characterizing a concentration of the first type of impurities; accordingly, S201 comprises the steps of:

[0130] S11: when the centralized heat-preservation method reaches the pyrolytic carbonization temperature for a first set time but has not yet reached the second duration T2, and the first concentration indicator falls within a first concentration threshold range X1, sending a first time-reduction signal to a gradient control module (or control unit) of the heating chamber, wherein the gradient control unit is capable of reducing the second duration T2 in response to the first time-reduction signal;

[0131] S12: when the centralized heat-preservation method has reached or exceeded the second duration T2 after reaching the pyrolytic carbonization temperature, and the first

concentration indicator falls within a corresponding second concentration threshold range X2, sending a first time-extension signal to the control unit, wherein the control unit is capable of extending the second duration T2 in response to the first time-extension signal.

[0132] As a preferred embodiment, in the present invention, the concentration of nitrogen (or a nitrogen-containing gas) is selected as the first concentration indicator.

[0133] In some embodiments, the second type of impurities comprises tar.

[0134] During the centralized heat-preservation method, the second type of impurities discharged from the heating chamber may also be monitored to obtain a second concentration indicator of the second type of impurities, and monitoring and parameter adjustment may be performed based on the second concentration indicator, the first concentration indicator, and the current process state. It should be understood that, in addition to being directly obtained from the thermogravimetric analysis results of the mesh precursor (as shown in FIG. 3), the temperature for the heat-preservation treatment may also be an empirical value collected by an engineer after process debugging.

[0135] In this embodiment, limited factors such as nitrogen and the second type of impurities are preferably used for state monitoring and automatic adjustment of the centralized heat-preservation method. This automatic adjustment process based on limited factors can also reduce, to a certain extent, the user's requirement for high precision in setting process parameters at the initial stage. For example, at the beginning of preparation, only a rough temperature for the heat-preservation treatment may be selected based on the pyrolysis data (or preliminarily selected based on the engineer's experience), and then the automatic adjustment process can relatively precisely adjust the heat-preservation temperature according to the actual processing state, thereby assisting the engineer in quickly exploring the preparation conditions and reducing the process application cost to a certain extent.

[0136] In some embodiments, the method further comprises the step of: during the heating stage of the mesh precursor, introducing an inert gas into the heating chamber to discharge the impurities out of the heating chamber through the exhaust pipe, wherein the introduction rate of the inert gas is about 10-60 cm³/min; and collecting a concentration indicator of the impurities by a gas monitoring device connected to the exhaust pipe.

[0137] In order to reduce the influence of rapid deformation during stress relief and pyrolytic carbonization on the mesh precursor during the centralized heat-preservation method, the mesh precursor has a symmetrical design. For example, in some embodiments, the mesh precursor comprises: a body, and a hollow region provided in the middle of the body, wherein the body is

uniformly arranged around the edge of the hollow region. The uniformly arranged mesh holes cooperate with the hollow region provided in the middle, thereby forming an impurity discharge space on the mesh precursor that facilitates uniform discharge of impurities.

[0138] For example, in some embodiments, the edge of the body may have one or more of the following shapes: circular, elliptical, or rounded rectangular. For example, in some embodiments, the base of the target to be formed may have one or more of the following shapes: circular, square, cross-shaped, asterisk-shaped, or a hollow structure (equivalent to a hollow structure).

[0139] In some embodiments, the method further comprises the steps of: providing a carbon-rich photopolymerizable material as a raw material, and obtaining process parameters for preparing the mesh precursor from the photopolymerizable material, wherein the process parameters comprise one or more of: a size of the mesh holes, a size of the target to be formed, and a thickness of the mesh precursor; inputting the process parameters into a photopolymerization-based 3D printing system, and discretely stacking the photopolymerizable material through the 3D printing system to prepare the corresponding mesh precursor.

[0140] For example, the mesh precursor can be prepared using 3D printing technology based on the principle of photopolymerization and photocuring molding technology based on a micro-template process. Among them, photopolymerization-based 3D printing technology for preparing microneedles includes one or more of: laser stereolithography (SLA), two-photon polymerization (TPP), digital light processing (DLP), liquid crystal display polymerization (LCD), continuous liquid interface production (CLIP), and static optical projection lithography (SOPL). Such technologies are based on digital models and produce three-dimensional entities by controlling a light source to discretely stack materials.

[0141] As another example, a polymer microneedle precursor may also be prepared using photocuring molding technology based on a micro-template process (for example, photocuring molding technology can be used to prepare microneedles with different bases as shown in FIG. 10, such as cross-shaped bases, or pentagram-shaped or polygonal star-shaped bases). A mold is pre-manufactured by etching, 3D printing, or the like, and then the microneedle structure is obtained by filling with a photopolymerizable material, exposure curing, and demolding. The microneedle products prepared by the present application using the 3D printing process, precursor optimization design, and centralized heat-preservation method have good surface continuity (almost no obvious defects, uniform mechanical properties), and improved strength and electrical conductivity, and the reliability and service life in practical applications are also enhanced.

[0142] In this embodiment, a 3D printing process is introduced for precursor preparation to facilitate customized production of microneedle products. Moreover, experimental verification has shown that the mesh design adopted in the present application, in cooperation with the low-temperature gradient heat-preservation method (i.e., the centralized heat-preservation method), can effectively alleviate or reduce defect problems that may occur during the sintering process of the precursor obtained by 3D printing. Of course, in other embodiments, a molding method may also be used to manufacture the microneedle precursor.

[0143] Further, in order to improve the synergy between the mesh design and the low-temperature gradient heat-preservation method, when the mesh precursor adopts a circular or rounded design, and the edge width L1 of the mesh holes of the precursor is less than or equal to about 2 mm, and the radius L2 of the body is less than or equal to about 100 mm, the mesh precursor still maintains a good overall morphology after being treated by the low-temperature gradient heat-preservation method, with no obvious defects. The verification results are shown in Table 2.

[0144] Table 2

Preparation Example	Shape of precursor	Line width L1 (mm)	Radius L2 (mm)	Defect area of microneedles (or defect generation rate)
1	Circular	0.1	1	Excellent
2	Annular	0.5	5	Excellent
3	Elliptical	0.8	10	Excellent
4	Rounded rectangular	1	20	Excellent
5	Circular	1.5	60	Excellent
6	Annular	2	100	Good
7	Circular	0.5	110	Poor
8	Annular	2.5	5	Poor
9	Pentagram-shaped	0.5	5	Poor

[0145] Note: Other preparation processes of the mesh precursor in Table 2 are the same as those in Verification Example 1; The experimental data in Table 2 further demonstrate that the mesh process design provided by the embodiments of the present invention can achieve uniform stress relief and proportional shrinkage deformation (e.g., the shrinkage rate in each local region is about 25%), and the defect area of the final product is significantly reduced.

[0146] In contrast, as shown in FIG. 8, using a preparation process similar to that of Verification Example 1, a circular design with a radius of 8 mm and a rectangular design with a length of 8 mm (both without a mesh design) were subjected to the low-temperature gradient

process, and the resulting microneedles exhibited severe deformation and could not meet the requirements for practical application.

[0147] Therefore, based on the mesh process design proposed in this embodiment, when applied to different process applications, the user can flexibly adjust the product shape and size in terms of morphological design, mesh distribution, etc., according to actual product requirements (e.g., when preparing medical devices, sensors, and other components of different sizes and properties), so as to ensure the reliability of the final molded product. For example, in some embodiments, when microneedle particles are to be prepared, the base of the microneedle may be configured as a cross-shaped base, or a pentagram-shaped or polygonal star-shaped base, or other adaptive adjustments may be made to the shape according to application requirements, so as to obtain independent microneedle particle products.

[0148] Correspondingly, the present invention provides a use of the glassy carbon microneedle in preparing a signal transmission device, wherein the glassy carbon microneedle is used to connect to or form the signal transmission device, and the signal transmission device is used to transmit one or more of the following signals: an electrical signal, a thermal signal. For example, in some embodiments, the glassy carbon microneedle (or the signal transmission device formed thereby) can be used in medical fields such as electrically mediated stimulation therapy, photothermal therapy, and gene transfection. For instance, it can transmit electrical signals during electrically mediated stimulation therapy. As another example, it can transmit thermal signals (i.e., heat) during photothermal therapy, such that when therapeutic light is irradiated onto the microneedle, the microneedle converts the light into heat.

[0149] In some embodiments, one end of the signal transmission device (also referred to as a signal sensing device) is connected to biological tissue, and the other end is connected to a biosensor and/or a brain-computer interface.

[0150] In the present invention, the adoption of the mesh design facilitates the formation of a uniform stress distribution in the structure of the precursor and the formation of a space for uniform discharge of impurities. Meanwhile, the corresponding adoption of the centralized heat-preservation treatment, in cooperation with the uniform stress distribution and the impurity discharge space, can sequentially and stepwise achieve core processes such as uniform and stable stress relief and pyrolytic carbonization.

[0151] Moreover, in the present invention, the spatial design for uniform impurity discharge and the centralized heat-preservation treatment are used in cooperation to concentrate the main stages of pyrolytic carbonization (first, concentration in terms of time and temperature range, and second, relatively concentrated exhaust from the perspective of gas discharge), so that the user

can more easily achieve centralized monitoring of the pyrolytic carbonization process during production.

[0152] Of course, in other embodiments, depending on different application scenarios or different process standards, the user may also adaptively configure the morphology of the precursor. For example, the precursor may be configured in the form of a microneedle patch, i.e., a plurality of microneedles (or microneedle-like structures) arranged at intervals on a substrate. In some embodiments, the plurality of microneedle structures may be radially arranged around a center point. In some embodiments, one or more post-treatments may also be performed on the microneedles to optimize their application performance. For example, the post-treatment method may be one or more of: chemical group modification, chemical group etching. For instance, the modification method may be: chemical modification, physical vapor deposition, laser surface modification, chemical vapor deposition, spraying, sputtering, etching, surface roughening treatment, electrochemical treatment, or plasma treatment.

[0153] Embodiment 2

[0154] In the centralized heat-preservation method of the present invention, firstly, centralized gradient heat preservation is selected in a low temperature range, and secondly, rapid temperature increase is performed in a subsequent high temperature stage. Moreover, in order to accelerate the process in the high temperature stage, the present invention further provides a preparation method that introduces a variable heating rate adjustment process, and the preparation method may comprise the same or similar steps as those in Embodiment 1.

[0155] In some embodiments, the preparation method further comprises the steps of:

[0156] monitoring and collecting a concentration indicator of impurities; when the concentration indicator is lower than a set first threshold range A, sending a first speed change signal to the heating chamber (which has a gradient control unit); the heating chamber, in response to the first speed change signal, switching a current first set sub-rate (i.e., a first heating rate) to a second set sub-rate (i.e., a second heating rate).

[0157] For example, in some embodiments, the first set sub-rate is about 0.5°C/min, and the second set sub-rate is about 2°C/min.

[0158] In this embodiment, the concentration indicator can be used to control the variable heating rate process in real time.

[0159] It is worth noting that, unlike the conventional glassy carbon preparation processes in the prior art, the present invention focuses on the preparation of glassy carbon for microneedle-

shaped products. For microneedle products with small dimensions, during the actual sintering process, excessive shrinkage speed can easily lead to undesirable deformation, thereby affecting the final surface morphology and strength of the microneedles, making them difficult to use in practice.

[0160] However, the present invention, by proposing the mesh design of the precursor and the centralized heat-preservation method, reduces to a certain extent the influence of the heating rate on the third heating stage, and accordingly, also reduces the fluctuation of the impurity concentration discharged during the third heating stage. Thus, in this embodiment, by combining the monitoring of key impurity parameters in the third heating stage with centralized heat preservation, the reliability and stability of the monitoring results can be ensured, thereby effectively optimizing product quality.

[0161] Embodiment 3

[0162] In order to improve the reliability of the centralized heat-preservation method (i.e., the low-temperature gradient heat-preservation method) and to reduce the labor cost during the preparation process to a certain extent, the present invention further provides an automatic monitoring system for glassy carbon preparation, as shown in FIG. 9, comprising:

[0163] a gradient control module 10 (or control unit) for controlling the heating process of the heating chamber;

[0164] a low-temperature gradient process monitoring subsystem (also referred to as a centralized heat-preservation monitoring subsystem), comprising:

[0165] an impurity monitoring module 20 connected to an exhaust pipe of the heating chamber and configured to monitor a concentration indicator of impurities discharged through the exhaust pipe; wherein the impurities comprise a first type of impurities, and the first type of impurities comprise one or more of: carbon monoxide, carbon dioxide, nitric oxide, nitrogen dioxide, and nitrogen;

[0166] a signal adjustment module 21 configured to automatically adjust the centralized heat-preservation method according to the concentration indicator and a current state of the centralized heat-preservation method; wherein the concentration indicator comprises a first concentration indicator for characterizing a concentration of the first type of impurities; accordingly, the signal adjustment module 21 comprises:

[0167] a first adjustment unit 11 configured to, when the centralized heat-preservation method has reached the pyrolytic carbonization temperature for a first set time but has not yet reached

the second duration T2 (i.e., the preset heat-preservation duration for pyrolysis), and the first concentration indicator falls within a first concentration threshold range X1, send a first time-reduction signal to the gradient control module of the heating chamber, wherein the control unit is capable of reducing the second duration T2 in response to the first time-reduction signal;

[0168] and/or a second adjustment unit 12 configured to, when the centralized heat-preservation method has reached or exceeded the second duration T2 after reaching the pyrolytic carbonization temperature, and the first concentration indicator falls within a corresponding second concentration threshold range X2, send a first time-extension signal to the control unit, wherein the control unit is capable of extending the second duration T2 in response to the first time-extension signal.

[0169] Wherein, when the first concentration indicator falls within the first concentration threshold range X1, the heat-preservation treatment is terminated and the rapid temperature increase stage is entered.

[0170] In some embodiments, the signal adjustment module 21 further comprises: a speed change unit 13 configured to, when the centralized heat-preservation method is raising the temperature from the pyrolytic carbonization temperature to the target heating temperature, and the first concentration indicator is monitored to fall within a third concentration threshold range X3, send a first speed adjustment signal to the control unit, wherein the control unit is capable of increasing the third set speed VIII (i.e., the heating rate in the third heating stage) in response to the first speed adjustment signal.

[0171] In some embodiments, the impurity monitoring module 20 is further configured to monitor a second type of impurities discharged from the heating chamber during the centralized heat-preservation method stage.

[0172] In some embodiments, the signal adjustment module 21 further comprises: a comprehensive adjustment unit 14 configured to, when the heating chamber has reached the pyrolytic carbonization temperature for a first set time but has not yet reached the second duration T2, and the first concentration indicator falls within the first concentration threshold range X1, and the second concentration indicator falls within a fourth concentration threshold range X4, send the first time-reduction signal to the control unit of the heating chamber, wherein the control unit is capable of reducing the second duration T2 in response to the first time-reduction signal.

[0173] Wherein, a first, a second, and a fifth concentration threshold ranges are sequentially set according to the concentration level of the first type of impurities. A fourth and a sixth concentration threshold ranges are sequentially set according to the concentration level of the

second type of impurities.

[0174] In some embodiments, the signal adjustment module 21 further comprises: a user adjustment unit 15 configured to, when the heating chamber has reached the pyrolytic carbonization temperature, and when the first concentration indicator falls within a fifth concentration threshold range X5, or the second concentration indicator falls within a sixth concentration threshold range X6, send a first prompt signal to the user to prompt the user to adjust the centralized heat-preservation method of the gradient control module.

[0175] In this embodiment, the heat-preservation treatment time for pyrolysis can be dynamically adjusted according to the ranges corresponding to the first and second concentration indicators. For example, when the concentration indicators are relatively low (i.e., the first concentration indicator is within the first concentration threshold range, and the second concentration indicator is within the fifth concentration threshold range), the heat-preservation time at the pyrolytic carbonization temperature is automatically reduced.

[0176] When at least one concentration indicator is too high, for example, when the first concentration indicator falls within the fifth concentration threshold range X5, or when the second concentration indicator falls within the sixth concentration threshold range X6, emergency manual intervention is introduced.

[0177] Alternatively, in some embodiments, the comprehensive adjustment unit 14 is further configured to, when the first concentration indicator falls within the second concentration threshold range, or the second concentration indicator falls within a seventh concentration threshold range (i.e., between the fourth and sixth concentration threshold ranges), similarly send the first time-extension signal to the control unit, and correspondingly, the control unit is capable of extending the second duration T2 in response to the first time-extension signal.

[0178] In actual processing, due to different processing environments, equipment models, and product requirements, frequent adjustment of preparation conditions may be involved. The present invention adopts an automatic adjustment process that only adjusts for key nodes (e.g., the heat-preservation duration for pyrolysis in the low temperature range), thereby flexibly and dynamically adjusting the preparation conditions, while also utilizing limited factors for multi-level adjustment. This enables more precise automatic adjustment of the heat-preservation duration for pyrolysis without increasing application costs, reducing the need for manual intervention by the user.

[0179] In some embodiments, the system further comprises: a mesh process monitoring subsystem, the mesh process monitoring subsystem comprising:

[0180] a first view acquisition module 30 configured to acquire morphological information of a mesh precursor, wherein the morphological information comprises a first image for showing dimensional features of the mesh precursor;

[0181] a view analysis module 40 configured to obtain characteristic indicators of the mesh precursor based on the morphological information; wherein the mesh precursor comprises: a body, and a hollow region provided in the middle of the body; the characteristic indicators comprise a first characteristic indicator for characterizing the dimensional features, and the first characteristic indicator comprises a line width of mesh holes;

[0182] an execution condition determination module 50 configured to determine, based on the characteristic indicators, whether the mesh precursor meets a preset execution condition for a centralized heat-preservation method (e.g., the execution condition is a standard line width of the mesh holes).

[0183] In some embodiments, the morphological information further comprises: a second image for showing morphological features of the mesh precursor; accordingly, the characteristic indicators further comprise a second characteristic indicator obtained from the second image for indicating a defect quantity.

[0184] For example, in some embodiments, an image dimension measuring instrument may be selected to obtain corresponding dimensional data.

[0185] In some embodiments, the execution condition determination module 50 comprises:

[0186] a first determination unit 51 configured to determine a monitoring level of the centralized heat-preservation method based on the first characteristic indicator, wherein the monitoring levels are divided into: a first-level monitoring and a second-level monitoring according to a difference between the first characteristic indicator and a standard dimensional feature;

[0187] a second determination unit 52 configured to determine a surveillance level of the centralized heat-preservation method based on the second characteristic indicator, wherein the surveillance levels are divided into: a first-level surveillance and a second-level surveillance according to a difference between the second characteristic indicator and a standard morphological feature;

[0188] an execution risk analysis unit 53 configured to determine an execution risk level of the centralized heat-preservation method based on the monitoring level and the surveillance level; wherein, when both the monitoring level and the surveillance level are the first level, the execution risk level is low, and a first start signal is sent to the gradient control module, and the gradient

control module, in response to the first start signal, starts the centralized heat-preservation method and activates the signal adjustment module 21;

[0189] when the monitoring level is the first level and the surveillance level is the second level, or when the monitoring level is the second level and the surveillance level is the first level, the execution risk level is medium, and a second start signal is sent to the gradient control module, and the gradient control module, in response to the second start signal, starts and executes the centralized heat-preservation method in response to gradient control parameters input by a user;

[0190] when both the monitoring level and the surveillance level are the second level, the execution risk level is high, and a prompt signal is sent to the user, and a control signal input by the user in real time is received within a set time.

[0191] In some embodiments, when a difference between the first characteristic indicator (e.g., the line width of the mesh holes) and a standard dimensional feature (e.g., a preset standard line width) is less than or equal to a preset first difference, the first-level monitoring (mode) is selected; when the difference is greater than the first difference and less than a preset second difference, the second-level monitoring (mode) is selected.

[0192] In some embodiments, when a difference between the second characteristic indicator (e.g., the defect quantity) and a standard morphological feature (a standard defect quantity) is less than or equal to a preset third difference, the first-level surveillance (mode) is selected; and when the corresponding difference is greater than the third difference and less than a preset fourth difference, the second-level surveillance (mode) is selected.

[0193] For example, in some embodiments, when facing batch process production, before performing the centralized heat-preservation method on a batch of mesh precursors, a portion of the mesh precursors may be selected as test samples, and the monitoring level (or surveillance level) during the low-temperature gradient process is determined by the mesh process monitoring subsystem, thereby improving the effectiveness of the entire preparation process.

[0194] Moreover, in this embodiment, by using two clear indicators, i.e., the line width and the defect quantity, standardized quality evaluation of the test samples can be performed quickly, thereby enabling flexible linkage with the subsequent low-temperature gradient process. For example, when the surveillance level and monitoring level of the test samples are both the first level, the signal adjustment module 21 is preferably activated to dynamically adjust the low-temperature process.

[0195] In some embodiments, the defect quantity may also be characterized by a defect area.

[0196] It should be noted that in this embodiment, the terms “monitoring” and “surveillance” have the same meaning, and different expressions are used only for the convenience of distinction.

[0197] In this embodiment, in order to improve the accuracy and reliability of the automatic monitoring, a monitoring scheme based on multi-level dynamic regulation of different types of parameters is proposed. Moreover, in order to reduce the difficulty of the monitoring process, the present invention mainly monitors key dimensional features in the mesh technology (e.g., the width of the mesh holes) and key output impurities in the centralized heat-preservation method (e.g., nitrogen), thereby using a combination of limited factors to form a multi-level monitoring mode. Thus, this multi-level dynamic regulation monitoring scheme can reduce the possibility of process failure caused by the combination of limited factors or by a single monitoring device failure; at the same time, it can also avoid, to a certain extent, the difficulty of monitoring and analysis that may be caused by multi-factor monitoring (on the contrary, the present invention uses limited and standardized factor comparison to quickly identify difficult problems (e.g., when the risk level is high), and then notify the user at the first time, achieving synergy between automatic control and manual monitoring).

[0198] In some embodiments, the system further comprises an evaluation subsystem, comprising:

[0199] a second view acquisition module 60 configured to acquire a third image of a mesh microneedle product prepared from the mesh precursor;

[0200] an image comparison module 70 configured to compare the third image with the first image to obtain shrinkage data and morphological difference data of the mesh microneedle product, wherein the morphological difference data is a difference in deformation ratios between the mesh precursor and the mesh microneedle product at at least two points;

[0201] a quality evaluation module 80 configured to perform product quality analysis on the mesh microneedle product based on the shrinkage data and the morphological difference data.

[0202] For example, in some embodiments, when both the shrinkage data and the morphological difference data fall within preset standard ranges, it is considered that the product quality meets expectations and the current preparation process is in compliance with the specifications.

[0203] In this embodiment, the image comparison technology can also be used to quickly evaluate the final prepared product. For example, if the product quality is monitored to be significantly lower than the expected quality, the user can be promptly notified to adjust the

process.

[0204] Embodiment 4

[0205] The present invention also correspondingly provides a semi-automatic monitoring method for glassy carbon preparation, comprising the steps of:

[0206] S200: when the glassy carbon preparation enters the centralized heat-preservation method step, monitoring a concentration indicator of impurities discharged through an exhaust pipe of the heating chamber; wherein the impurities comprise a first type of impurities, and the first type of impurities comprise one or more of: carbon monoxide, carbon dioxide, nitric oxide, nitrogen dioxide, and nitrogen;

[0207] S201: automatically adjusting the centralized heat-preservation method according to the concentration indicator and a current state of the centralized heat-preservation method; wherein the concentration indicator comprises a first concentration indicator for characterizing a concentration of the first type of impurities; accordingly, S201 comprises the steps of:

[0208] S11: when the low-temperature gradient heat-preservation method (i.e., the centralized heat-preservation method) reaches the pyrolytic carbonization temperature for a first set time but has not yet reached the second duration T2 (i.e., the heat-preservation duration for pyrolysis), and the first concentration indicator falls within a first concentration threshold range X1, sending a first time-reduction signal to the gradient control module of the heating chamber, wherein the control unit is capable of reducing the second duration T2 in response to the first time-reduction signal;

[0209] S12: when the heating chamber has reached or exceeded the second duration T2 after reaching the pyrolytic carbonization temperature, and the first concentration indicator falls within a corresponding second concentration threshold range X2, sending a first time-extension signal to the control unit, wherein the control unit is capable of extending the second duration T2 in response to the first time-extension signal.

[0210] In some embodiments, S201 further comprises the step of:

[0211] S13: when the heating chamber is raising the temperature from the pyrolytic carbonization temperature to the target heating temperature, and the first concentration indicator is monitored to fall within a third concentration threshold range X3, sending a first speed adjustment signal to the control unit, wherein the control unit is capable of increasing the third set speed VIII (i.e., the heating rate in the third heating stage) in response to the first speed adjustment signal.

[0212] In some embodiments, S200 further comprises the step of:

[0213] during the centralized heat-preservation method step (e.g., the second heating stage or the third heating stage), monitoring a second type of impurities discharged from the heating chamber.

[0214] In some embodiments, S201 comprises the steps of:

[0215] when the heating chamber has reached the pyrolytic carbonization temperature for a first set time but has not yet reached the second duration T2, and the first concentration indicator falls within the first concentration threshold range X1, and the second concentration indicator falls within a fourth concentration threshold range X4, sending a first time-reduction signal to the control unit of the heating chamber, wherein the control unit is capable of reducing the second duration T2 in response to the first time-reduction signal;

[0216] and/or, when the heating chamber has reached the pyrolytic carbonization temperature, and when the first concentration indicator falls within a fifth concentration threshold range X5, and the second concentration indicator falls within a sixth concentration threshold range X6, sending a first prompt signal to the user to prompt the user to adjust the centralized heat-preservation method of the gradient control module.

[0217] In some embodiments, before S200, the method further comprises the steps of:

[0218] S203: acquiring morphological information of a mesh precursor, wherein the morphological information comprises a first image for showing dimensional features of the mesh precursor;

[0219] S204: obtaining characteristic indicators of the mesh precursor based on the morphological information; wherein the mesh precursor comprises: a body, and a hollow region provided in the middle of the body; the characteristic indicators comprise a first characteristic indicator for characterizing the dimensional features, and the first characteristic indicator comprises: an edge width of mesh holes on the body, and a radius of the body;

[0220] S205: determining, based on the characteristic indicators, whether the mesh precursor meets a preset execution condition for the low-temperature gradient heat-preservation method (i.e., the centralized heat-preservation method).

[0221] In some embodiments, the morphological information further comprises: a second image for showing morphological features of the mesh precursor; accordingly, the characteristic indicators further comprise a second characteristic indicator for indicating a defect quantity. The

defect quantity may be characterized by a defect area. The defects may include: foaming, cracking, deformation, and the like.

[0222] The defect area may be calculated by image comparison. For example, points with pixel differences between a test sample photograph (i.e., a surface photograph of the prepared glassy carbon product) and a standard sample photograph (a surface photograph of a glassy carbon product selected as a standard sample) may be used as a defect region, thereby calculating the defect area. Alternatively, other automated defect detection equipment or automated defect detection techniques may also be used to calculate the defect area (or defect quantity).

[0223] In some embodiments, S205 comprises the steps of:

[0224] S51: determining a monitoring level of the low-temperature gradient heat-preservation method according to the first characteristic indicator, wherein the monitoring levels are divided into: first-level monitoring and second-level monitoring based on a difference between the first characteristic indicator and a standard dimensional feature;

[0225] S52: determining a surveillance level of the low-temperature gradient heat-preservation method according to the second characteristic indicator, wherein the surveillance levels are divided into: first-level surveillance and second-level surveillance based on a difference between the second characteristic indicator and a standard morphological feature;

[0226] S53: determining an execution risk level of the low-temperature gradient heat-preservation method according to the monitoring level and the surveillance level;

[0227] wherein, when both the monitoring level and the surveillance level are the first level, a first start signal is sent to the gradient control module, and the gradient control module, in response to the first start signal, starts the low-temperature gradient heat-preservation method and executes S200;

[0228] when the monitoring level is the first level and the surveillance level is the second level, or when the monitoring level is the second level and the surveillance level is the first level, a second start signal is sent to the gradient control module, and the gradient control module, in response to the second start signal, starts and executes the low-temperature gradient heat-preservation method in response to gradient control parameters input by a user (e.g., the heat-preservation duration for pyrolysis, the heating rate in the third heating stage);

[0229] when both the monitoring level and the surveillance level are the second level, a prompt signal is sent to the user, and a control signal input by the user in real time is received

within a set time.

[0230] In some embodiments, the method further comprises the steps of:

[0231] S206: acquiring a third image of a mesh microneedle product prepared from the mesh precursor;

[0232] S207: comparing the third image with the first image to obtain shrinkage data and morphological difference data of the mesh microneedle product, wherein the morphological difference data is a difference in deformation ratios between the mesh precursor and the mesh microneedle product at at least two points;

[0233] S208: performing product quality analysis on the mesh microneedle product based on the shrinkage data and the morphological difference data.

[0234] It should be noted that the threshold values or ranges used in the present invention can be adjusted by the user according to the actual process conditions.

[0235] It should be noted that the temperature values actually selected in the present invention may be the recommended temperatures or values close to the recommended temperatures.

[0236] The microneedle products prepared by using the mesh precursor and the heat-preservation treatment in the present invention have multiple advantages such as high rigidity, good biocompatibility, heat resistance, chemical resistance, good electrical conductivity, and high purity. They can be applied not only to conventional solid or hollow microneedle arrays but also to the preparation of components for precision devices such as electrospinning nozzles, extrusion printing nozzles, brain-computer interfaces, and biosensors.

[0237] Correspondingly, the present invention provides a use of the glassy carbon microneedle in preparing a delivery medium, wherein the delivery medium comprises one or more of: a drug delivery medium, a biological sample delivery medium (or a biological sample extraction medium). The drug delivery medium may be connected to a pressure conduction system. In some embodiments, the glassy carbon microneedle is loaded with a drug and/or a biological agent by at least one of coating, deposition, filling, wrapping, and chemical bonding. In some embodiments, in order to improve the drug-loading performance of the glassy carbon, at least one post-treatment may be performed on the glassy carbon, so as to facilitate loading of the drug and/or the biological agent thereon by coating, deposition, filling, wrapping, or chemical bonding.

[0238] Embodiment 5

[0239] It is worth noting that this centralized heat-preservation method enables the roller microneedle product to maintain good morphological and strength characteristics even when preparing a relatively large-sized roller microneedle. For example, even when the length of the roller microneedle precursor is increased to 200 mm and the width (equivalent to the radius) is increased to 100 mm, it can still maintain stable deformation during the heating process.

[0240] The present invention also provides a method for preparing a roller microneedle, comprising:

[0241] S401: obtaining a precursor prepared from a carbon-based polymer, as shown in Fig. 14 and Fig. 15, wherein the precursor comprises: a plurality of first supports and a plurality of second supports arranged at intervals, the first supports and the second supports intersecting to form a plurality of mesh holes at intervals, and at least one support being provided with a plurality of microneedles or microneedle-like structures;

[0242] S402: performing a centralized heat-preservation treatment on the precursor; wherein S402 comprises the steps of:

[0243] in a first heating stage, selecting a stress-relief temperature to perform a heat-preservation treatment on the precursor, so as to relieve stress in the precursor; wherein the stress-relief temperature is selected according to a first selection rule;

[0244] raising temperature to enter a second heating stage, and in the second heating stage, selecting the pyrolytic carbonization temperature to perform another heat-preservation treatment on the precursor, so as to cause the precursor to undergo pyrolytic carbonization, wherein the precursor undergoes shrinkage deformation during the pyrolytic carbonization; the pyrolytic carbonization temperature is selected according to a second selection rule;

[0245] wherein the first selection rule is: selecting the stress-relief temperature from a weight-loss-rate fluctuation temperature; wherein the weight-loss-rate fluctuation temperature corresponds to one or more temperature values of at least one curve segment having a greatest curvature change in a derivative thermogravimetry curve, and the derivative thermogravimetry curve is a curve representing the rate of weight change as a function of temperature; and the second selection rule is: selecting the pyrolytic carbonization temperature from a weight-loss fluctuation temperature; wherein the weight-loss fluctuation temperature corresponds to one or more temperature values of a curve segment having a greatest curvature change in a thermogravimetric analysis curve in an interval in which a slope gradually decreases, and the thermogravimetric analysis curve is a curve representing weight change as a function of temperature.

[0246] In some embodiments, the width of the supports of the precursor (i.e., the line width) is less than or equal to 3 mm.

[0247] In some embodiments, the precursor may be prepared using photocuring 3D printing technology. Correspondingly, before S402, the method further comprises the step of: immersing the precursor in a cleaning liquid (e.g., an alcohol-based liquid) for a first period of time, wherein the alcohol-based liquid refers to an alcohol solution or an alcohol solvent.

[0248] In some embodiments, the alcohol solution may be ethanol, propanol, methanol, etc., at various concentrations.

[0249] Among them, the alcohol solution is preferably high-concentration ethanol, such as absolute ethanol.

[0250] In some embodiments, the first period of time may be set by the user. For example, the first period of time may be about 5 minutes, during which shaking or ultrasonic cleaning may be used to accelerate the cleaning until residual liquid on the surface of the precursor (i.e., the liquid raw material that adhered to the surface of the precursor and was not formed during the photopolymerization printing process) is completely removed.

[0251] In some embodiments, after the immersion treatment and drying, a secondary photocuring is further performed to fully crosslink and cure the material (in this step, high-pressure air blowing or high-speed centrifugation may also be used to remove residual resin material inside the supports).

[0252] In some embodiments, the precursor may also be prepared by methods such as fused deposition modeling or mold forming.

[0253] In some embodiments, the precursor has a columnar design, wherein a plurality of the first supports are arranged around at least one circle, and a plurality of the second supports are arranged at intervals along the length direction of the first supports and intersect with the plurality of first supports, so as to combine with the first supports to form a columnar frame. The precursor further comprises: a third support and a fourth support disposed inside the columnar frame, wherein the third support and the fourth support are cross-arranged in at least two directions, and two ends of the third support and the fourth support are respectively connected to the first supports or the second supports to support the columnar frame. A plurality of microneedles or microneedle-like structures are provided on side surfaces of the first supports and/or the second supports.

[0254] In some embodiments, the length of the first supports of the precursor is less than or

equal to 200 mm, and the width of the columnar frame (for example, when the columnar frame is a cylindrical structure, the width may refer to the radius) is less than or equal to 100 mm.

[0255] It is worth noting that for microneedle products, even small defects can have a severe impact on their quality, and as the size of the precursor gradually increases, the processing difficulty also increases (defects are more likely to occur due to deformation). The centralized heat-preservation method proposed in the present invention can increase the size of the product while ensuring the quality of the microneedles (i.e., controlling the number of defects).

[0256] It has been verified that even when the width of the precursor reaches 100 mm and the length reaches 200 mm, the final roller microneedle product obtained after the heat treatment can still maintain good morphology and performance during the rapid heating process.

[0257] Table 3

Preparation Example	Width of the columnar frame	Length of the first support	Width of the support (line width)	Quality
2-1	20mm	80mm	1mm	Excellent
2-2	90mm	80mm	1mm	Excellent
2-3	20mm	190mm	1mm	Excellent
2-4	20mm	80mm	3mm	Excellent
2-5	100mm	200mm	3mm	Excellent

[0258] The heating process parameters used in Table 3 are shown in Fig. 2b.

[0259] In some embodiments, S402 further comprises the step of: in a subsequent third heating stage, continuously raising the temperature from the pyrolytic carbonization temperature to the target heating temperature.

[0260] In some embodiments, in the third heating stage, a first heating rate is used to raise the temperature to a speed change temperature point, and then a second heating rate is used to raise the temperature to the target heating temperature, wherein the second heating rate is greater than the first heating rate, and the speed change temperature point is a temperature point corresponding to a numerical point on the thermogravimetric analysis curve where the slope is less than a preset slope threshold during a process of gradually increasing slope.

[0261] In some embodiments, the method further comprises: during the second heating stage, introducing a gas into the heating chamber where the precursor is located.

[0262] In some embodiments, the introduction rate of the gas is 10-60 cm³/min.

[0263] In some embodiments, the method further comprises:

[0264] during the second heating stage, collecting, via the gas, a concentration indicator of impurities generated during the pyrolytic carbonization of the precursor; wherein the impurities comprise a first type of impurities, and the first type of impurities comprise one or more of: carbon monoxide, carbon dioxide, nitric oxide, nitrogen dioxide, and nitrogen;

[0265] when the pyrolytic carbonization temperature is reached for a first set time but the second duration T2 has not yet been reached, and the first concentration indicator falls within a first concentration threshold range X1, sending a first time-reduction signal to the heating chamber;

[0266] or, when the centralized heat-preservation method has reached or exceeded the second duration T2 after reaching the pyrolytic carbonization temperature, and the first concentration indicator falls within a corresponding second concentration threshold range X2, sending a first time-extension signal to the heating chamber; wherein the second duration T2 is a preset heat-preservation duration for pyrolysis.

[0267] Embodiment 6

[0268] The present invention also corresponds to Embodiment 5 above and provides a system for preparing a roller microneedle, comprising:

[0269] a centralized heat-preservation module configured to perform a centralized heat-preservation treatment on a precursor; wherein the precursor is prepared from a carbon-based polymer, and the precursor comprises: a plurality of first supports and a plurality of second supports arranged at intervals, the first supports and the second supports intersecting to form a plurality of mesh holes at intervals, and at least one support being provided with a plurality of microneedles or microneedle-like structures; and the centralized heat-preservation module comprises:

[0270] a first heating unit configured to, in a first heating stage, select a stress-relief temperature to perform a heat-preservation treatment on the precursor, so as to relieve stress in the precursor; wherein the stress-relief temperature is selected according to a first selection rule;

[0271] a second heating unit configured to raise temperature to enter a second heating stage, and in the second heating stage, select the pyrolytic carbonization temperature to perform another heat-preservation treatment on the precursor, so as to cause the precursor to undergo pyrolytic carbonization, wherein the precursor undergoes shrinkage deformation during the pyrolytic carbonization; the pyrolytic carbonization temperature is selected according to a second selection rule;

[0272] wherein the first selection rule is: selecting the stress-relief temperature from a weight-loss-rate fluctuation temperature; wherein the weight-loss-rate fluctuation temperature corresponds to one or more temperature values of at least one curve segment having a greatest curvature change in a derivative thermogravimetry curve, and the derivative thermogravimetry curve is a curve representing the rate of weight change as a function of temperature; and the second selection rule is: selecting the pyrolytic carbonization temperature from a weight-loss fluctuation temperature; wherein the weight-loss fluctuation temperature corresponds to one or more temperature values of a curve segment having a greatest curvature change in a thermogravimetric analysis curve in an interval in which a slope gradually decreases, and the thermogravimetric analysis curve is a curve representing weight change as a function of temperature.

[0273] It should be understood that the centralized heat-preservation method for preparing a roller microneedle in the present invention may also adopt the same or similar steps as those in any of the above embodiments. Therefore, the methods and systems in Embodiment 5 and Embodiment 6 may also include the steps or unit modules in any of the above embodiments.

[0274] It should be noted that the microneedles provided by the present invention are preferably applicable to the fields of drug delivery, biosensing, tissue repair, medical aesthetics, etc., penetrating the skin or other biological barriers through the needle structure to achieve efficient substance delivery or signal acquisition. For example, in drug delivery, the microneedles form microchannels to deliver the drug directly to the target site, avoiding the first-pass effect and improving efficacy; in biosensing, the microneedles can directly contact body fluids to achieve precise signal detection; in tissue repair and medical aesthetics, through the physical stimulation mediated by the microneedles in combination with drugs, tissue regeneration and repair can be promoted, skin quality improved, and skin diseases treated, etc. Of course, the microneedles provided by the present invention can also be applied to other application scenarios, such as electronics, chemical industry, etc., and the present invention does not impose limitations in this regard.

[0275] From the description of the above embodiments, those skilled in the art can clearly understand that the methods of the above embodiments can be implemented by means of software plus a necessary general hardware platform, and of course also by hardware, but in many cases the former is a better implementation. Based on such understanding, the technical solutions of the present invention, or the part that contributes to the prior art, can be embodied in the form of a software product. The computer software product is stored in a storage medium (e.g., ROM/RAM, magnetic disk, optical disk) and includes several instructions for causing a computer terminal (which may be a mobile phone, a computer, a server, or a network device,

etc.) to execute the methods described in the various embodiments of the present invention. The embodiments of the present invention have been described above with reference to the accompanying drawings, but the present invention is not limited to the specific embodiments described above. The specific embodiments described above are merely illustrative rather than restrictive. Under the teaching of the present invention, those of ordinary skill in the art may make many modifications without departing from the spirit of the present invention and the scope of protection of the claims, and such modifications fall within the protection of the present invention.

CLAIMS

1. A method for preparing a glassy carbon microneedle, wherein the method comprises:
preparing a precursor using a carbon-based polymer raw material, wherein the precursor has a microneedle or microneedle-like structure;

placing the precursor in a heating chamber and starting a centralized heat-preservation method, wherein starting the centralized heat-preservation method comprises: in a first heating stage, selecting a stress-relief temperature to perform a heat-preservation treatment on the precursor, so as to relieve stress in the precursor; wherein the stress-relief temperature is selected according to a first selection rule; wherein the first selection rule is: selecting the stress-relief temperature from a weight-loss-rate fluctuation temperature; and wherein the weight-loss-rate fluctuation temperature corresponds to a temperature value of a data point, in a derivative thermogravimetry curve, having a greatest curvature change in an interval less than a pyrolytic carbonization temperature;

raising temperature to enter a second heating stage, and in the second heating stage, selecting the pyrolytic carbonization temperature to perform another heat-preservation treatment on the precursor, so as to cause the precursor to undergo pyrolytic carbonization, wherein the microneedle or the microneedle-like structure shrinks during the pyrolytic carbonization; wherein the pyrolytic carbonization temperature is selected according to a second selection rule; wherein the second selection rule is: selecting the pyrolytic carbonization temperature from a weight-loss fluctuation temperature; wherein the weight-loss fluctuation temperature corresponds to a temperature value of a curve segment, in a thermogravimetric analysis curve, having a greatest curvature change in an interval in which a slope gradually decreases;

in a subsequent third heating stage, continuously raising temperature from the pyrolytic carbonization temperature to a target heating temperature, so that the precursor prepared from the carbon-based polymer is finally converted into the glassy carbon microneedle.

2. The method according to claim 1, further comprising:
during a heating stage of the precursor, introducing an inert gas into the heating chamber to protect the precursor and discharge impurities generated during the heating stage; and,
collecting a concentration indicator of the impurities by a gas monitoring device.
3. The method according to claim 2, wherein the method further comprises:
in the third heating stage, when the concentration indicator of the impurities is monitored to be lower than a preset concentration range, selecting a switching time according to a current time, wherein a difference between the switching time and the current time is less than a preset difference range;

at the switching time, increasing a current first heating rate to a second heating rate, and continuing to raise temperature to the target heating temperature.

4. The method according to claim 1, wherein the carbon-based polymer comprises:
 - (1) a carbon-rich polymer, wherein the carbon-rich polymer comprises one or more of: furan resin, furfuryl alcohol resin, furfuryl ketone resin, phenolic resin, epoxy resin, polyurethane, polyimide, polyethylene glycol, acrylic resin, polylactic acid, polycaprolactone, polyethylene, polyether ether ketone, nylon, polycarbonate, polymethyl methacrylate, polyvinyl butyral, polyethylene terephthalate, polyacrylonitrile, polyvinylidene fluoride, polyvinylidene chloride, polystyrene, polytetrafluoroethylene, polybutadiene, polyphenylene ether, polyphenylene sulfide, polybutene-1, polybenzimidazole, polyaryletherketone, polyarylsulfone, polyethylene naphthalate, polyaniline, polyacetylene, poly(p-phenylene), polyphthalimide, poly(phenylene ethynylene), polylactide, polychloroprene, polycyanoacrylate, poly(naphthylene ethynylene), poly(p-xylylene), polymethylphenylsiloxane, liquid crystal polymer, polythiophene, polyvinylacetylene, polyoxadiazole, poly(bisphenol A), acrylonitrile-butadiene-styrene copolymer, polychlorotrifluoroethylene, epoxy resin-acrylate copolymer, polyquinone, poly(p-phenylene sulfone), polyphenylene, polybenzoxazole, polypiperidine, polyvinyl acetal, polybenzothiazole, and polyvinylpyrrolidone; or (2) a product obtained by further modifying the carbon-rich polymer.
5. The method according to claim 1, wherein a method for preparing the precursor comprises mold forming and/or 3D printing.
6. The method according to claim 5, wherein the 3D printing is performed by laser stereolithography, two-photon polymerization, digital light processing, liquid crystal display polymerization, continuous liquid interface production, fused deposition modeling, selective laser sintering, computed axial lithography, powder binder jetting, electric-field direct writing, inkjet direct writing, or static optical projection lithography.
7. The method according to claim 1, wherein a base of the microneedle or the microneedle-like structure is capable of having one or more of the following shapes: circular, rectangular, cross-shaped, asterisk-shaped, or a hollow structure.
8. The method according to claim 1, wherein the precursor has a substrate, and a plurality of microneedles or microneedle-like structures are arranged on the substrate at intervals; or the precursor is a microneedle particle.

9. The method according to claim 8, wherein the substrate comprises a plurality of mesh holes arranged at intervals, the mesh holes intersect with each other to form a mesh arrangement, and the microneedle or the microneedle-like structure to be formed is provided at edges of the mesh holes.
10. The method according to claim 9, wherein the mesh holes are filled with a polymer film.
11. The method according to claim 9, wherein the substrate comprises: a body, wherein a hollow region is provided in the body; the plurality of mesh holes are arranged on the body at intervals, and the body is capable of having one or more of the following shapes: circular, annular, elliptical, rounded rectangular, or regular polygonal.
12. The method according to claim 11, wherein a line width L1 of the mesh holes is less than or equal to 2 mm, and a radius L2 of the body of the precursor is less than or equal to 100 mm.
13. A glassy carbon microneedle, wherein the glassy carbon microneedle is prepared by the method according to any one of claims 1 to 12.
14. Use of the glassy carbon microneedle according to claim 13 in preparing a signal transmission device, wherein the glassy carbon microneedle is used to connect to or form the signal transmission device, and the signal transmission device is used to transmit one or more of the following signals: an electrical signal, an optical signal, and a thermal signal.
15. The use according to claim 14, wherein one end of the signal transmission device is connected to biological tissue, and another end of the signal transmission device is connected to a signal processing device to form a biosensor and/or a brain-computer interface.
16. Use of the glassy carbon microneedle according to claim 13 in preparing a delivery medium, wherein the delivery medium comprises one or more of: a drug delivery medium and a biological sample delivery medium.
17. The use according to claim 16, wherein the drug delivery medium is connected to a pressure conduction system.
18. The use according to claim 15, wherein the glassy carbon microneedle is loaded with a drug and/or a biological agent by at least one of coating, deposition, filling, wrapping, and chemical bonding.