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(54) Title: A FLEXIBLE AND ELECTRICALLY CONDUCTIVE COMPOSITE

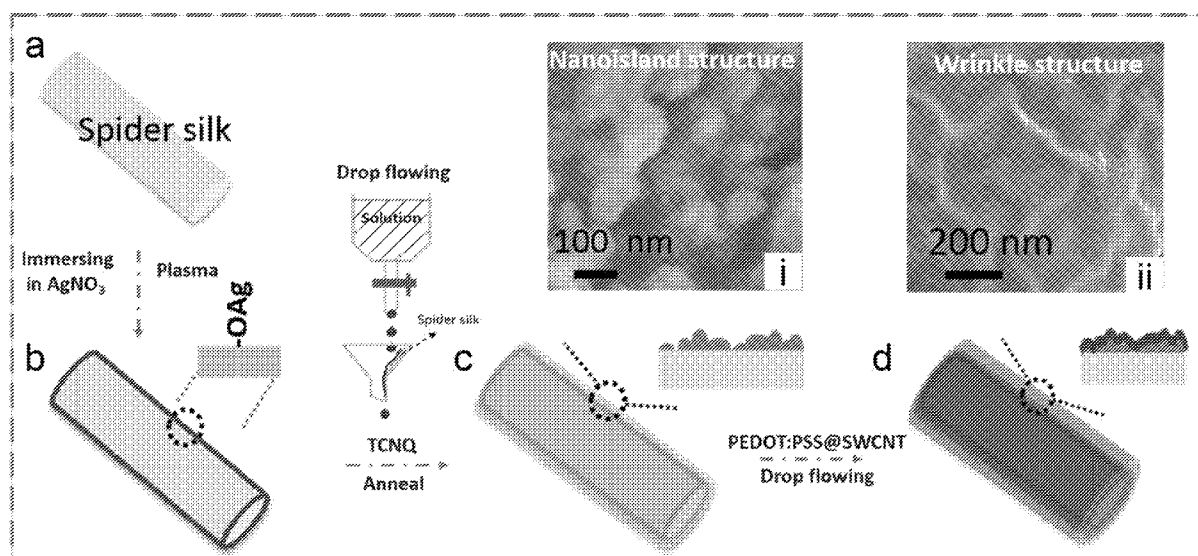


FIG. 2A

(57) Abstract: Various embodiments refer to a flexible and electrically conductive composite, a method of preparing the composite, and a prosthesis comprising the composite. The flexible and electrically conductive composite comprises silk fiber and a coating material comprising an electrically conducting polymer and an electrically conducting nanostructured material disposed on a surface of the silk fiber.

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A FLEXIBLE AND ELECTRICALLY CONDUCTIVE COMPOSITE

CROSS-REFERENCE TO RELATED APPLICATION

[001] This application claims the benefit of priority of Singapore patent application number 10201807020R, filed 20 August 2018, the contents of which being hereby incorporated by reference in its entirety for all purposes.

TECHNICAL FIELD

[002] The invention relates to a flexible and electrically conductive composite, and in particular, to a flexible and electrically conductive composite for use in an electro-tendon of a prosthesis.

BACKGROUND

[003] Inspired by the biological model of human hands, tendon-driven humanoid robotic hands have been designed and developed to feel precisely and work dexterously as human hands, and their use as prostheses have helped disabled people regain their confidence in life. As core components of transmission and sensing systems in robotic hands, tendons and wires play fundamental roles of transmitting force and electrical signal from servo motor and sensor, respectively, to make the robotic hands move and feel.

[004] With rapid growth in demand for better performance and functionality, it is challenging to build a multi-functional actuating layout and sensing circuit on a slender robotic finger with high durability and reasonable size similar to human hands. In terms of the materials used, even though polydimethylsiloxane (PDMS)-based and metal-based materials have been developed, their mechanical properties, especially toughness,

are unable to satisfy requirements of humanoid robotic hands, which require energy storage and recovery at high efficiency in order to mimic that of a human hand. Therefore, it remains a challenge to develop a tough material for use in electro-tendon for robotic hands having high endurance when grasping weights and good stability when stimulated, and which is able to balance the limited design space constraint while at the same time exhibiting improved performance.

[005] In view of the above, there remains a need for an improved material that addresses or at least alleviates one or more of the above-mentioned problems.

SUMMARY

[006] In a first aspect, a flexible and electrically conductive composite is provided. The flexible and electrically conductive composite comprises silk fiber and a coating material comprising an electrically conducting polymer and an electrically conducting nanostructured material disposed on a surface of the silk fiber.

[007] In a second aspect, a method of preparing a flexible and electrically conductive composite is provided. The method comprises

- a) providing silk fiber, and
- b) disposing a coating material comprising an electrically conducting polymer and an electrically conducting nanostructured material on a surface of the silk fiber.

[008] In a third aspect, a flexible and electrically conductive composite prepared by a method according to the second aspect is provided.

[009] In a fourth aspect, a prosthesis comprising a flexible and electrically conductive composite according to the first aspect or prepared by a method according to the second aspect is provided.

[0010] In a fifth aspect, use of a flexible and electrically conductive composite according to the first aspect or prepared by a method according to the second aspect in prosthesis, stretchable electronics, biomedical devices, implantable electronics, photodetectors, capacitors, electrochromic devices, strain gauges, sensors, wearable electronics, clean energy devices, smart clothes, and sensory skin for robotic systems, is provided.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] In the drawings, like reference characters generally refer to the same parts throughout the different views. The drawings are not necessarily drawn to scale, emphasis instead generally being placed upon illustrating the principles of various embodiments. In the following description, various embodiments of the invention are described with reference to the following drawings.

[0012] **FIG. 1A** shows a photograph of a spider, *Nephila pilipes*, which produced the spider silk used in the experiments.

[0013] **FIG. 1B** shows an optical image depicting morphology of a single dragline silk according to an embodiment. The diameter was about 3 μm to 4 μm , and the surface was smooth. Scale bar denotes 10 μm . The insert in the image shows cross-section scanning electron microscopy (SEM) image of the single dragline silk along the line shown in the optical image. Scale bar of the insert denotes 2 μm .

[0014] **FIG. 1C** shows an optical image of a bundle of raw dragline silk from *Nephila pilipes* (top) and SEM images of a single spider silk (bottom left and right). Scale bar of the bottom left SEM image is 10 μm and scale bar of the bottom right SEM image is 2 μm . As can be seen from the bottom right SEM image, surface of the spider silk is smooth.

[0015] FIG. 2A shows schematic diagrams **a** to **d** for preparing a conductive spider silk composite according to embodiments. In **a**, spider silk, which was processed by rinsing with ethanol and dried, was hydrophilized by plasma in an oxygen (O_2) atmosphere, forming hydrophilic groups, such as hydroxyl groups on the surface of spider silk. In **b**, the modified spider silk was immersed in a solution of silver nitrate ($AgNO_3$) in ethanol, whereby the hydrophilic group $-OH$ was changed into $-OAg$ as the seeds for nano-island structure growth. In **c**, the spider silk- OAg was immersed in a solution of 0.01 mol/L tetracyanoquinodimethane (TCNQ) in ethanol, through drop flowing and annealed to form a layer of nano-island structure. In **d**, the spider silk of **c** was immersed in an aqueous solution of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) and single-walled carbon nanotubes (SWCNT) also via drop flowing, and annealed. Also shown are SEM images (i) and (ii), respectively depicting nano-island structure formed after **c**, and wrinkle structure formed after **d**, of various embodiments. A reason for the wrinkle structure was intrinsic shrinkage of spider silk induced by water present in the aqueous solution of PEDOT:PSS. Scale bar in image (i) denotes 100 nm, while the scale bar in image (ii) denotes 200 nm.

[0016] FIG. 2B shows a SEM image of the wrinkled surface of a single fiber of spider silk with 10 % SWCNT composite formed resulting from the intrinsic shrinkage of the spider silk after immersion in water during PEDOT:PSS and SWCNT coating. Unless otherwise defined herein, % SWCNT refers to wt % SWCNT. Scale bar denotes 2 μm .

[0017] FIG. 2C shows a cross-sectional SEM image of a spider silk composite having a core and an outer layer. The spider silk was held in place using epoxy resin for the cross-sectional SEM imaging. As indicated in the figure, the core (area defined by the inner dashed line) is formed of spider silk, and the core diameter is about 3 μm to 4 μm . The outer layer (area between the outer dashed line and the inner dashed line) is a

conducting layer having a thickness of about 2 μm . Area beyond the outer dashed line is epoxy resin. Scale bar denotes 2 μm .

[0018] FIG. 3A is a graph depicting mechanical properties of spider silk composite according to an embodiment, by way of stress (GPa) vs strain (%) information of virgin spider silk, i.e. unmodified spider silk (VS), virgin spider silk which was dried after immersing in water (VS (Dry after immersing in water)), spider silk coated with a coating material of PEDOT:PSS and 0 wt% SWCNT (VS@0% SWCNT), and spider silk coated with a coating material of PEDOT:PSS and 7.5 wt% SWCNT (VS@7.5% SWCNT). As can be seen, stretchability of spider silk, measured in terms of strain (%) performance, improved nearly two times from 33 % for VS, to 56 % for VS@7.5% SWCNT. Further, the mechanical properties were successfully tuned by the content of SWCNT. As shown, toughness of the silk corresponds to energy needed to break the silk, and represented by area underneath each curve, is highest for VS@7.5% SWCNT.

[0019] FIG. 3B is a graph depicting mechanical properties of spider silk composite according to embodiments, by way of toughness ($\times 100 \text{ MJ/m}^3$) vs SWCNT (wt %), measured for unmodified spider silk (0 wt% SWCNT) and spider silk composites with varying wt % SWCNT. Compared with VS, toughness increased nearly 2 to 3 times to 420 MJ/m^3 when wt% of SWCNT was 10 wt%. Generally, based on the experiments carried out, toughness of the spider silk composites improved with increasing wt% of SWCNT.

[0020] FIG. 3C is a graph depicting mechanical properties of spider silk composite according to an embodiment, by way of Young's modulus (GPa) vs SWCNT (%). Generally, based on the experiments carried out, Young's modulus of the spider silk composites improved with increasing wt% of SWCNT with maximum at 10 wt% SWCNT.

[0021] **FIG. 3D** is a graph depicting mechanical properties of spider silk composite according to an embodiment, by way of tensile strength (GPa) vs SWCNT (%). Generally, based on the experiments carried out, tensile strength of the spider silk composites improved with increasing wt% of SWCNT.

[0022] **FIG. 3E** is a graph depicting mechanical properties of spider silk composite according to an embodiment, by way of stress (GPa) vs strain (%) information of Virgin spider silk (VS), VS (Dry after immersing in water), spider silk coated with a coating material of PEDOT:PSS and 0 wt% SWCNT (VS/PEDOT:PSS@0% SWCNT) and spider silk coated with a coating material of PEDOT:PSS and 10 wt% SWCNT (VS/...@10% SWCNT). As can be seen from the figure, the toughness and tensile strength when the content of SWCNT is at 10 % are respectively 420 MJ/m³ and 1.46 GPa, amounting to improvements of about 120 % and 95 %.

[0023] **FIG. 3F** shows a strain-stress curve in terms of nominal stress vs nominal strain of common spider silk. Area in gray under curve represents toughness of spider silk. Toughness is defined as the energy needed to break the spider silk.

[0024] **FIG. 4A** is a graph depicting electrical properties of spider silk composite according to an embodiment, by way of electrical conductivity (x1000 S/cm) vs SWCNT (%). Due to a layer of PEDOT:PSS, VS which was coated with the layer of PEDOT:PSS became electrically conductive and the electrical conductivity was about 370 S/cm. With incorporation of increasing amounts of SWCNT in PEDOT:PSS, electrical conductivity was further enhanced and achieved 1077 S/cm at 7.5 wt% SWCNT.

[0025] **FIG. 4B** is a graph depicting electrical properties of spider silk composite with 10 % SWCNT according to an embodiment, by way of resistance (R, Ohm) and Strain (%) vs Cycles. Electrical conductivity of the composite was nearly unchanged when it

underwent stretching and compression from 0 to 20 % (the maximum strain of human tendon is generally in the range of about 13 % to 18 %) under more than 1000 cycles. After releasing the stretching force at 0 %, it was able to resume to its original state.

[0026] FIG. 4C shows SEM images of a spider silk composite with 10 % SWCNT at various strain levels of (i) 0 %; (ii) 10 %; (iii) 20 %; (iv) 30 %; (v) 40 %; and (vi) 50 %. Scale bar in (i) denotes 2 μm , whereas scale bar in (ii) to (vi) denotes 200 nm. From the SEM images of the evolution of microstructure at same area under different strain, the wrinkle structure of conductive layer of PEDOT:PSS@SWCNT gradually flattened as shown by gradual reduction in height of the wrinkles, which resulted in no change of the conductive path. Therefore, electrical conductivity of the sample remained stable with increase in strain.

[0027] FIG. 4D is a graph showing the rate of change of resistance of spider silk composite with 10 % SWCNT under strain from 0 % to breakage. The ratio of $\Delta R/R$ was about 5 % even at 60 % strain. This low change in resistance is due to the wrinkled structure of the conductive layer, formed as a result of intrinsic shrinkage of spider silk in aqueous solution.

[0028] FIG. 4E is a graph showing that the conductivity of the spider silk with 10 wt% SWCNT remained at 1,070 S/cm even after 1,000 cycles of 0 to 20 % strain. Here, 20 % was chosen as reference because the maximum strain a human tendon can withstand is generally in the range of about 13 % to 18 %.

[0029] FIG. 5A shows a schematic diagram and a photograph of a specific structure of a humanoid robotic hand that the inventors have fabricated, to demonstrate performance of humanoid robotic hands based on the conductive spider silk (C-spider silk with 10 % SWCNT) as electro-tendon.

[0030] **FIG. 5B** shows a photograph of a humanoid robotic hand that the inventors have fabricated, whereby index finger (IF) is connected with C-spider silk with 10 % SWCNT as electro-tendon, middle finger (MF) is connected with silicone rubber as electro-tendon, ring finger (RF) is connected with steel fiber as electro-tendon and little finger (LF) is connected with carbon fiber as electro-tendon. Also shown is a graph of loading weight (kg/mm^2) (meaning the maximum weight that the tendon may be loaded per 1 mm^2) performance vs the different electro-tendons of C-spider silk with 10 % SWCNT, steel fiber, carbon fiber, and silicone rubber, and that of electro-tendons of nylon and spider silk. Surprisingly, the loading weight of the finger based on C-spider silk with 10 % SWCNT was about 107.3 kg/mm^2 which nearly came up to that based on steel fiber of about 131.9 kg/mm^2 , and was clearly better than that exhibited by electro-tendons of nylon, carbon fiber, spider silk and silicone rubber.

[0031] **FIG. 5C** shows photographs of index finger of the humanoid robotic hand shown in **FIG. 5B** under natural state (left) as compared to it being bent to final state dragged by an electro-tendon (right). As can be seen, the bending angle was about 8° when the index finger was under natural state. Correspondingly, the bending angle gradually changed to 73° when it was bent to final state dragged by an electro-tendon. Also shown are graphs of bending angle ($^\circ$) and relative length (cm) as a function of time (s). Relative length refers to the change in length of the tendon dragged by the motor when the finger was moving. This data was obtained from the controlling software. As can be seen from the graphs, during the full bending process, the robotic finger changed from natural state to final state, then back to natural state.

[0032] **FIG. 5D** shows graphs of bending angle ($^\circ$) vs relative length of tendon (cm) for fingers of the humanoid robotic hand shown in **FIG. 5B** of (i) C-spider silk with 10 % SWCNT, (ii) steel fiber, (iii) carbon fiber, and (iv) silicone rubber. As can be seen,

fingers based on C-spider silk and carbon fiber were able to successfully finish a full bending process. For the finger based on steel fiber, it cannot complete a full bending action due to its irreversibility, poor flexibility and stretchability. For the finger based on silicone rubber, it only bent at a very small angle of about 27° when pulled by electro-tendon, even at larger relative lengths, which may have originated due to low toughness of silicone rubber.

[0033] **FIG. 5E** is a graph showing maximum bending angle, $\theta_{\text{Max}} (^{\circ})$ and Cycles for fingers of the humanoid robotic hand shown in **FIG. 5B** of C-spider silk with 10 % SWCNT, steel fiber, carbon fiber, and silicone rubber. Although the finger based on C-spider silk and carbon fiber could successfully finish a full bending process, the poor shear strength of the carbon fiber only allows the finger to repeat the bending action several times, whereas the finger based on C-spider silk exhibited the best repeatability in bending action.

[0034] **FIG. 5F** is a graph showing results of an endurance experiment for the finger of the humanoid robotic hand shown in **FIG. 5B** of C-spider silk with 10 % SWCNT. Bending angle ($^{\circ}$) is shown against time (s). As shown, the finger based on C-spider silk was able to repeat the bending action for more than 1000 s.

[0035] **FIG. 5G** is a graph showing results of an endurance experiment for the finger of the humanoid robotic hand shown in **FIG. 5B** of carbon fiber. Bending angle ($^{\circ}$) is shown against time (s). As shown, the poor shear strength of the carbon fiber only allows the finger to repeat the bending action several times, before breaking at about 110 s.

[0036] **FIG. 6A** is a schematic diagram of a pressure feedback system designed by the inventors and which is configured to provide feedback processes of the anatomic robotic hand when it is touched, and when it grasps an object.

[0037] **FIG. 6B** is a photograph of a humanoid robotic hand. The dotted area shows a pressure sensor based on a pyramid structure which was assembled on the tip of index finger and connected with a reference resistor by the electro-tendon.

[0038] **FIG. 6C** shows a graph of resistance (R, ohm) and angle (°) against time (s) of the index finger (IF) connected with C-spider silk with 10 % SWCNT shown in **FIG. 6B**. As can be seen, resistance of the electro-tendon was nearly unchanged for the finger under bending.

[0039] **FIG. 6D** illustrates a feedback system based on electro-tendons according to embodiments disclosed herein. All the fingers of the robotic hand were connected with tendons of C-spider silk with 10 % SWCNT. TF denotes thumb, IF denotes index finger, and MF denotes middle finger. As can be seen, the robotic hand could catch the balloon with no deformation because of the pressure feedback system which made the fingers stop at a suitable pressure. Here, U_{out} is the voltage obtained shown in the pressure feedback system of **Fig. 6A**.

[0040] **FIG. 6E** shows comparative results of that shown in **FIG. 6D** using a robotic hand based on electrically non-conductive nylon. All the fingers of the robotic hand were connected with tendons of nylon. TF denotes thumb, IF denotes index finger, and MF denotes middle finger. As can be seen, the robotic hand with tendons of electrically non-conductive nylon bent over and the balloon even dropped out due to absence of signal from a pressure feedback system to stop the motion of the fingers.

[0041] **FIG. 7A** shows a snapshot of the coarse-grained spider silk composite comprising crystalline structure or beta-sheet structure; amorphous structure (3₁-helices and beta-turns); SWCNT.

[0042] FIG. 7B depicts dissipative particle dynamic simulation (DPD) simulated images showing the structural evolution of spider silk along the x-axis with increasing strain.

[0043] FIG. 7C depicts DPD simulated images showing the structural evolution of spider silk composite with 10% SWCNT along the x-axis with increasing strain. As can be seen from the figure, SWCNT introduced in spider silk induced improvement of mechanical properties of spider silk.

[0044] FIG. 7D shows Raman spectra for virgin spider silk (VS), spider silk with 2.5 wt% SWCNT (VS@2.5% SWCNT), spider silk with 7.5 wt% SWCNT (VS@7.5% SWCNT), and spider silk with 10.0 wt% SWCNT (VS@10.0% SWCNT).

[0045] FIG. 8A is a graph showing Young's modulus (GPa) and simulated Young's modulus (GPa) vs SWCNT (%). The graph shows the trend of Young's modulus with wt% of SWCNT based on simulation and experiments.

[0046] FIG. 8B is a graph showing strength (GPa) and simulated strength (GPa) vs SWCNT (%). The graph shows the trend of strength with wt% of SWCNT based on simulation and experiments.

[0047] FIG. 8C is a graph showing toughness ($\times 100 \text{ MJ/m}^3$) and simulated toughness ($\times 100 \text{ MJ/m}^3$) vs SWCNT (%). The graph shows the trend of toughness with wt% of SWCNT based on simulation and experiments.

[0048] FIG. 9 is a graph providing a comparison of conductivity and toughness performance of an embodiment of a composite disclosed herein (star) as compared to state of the art flexible conductive materials. Results show that the composite disclosed herein has both conductivity and toughness properties which are superior to the state of the art flexible conductive materials, and which is very suitable for electro-tendons.

[0049] **FIG. 10A** is a schematic diagram showing the fabrication process for a pressure sensor according to an embodiment. A silicon (Si) master was prepared, after which silver nanowires (AgNWs) were deposited on the Si master (Step 1) to form a modified silicon master. Then, an elastomer mixture comprising polydimethylsiloxane (PDMS) elastomer and cross-linker was cast on the modified silicon master (Step 2). After degassing under vacuum, the elastomer mixture with the silver nanowires embedded thereto (Ag-nanofiber/PDMS) was cured at 90 °C for 1 hour before being peeled off from the silicon master to form a Ag-nanofiber /PDMS film (Step 3). Finally, Ag-nanofiber /PDMS films were placed face-to-face on a piece of indium tin oxide (ITO)-coated polyethylene terephthalate (PET) film (Sigma Aldrich). Silver paint (Structure Probe, Inc.) was applied to connect graphene or ITO electrodes to copper wires (Step 4). The device was then packaged with two PDMS films to avoid interference (Step 5).

[0050] **FIG. 10B** shows SEM images showing the pyramidal structures of the pressure sensor at different scales. Scale bar in the figures denote 100 μm and 10 μm , respectively.

[0051] **FIG. 10C** shows the index finger of a humanoid robotic hand bending in response to different pressures (0, 117, 327 and 749 Pa). Bottom panels show the voltage signals produced when the pressure sensor was touched. Higher forces resulted in greater bending angles.

DESCRIPTION

[0052] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practised. These embodiments are described in sufficient detail to enable those skilled in the art to practise the invention. Other embodiments may be utilized and

structural, logical, and electrical changes may be made without departing from the scope of the invention. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

[0053] In a first aspect, a flexible and electrically conductive composite is provided. The flexible and electrically conductive composite comprises silk fiber and a coating material comprising an electrically conducting polymer and an electrically conducting nanostructured material disposed on a surface of the silk fiber.

[0054] Examples of silk fibers include silk fibers produced from silkworms and from spiders. In various embodiments, the silk fiber is spider silk. Spider silk, which has been hailed as a “super fiber”, exhibits outstanding mechanical properties due to its unique hierarchical structure based on hydrogen-bonded β -sheet nanocrystals that universally consist of highly conserved poly-(Gly-Ala) and poly-Ala domains. Generally, spider silk may have a density of about 1 g/cm³; strength of about 1 GPa to 2 GPa; modulus of about 2.2 GPa to 10 GPa; toughness of about 160 MJ/m³; and maximum strain of about 30 % to 40 %. For the silk from silkworms, it has a density of about 1 g/cm³; strength of about 400 MPa to 800 MPa; modulus of about 1 GPa to 8 GPa; toughness of about 30 MJ/m³ to 50 MJ/m³; and maximum strain of about 10 % to 25 %.

[0055] In particular, of the various attributes of silk fibers, toughness of spider silk is better than any of the best synthetic high-performance fibers available today, including Kevlar (Dupont Advanced Fiber Systems) which is mainly applied in body armor.

[0056] By disposing a coating material comprising an electrically conducting polymer and an electrically conducting nanostructured material on a surface of the silk fiber, the resultant flexible and electrically conductive composite according to embodiments disclosed herein has high toughness and high electrical conductivity. In particular, when

the silk fiber is spider silk, the flexible and electrically conductive composite disclosed herein has demonstrated a toughness value of up to 420 MJ/m^3 , and an electrical conductivity value of up to 1077 S/cm . These properties are far better than that of present conductive materials. Moreover, the electrical conductivity of the presently disclosed flexible and electrically conductive composite remains nearly unchanged when stretched or compressed, which is helpful for signal transmission.

[0057] The flexible and electrically conductive composite disclosed herein may advantageously be used in an electro-tendon for prostheses. In this regard, an innovative electro-tendon for anatomic robotic hands comprising the flexible and electrically conductive composite was designed by the inventors to make use of these excellent properties to perform dual function of transmitting force from servo motor of dynamical system, as well as electrical signal from pressure sensor of feedback system, which fills the gap towards design and application of tough electrodes for robotic industry. Since the flexible and electrically conductive composite disclosed herein is able to transmit both traction and electrical signal, complex process designs involved with robotic prostheses may be simplified.

[0058] The high toughness property of the flexible and electrically conductive composite renders it particularly attractive for use in fabrication of electro-tendons in prostheses such as humanoid robotic hands, whereby the high toughness property may be exploited to enable bearing of force by the robotic hands from a driving motor to make the robotic hands grasp weights under stretching or compressing of the electro-tendons. Benefitting from these excellent properties of the tendons, the anatomic hand which was assembled by the inventors exhibited reversible, reproducible and durable performance, and was able to accurately feel the stable signals from feedback system when grasping things.

[0059] The flexible and electrically conductive composite disclosed herein is therefore able to address or at least alleviate problems relating to state of the art materials which do not possess good toughness properties, stretchability and/or are not electrically conductive, in order that the robotic hands may store and recover energy at high efficiency.

[0060] With the above in mind, various embodiments disclosed herein refer to a flexible and electrically conductive composite. The term “composite” refers to a material formed of a combination of two or more different materials. The term “flexible” as used herein refers to materials that are compliant and respond in the presence of external forces by deforming readily. For example, the flexible and electrically conductive composite may flex or bend readily upon application of a force on the composite.

[0061] In various embodiments, the flexible and electrically conductive composite is stretchable. The term “stretchable” as used herein refers to the flexible and electrically conductive composite having ability to deform elastically in response to a force such that it extends in length, width and/or other dimensions, and are able to return at least substantially to its original non-extended configuration after removal of the force. By the term “substantially”, this means that the flexible and electrically conductive composite is able to return to at least about 90 % of its original non-extended configuration after removal of the force, such as at least about 93 %, at least about 95 %, at least about 97 %, at least about 99 %, or return to 100 % of its original non-extended configuration after removal of the force.

[0062] For example, the force may be a tension force acting on two portions of a flexible and electrically conductive composite, such that the flexible and electrically conductive composite elongates between the two portions. In various embodiments, the flexible and electrically conductive composite may be stretched such that one or more

dimensions such as length and/or width of the composite has an increase of about 50 % to about 1000 % of its original dimension.

[0063] The flexible and electrically conductive composite comprises silk fiber and a coating material comprising an electrically conducting polymer and an electrically conducting nanostructured material disposed on a surface of the silk fiber.

[0064] In various embodiments, the silk fiber is a silkworm silk or spider silk. Depending on intended application, silkworm silk, spider silk, or a blend of silkworm silk and spider silk may be used as the silk fiber. In some embodiments, the silk fiber is spider silk. The spider silk may be obtained from *Nephila pilipes*.

[0065] The silk fiber may have any suitable length and thickness. In various embodiments, the silk fiber has a thickness in the range of about 2 μm to about 5 μm . For example, the silk fiber may have a thickness in the range of about 3 μm to about 5 μm , about 2 μm to about 4 μm , or about 3 μm to about 4 μm . In some embodiments, the silk fiber has a thickness in the range of 3 μm to about 4 μm .

[0066] The silk fiber may be used singly, or in plurality as a bundle of silk fibers made up from 2, 3, 4, 5, 10, 20, 50, 100, or more fibers.

[0067] Generally, silk fibers obtained directly from a silkworm or from a spider may have a smooth surface. By the term “smooth”, this means that the surface of the silk fiber may have a surface roughness value of less than or equal to 0.25 microns, such as less than 0.15 microns, less than 0.1 microns, or less than 0.05 microns. In some embodiments, surface of the silk fiber has a surface roughness value of a few nanometers, such as a roughness in the range of about 10 nm to about 50 nm, or about 5 nm to about 30 nm. In various embodiments, the surface of the silk fiber may be textured before disposing of the coating material thereon. In so doing, the surface roughness value of the surface of the silk fiber may increase to a value greater than 0.25

microns, such as greater than 0.4 microns, greater than 0.5 microns, or greater than 0.75 microns. Advantageously, texturing of the surface of the silk fiber may allow improved adherence of the coating material which is subsequently disposed thereon due to increase in contact surface area between the surface of the silk fiber and the coating material.

[0068] For example, the surface of the silk fiber may be textured with a nano-island structure before disposing of the coating material thereon. As used herein, the term "nano-island" refers to a distinct area of a layer having a defined geometric shape that is protruding from the layer. A plurality of nano-islands may be present on the surface of the silk fiber. Each of the nano-islands may have a feature size defined herein as a maximal length across the defined geometric shape that is protruding from the layer. Advantageously, it has been demonstrated herein that the nano-island structure of the silk fiber surface also facilitates formation of a wrinkle structure of a coating material that is subsequently disposed on the silk fiber.

[0069] In various embodiments, the nano-island structure may have a feature size in the range of about 10 nm to about 100 nm, such as about 20 nm to about 100 nm, about 30 nm to about 100 nm, about 50 nm to about 100 nm, about 75 nm to about 100 nm, about 10 nm to about 80 nm, about 10 nm to about 70 nm, about 10 nm to about 50 nm, about 10 nm to about 30 nm, about 20 nm to about 80 nm, about 30 nm to about 70 nm, or about 40 nm to about 60 nm.

[0070] A coating material comprising an electrically conducting polymer and an electrically conducting nanostructured material is disposed on a surface of the silk fiber.

[0071] In various embodiments, the electrically conducting polymer is selected from the group consisting of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS), a poly(thiophene), a polycarbazole, a polyindole, a polyazepine, a

polyaniline, a copolymer thereof, and a combination thereof. In some embodiments, the electrically conducting polymer comprises or consists of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS).

[0072] In specific embodiments, the electrically conducting polymer is poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS).

[0073] In addition to the electrically conducting polymer, the coating material further comprises an electrically conducting nanostructured material. As used herein, the term “nanostructured material” refers to a material having a size in the nanometer range. The term “electrically conducting nanostructured material” as used herein refers to a nanostructured material that allows flow of electric charges in one or more directions within or through the material.

[0074] The electrically conducting nanostructured material may be present in the coating material at an amount of up to 12.5 wt%. For example, the electrically conducting nanostructured material may be present in the coating material at an amount in the range of about 2.5 wt% to about 12.5 wt%, such as about 3.5 wt% to about 12.5 wt%, about 5 wt% to about 12.5 wt%, about 7.5 wt% to about 12.5 wt%, or about 7.5 wt% to about 10 wt%. In various embodiments, the electrically conducting nanostructured material is present in the coating material at an amount in the range of about 7.5 wt% to about 10 wt%.

[0075] The electrically conducting nanostructured material may be selected from the group consisting of nanotubes, nanowires, nanofibers, nanoparticles, and combinations thereof. In some embodiments, the electrically conducting nanostructured material comprises or consists of nanotubes.

[0076] Generally, any electrically conducting nanomaterial may be used for the electrically conducting nanostructured material. For example, the electrically

conducting nanostructured material may comprise or consist of a metal, a metal oxide, graphene, carbon nanotubes, or combinations thereof.

[0077] In various embodiments, the metal or metal oxide comprises or consists of a metal selected from the group consisting of Ag, Au, Pt, Cu, Ni, Ti, Cr, Co, Fe, Al, Zn, W, V, and combinations thereof.

[0078] In various embodiments, the electrically conducting nanostructured material comprises or consists of carbon nanotubes, such as multi-walled carbon nanotubes or single-walled carbon nanotubes. The carbon nanotubes may or may not be functionalized.

[0079] In some embodiments, the electrically conducting nanostructured material comprises or consists of single-walled carbon nanotubes. The single-walled carbon nanotubes may be metallic single-walled carbon nanotubes, semiconducting single-walled carbon nanotubes or combinations thereof.

[0080] Single-walled carbon nanotubes refer generally to seamless cylinders formed from one graphene layer. For example, carbon nanotubes may be described as a graphene sheet rolled into a hollow cylindrical shape so that the structure is one-dimensional with axial symmetry, and in general exhibiting a spiral conformation, called chirality. Other structural types of single-walled carbon nanotubes, such as zigzag or armchair, may also be used. A single-walled carbon nanotubes may be defined by a cylindrical sheet with a diameter of about 0.7 nm to about 20 nm, such as about 1 nm to about 20 nm.

[0081] Size of the single-walled carbon nanotubes may be characterized by their diameter and/or their length. The term "diameter" as used herein refers to the maximal length of a straight line segment, when applied to a cross-section of each single-walled carbon nanotube, which passes through the center of the single-walled carbon nanotubes

and terminating at the periphery. Average diameter of the single-walled carbon nanotubes may be calculated by dividing the sum of the diameter of each nanotube by the total number of nanotubes.

[0082] In various embodiments, the single-walled carbon nanotubes have an average diameter in the range of about 1 nm to about 20 nm, such as about 5 nm to about 20 nm, about 10 nm to about 20 nm, about 1 nm to about 15 nm, about 1 nm to about 10 nm, or about 5 nm to about 10 nm.

[0083] The single-walled carbon nanotubes may be of any desired length, such as in the range from about 0.1 nm to about 10 μm , about 1 nm to about 5 μm , or about 10 nm to about 1 μm . In some embodiments, the single-walled carbon nanotubes may be at least 1 μm or at least 2 μm , or between about 0.5 μm and about 1.5 μm , or between about 1 μm and about 5 μm .

[0084] In specific embodiments, the flexible and electrically conductive composite comprises silk fiber and a coating material formed of PEDOT:PSS and single-walled carbon nanotubes disposed on a surface of the silk fiber.

[0085] The coating material comprising an electrically conducting polymer and an electrically conducting nanostructured material which is disposed on a surface of the silk fiber may form a continuous layer on the surface of the silk fiber. By the term “continuous”, this means that the coating material at least substantially covers an entire surface of the silk fiber, such as at least about 80%, at least about 90 %, at least about 95 %, at least about 98 % or 100 % of an entire surface of the silk fiber.

[0086] Thickness of the layer formed by the coating material on the silk fiber may be in the range of about 1 μm to about 100 μm . For example, thickness of the layer may be in the range of about 5 μm to about 100 μm , about 10 μm to about 100 μm , about 20 μm to about 100 μm , about 50 μm to about 100 μm , about 1 μm to about 80 μm , about 1

μm to about 50 μm , about 1 μm to about 30 μm , about 10 μm to about 80 μm , or about 30 μm to about 70 μm .

[0087] In various embodiments, the coating material forms a layer having a wrinkle structure on the surface of the silk fiber. By the term “wrinkle structure”, this means that the coating material does not form a smooth surface on the surface of the silk fiber, and instead forms ripples or creases on the surface of the silk fiber. In embodiments wherein the coating material forms a layer having a wrinkle structure, thickness of the coating material is measured from the underlying surface and includes a height of the wrinkles comprised in the wrinkle structure. The height of the wrinkles may range from about 10 nm to about 10 μm , such as about 50 nm to about 10 μm , about 100 nm to about 10 μm , about 1 μm to about 10 μm , about 2 μm to about 10 μm , about 5 μm to about 10 μm , about 10 nm to about 8 μm , about 10 nm to about 5 μm , about 10 nm to about 3 μm , about 10 nm to about 1 μm , about 500 nm to about 5 μm , about 1 μm to about 8 μm , or about 1 μm to about 5 μm .

[0088] The wrinkle structure of the coating material may be formed through contacting of the silk fiber with a liquid such as an organic solvent, or an aqueous solution comprising water, or water so as to result in shrinkage of the silk fiber. The wrinkle structure may be obtained upon drying of the liquid from the silk fiber. Examples of organic solvent may include acetone, and an alcohol such as methanol, ethanol, propanol, and isopropanol. In various embodiments, the wrinkle structure of the coating material is formed through contacting of the silk fiber with water. Advantageously, the wrinkle structure may allow electrical conductivity of the flexible and electrically conductive composite to remain stable with increase in strain, as conductive path of the coating material may remain unchanged due to gradual flattening of the wrinkles when the composite is under strain, such as when it is being stretched.

[0089] In various embodiments, the electrical conductivity of the composite remains essentially constant or constant when the composite is subjected to a strain of up to 20 %. By the term “essentially constant”, this means that the electrical conductivity of the composite may have a variance of less than about 5 %, such as less than about 2 %, preferably less than about 1 %, even more preferably less than about 0.5 %.

[0090] According to a second aspect, a method of preparing a flexible and electrically conductive composite is provided. The method comprises providing silk fiber, and disposing a coating material comprising an electrically conducting polymer and an electrically conducting nanostructured material on a surface of the silk fiber. The silk fiber may be used singly, or in plurality as a bundle of silk fibers made up from 2, 3, 4, 5, 10, 20, 50, 100, or more fibers.

[0091] In various embodiments, providing the silk fiber comprises forming a texture on a surface of the silk fiber. For example, forming a texture on the surface of the silk fiber may comprise forming a nano-island structure on the surface of the silk fiber. As mentioned above, the nano-island structure may have a feature size in the range of about 10 nm to about 100 nm.

[0092] In various embodiments, providing the silk fiber comprises hydrophilicizing a surface of the silk fiber; contacting the hydrophilicized silk fiber with a metal ion to form a metal ion-modified silk fiber; contacting the metal ion-modified silk fiber with an organic acceptor to form an organic acceptor-modified silk fiber; and annealing the organic acceptor-modified silk fiber.

[0093] Hydrophilicizing the surface of the silk fiber may comprise subjecting the surface of the silk fiber to plasma in an oxygen atmosphere. The plasma treatment may be carried out for any suitable period of time, such as about 5 minutes, about 10 minutes, about 20 minutes, or about 30 minutes.

[0094] Following hydrophilicizing, the hydrophilicized silk fiber may be contacted with a metal ion to form a metal ion-modified silk fiber. Contacting the hydrophilicized silk fiber with a metal ion may comprise immersing the hydrophilicized silk fiber in a solution comprising the metal ion. The metal ion may be selected from the group consisting of silver ion, cupric ion, aluminium ion, iron ion, and a combination thereof.

[0095] In various embodiments, the solution comprising the metal ion is a solution comprising a salt of the metal. The salt of the metal may be at least substantially dissolved in an aqueous solution, an organic solvent, such as acetone, and/or an alcohol-based solvent such as methanol, ethanol, propanol, and isopropanol. In some embodiments, the solution comprising the metal ion is a solution comprising a salt of the metal and an alcohol-based solvent. The salt of the metal may, for example, be selected from the group consisting of metal nitrate, metal sulfate, metal phthalate, metal phosphate, metal carbonate, and a combination thereof.

[0096] Examples of an alcohol-based solvent include, but are not limited to, methanol, ethanol, propanol, and isopropanol. In various embodiments, the alcohol-based solvent comprises or consists of ethanol.

[0097] In specific embodiments, the metal salt is silver nitrate and the alcohol-based solvent is ethanol.

[0098] Concentration of the metal salt in the solution may be any suitable value, such as in the range of about 0.05 mol/L to about 0.2 mol/L, for example, about 0.1 mol/L to about 0.2 mol/L, about 0.05 mol/L to about 0.1 mol/L, or about 0.1 mol/L.

[0099] The metal ion-modified silk fiber may be contacted with an organic acceptor to form an organic acceptor-modified silk fiber. Contacting the metal ion-modified silk fiber with an organic acceptor may comprise immersing the metal ion-modified silk fiber in a mixture comprising the organic acceptor. The mixture comprising the organic

acceptor may comprise the organic acceptor and a suitable solvent such as an aqueous solution or an alcohol. In some embodiments, the mixture comprising the organic acceptor comprises the organic acceptor and an alcohol.

[00100] The organic acceptor may be selected from the group consisting of tetracyanoquinodimethane, tetracyanoethylene, and a combination thereof. In some embodiments, the organic acceptor comprises or consists of tetracyanoquinodimethane.

[00101] Examples of an alcohol include, but are not limited to, methanol, ethanol, propanol, and isopropanol. In various embodiments, the alcohol comprises or consists of ethanol.

[00102] In specific embodiments, the organic acceptor is tetracyanoquinodimethane, and the alcohol is ethanol.

[00103] Concentration of the organic acceptor in the mixture may be any suitable value, such as in the range of about 0.001 mol/L to about 0.1 mol/L, for example, about 0.005 mol/L to about 0.1 mol/L, about 0.01 mol/L to about 0.1 mol/L, or about 0.01 mol/L.

[00104] In some embodiments, immersing the metal ion-modified silk fiber in the mixture comprising the organic acceptor is carried out by drop flowing. For example, the mixture may contact the metal ion-modified silk fiber in a drop flow arrangement, so that each drop of the mixture is allowed to flow along the length of the metal ion-modified silk fiber from an end region to an opposing end region of the silk fiber. The flow rate may range from about 1 to about 3 drops per second, and may take place for a time period of about 3 to 10 minutes.

[00105] The organic acceptor-modified silk fiber may be annealed. Advantageously, annealing the organic acceptor-modified silk fiber in an inert environment is not required, as the annealing may be carried out in air. Annealing the

organic acceptor-modified silk fiber may be carried out at a temperature in the range of about 80 °C to about 120 °C, such as about 90 °C to about 120 °C, about 100 °C to about 120 °C, about 80 °C to about 110 °C, about 80 °C to about 100 °C, about 90 °C to about 110 °C, or about 100 °C. In various embodiments, annealing the organic acceptor-modified silk fiber is carried out at a temperature of about 100 °C. The annealing may be carried out for a time period in the range of about 3 minutes to about 10 minutes, such as about 5 minutes to about 10 minutes, about 7 minutes to about 10 minutes, or about 5 minutes to about 8 minutes.

[00106] The method of preparing a flexible and electrically conductive composite comprises disposing a coating material comprising an electrically conducting polymer and an electrically conducting nanostructured material on a surface of the silk fiber.

[00107] In various embodiments, disposing the coating material comprises immersing the silk fiber in a solution comprising the coating material and a suitable solvent such as an aqueous solution or an organic solvent. Examples of suitable organic solvent include acetone and an alcohol such as methanol, ethanol, propanol, and isopropanol. In some embodiments, disposing the coating material comprises immersing the silk fiber in an aqueous solution comprising the coating material. As mentioned above, contacting of the silk fiber with an organic solvent or with water present in an aqueous solution may result in shrinkage of the silk fiber so that the silk fiber having the coating material disposed thereon may have a wrinkle structure.

[00108] Immersing the silk fiber in the solution comprising the coating material may be carried out by drop flowing. For example, the solution may contact the silk fiber in a drop flow arrangement, so that each drop of the solution is allowed to flow along the length of the silk fiber from an end region to an opposing end region of the silk fiber. Advantageously, drop flowing allows conformal contact between the silk fiber

and electrically conductive layer, such as that shown in **FIG. 2C**. The flow rate may range from about 1 to about 5 drops per 1 to 5 seconds, such as about 1 to 3 drops per 2 to 5 seconds, and may take place for a time period of about 5 to 10 minutes. Speed at which the drop flowing is carried out and concentration of the electrically conducting nanostructured material in the solution, for example, may be controlled to affect morphology of the resultant wrinkle structure. In some embodiments, the flow rate may range from 1 to 5 drops per 1 to 5 seconds, while concentration of the electrically conducting nanostructured material in the coating material may be present at an amount of up to 12.5 wt%.

[00109] The coating material comprising the electrically conducting polymer and the electrically conducting nanostructured material may be dispersed in the solution. In various embodiments, the coating material may be well dispersed. Methods such as agitation, stirring or sonication may be used to disperse coating material in the solution. Concentration of the electrically conducting nanostructured material in the solution may be of any suitable value, so that the electrically conducting nanostructured material may be present in the coating material at an amount of up to 12.5 wt%, such as in the range of about 2.5 wt% to about 12.5 wt%.

[00110] Examples of suitable electrically conducting polymer and electrically conducting nanostructured material have already been discussed above.

[00111] In various embodiments, the electrically conducting polymer is selected from the group consisting of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS), a poly(thiophene), a polycarbazole, a polyindole, a polyazepine, a polyaniline, a copolymer thereof, and a combination thereof. In some embodiments, the electrically conducting polymer comprises or consists of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS).

[00112] In various embodiments, the electrically conducting nanostructured material is selected from the group consisting of nanotubes, nanowires, nanofibers, nanoparticles, and combinations thereof. The electrically conducting nanostructured material may comprise or consist of a metal, a metal oxide, graphene, carbon nanotubes, or combinations thereof. In various embodiments, the electrically conducting nanostructured material comprises or consists of carbon nanotubes. For example, the electrically conducting nanostructured material may comprise or consist of single-walled carbon nanotubes.

[00113] The method of preparing a flexible and electrically conductive composite may further comprise annealing the silk fiber having the coating material disposed thereon. As in the case for annealing the organic acceptor-modified silk fiber mentioned above, annealing the silk fiber having the coating material in an inert environment is not required, as the annealing may be carried out in air. Annealing the silk fiber having the coating material disposed thereon may be carried out at any suitable temperature. In various embodiments, annealing the silk fiber having the coating material disposed thereon is carried out at a temperature in the range of about 60 °C to about 100 °C, such as about 70 °C to about 100 °C, about 80 °C to about 100 °C, about 60 °C to about 90 °C, about 60 °C to about 80 °C, about 70 °C to about 90 °C, or about 80 °C. The annealing may be carried out for a time period in the range of about 3 minutes to about 15 minutes, such as about 5 minutes to about 15 minutes, about 7 minutes to about 15 minutes, about 3 minutes to about 12 minutes, about 3 minutes to about 10 minutes, or about 5 minutes to about 10 minutes.

[00114] In a third aspect, a flexible and electrically conductive composite prepared by a method according to the second aspect is provided.

[00115] According to a fourth aspect, a prosthesis comprising a flexible and electrically conductive composite according to the first aspect or prepared by a method according to the second aspect is provided.

[00116] The prosthesis may, for example, be a robotic hand. The flexible and electrically conductive composite may be comprised in the prosthesis as an electro-tendon. The electro-tendon may be of any suitable length and thickness, which may be tailored according to the dimensions of the prosthesis.

[00117] In a fifth aspect, use of a flexible and electrically conductive composite according to the first aspect or prepared by a method according to the second aspect in prosthesis, stretchable electronics, biomedical devices, implantable electronics, photodetectors, capacitors, electrochromic devices, strain gauges, sensors, wearable electronics, clean energy devices, smart clothes, and sensory skin for robotic systems, is also provided.

[00118] In order that the invention may be readily understood and put into practical effect, particular embodiments will now be described by way of the following non-limiting examples.

EXAMPLES

[00119] It remains a big challenge to develop a super/highly tough conducting material for use in prostheses such as robotic hands.

[00120] Various embodiments disclosed herein refer to a flexible conducting composite, comprising: silk fiber, such as spider silk, coated with a coating of conducting polymer, such as poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) and single-walled carbon nanotubes (SWCNTs). The coating may comprise a layer of wrinkled structures, and/or the conductivity of the composite may remain almost unchanged when stretched/compressed to a strain of 0 to 20 %.

[00121] Various embodiments disclosed herein refer to a method of forming a flexible conducting composite, comprising: a) providing a cleaned silk fiber, such as spider silk; b) treating the silk fiber with plasma under oxygen gas atmosphere; c) immersing the plasma-treated silk fiber in a solution of silver ions to form silver ion-modified silk fiber; d) coating the silver ion-modified silk fiber with a solution of tetracyanoquinodimethane (TCNQ), such as 0.001 mol/L to 0.1 mol/L of TCNQ in ethanol, to form TCNQ-coated silk fiber, wherein the coating may be carried out via drop flowing method with a flow rate of 1 to 3 drop per second for about 3 to 10 minutes; e) annealing the TCNQ-coated silk fiber at 80 °C to 120 °C for 3 to 10 minutes in air atmosphere; f) coating the annealed silk fiber with a solution of conducting polymer, including PEDOT:PSS, and 2.5 wt% to 12.5 wt% of SWCNTs to form conducting polymer/SWCNT-coated silk fiber, wherein the coating may be carried out via drop flowing method with a flow rate of 1 to 3 drops per 2 to 5 second for about 5 to 10 minutes; and g) annealing the conducting polymer/SWCNT-coated silk fiber at 80 to 100 °C for 3 to 15 minutes in air atmosphere.

[00122] High conductive of spider silk composites unchanged under stretching and compressing.

[00123] Spider silk, which has been hailed as a “super fiber”, exhibit outstanding mechanical properties due to the unique hierarchical structure based on hydrogen-bonded β -sheet nanocrystals that universally consist of highly conserved poly-(Gly-Ala) and poly-Ala domains.

[00124] According to various embodiments disclosed herein, spider silk from *Nephila pilipes*'s, a common spider in Singapore, was collected for the experiments. The surface of the virgin spider silk (VS) was very smooth and the diameter was about 3 μm to 4 μm . However, a layer of wrinkle structure tend to be formed after coating

PEDOT:PSS@SWCNT due to the intrinsic shrinkage of spider silk induced by the solution of water. Consequently, the stretchability of the modified silk composite improved nearly two times from 33 % to 56 %. On the other hand, due to the layer of PEDOT:PSS, VS became conductive and the conductivity was about 370 S/cm. By adding more SWCNT in PEDOT:PSS, the conductivity can be further enhanced and a conductivity of 1077 S/cm was achieved with 7.5 % SWCNT. Interestingly, the conductivity of the composite was nearly unchanged when it was stretched/compressed from 0 to 20 % (the maximum strain of human tendon is 13 % to 18 %) for more than 1000 cycles. From the scanning electron microscope (SEM) images of the evolution of microstructure at same area under different strain, the wrinkle structure of conductive layer of PEDOT:PSS@SWCNT gradually flattened which resulted in no change in the conductive path. Therefore, the conductivity of the sample remained stable when the strain increased.

[00125] Excellent mechanical properties of the conductive spider silk composite

[00126] Besides the conductivity of the spider silk, the mechanical properties were successfully tuned by the content of SWCNT as observed from strain-stress loops. Especially, the toughness (the area of strain-stress curves is toughness, also means breaking energy) of the spider silk was enhanced when coated with PEDOT:PSS with more SWCNT. From 200 to 300 samples, compared with VS, the toughness increased nearly 2 to 3 times to 420 MJ/m³ when wt% of SWCNT was 10 %. In addition, Young's modulus and tensile strength of the spider silk composites also improved with increasing of wt% of SWCNT, with tensile strength at 1.48 GPa when wt% of SWCNT was 10 %.

[00127] Highly tough conductive spider silk used as the tendon in prosthesis

[00128] Encouraged by the excellent properties with toughness of 420 MJ/m³, stretchability of 56 %, Young's modulus of 5.7 GPa, tensile strength of 1.48 GPa and conductivity of 1077 S/cm, the inventors used the spider silk coated with PEDOT:PSS@ 10 % SWCNT as tendon and ligament to assemble an anatomic robotic hand to perform some basic works like human hands. Surprisingly, the loading weight of the finger based on modified spider silk composite (C-spider silk) was about 8 kg. And the anatomic hand the inventors assembled not only exhibit reversible, reproducible and durable performance but also accurately feel the stable signals from feedback system when grasping things. Supertough electro-tendons based on spider silk composites may be obtained.

[00129] **Example 1: Preparation of conductive spider silk composite**

[00130] **A) Feeding the spider and collection of the spider silk**

[00131] The spider was kept in an 80 × 60 × 40-cm vivarium, consisting of wood panels and artificial plants (shown in **FIG. 1A**). The spider was kept at humidity above 65 % and temperature about 25 °C. The spider was fed live locusts and flies three time a week. The inventors collected the spider silk every two weeks using a scalpel for transfer within a rigid frame. Herein, a classic spider silk, dragline, as an example was used. The diameter was about 3 μm to 4 μm (**FIG. 1B**), and the surface was smooth.

[00132] **B) Preparation of nano-island structure on the spider silk**

[00133] Firstly, the collected raw spider silk was rinsed by ethanol (Absolute, 99.9%) three times and dried at 80 °C for about 12 hours. Then, the spider silk was hydrophilized by the plasma under O₂ atmosphere for 10 min, forming hydrophilic groups, such as hydroxyl groups on the surface of spider silk (**FIG. 2A, a**).

[00134] Secondly, the modified spider silk was immersed in 0.1 mol/L silver nitrate (AgNO_3) in ethanol for 5 min. The hydrophilic group -OH was changed into -OAg as the seeds for nano-island structure growth (**FIG. 2A, b**).

[00135] Thirdly, the spider silk-OAg was immersed in 0.01 mol/L tetracyanoquinodimethane (TCNQ) in ethanol through the method of drop flowing and annealed (5 min, 100 °C) to form a layer of nano-island structure. Specifically, the spider silk-OAg was laid along the beaker. The 0.01 mol/L TCNQ dropped from the funnel and flowed past the spider silk-OAg at a flow rate of about 1 drop per 1 second. The whole process took about 10 min. After that, the modified spider silk-OAg was annealed for 5 min at 100 °C. At last, a nano-island structure formed on the surface of spider silk (**FIG. 2A, c**, and image (i) shown in **FIG. 2A**).

[00136] **C) Preparation of conductive composite spider silk**

[00137] The inventors prepared PEDOT:PSS solution with 2.5 %, 5 %, 7.5 %, 10 %, and 12.5 % SWNCT. And then, the spider silk of **FIG. 2A, c** was immersed in the PEDOT:PSS solution also via the method of drop flowing. The rate was 1 drop per 5 second. After annealing at 80 °C for 5 min, the diameter changed from a range of about 3 μm to 4 μm , to a range of about 6 μm to 7 μm and a conducting wrinkle structure was formed on the surface of spider silk which was very helpful for unchanged conductivity during stretching/compression. The reason for the wrinkle structure was the intrinsic shrinkage of spider silk induced by the solution of water in PEDOT:PSS (**FIG. 2A, d** and image ii shown in **FIG. 2A**).

[00138] **Example 2: Detailed principle of design and fabrication, and related testing results**

[00139] **A) Mechanical and electrical properties of spider silk composite**

[00140] After modifying, the stretchability of the modified spider silk composite (C-spider silk) improved nearly two times from 33 % to 56 %. More importantly, the mechanical properties were successfully tuned by the content of SWCNT from strain-stress loops (**FIG. 3A**). Especially, the toughness (the area of strain-stress curves is toughness, also means breaking energy) of the spider silk was enhanced when coating PEDOT:PSS with more SWCNT. From the 200 to 300 samples tested by the inventors (**FIG. 3B**), compared with VS, the toughness increased nearly 2 to 3 times to 420 MJ/m³ when wt% of SWCNT was 10 %. In addition, Young's modulus (**FIG. 3C**) and tensile strength (**FIG. 3D**) of the spider silk composites also improved with increasing of wt% of SWCNT.

[00141] Due to the layer of PEDOT:PSS, VS coated with the layer of PEDOT:PSS without SWCNT became electrically conductive, but the electrical conductivity was about 370 S/cm. With incorporation and increasing amount of SWCNT in PEDOT:PSS, the electrical conductivity further enhanced and achieved 1077 S/cm at 7.5% SWCNT (**FIG. 4A**).

[00142] It was surprisingly found by the inventors that the electrical conductivity of the composite was nearly unchanged when it stretched/compressed from 0 to 20 % (the maximum strain of human tendon is 13 % to 18 %) under more 1000 cycles (**FIG. 4B**). From the SEM (scanning electron microscope) images of the evolution of microstructure at same area under different strain (**Fig. 4C**), the wrinkle structure of conductive layer of PEDOT:PSS@SWCNT gradually flattened which resulted in no change of the conductive path. Therefore, the conductivity of the sample remained stable along the strain increased.

[00143] **Example 3: Feedback action of anatomic robotic hand with highly tough conductive spider silk composite**

[00144] Encouraged by the excellent properties with toughness of 420 MJ/m³, stretchability of 56 %, Young's modulus of 5.7 GPa, tensile strength of 1.48 GPa and conductivity of 1077 S/cm, spider silk coated with PEDOT:PSS@ 10% SWCNT was used as tendon and ligament to assemble an anatomic robotic hand to perform some basic works like human hands.

[00145] **FIG. 5A** shows a specific structure of the humanoid robotic hand that the inventors have fabricated. Firstly, besides the C-spider silk (modified spider silk composite), some other conductive materials/matrix were used such as steel fiber which represents the metal materials, silicone rubber fiber which represents the materials based on PDMS and commercial carbon fiber which represents the target materials with lower toughness to compare with the performance of the robotic hands (**FIG. 5B**) made from these materials. The diameter of these fibers was about 0.3 mm. Surprisingly, the loading weight of the finger based on C-spider silk was about 8 kg which nearly came up to that based on steel fiber of about 9.5 kg (**FIG. 5B**).

[00146] The loading weight of finger based on commercial carbon fiber, natural spider silk and silicone rubber fiber was about 4.2 kg, 4 kg, and about 0.7 kg, respectively. The measured values of the loading weight of the five materials were lower than the theoretical values and it may be due to the knots of the tendons and structure of the hands.

[00147] When the tendons transmitted the force from the motor, the finger bent and then the angle between it and vertical direction increased. As shown in **FIG. 5C**, the angle was about 8 ° when index finger under natural state. Correspondingly, the angle gradually changed to 73 ° when it bent to final state dragged by tendons. The same bending procedure was carried out for the other fingers. However, as shown for the

irreversible steel fiber, the finger cannot complete a full bending action (**FIG. 5D ii**) due to the poor flexibility and stretchability.

[00148] For the finger based on silicone rubber fiber (**FIG. 5D iv**), it only bent at very small angle of about 27 ° even under larger relative length pulled by tendons which originated from the low toughness. Although the finger based on C-spider silk and carbon fiber could successfully finished a full bending process (**FIG. 5D i and iii**), the poor shear strength of the carbon fiber only allows the finger to repeat the bending action several times (**FIG. 5E**). From the results of endurance experiment shown in **FIG. 5F** and **FIG. 5G**, it was apparent that C-spider silk could complete over 1000 cycles tests and was more suitable for tendons of anatomic robotic hands.

[00149] Besides transmitting the traction from motor mentioned above, the other important function of the electro-tendons is to stably transfer the signal from the feedback system when the robotic hands moving. To check this performance, the inventors designed a pressure feedback system, using the procedure described below (**FIG. 6A**).

[00150] **A) Fabrication of the pressure sensor – preparing the silicon master**

[00151] (100) Si wafers with 280 nm silicon dioxide (SiO₂) layer were inlaid with grid patterns by photolithography (SUSS MJB4 Mask Aligner, Garching). The exposed SiO₂ patterns were etched by a buffered oxide etch (BOE) (NH₄F: HF = 7:1, v/v). The substrate was then anisotropically etched by a wet etching solution (35 wt% KOH in H₂O: Isopropanol = 4:1, v/v) at 80 °C under vigorous stirring to form recessed pyramid patterns. The remaining SiO₂ layer was removed by BOE. After washing with DI water, the Si masters were modified with 1H,1H,2H,2H-perfluorodecyltrichlorosilane (Gelest, Inc.) by gas phase silanization to prevent adhesion.

[00152] B) Fabrication of the pressure sensor – preparation of the microstructured Ag-nanofiber PDMS films

[00153] Ag-nanofiber suspensions (0.5 g/L) was sprayed on the Si master to form a modified silicon master. Then PDMS elastomer and cross-linker (Sylgard 184, Tow Corning) were mixed (10:1, w/w) and stirred for 10 min, and then cast on the modified silicon master. After degassing under vacuum, the elastomer mixture is cured at 90 °C for 1 hour before being peeled off from the silicon master.

[00154] C) Fabrication of the pressure sensor device

[00155] Ag-nanofiber /PDMS films were placed face-to-face on a piece of ITO-coated PET film (Sigma Aldrich). Silver paint (Structure Probe, Inc.) was applied to connect graphene or ITO electrodes to copper wires. The device was then packaged with two PDMS films to avoid interference.

[00156] The pressure sensor based on the pyramid structure prepared using the procedure described above had sensitivity of about 24.8 kPa⁻¹. This sensor can detect pressures from 0 to 1 kPa in less than 4 ms, which is enough for the grasping experiments described herein. As mentioned, the pressure sensor is based on a pyramid structure which assembled on the tip of index finger connected with a reference resistor by the electro-tendon (the demo shown in **FIG. 6B**). Firstly, the sensor was bonded on the tip of finger by superglue. Then, the pins of sensors were bonded onto the electro-tendons by conductive silver paste. The resistance of the electro-tendon was nearly unchanged for the finger under bending (**FIG. 6C**).

[00157] The inventors touched the pressure sensor with different force, the finger bent at different relative angles. The result showed that the electro-tendons were able to transmit the electrical signal from pressure sensor.

[00158] Next, the inventors used the anatomic robotic hand based on the electro-tendon to grasp a green balloon and compared with another robotic hand based on non-conductive materials nylon which is a common material for tendon. It was found that the robotic finger with C-spider silk could catch the balloon with no deformation because of the pressure feedback system to make the hand stop at a suitable pressure (**FIG. 6D**). For tendon with non-conductive nylon, the fingers have bent over and even the balloon have dropped out due to no signal from pressure feedback system to make hand stop (**FIG. 6E**).

[00159] **Example 4: Commercial applications of the invention**

[00160] Supertough conductive spider silk composite in this work have filled the gap of flexible and stretchable tough conductor for robots. Benefitting from the toughness of 420 MJ/m^3 and conductivity of 1077 S/cm , the inventors realized an electro-tendon with dual-function of transmitting force from servo motor from dynamical system and electrical signal from press sensor of feedback system. And the anatomic hands assembled by electro-tendons could well perform a whole process of grasping things including how to make the finger move and when to stop the finger. Although this work focused on the implementation of electro-tendons, the supertough flexible conductor could also serve as electrode for interconnector for highly tough flexible electronic circuits, anti-static durable woven and tough cables of mechanics.

[00161] Advantageously, benefitting from the toughness of 420 MJ/m^3 and conductivity of 1077 S/cm , the modified spider silk can be applied as an electro-tendon with dual function of transmitting force from motor and electrical signal from feedback system in robots. The anatomic hands assembled by electro-tendons could well perform a whole process of grasping things including how to make the finger move and when to

stop the finger. Supertough conductive spider silk composite according to embodiments disclosed herein have filled the gap of flexible conductor for robots.

[00162] By “comprising” it is meant including, but not limited to, whatever follows the word “comprising”. Thus, use of the term “comprising” indicates that the listed elements are required or mandatory, but that other elements are optional and may or may not be present.

[00163] By “consisting of” is meant including, and limited to, whatever follows the phrase “consisting of”. Thus, the phrase “consisting of” indicates that the listed elements are required or mandatory, and that no other elements may be present.

[00164] The inventions illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms “comprising”, “including”, “containing”, etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the inventions embodied therein herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention.

[00165] By “about” in relation to a given numerical value, such as for temperature and period of time, it is meant to include numerical values within 10% of the specified value.

[00166] The invention has been described broadly and generically herein. Each of the narrower species and sub-generic groupings falling within the generic disclosure also form part of the invention. This includes the generic description of the invention with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

[00167] Other embodiments are within the following claims and non-limiting examples. In addition, where features or aspects of the invention are described in terms of Markush groups, those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

CLAIMS

1. A flexible and electrically conductive composite comprising silk fiber and a coating material comprising an electrically conducting polymer and an electrically conducting nanostructured material disposed on a surface of the silk fiber.
2. The flexible and electrically conductive composite according to claim 1, wherein the silk fiber is spider silk.
3. The flexible and electrically conductive composite according to claim 1 or 2, wherein the surface of the silk fiber was textured before disposing of the coating material thereon.
4. The flexible and electrically conductive composite according to claim 3, wherein the surface of the silk fiber was textured with a nano-island structure before disposing of the coating material thereon.
5. The flexible and electrically conductive composite according to any one of claims 1 to 4, wherein the electrically conducting polymer is selected from the group consisting of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS), a poly(thiophene), a polycarbazole, a polyindole, a polyazepine, a polyaniline, a copolymer thereof, and a combination thereof.

6. The flexible and electrically conductive composite according to any one of claims 1 to 5, wherein the electrically conducting polymer comprises or consists of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS).
7. The flexible and electrically conductive composite according to any one of claims 1 to 6, wherein the electrically conducting nanostructured material is selected from the group consisting of nanotubes, nanowires, nanofibers, nanoparticles, and a combination thereof.
8. The flexible and electrically conductive composite according to any one of claims 1 to 7, wherein the electrically conducting nanostructured material comprises or consists of a metal, a metal oxide, graphene, carbon nanotubes, or a combination thereof.
9. The flexible and electrically conductive composite according to any one of claims 1 to 8, wherein the electrically conducting nanostructured material comprises or consists of carbon nanotubes.
10. The flexible and electrically conductive composite according to any one of claims 1 to 9, wherein the electrically conducting nanostructured material is present in the coating material at an amount of up to 12.5 wt%.
11. The flexible and electrically conductive composite according to any one of claims 1 to 10, wherein the coating material forms a continuous layer on the surface of the silk fiber.

12. The flexible and electrically conductive composite according to any one of claims 1 to 11, wherein the coating material forms a layer having a wrinkle structure on the surface of the silk fiber.

13. The flexible and electrically conductive composite according to any one of claims 1 to 12, wherein the flexible and electrically conductive composite is stretchable.

14. The flexible and electrically conductive composite according to any one of claims 1 to 13, wherein electrical conductivity of the composite remains essentially constant or constant when the composite is subjected to a strain of up to 20 %.

15. A method of preparing a flexible and electrically conductive composite, the method comprising

- a) providing silk fiber, and
- b) disposing a coating material comprising an electrically conducting polymer and an electrically conducting nanostructured material on a surface of the silk fiber.

16. The method according to claim 15, wherein providing the silk fiber comprises forming a texture on a surface of the silk fiber.

17. The method according to claim 16, wherein forming a texture on the surface of the silk fiber comprises forming a nano-island structure on the surface of the silk fiber.

18. The method according to any one of claims 15 to 17, wherein providing the silk fiber comprises

- a) hydrophilicizing a surface of the silk fiber;
- b) contacting the hydrophilicized silk fiber with a metal ion to form a metal ion-modified silk fiber;
- c) contacting the metal ion-modified silk fiber with an organic acceptor to form an organic acceptor-modified silk fiber; and
- d) annealing the organic acceptor-modified silk fiber.

19. The method according to claim 18, wherein hydrophilicizing the surface of the silk fiber comprises subjecting the surface of the silk fiber to plasma in an oxygen atmosphere.

20. The method according to claim 18 or 19, wherein contacting the hydrophilicized silk fiber with a metal ion comprises immersing the hydrophilicized silk fiber in a solution comprising the metal ion.

21. The method according to any one of claims 18 to 20, wherein the metal ion is selected from the group consisting of silver ion, cupric ion, aluminium ion, iron ion, and a combination thereof.

22. The method according to any one of claims 18 to 21, wherein contacting the metal ion-modified silk fiber with an organic acceptor comprises immersing the metal ion-modified silk fiber in a mixture comprising the organic acceptor.

- 23.** The method according to claim 22, wherein immersing the metal ion-modified silk fiber in the mixture comprising the organic acceptor is carried out by drop flowing.
- 24.** The method according to any one of claims 18 to 23, wherein the organic acceptor is selected from the group consisting of tetracyanoquinodimethane, tetracyanoethylene, and a combination thereof.
- 25.** The method according to any one of claims 18 to 24, wherein annealing the organic acceptor-modified silk fiber is carried out at a temperature in the range of about 80 °C to about 120 °C.
- 26.** The method according to any one of claims 15 to 25, wherein disposing the coating material comprises immersing the silk fiber in a solution comprising the coating material.
- 27.** The method according to claim 26, wherein immersing the silk fiber in the solution comprising the coating material is carried out by drop flowing.
- 28.** The method according to any one of claims 15 to 27, wherein the electrically conducting polymer is selected from the group consisting of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS), a poly(thiophene), a polycarbazole, a polyindole, a polyazepine, a polyaniline, a copolymer thereof, and a combination thereof.

- 29.** The method according to any one of claims 15 to 28, wherein the electrically conducting polymer comprises or consists of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS).
- 30.** The method according to any one of claims 15 to 29, wherein the electrically conducting nanostructured material is selected from the group consisting of nanotubes, nanowires, nanofibers, nanoparticles, and combinations thereof.
- 31.** The method according to any one of claims 15 to 30, wherein the electrically conducting nanostructured material comprises or consists of a metal, a metal oxide, graphene, carbon nanotubes, or combinations thereof.
- 32.** The method according to any one of claims 15 to 31, wherein the electrically conducting nanostructured material comprises or consists of carbon nanotubes.
- 33.** The method according to any one of claims 15 to 32, further comprising annealing the silk fiber having the coating material disposed thereon.
- 34.** The method according to claim 33, wherein annealing the silk fiber having the coating material disposed thereon is carried out at a temperature in the range of about 60 °C to about 100 °C.
- 35.** A flexible and electrically conductive composite prepared by a method according to any one of claims 15 to 34.

36. A prosthesis comprising a flexible and electrically conductive composite according to any one of claims 1 to 14 or prepared by a method according to any one of claims 15 to 34.

37. The prosthesis according to claim 36, wherein the flexible and electrically conductive composite is comprised in the prosthesis as an electro-tendon.

38. The prosthesis according to claim 36 or 37, wherein the prosthesis is a robotic hand.

39. Use of a flexible and electrically conductive composite according to any one of claims 1 to 14 or prepared by a method according to any one of claims 15 to 34 in prosthesis, stretchable electronics, biomedical devices, implantable electronics, photodetectors, capacitors, electrochromic devices, strain gauges, sensors, wearable electronics, clean energy devices, smart clothes, and sensory skin for robotic systems.

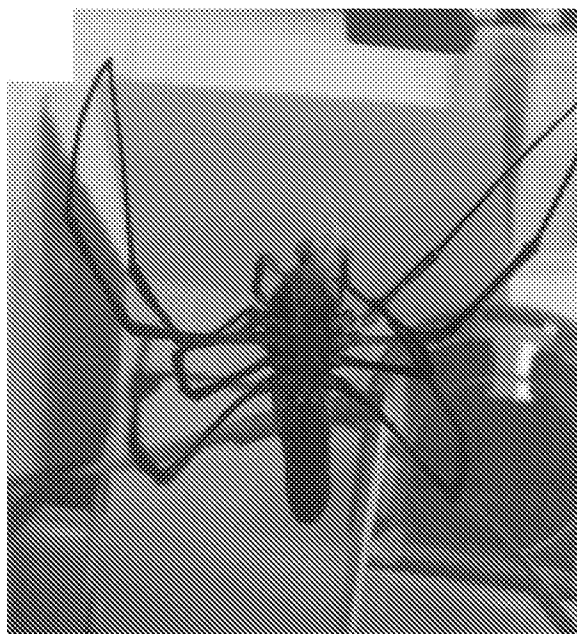


FIG. 1A

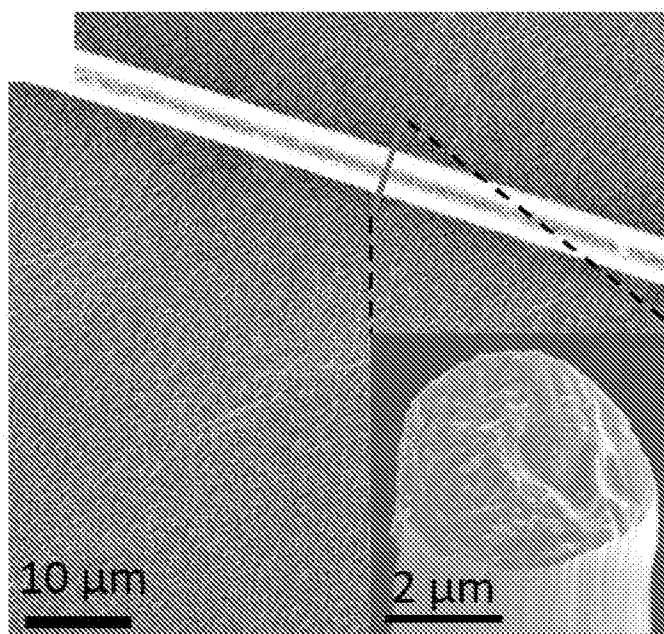


FIG. 1B

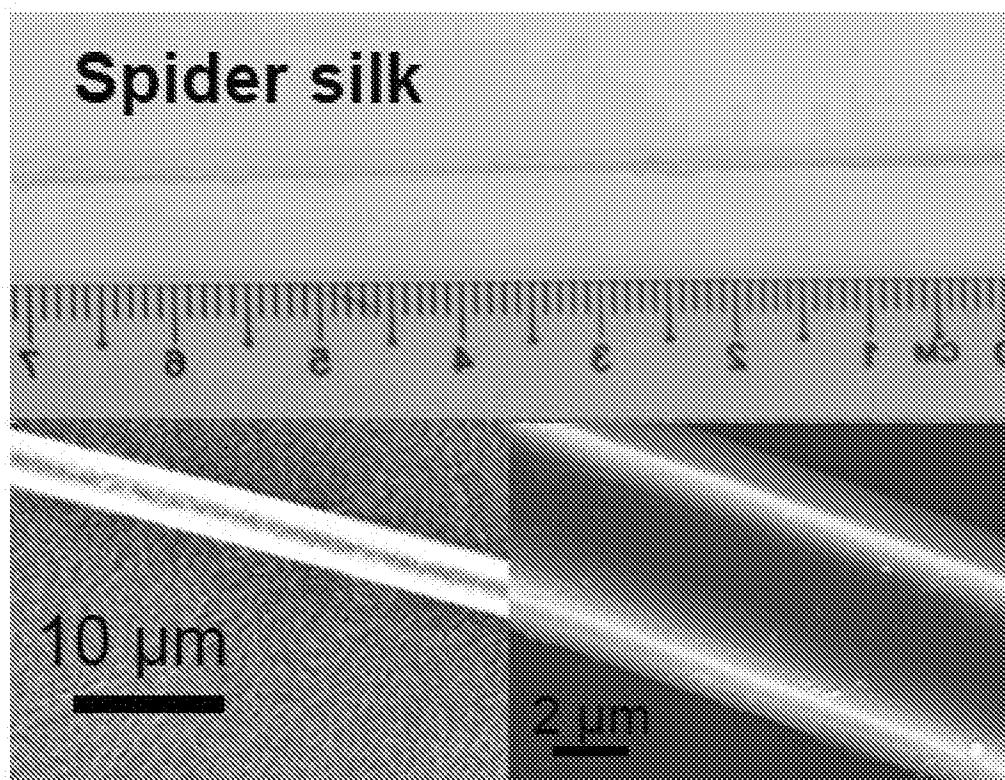


FIG. 1C

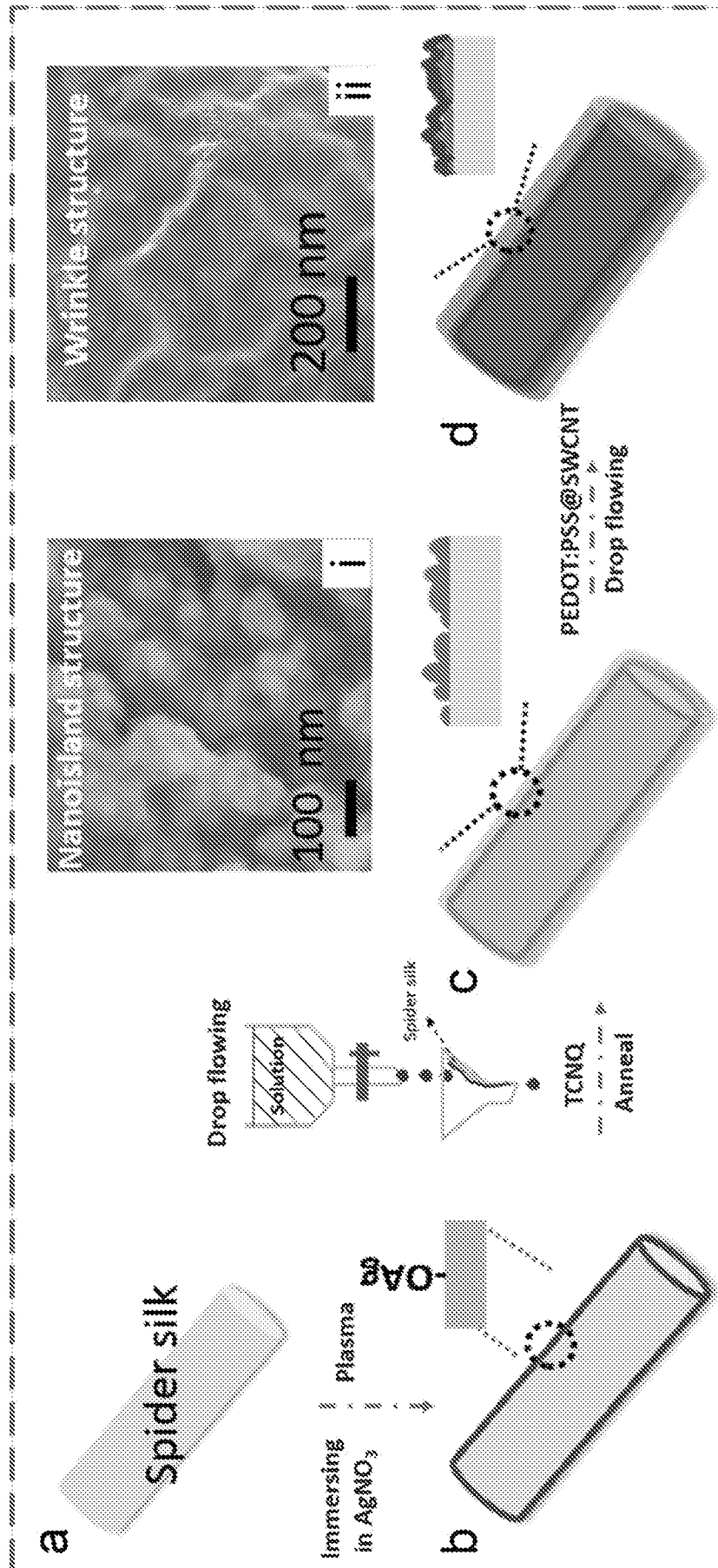


FIG. 2A

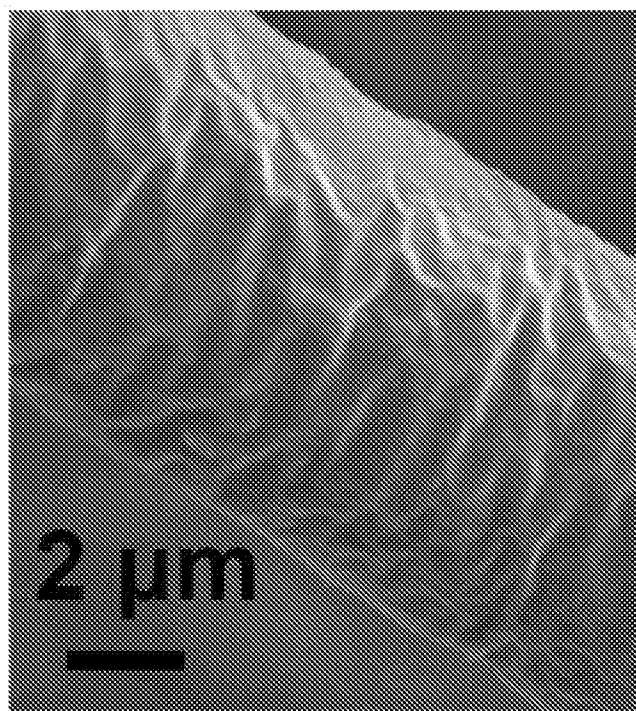


FIG. 2B

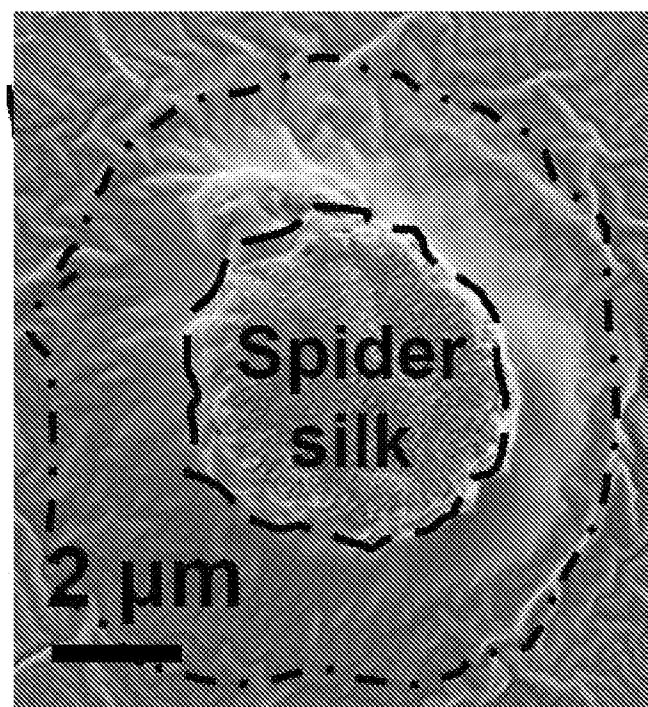


FIG. 2C

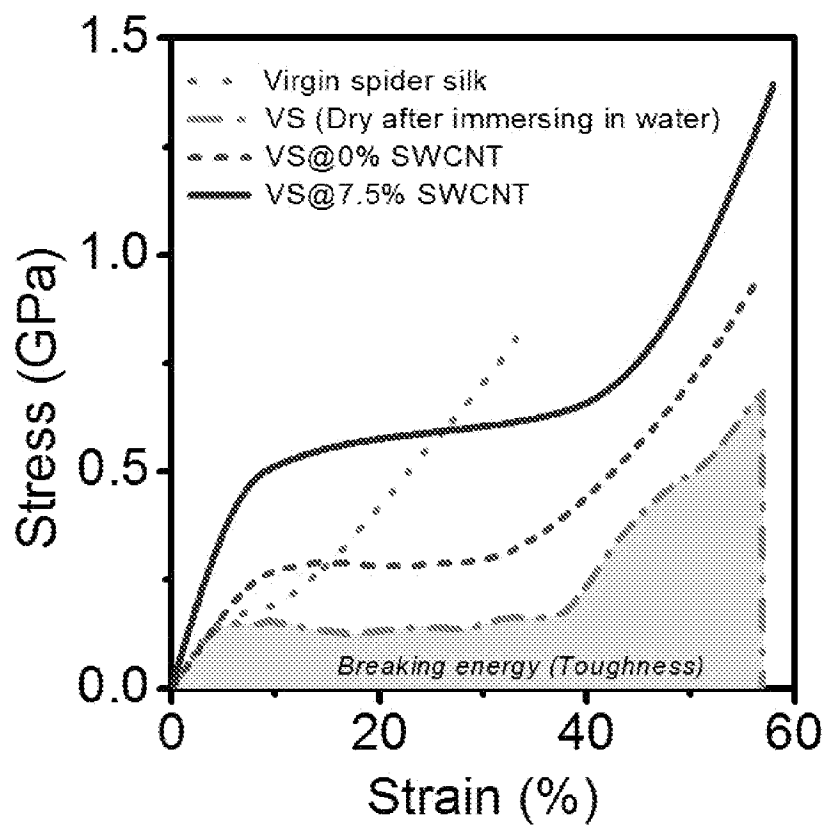


FIG. 3A

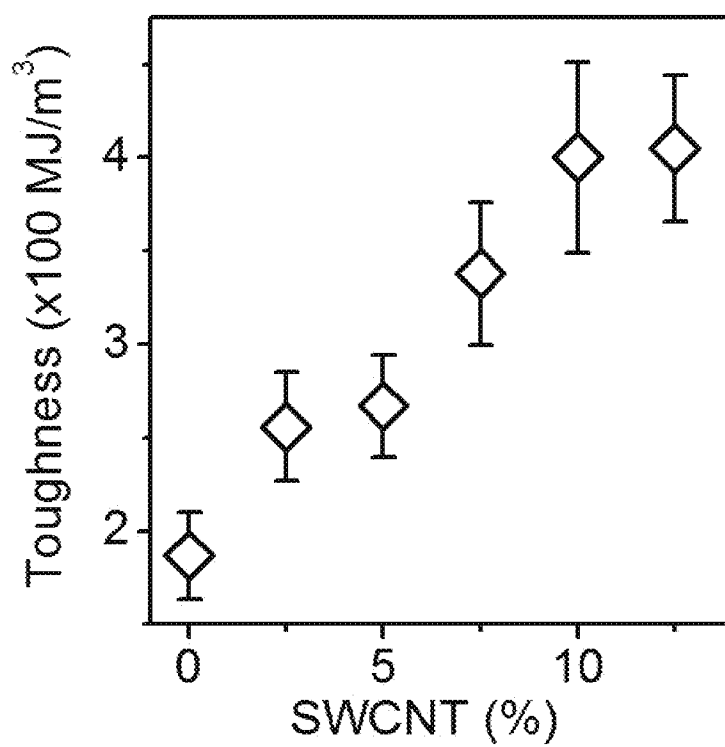


FIG. 3B

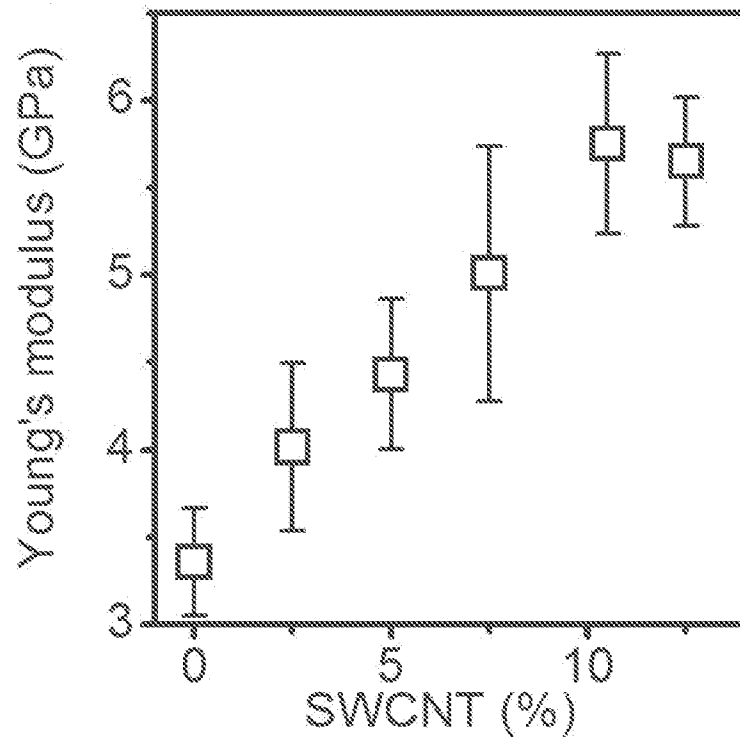


FIG. 3C

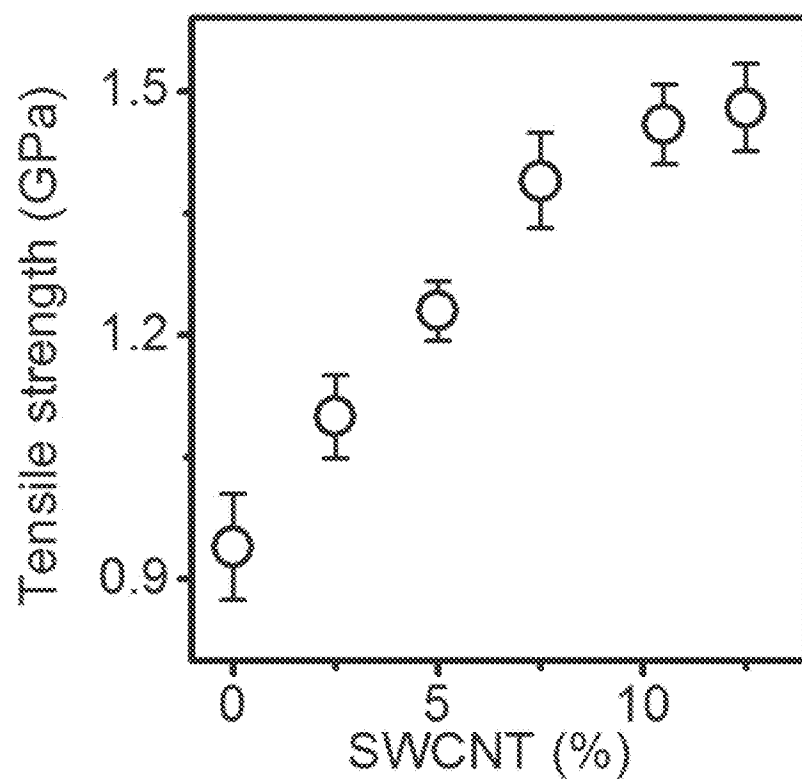


FIG. 3D

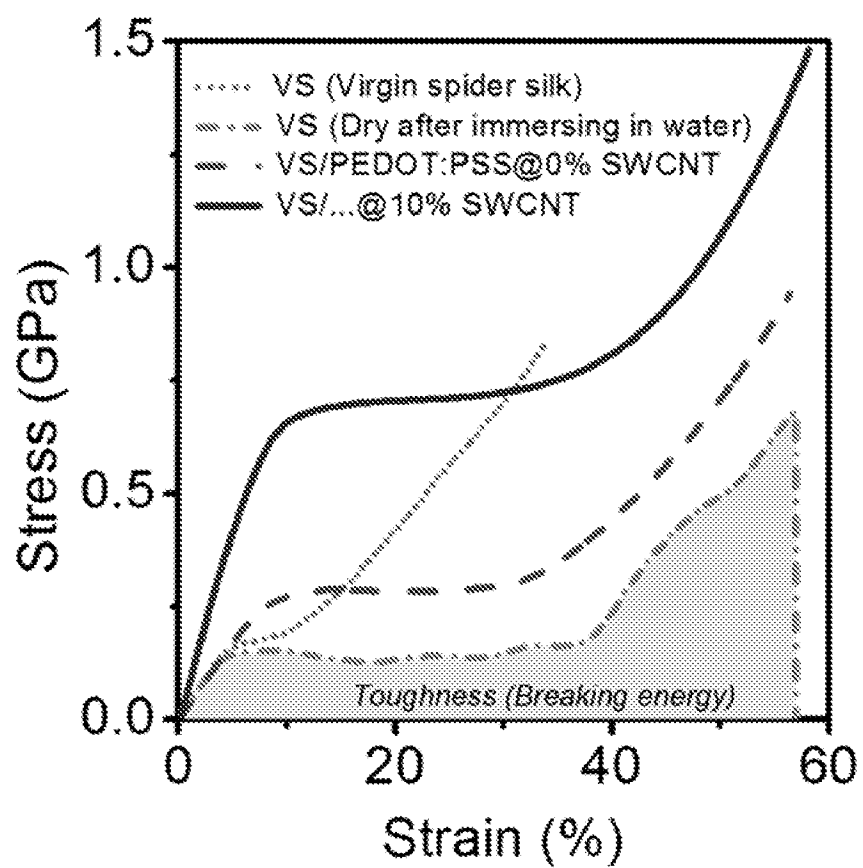


FIG. 3E

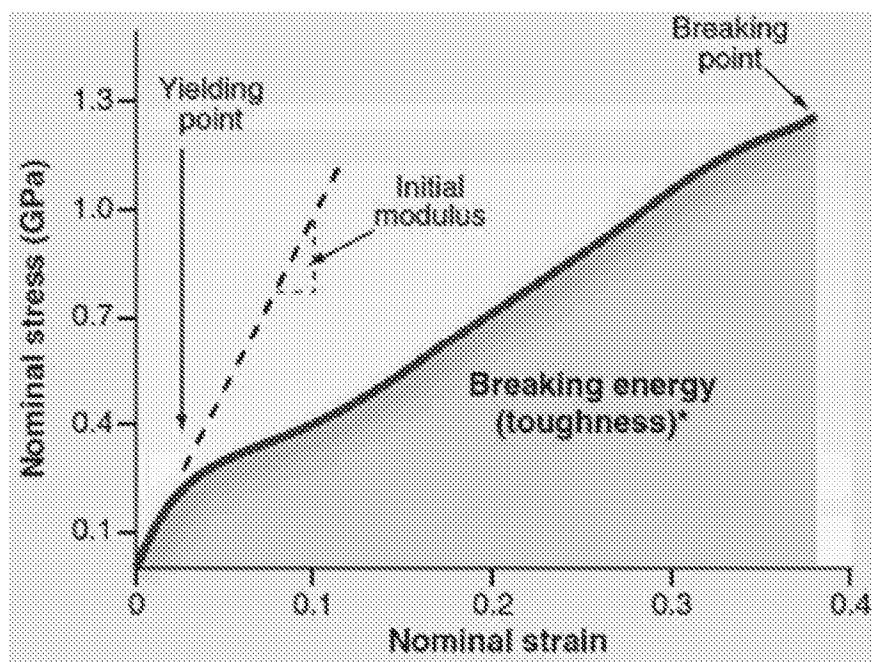


FIG. 3F

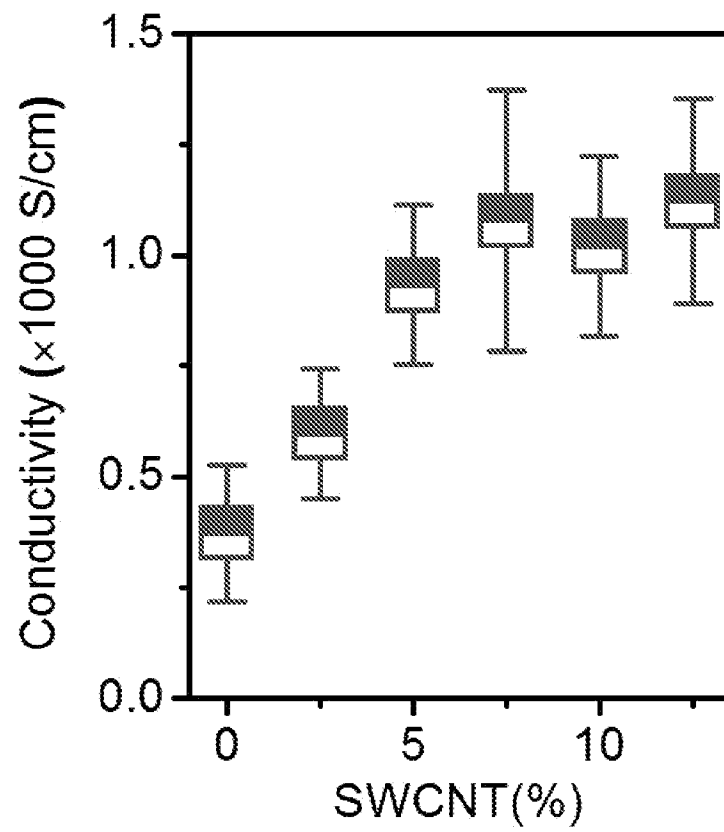


FIG. 4A

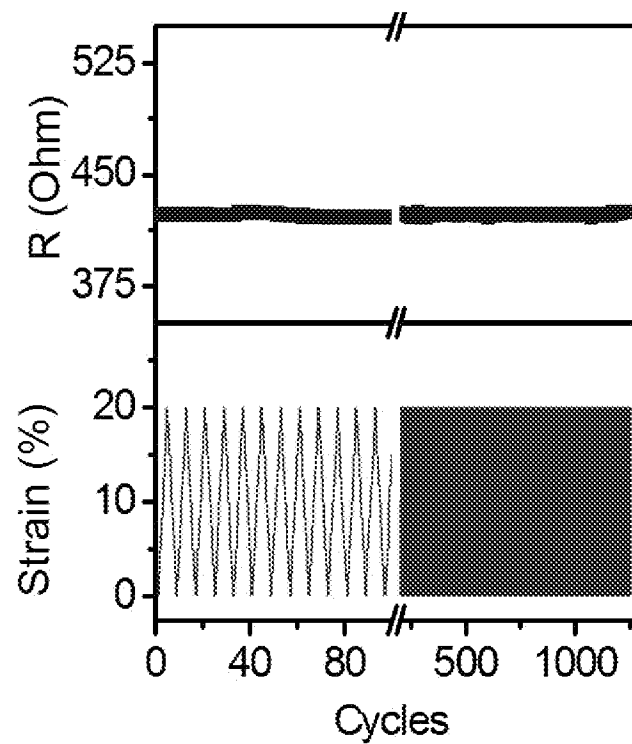


FIG. 4B

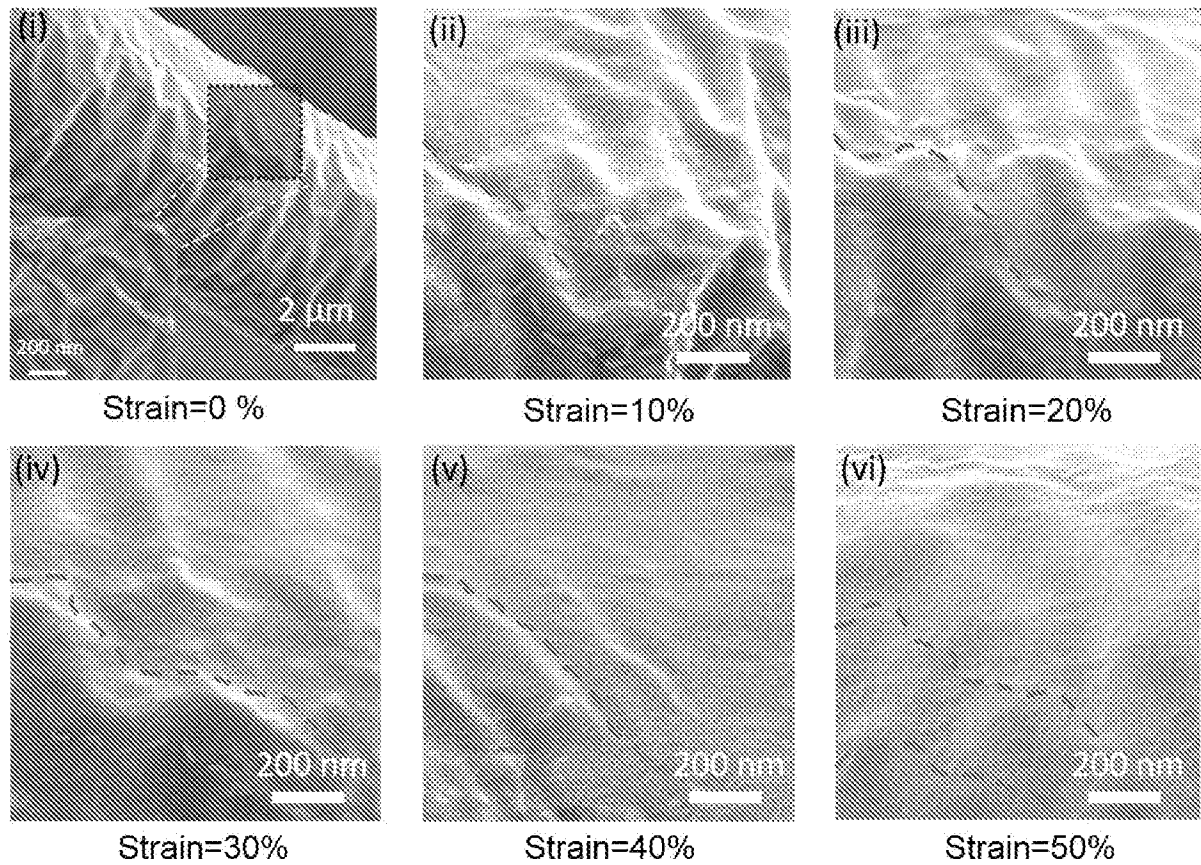


FIG. 4C

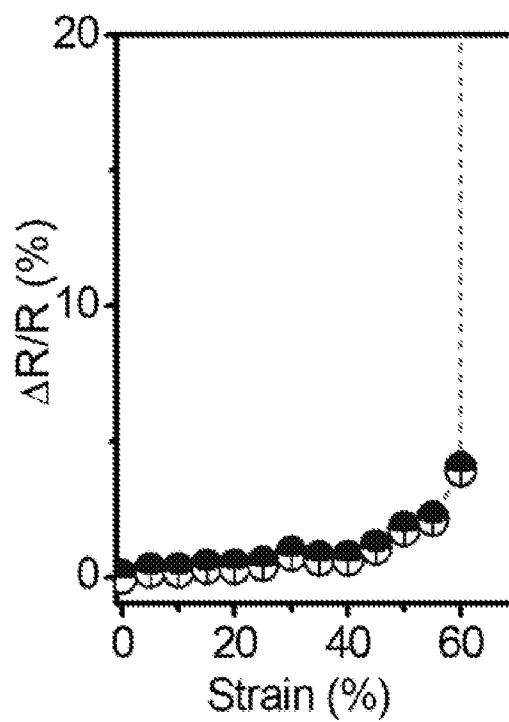


FIG. 4D

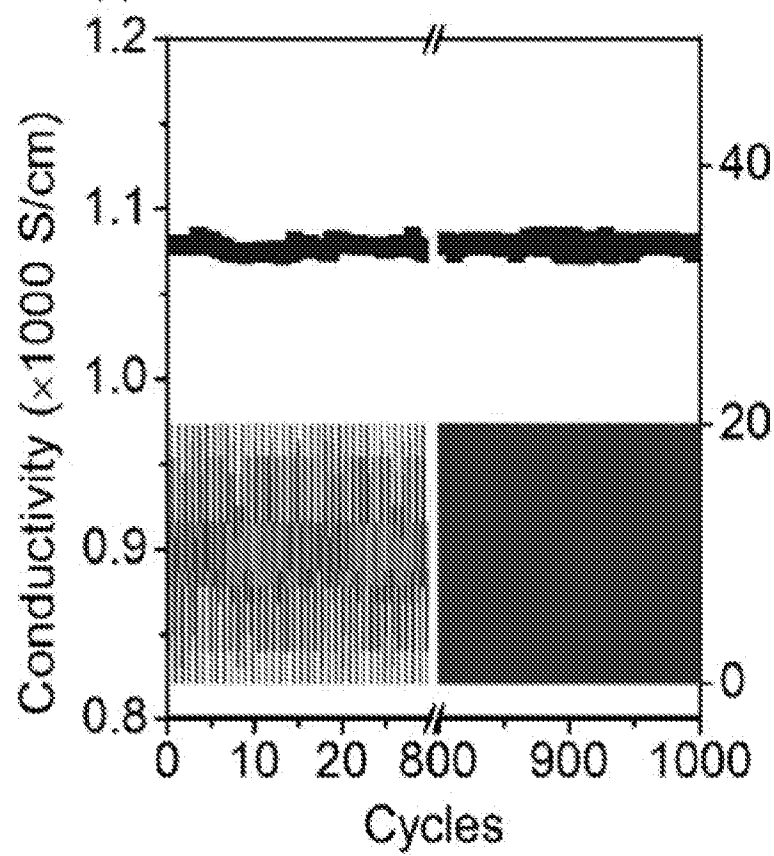


FIG. 4E

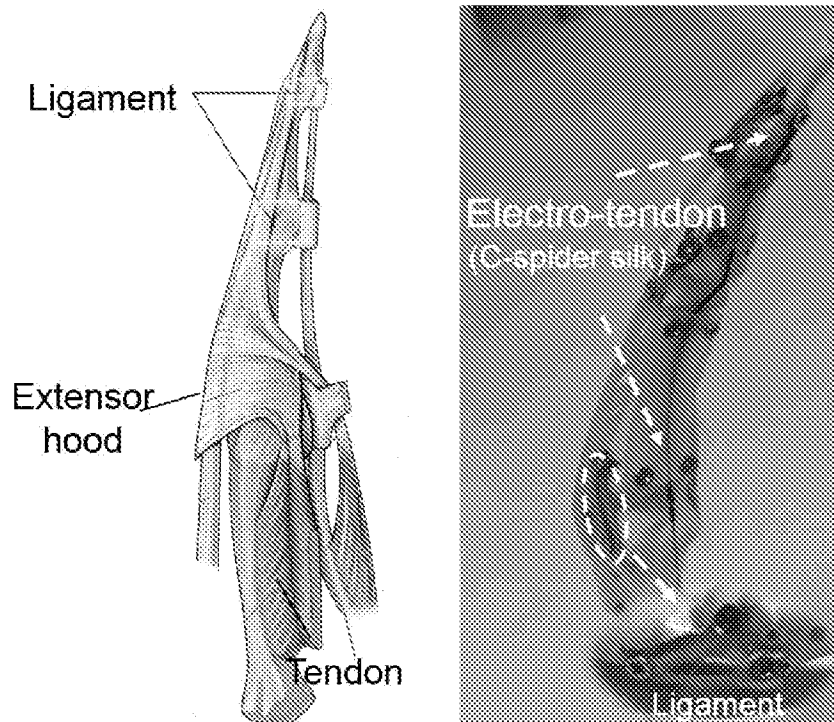
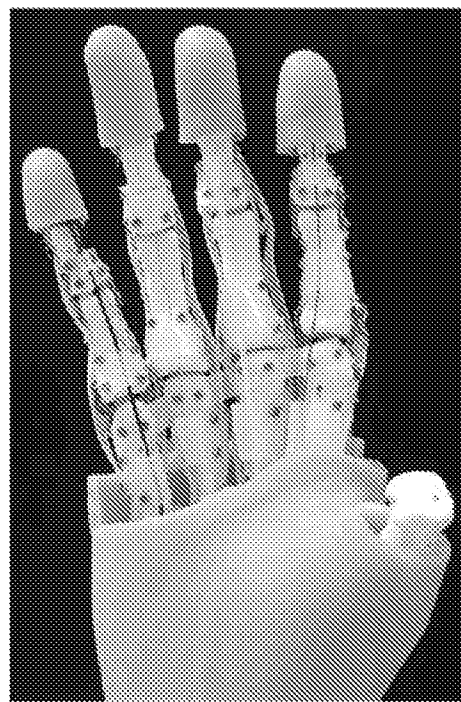


FIG. 5A



IF: C-spider silk MF: Silicone rubber
RF: Steel fiber LF: Carbon fiber

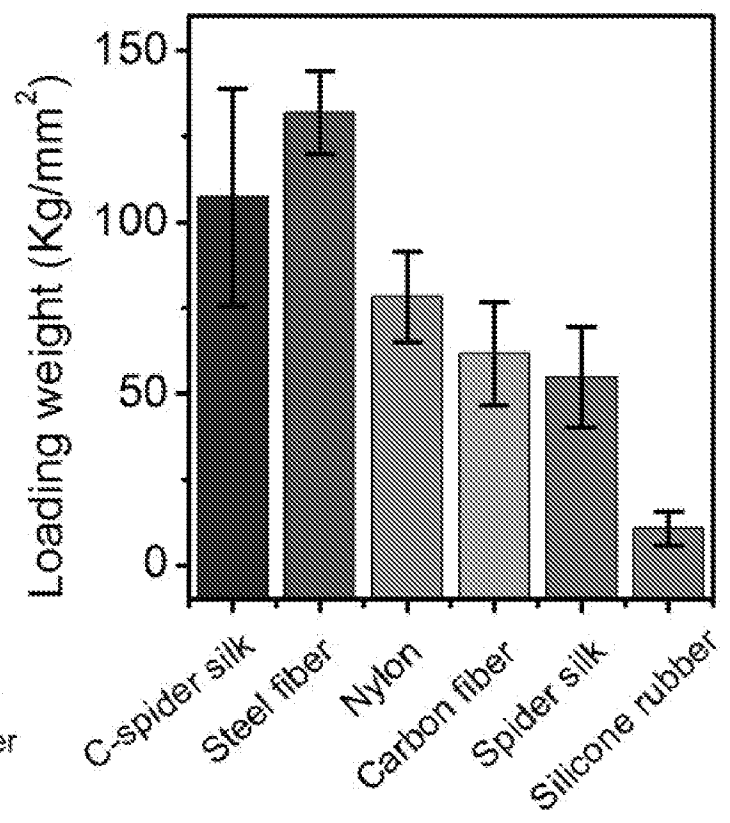


FIG. 5B

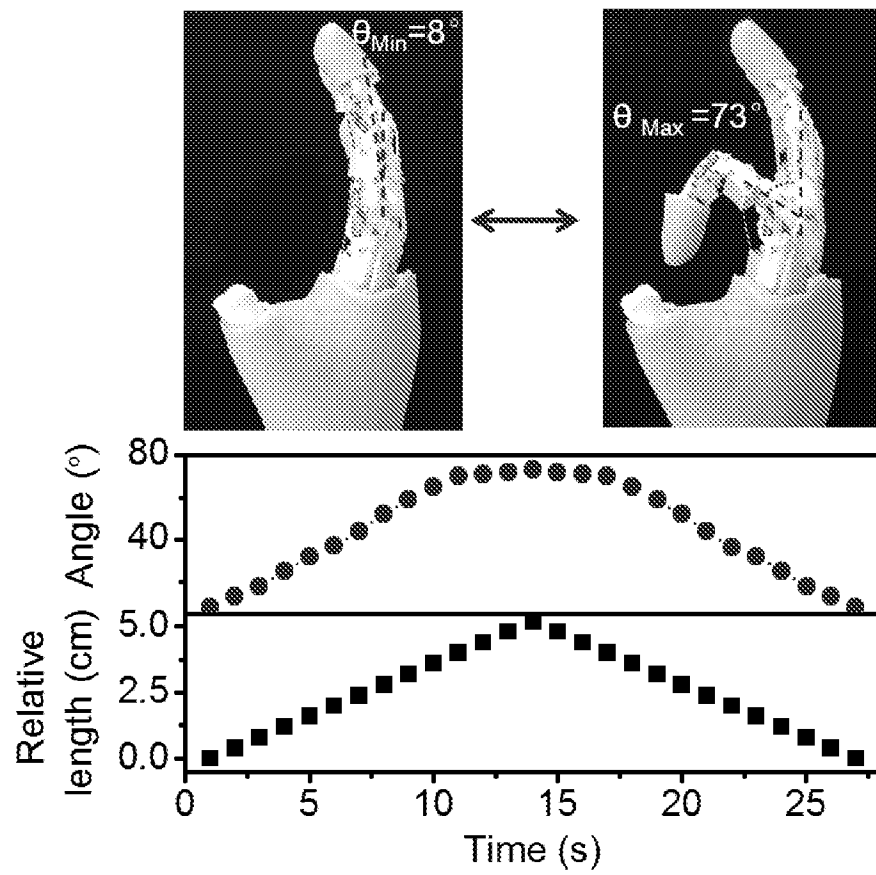


FIG. 5C

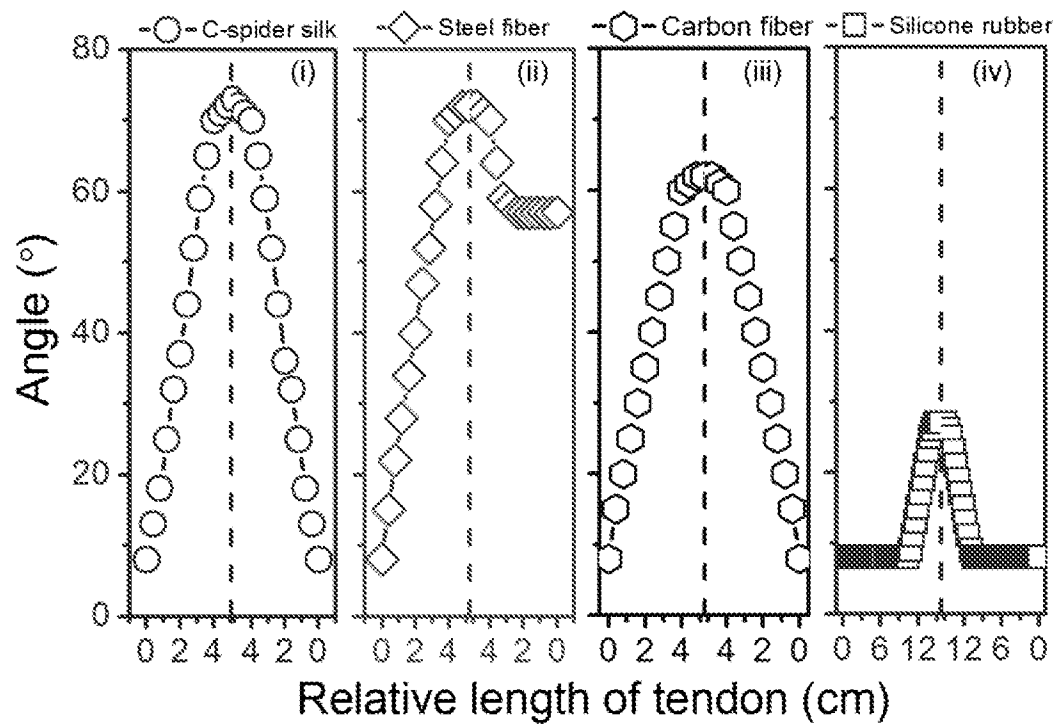


FIG. 5D

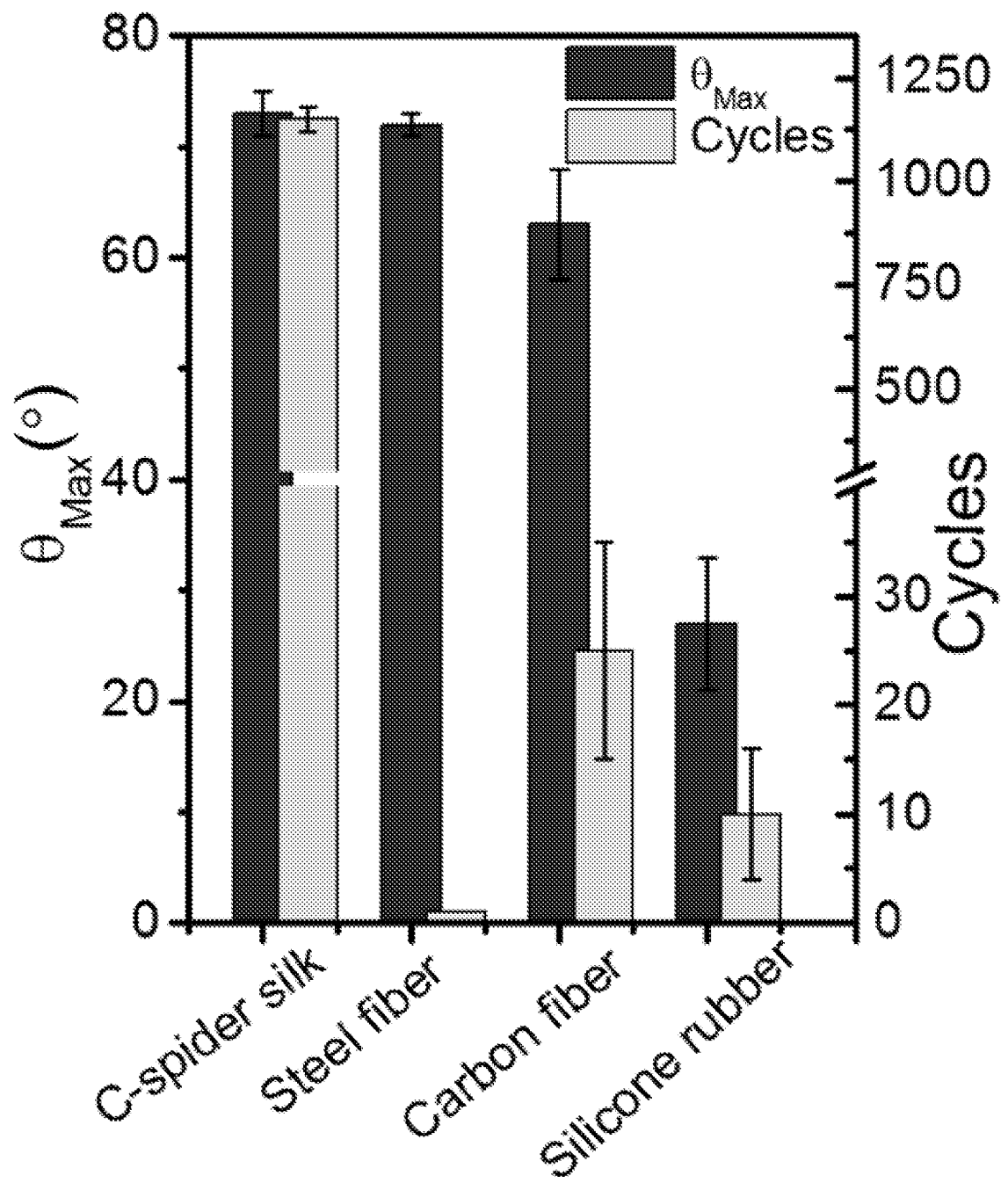


FIG. 5E

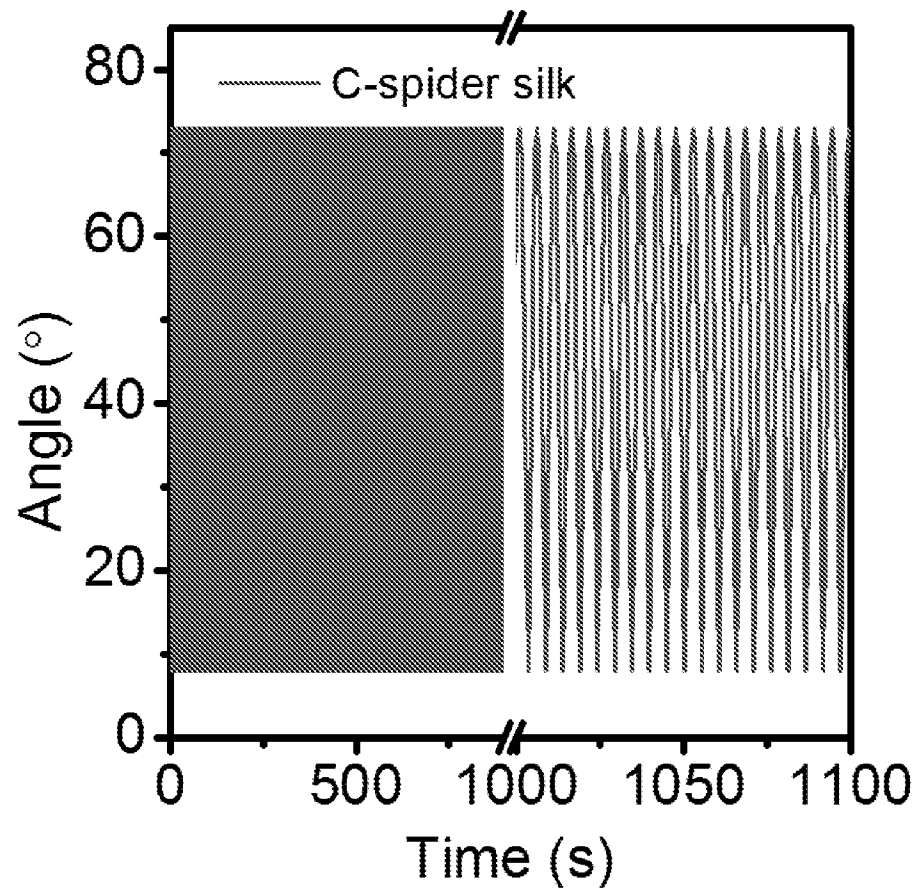


FIG. 5F

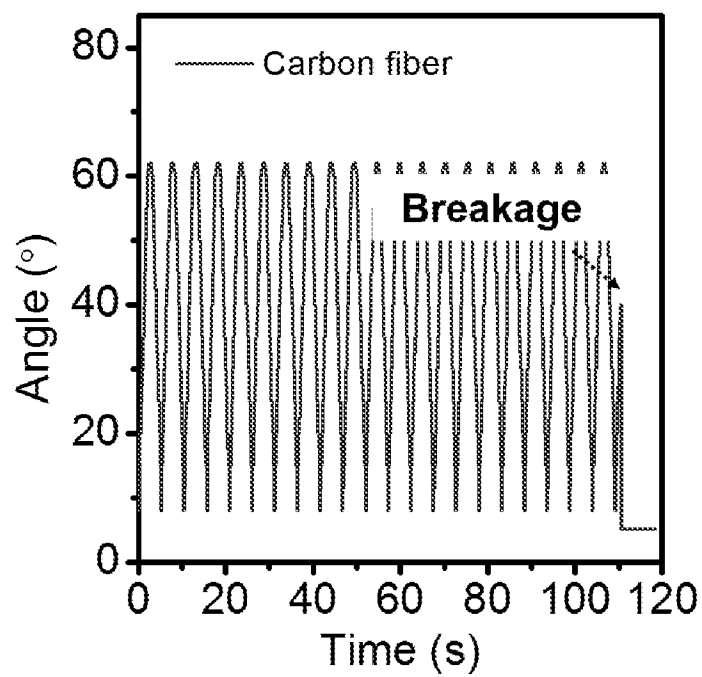


FIG. 5G

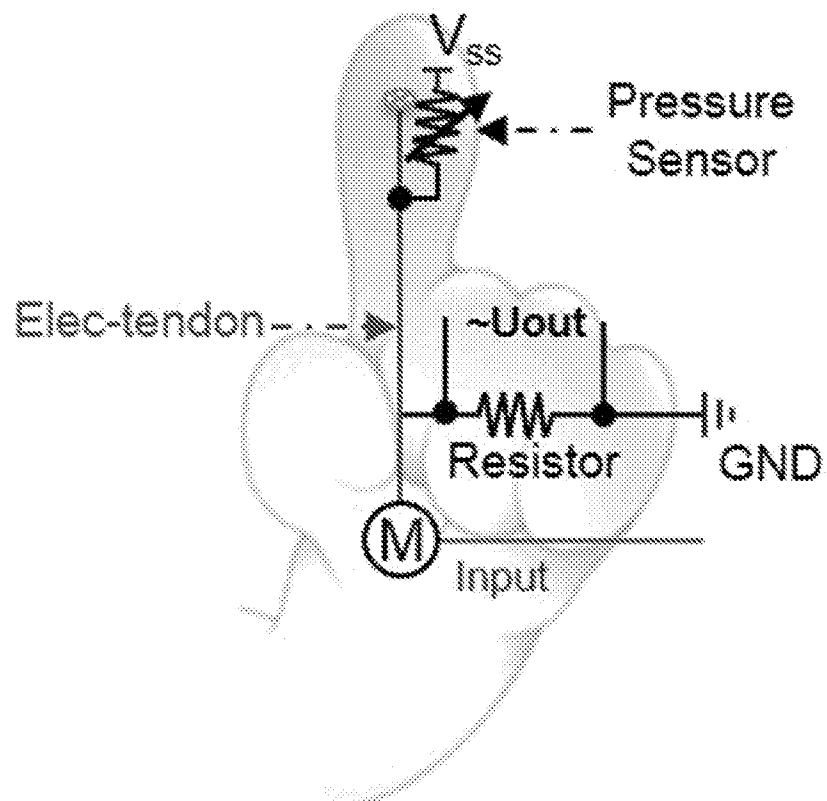


FIG. 6A

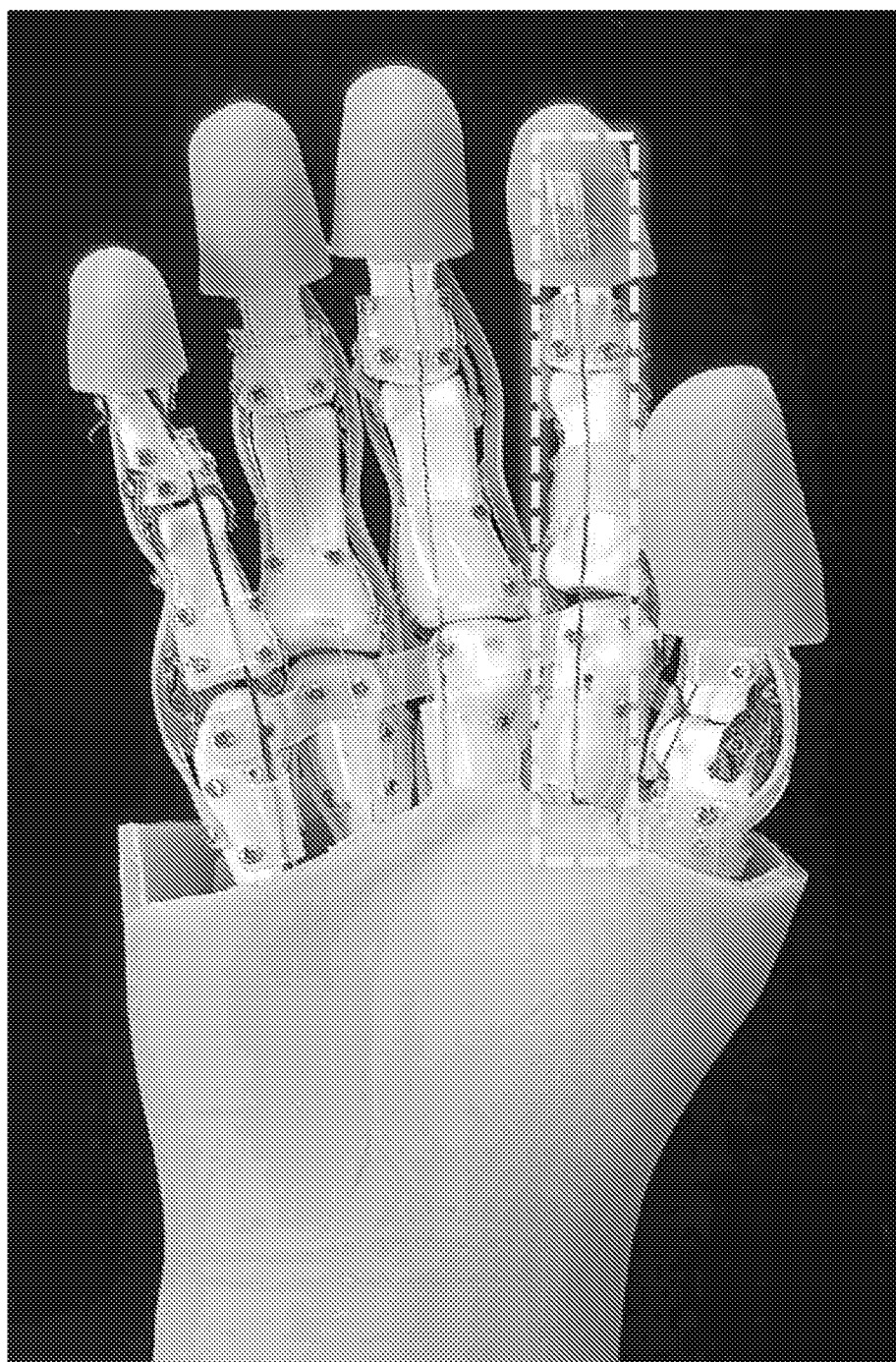


FIG. 6B

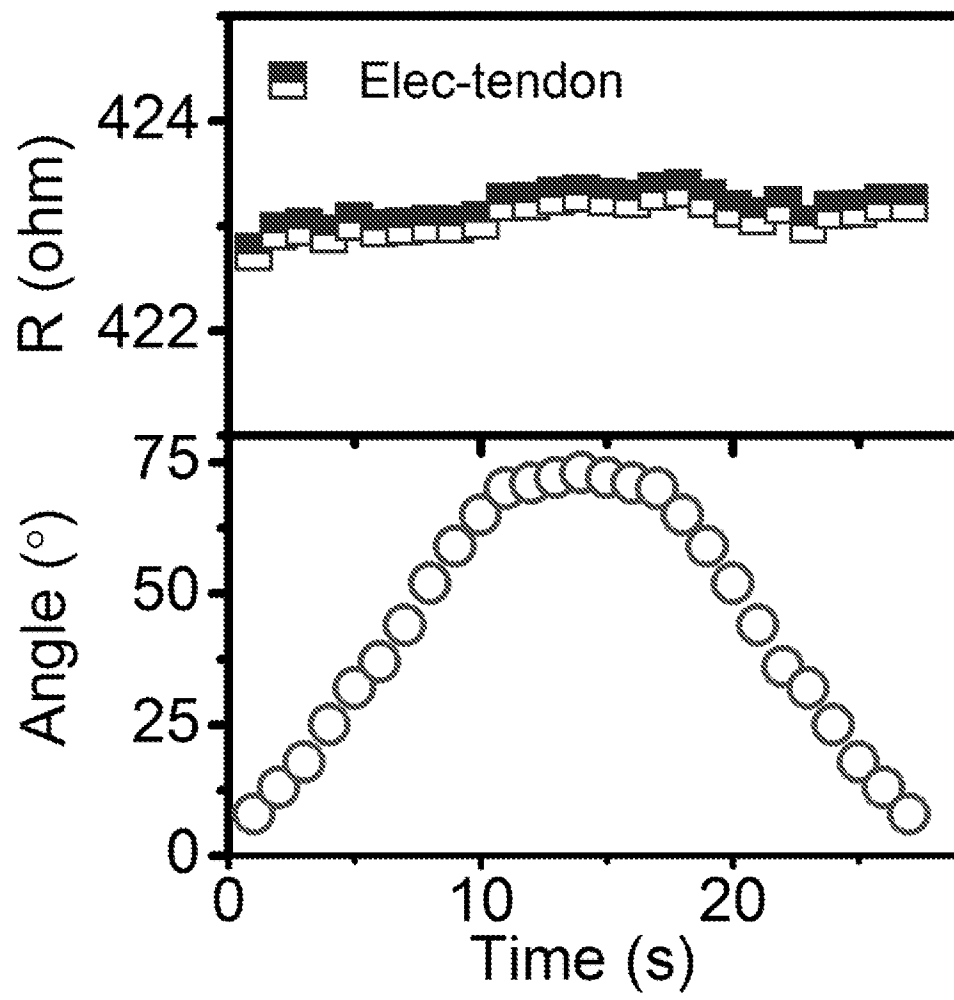


FIG. 6C

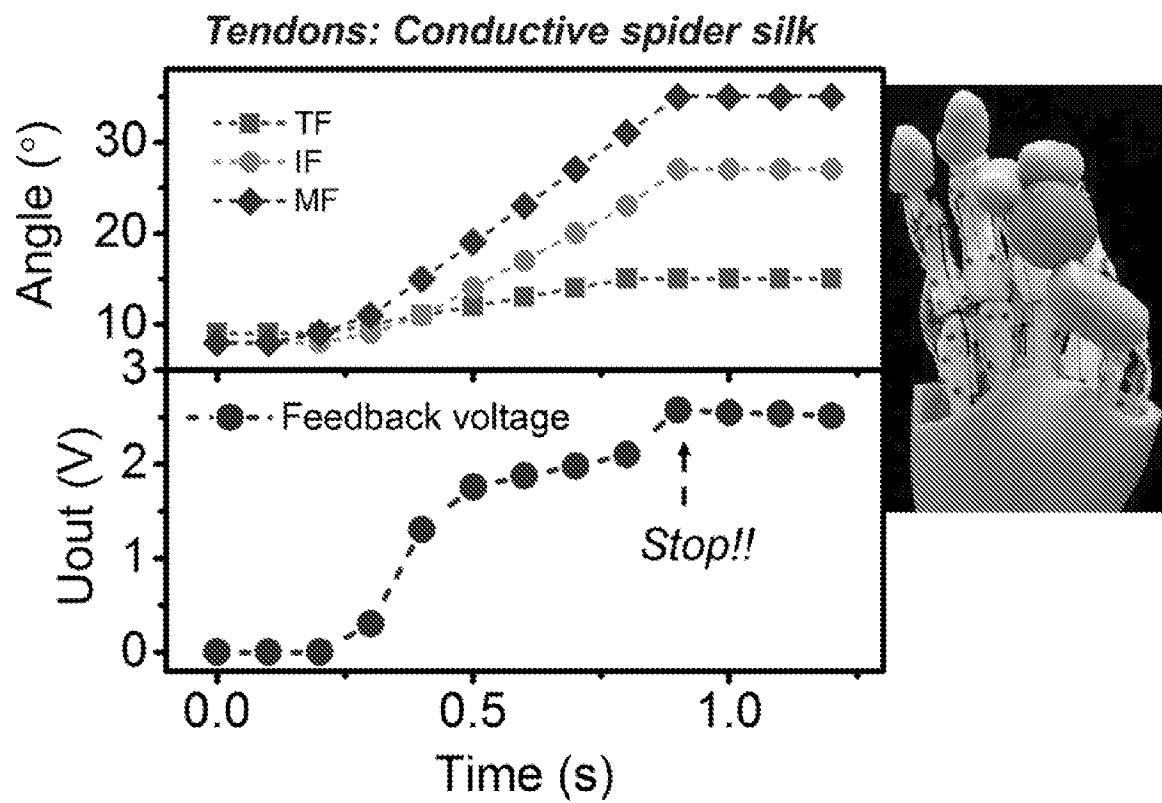


FIG. 6D

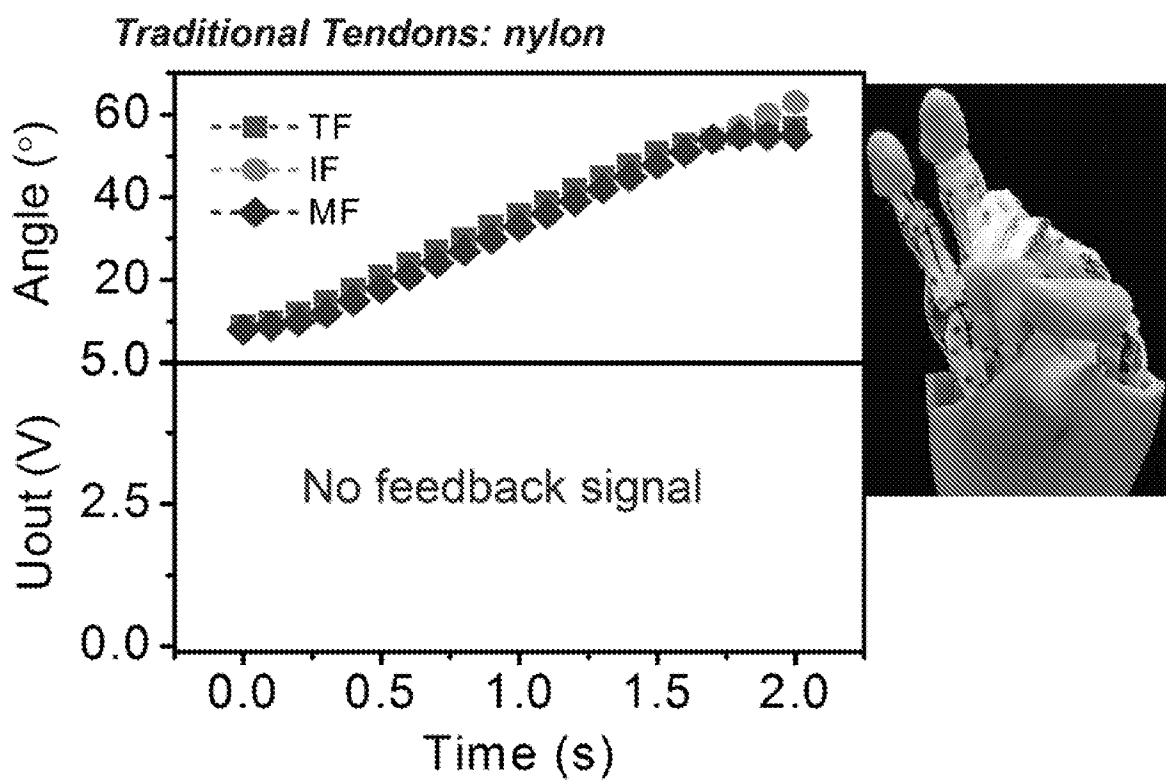


FIG. 6E

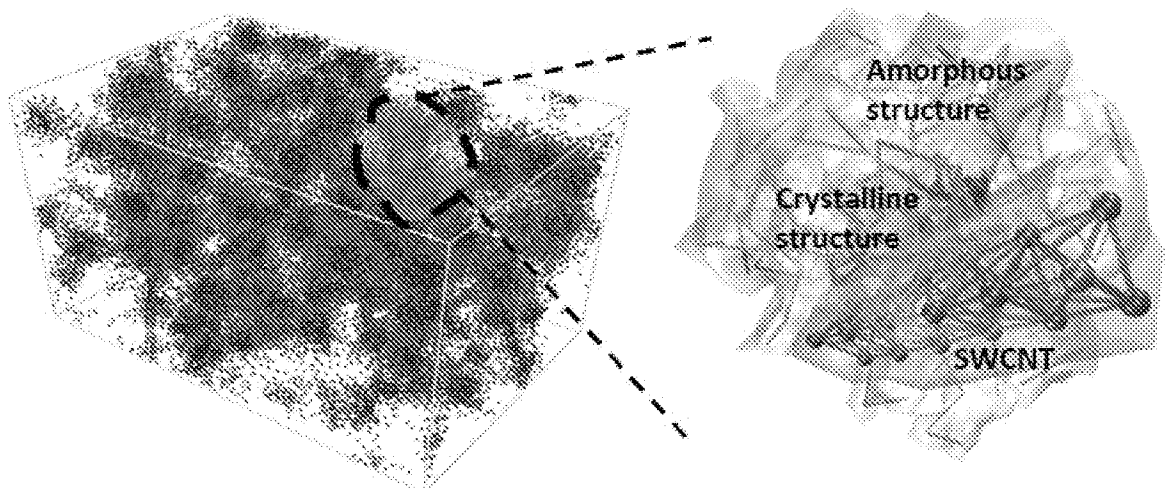


FIG. 7A

Spider silk without SWCNT

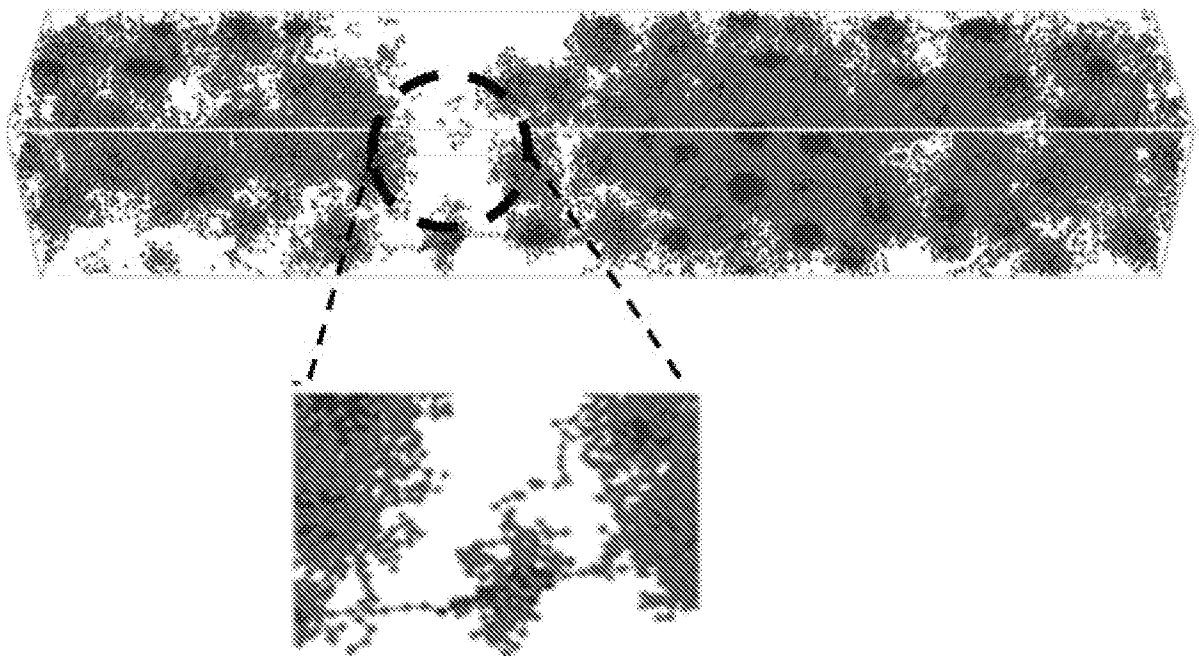


FIG. 7B

Spider silk with SWCNT

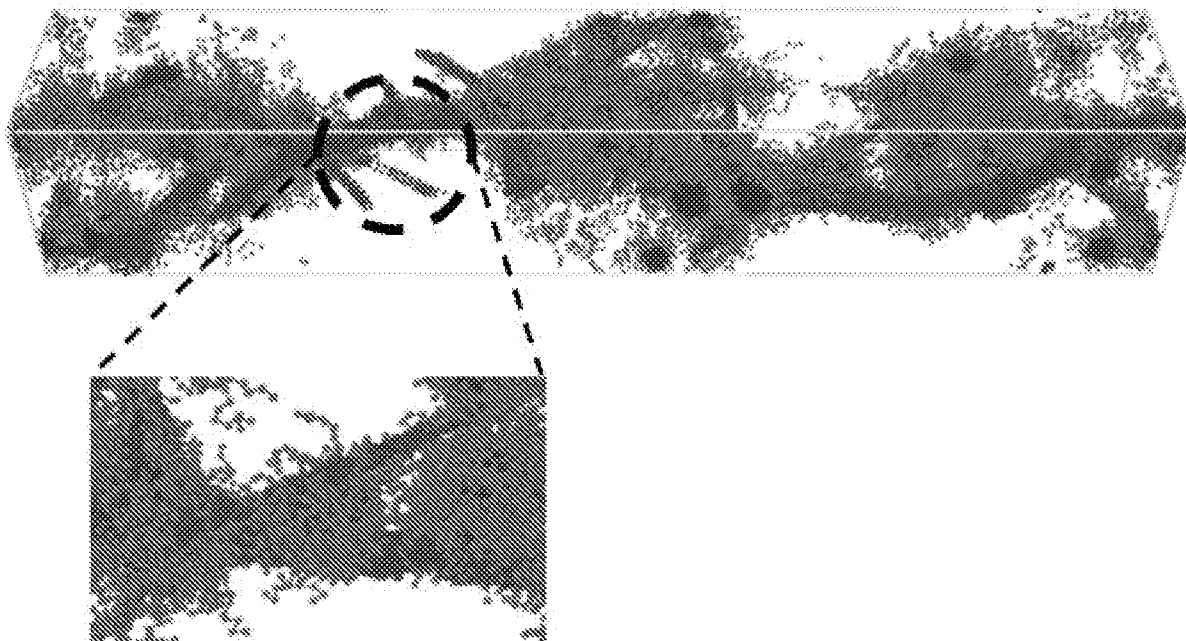


FIG. 7C

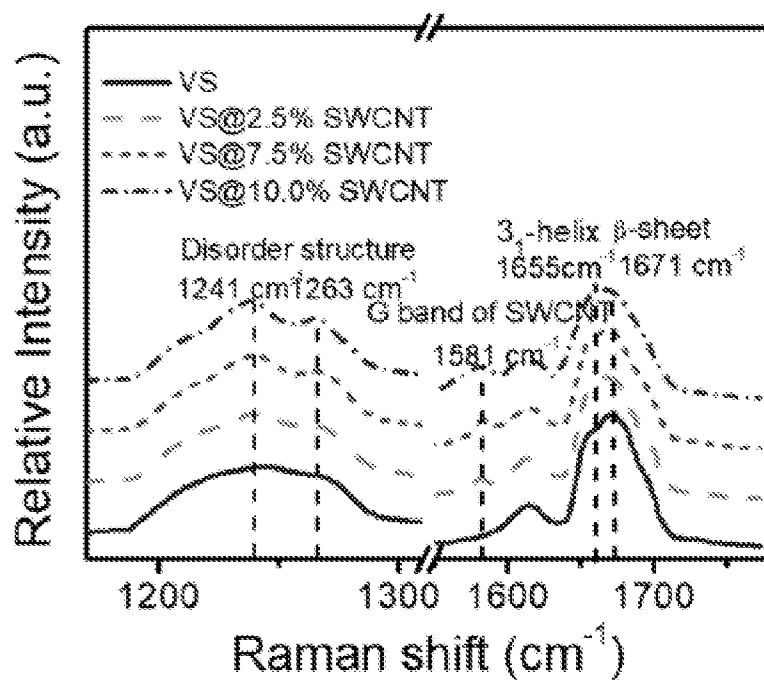


FIG. 7D

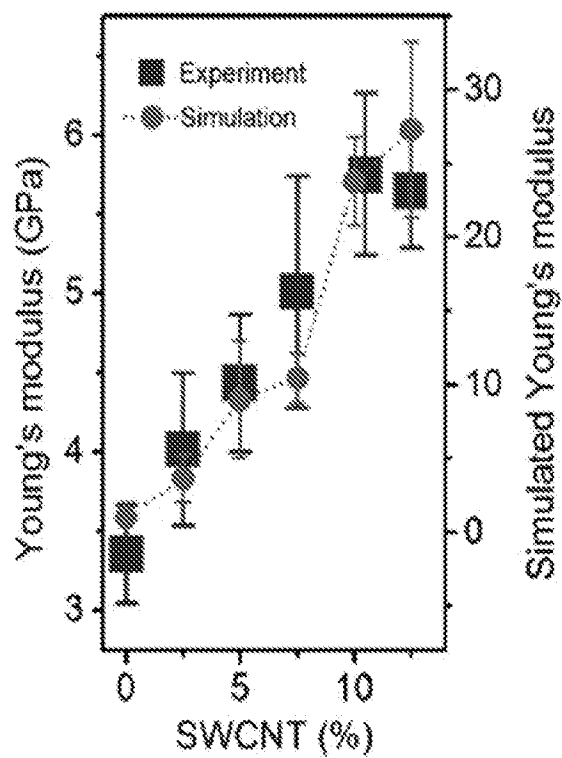


FIG. 8A

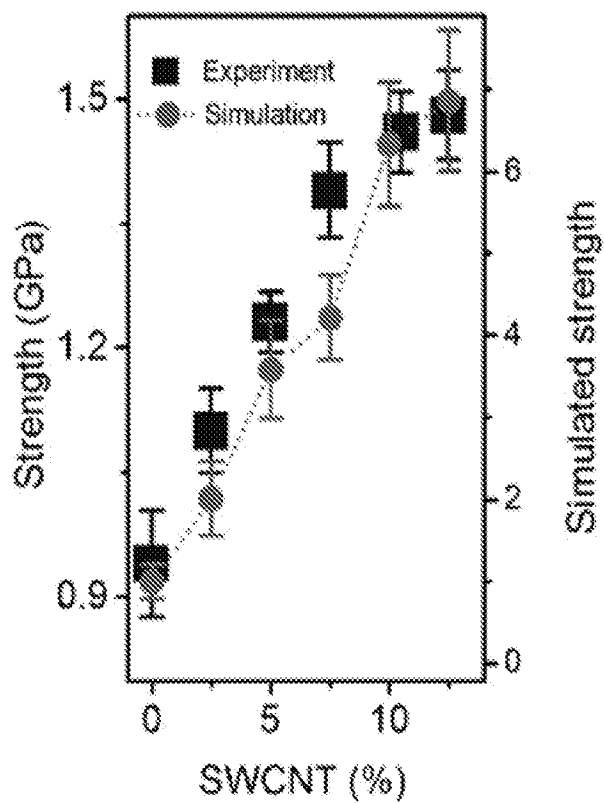


FIG. 8B

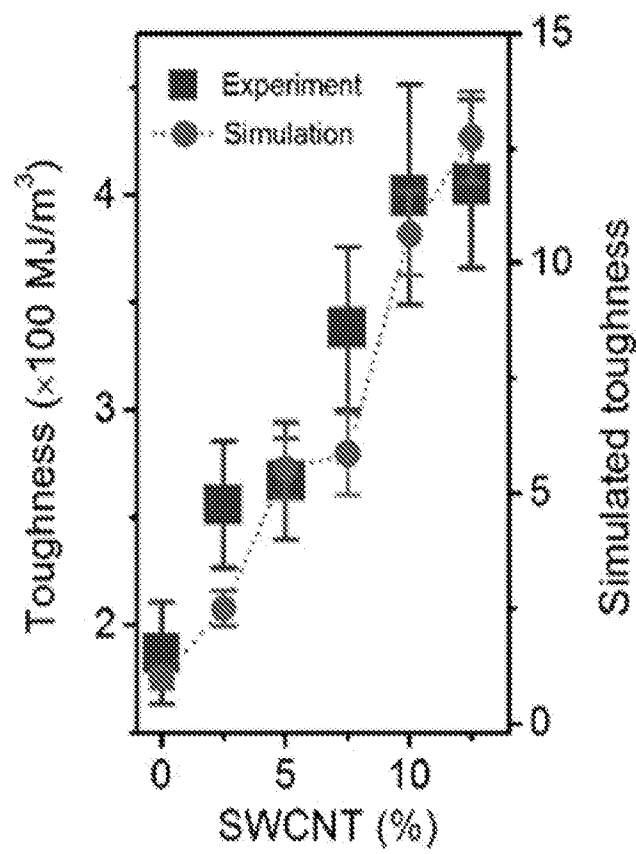


FIG. 8C

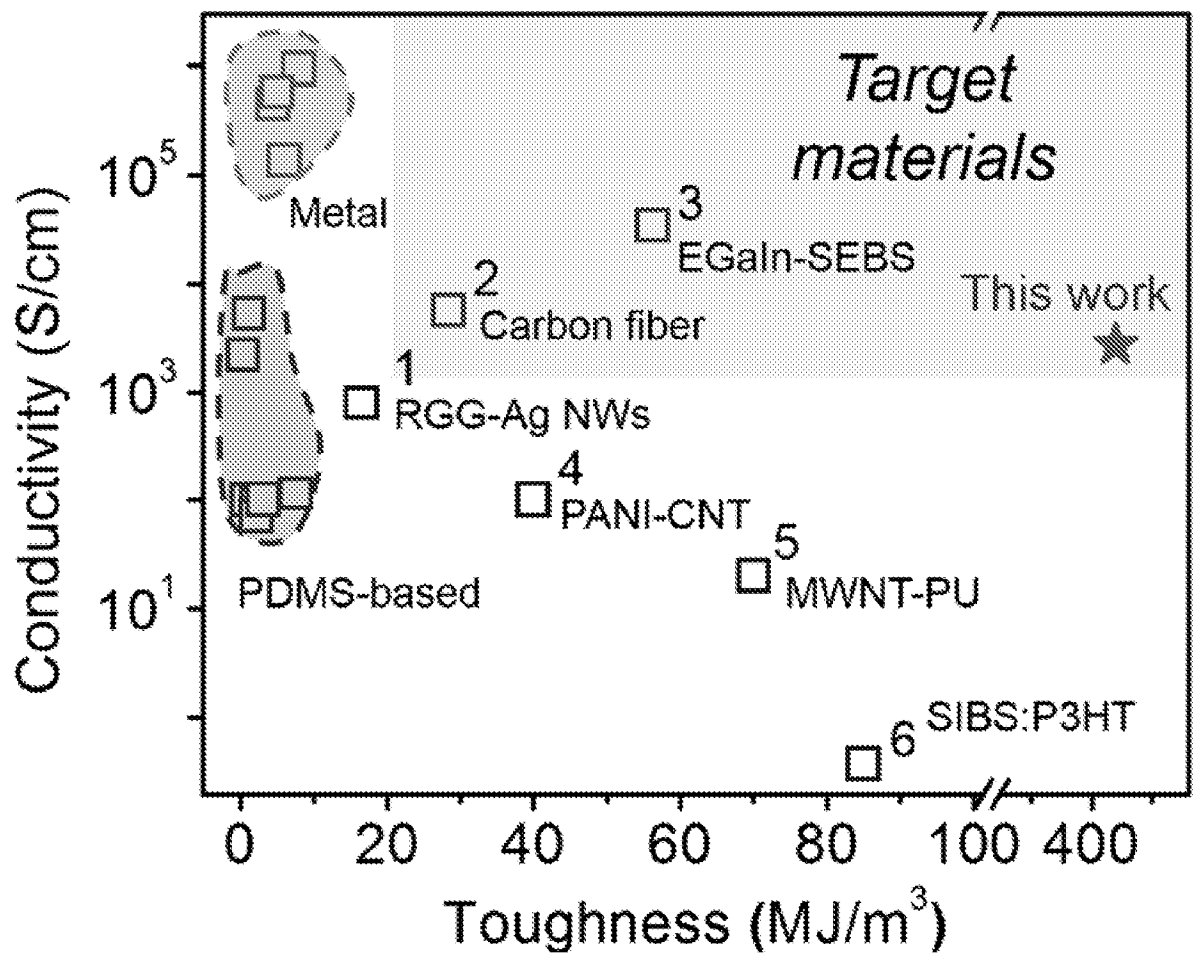


FIG. 9

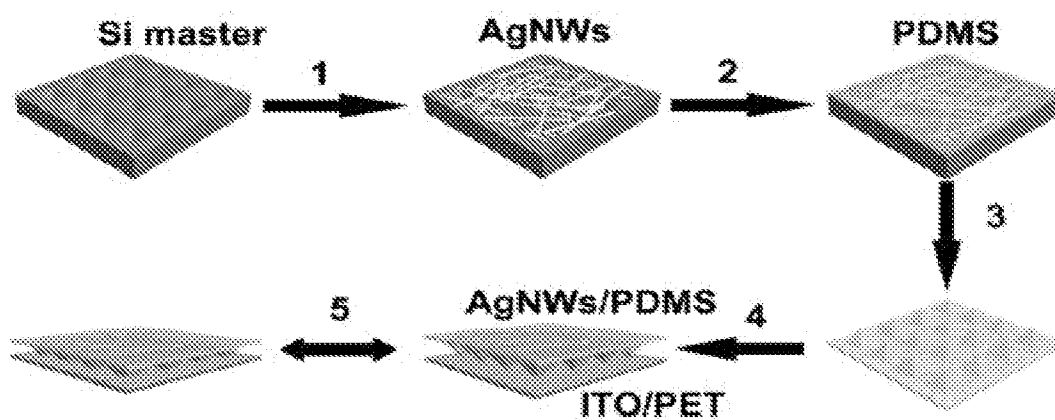


FIG. 10A

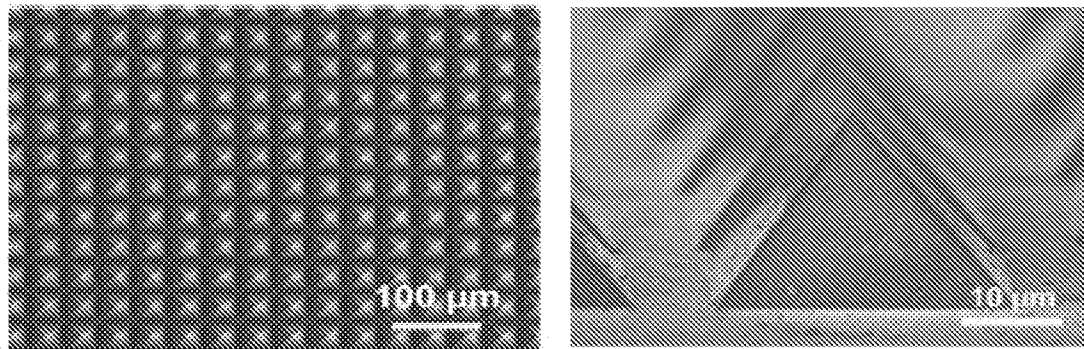


FIG. 10B

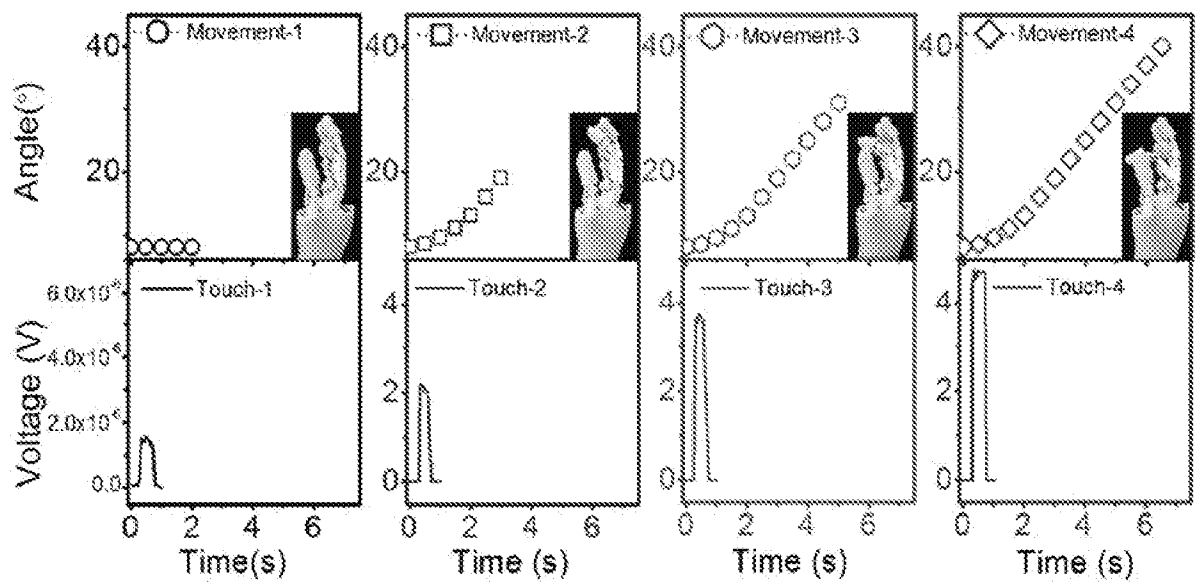


FIG. 10C

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2019/050411

A. CLASSIFICATION OF SUBJECT MATTER

See Supplemental Box

According to International Patent Classification (IPC)

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Database: EPODOC, DWPI, FAMPAT, CAPLUS, COMPENDEX, INSPEC

Keywords: silk fiber, conductive polymer, metal, metal oxide, graphene, carbon nanotubes and related terms.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	ADHIKARI, S. ET AL., Organic Conductive Fibers as Nonmetallic Electrodes and Neural Interconnects. <i>Industrial & Engineering Chemistry Research</i> , 24 May 2018, Vol. 57, No. 23, pages 7866-7871 [Retrieved on 2019-10-18] <DOI: 10.1021/ACS.IECR.8B00786> see Section 2, and Table 1	1-3, 5-16 and 26-39 4 and 17-25
X A	CN 104313873 A (UNIV JIANGNAN) 28 January 2015 see Table 1, Examples 1-4 of the machine translation	1-3, 5-16 and 26-39 4 and 17-25
X A	FUJII, S. ET AL., Conducting Polymer-Metal Nanocomposite Coating on Fibers. <i>Advances in Nanocomposite Technology</i> , 27 July 2011, pages 47-72 [Retrieved on 2019-10-18] <DOI: 10.5772/16911> see Section 2, Schemes 1 and 2, and Table 1	1-3, 5-16 and 26-39 4 and 17-25
X A	XIA, Y. ET AL., Silk Fibroin Fibers Supported with High Density of Gold Nanoparticles: Fabrication and Application as Catalyst. <i>Gold Bulletin</i> , 25 August 2011, Vol. 44, pages 171-176 [Retrieved on 2019-10-18] <DOI: 10.1007/S13404-011-0024-7> see whole document	1-3, 5-16 and 26-39 4 and 17-25

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

☒ See patent family annex.

*Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"D" document cited by the applicant in the international application

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

18/10/2019

(day/month/year)

Date of mailing of the international search report

29/10/2019

(day/month/year)

Name and mailing address of the ISA/SG

IPOS Intellectual Property Office of Singapore
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Singapore 408533

Email: pct@ipos.gov.sg

Authorized officer

Joan Toh (Dr)

IPOS Customer Service Tel. No.: (+65) 6339 8616

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2019/050411

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	STEVEN, E. ET AL., Carbon nanotubes on a spider silk scaffold. <i>Nature communications</i> , 10 September 2013, Vol. 4, pages 2435: 1-8 [Retrieved on 2019-10-18] <DOI: 10.1038/NCOMMS3435> see whole document	-
A	CN 104894681 A (SUZHOU WEIERDE COMMERCIAL & TRADE CO LTD) 9 September 2015 see abstract of the machine translation	-
A	US 2014/0303470 A1 (TSUKADA, S. ET AL.) 9 October 2014 see paragraphs [0222], [0227]-[0230], and [0269]-[0284], and Fig. 5	-
A	CHEN, G. ET AL., Plasticizing Silk Protein for On-Skin Stretchable Electrodes. <i>Advanced Materials</i> , 30 March 2018, Vol. 30, No. 21, pages 1800129: 1-7 [Retrieved on 2019-10-18] <DOI: 10.1002/ADMA.201800129> see page 1800129 (5 of 7), left column, 2nd paragraph, and Figure 1	-

INTERNATIONAL SEARCH REPORT

International application No.

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Supplemental Box (Classification of Subject Matter)

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D06M 11/74 (2006.01)

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Note: This Annex lists known patent family members relating to the patent documents cited in this International Search Report. This Authority is in no way liable for these particulars which are merely given for the purpose of information.

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