Review Article

Yunqing Gu, Lingzhi Yu, Jiegang Mou*, Denghao Wu, Peijian Zhou, and Maosen Xu

Mechanical properties and application analysis of spider silk bionic material

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Abstract: Spider silk is a kind of natural biomaterial with superior performance. Its mechanical properties and biocompatibility are incomparable with those of other natural and artificial materials. This article first summarizes the structure and the characteristics of natural spider silk. It shows the great research value of spider silk and spider silk bionic materials. Then, the development status of spider silk bionic materials is reviewed from the perspectives of material mechanical properties and application. The part of the material characteristics mainly describes the biocomposites based on spider silk proteins and spider silk fibers, nanomaterials and man-made fiber materials based on spider silk and spider-web structures. The principles and characteristics of new materials and their potential applications in the future are described. In addition, from the perspective of practical applications, the latest application of spider silk biomimetic materials in the fields of medicine, textiles, and sensors is reviewed, and the inspiration, feasibility, and performance of finished products are briefly introduced and analyzed. Finally, the research directions and future development trends of spider silk biomimetic materials are prospected.

Keywords: spider silk, characteristics, biomimetic materials, composite, structural material

1 Introduction

For more than half a century, the rise of synthetic polymer materials has not only brought many conveniences to people's lives, but also caused serious "white pollution" problems due to their inability to recycle and the lack of biodegradability. Now that sustainable development has become a common theme in today's world, it is increasingly urgent to develop materials that meet sustainable development. So, the research and development of biomaterials has become a research hotspot (1,2). Among the natural biological materials, spider silk has attracted more and more scholars with its excellent comprehensive properties.

Natural spider silk is a natural protein biomaterial secreted by spiders through their silk glands. It belongs to a type of bioelastic fiber. It is one of the best materials produced in nature (3). As early as thousands of years ago, people had a certain understanding of the application value of spider silk. The ancient Greeks used spider silk to stop bleeding and heal wounds. Indigenous people used spider silk as a fishing line. By the time of World War II, spider silk was used as a crosshair in the optical device of the sighting system of telescopes, guns (4–7), etc. It can be seen that there have been many research works on spider silk and it has obtained preliminary applications in many fields. Spider silk has also been one of the hot research topics in recent years and has shown great application and commercial value in various fields (8–10).

Natural spider silk is favored by researchers mainly for its outstanding mechanical strength, temperature adaptability, and its composition, while spider silk fiber has high specific strength, excellent elasticity, and super toughness, which is incomparable to those of other natural fibers and synthetic fibers (11). The unit weight of spiderline (Dragline silk) is three times stronger than that of aramid, five times stronger than that of steel, and two times more flexible than nylon (12). It is no exaggeration to say that spider silk is one of the best structural materials produced in nature. The excellent comprehensive performance of spider silk makes it to be considered an ideal material for parachutes and body armor. In addition, the good biodegradability and biocompatibility of spider silk also make it to have good medical applications (13), such as artificial tendons

*** Corresponding author: Jiegang Mou,** College of Metrology & Measurement Engineering, China Jiliang University, Hangzhou, 310018, China, e-mail: mjg@cjlu.edu.cn
Yunqing Gu, Lingzhi Yu, Denghao Wu, Peijian Zhou, Maosen Xu: College of Metrology & Measurement Engineering, China Jiliang University, Hangzhou, 310018, China

and ligaments, tissue repair materials, surgical sutures, etc.

Because spiders are carnivorous animals and do not like to live in groups, it is difficult to raise them in large quantities (14). An effective method is to use the bionic technology to apply the spider silk structure and principle to other man-made materials. In recent years, with the development of high-tech such as genetic modification, polymers, and nanotechnology, researchers have conducted an in-depth exploration of the composition, structure, and characteristics of spider silk. For example, the DNA sequence of spider silk proteins has long been determined (15); spider genes are transferred to silkworms or other animals and plants and microorganisms to produce a large amount of spider silk protein by transgenic technology (16). With the development of science and technology and people's demand for new materials, the research and development of spider silk materials have received more and more attention, and new materials related to spider silk appear sequentially. This article summarizes the research status and application of typical bionic structural materials of spider silk in different fields from the perspective of research value and application methods, and further looks forward to its development prospects.

2 Characteristics and structure of spider silk

As one of the oldest species in the world, spiders have been living on earth for 400 million years. Except in Antarctica, they are distributed all over the world. Up to 3,000 spider species are currently recorded (17). Spider silk is secreted by the glands of spiders. Spiders use spider silk to carry out predation, reproduction, nesting, and other life activities, which are important tools for spiders to survive. At present, there are more research studies on Nephila clavipes (18,19), Araneus diadematus (20), Araneus ventricosus (21), Latrodectus hesperus (22), etc. These spiders have a similar tossing mechanism and their towing wire is the main research object.

2.1 The characteristics of natural spider silk

The net structure of natural spider silk in its natural state is shown in Figure 1. The main chemical components of

Figure 1: Appearance of natural spider silk.

spider silk are glycine, alanine, and a small amount of serine. It is thin and soft in appearance and has excellent elasticity and strength.

Natural spider silk is similar to natural silk, but its performance is slightly better than that of natural silk in all aspects (23). The mechanical properties of spider silk are shown in Table 1. The elongation of spider silk is slightly higher than those of silk and nylon, and the elongation at break can even reach two to four times its length (24), which is much higher than those of steel and Kevlar, so spider silk is very elastic. The tensile strength of spider silk is about five times that of steel, similar to that of Kevlar, and far better than those of silk, rubber, and nylon. Spider silk has the highest breaking energy, so its toughness is much better than those of other materials (25). Based on the above characteristics, the spider web can withstand great impact forces without being damaged, and its static load and impact resistance are better than those of other artificial and natural materials (26).

In addition, the ability of silk to absorb vibration after forming a spider web is also amazing. When flies,

Table 1: Comparison of the mechanical properties of spider silk and other materials (25–29)

Material	Elongation at break (%)	Tensile Strength (N/m^2)	Breaking energy (J/kg)
Spider silk	35–50	5×10^9	1×10^5
Nylon	18–26	5×10^8	8×10^4
Kevlar	2–5	4×10^9	3×10^4
Silkworm silk	15–35	6×10^8	7×10^4
Steel	8.0	1×10^9	5×10^3

moths, and other flying insects hit the spider web, the spider silk is stretched and tends to shrink back to its original state. When the silk shrinks, part of the mechanical energy will be converted into thermal energy, which will prevent the spider web from rebounding. With the cohesiveness of the spider web, it will be difficult for flying insects to escape once they enter the web (30).

Spider silk has good temperature characteristics. The spider silk still has good stability at 200°C, and its structure will be destroyed when the temperature goes beyond 300°C. Spider silk also performs well in low-temperature environments and still retains the elasticity at low temperatures of −40°C (31,32), and will not harden until reaching lower temperatures. Therefore, the advantages of spider silk materials are particularly significant in certain high- and low-temperature applications.

Spider silk is biocompatible (33). The main component of spider silk is spider silk protein, which is protein in nature and non-toxic. At present, no immune rejection reaction to spider silk protein has been found in the human body, so it has good biocompatibility. And spider silk can be degraded under specific conditions, and the degradation products can be absorbed by human tissues (34), so it is an ideal wound suture and prosthesis making material.

Spider silk is very sensitive to water. When immersed in water, spider silk fibers will shrink and affect the mechanical properties of spider silk. This shrinkage phenomenon of spider silk is called super contraction. Influenced by humidity, the size of spider silk fibers will change, and its tensile properties will also change (35).

These excellent properties of spider silk are not available in many natural or artificial materials. Through an in-depth research work on its structure and characteristics, researchers have concluded the relationship between its structure and function (36–39). Optimize or compound spider silk to obtain more powerful and more complete spider silk materials, or apply its structural theory to other man-made materials to improve certain characteristics of the material. These are two important directions for the development of spider silk bionic materials today.

2.2 Microstructure of spider silk

Spiders generally have seven glands for the production of spider silk proteins, which can secrete spider silk with different functions according to different needs. The glands used in spider webs and the types of spider silk they secrete are shown in Table 2. Among the various types of spider silk secreted by spiders, the dragline silk is the best and most representative natural protein fiber and one of the most used research objects by researchers.

Take the dragline silk produced by the major ampullate gland as an example, whose constituent proteins are MaSp1 and MaSp2. Both of these proteins have a repeating sequence consisting of approximately 3,500 amino acid residues (48), and on both sides of the protein repeating sequence region are non-repetitive regions consisting of approximately 100 amino acid residues. The molecular weight of natural MaSp1 and MaSp2 proteins is roughly 250–320 kDa (42).

In order to better understand the characteristics of spider silk, an in-depth analysis of the high-level structure of the secondary structure of different regions of the protein is necessary. The atoms of the polypeptide chain in the spider silk protein form a certain spatial arrangement due to rotation of the single chain, forming a peculiar spatial structure of the spider silk protein. According to the different angles between the various amide planes, different main chain conformations are formed. These different molecular conformations are related to its physical properties and biological functions. The spatial configurations of spider silk include (49): (1) α-spiral: the helix formed by the backbone of the polypeptide chain rising around the helix axis. (2) β-Sheet (50): multiple peptide chains or several peptide segments of a chain are arranged in parallel, and a certain fold is formed to form a sheet structure. (3) Irregular curl: that is, there is no regular partial peptide

Table 2: Types and composition of spider silk secreted by different glands (40–47)

Glands	Type of spider silk	Composition
Aggregate	Aqueous cement	ASG1, ASG2
Pyriform	Core fiber of capture spiral	PySp1, PySp2
Tubuliform	Egg-case silk	TuSp1, ECP-1, ECP-2
Flagelliform	Spiral silk	Flag
Aciniform	Capture silk	AcSp1
Minor ampullate	Dragline silk, framework silk	MiSp1, MiSp2
Major ampullate	Dragline silk, framework silk, radial silk	MaSp1, MaSp2

chain conformation except the above two conformations, including random coils, free folding, free rotation, U-shaped structure, etc.

There are three main types of amino acid sequence modules in the dragline silk: GPGXX, $A_n/(GA)_n$, and GGX (51). Among them, the arrangement of GPGXX amino acids will form a β-turn structure. The aggregation of multiple structures will cause a series of β-turns to fold together in series to form a β-turn spiral. This structure is similar to a “spring” and will greatly enhance the elastic properties of the protein (52). When β-turn is subjected to an external stress, a “spring” structure of proline will produce a corresponding restoring force to balance the torque acting on it. $A_n/(GA)_n$ is a sequence of alanine and glycine abundance, and the amino acid sequence will be neatly arranged to form a β-turn sheet structure (53). A sequence will form a “cable-like” structure, which will greatly enhance the stability of the crystalline region. The β-turn lamellar area also determines the strength properties of the spider silk, and due to the large amount of this area, the spider silk is also difficult to dissolve in water. GGX is a rich region of glycine, which will form a 3_{10} helix structure, that is, every three amino acids will form a helix structure by the action of covalent bonds. This structure is the transitional connection between the rigid region and the elastic region of the crystalline region. In short, the $A_n/(GA)_n$ sequence constitutes the hydrophobic crystalline region of the protein, giving spider silk protein its high tensile strength, while the GPGXX sequence forms the hydrophilic region of the protein, contributing to the excellent elastic properties of the protein. Together, they guarantee many excellent properties such as high strength and high elasticity of spider silk (48).

3 Mechanical properties of spider silk bionic material

Natural spider silk originates from the web formed by the spider or is manually drawn from the silk gland of the spider, but the yield is very low and cannot meet the actual application requirements. Spiders are carnivorous animals and are highly combative. When put together, spiders often attack each other. The survival rate of rearing is extremely low, so it is difficult to raise spiders in large numbers like domestic silkworms (54). There are many silk gland organs in spiders, and the properties of silk produced by different glands are different, so it is difficult to collect spider silk with a completely uniform performance; and due to the differences among spider individuals, the living environment, survival mode, self-control ability, and silk forming conditions will affect the quality of spider silk, so there is no uniform performance standard for natural spider silk. In addition, the processing of natural spider silk is extremely difficult, and the formed spider silk is difficult to be processed into other specific shapes. Therefore, the application range of natural spider silk is greatly limited, and new methods and approaches need to be sought to obtain a large number of new materials with similar structure and function to natural spider silk. Based on the principles of bionics and the understanding of the structure and function of natural spider, the design of new bionic materials with the advantages of natural spider silk has great scientific significance and application value.

3.1 Biocomposite

High stiffness and toughness are usually two mutually exclusive properties in a material. At the same time, achieving the strength and elasticity of a material is an extremely important and complex task (55,56). With the development of biocomposites, researchers have begun to try to produce materials with both high stiffness and toughness. Pezhman et al. (57) combined the silk-inspired triblock proteins with aligned nanocellulose to develop a nanocomposite material with high stiffness, high strength, and high toughness. First, they used a repetitive region from the ADF3 dragline spidroin from Araneus diadematus. A part of the wild-type spidroin sequence (called ADF3) and an engineered version having a repeating consensus sequence (called eADF3) were used. Then, cellulose-binding modules (CBMs) were added at each of its two ends. Finally, the modified DNA was used to produce proteins, CBM-ADF3-CBM and CBM-eADF3-CBM, with a triblock protein structure. Recombinant proteins with triblock architecture combine structurally modified spider silk with terminal cellulose affinity modules. Flow alignment of cellulose nanofibrils (CNFs) and triblock protein allowed continuous fiber production. Protein assembly involved phase separation into concentrated coacervates, with subsequent conformational switching from disordered structures into β-sheets. This process gave the matrix a tough adhesiveness, forming a new composite material with high strength and stiffness combined with increased toughness. Figure 2 shows the performance test results of this new material. It can be seen from Figure 2 that

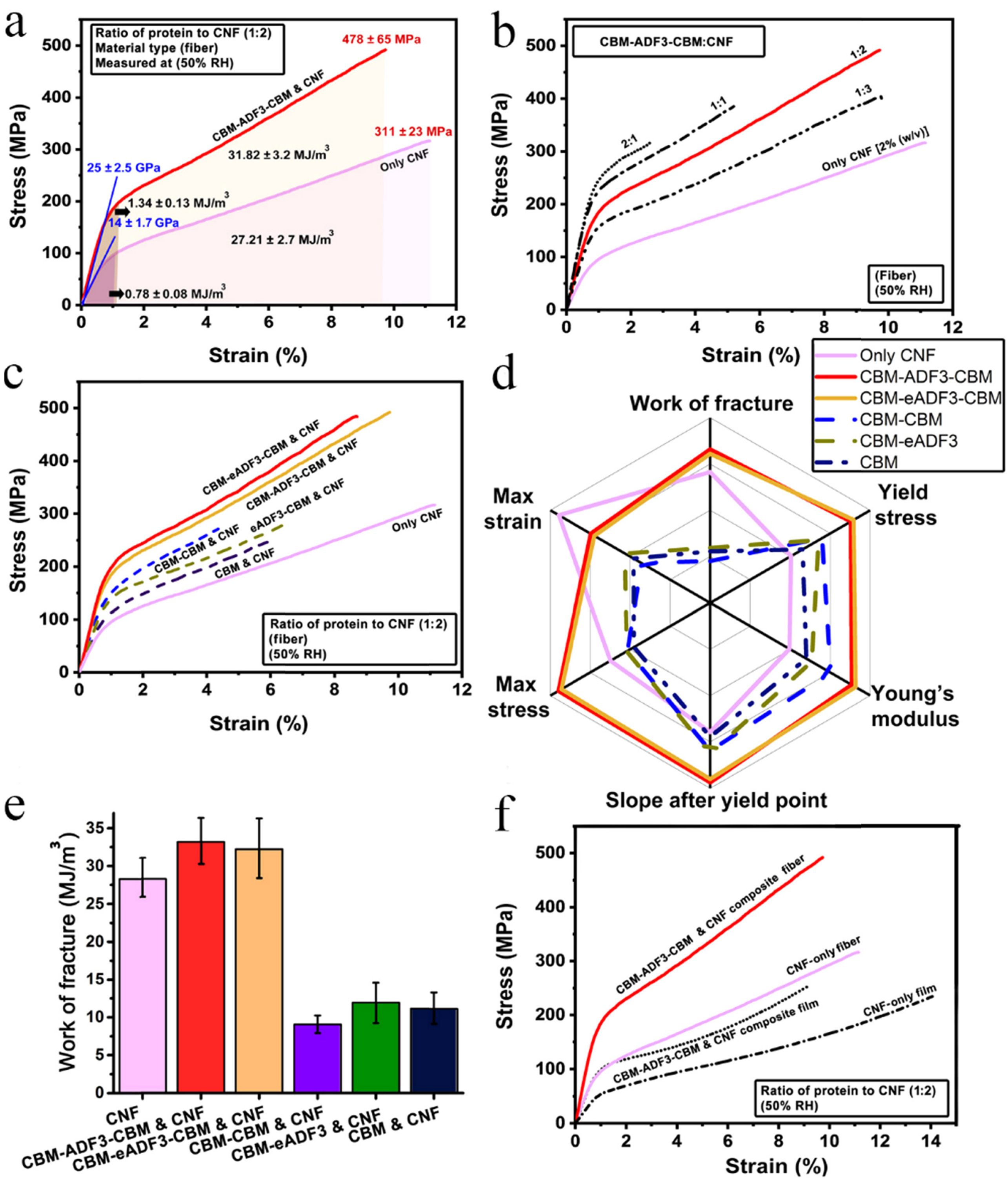

Figure 2: Properties of composites of spidroin proteins and nanocellulose (57). (a) Stress–strain curves of triblock spidroin composites and CNF fibers. (b) Stress–strain curves of protein and CNF composites with different protein-to-CNF ratios. (c) Stress–strain curves of composite fibers from different protein variants. (d) Performance comparison of composite fibers from different protein variants. (e) Toughness values of composite fibers from different protein variants. (f) Stress–strain curves of the oriented (fiber) and non-oriented composites and CNF. Copyright 2019, American Association for the Advancement of Science (AAAS).

after the triblock spider silk protein is compounded with nanocellulose, its toughness and tensile strength are greatly improved. With the increase in the proportion of spider silk protein, the hardness of the composite fiber increased significantly. By comparison, it was found that only the triblock structure of the spider silk protein can increase the fracture energy, stiffness, and yield strength at the same time. Comprehensive test results show that the composite material achieves the bionic goal of combining strength and toughness. Currently, this material is expected to be made into cloth, packaging, and even medical implants. In the future, this composite material can also become a substitute for ordinary plastic, which is convenient and environmentally friendly.

Another research result further amplifies the excellent properties of spider silk and produces materials with a better performance based on the natural spider silk. In recent years, graphene and its modified materials have attracted much attention (58,59). Luca et al. (60) dispersed graphene micro flakes and carbon nanotubes in water to make a special breeding solution to feed spiders, which successfully increased the strength of spider silk by three times and the toughness by ten times. Finally, a reinforced spider silk composited with graphene and carbon nanotubes was obtained. So far, this is the toughest fiber with strength comparable to that of the strongest carbon fiber. The study paves the way for the production of enhanced bionic silk fibers using a natural and efficient spider spinning process, thereby further improving one of the most promising strong materials.

There is a new research result that creatively uses the super contraction phenomenon of spider silk and cleverly exerts the huge value of the super contraction characteristics of spider silk. Super contraction of spider silk has a typical water-responsive shape memory function. Based on the existing research work on super contraction mechanism and the understanding of shape memory polymers, Gu et al. (61) were inspired by the shape memory behavior of spider silk and proposed a heat-responsive shape memory peptide with a β-sheet structure. A novel water-sensitive two-way shaped memory material was developed by incorporating the spider silk protein with a β-sheet structure into polyvinyl alcohol. The β-fold structure makes the material have good shape recovery ability and high shape fixability. This material not only has the characteristics of biocompatibility and non-toxicity, but is also easy to manufacture and has a high application potential in biomedical fields.

3.2 Cobweb-like structure material

Spider silk bionic materials are not limited to biological materials, and their composition is not limited to proteins. In fact, the composition of spider silk fibers and the structure of spider webs have a greater appeal for materials science. Through an in-depth understanding of the cobweb structure and the use of the principles of the cobweb structure to build other molecules, it is often possible to enhance the original material or to obtain new materials with a better performance than natural cobwebs.

Spider silk has good mechanical properties. The reason for such good properties is that it contains many nanosized crystals. These tiny crystals are oriented and dispersed in the spider silk protein matrix, which plays a good role in enhancement. Liff et al. (62) embedded the laponite into elastane by imitating the special structure of spider silk to produce a nanomaterial with good elasticity and toughness. They first dissolved clay flakes in water, exchanged it with water by solvent replacement using dimethylacetamide (DMAc) solvent capable of dissolving polyurethane, and then added the polyurethane elastomer to the laponite–DMAc mixture. By evaporation, a clay sheet–polyurethane elastomer nanocomposite film with a thickness of 80–120 μm can be obtained. Hard clay sheets are randomly distributed in the composite film, strengthening the material in all directions.

Three-dimensional carbon materials have great application prospects as electrode materials for supercapacitors due to their advantages such as high electrical conductivity and fast electrolyte diffusion rate (63–66). During the electric double-layer capacitor reaction, the diffusion of electrolyte ions and the rate of electron transfer have important effects on the electrochemical reaction speed, and the electrode/electrolyte interface greatly affects the performance of electrochemical energy storage (67–70). Deng et al. (71) were inspired by the spider-web structure and used the zeolite imidazolate framework (ZIF) as a precursor to fabricate a 3D carbon network (3DCN) with a bionic surface. The preparation process is shown in Figure 3. 3DCN is produced as the matrix by the salt-template method. ZIF-8 particles are added and fused into a continuous network-like, which is closely attached to 3DCN by a calcination process. The ZIF-8 particles act as the “spider” to introduce a “spider web” pattern on the surface of 3DCN. After the metal elements of ZIF were etched, a spider-web-like carbon pattern was formed on the surface of 3DCN. Such a modified surface morphology endows the carbon hybrid (S-3DCN) with enhanced mass-transfer ability and fully takes advantage of the ZIF-derived carbon. Further research work shows that the Laplace force differences in microstructures enable the liquid drops to arrange quickly, and the carbon hybrid material can deliver energy much faster in supercapacitors and exert a promising performance in electrolyte-based energy storage devices. This work has universal significance on carbon-based applications, such as catalysis, sensing, and energy conversion.

The spider-web structure is responsible for increasing the mechanical strength. Pant et al. (72) reported for the first time the preparation of a hybrid spider-web-like mat of polymer and oligomer using a simple electrospinning technique. They added viscous nylon-6 to methoxy poly(ethylene glycol) (MPEG) and applied a high voltage to the spinning solution during the electrospinning. The hydrogen bonds between MPEG and nylon-6 molecules appeared. And finally, a MPEG oligomer with a viscous nylon-6 supporting solution was fabricated. Strongly interconnected thin MPEG spider-web-like nanofibers with thick nylon-6 nanofibers are responsible for increasing the mechanical strength and hydrophilic nature of the nylon-6 mat. This material can be used for effective air filtration and different biomedical applications.

Spider silk is rich in alanine and glycine, and the protein molecules containing alanine are tightly arranged and crystalline, which make the spider silk extremely strong. The glycine-containing protein molecules are arranged in a disorderly manner, which makes the spider silk have good elasticity and stretchability. Gu et al. (73) proposed a method for synthesizing spider silk fibers by connecting a polypeptide to a compliant polymer segment. They used polybenzyl glutamate to simulate the structures of α-helix and β-sheet in spider silk, and further connected to the random coiled segments composed of polytetramethylene ether glycol. The resulting material has extremely high toughness and tensile strength. Tensile experiments show that the modulus of the polymer increases with the increase in the peptide component. The polymer fiber with a polypeptide content of 41.5% has a tensile strength of about 100 MPa and an elongation at break of 750%. The toughness of the obtained spider silk fibers (387 MJ/m^3) is more than twice that of ordinary spider silk drawing toughness (160 MJ/m^3). Compared with polyurethane materials with a similar structure, this material has an unprecedented tensile strength, and its fracture strain and strength have also been significantly improved.

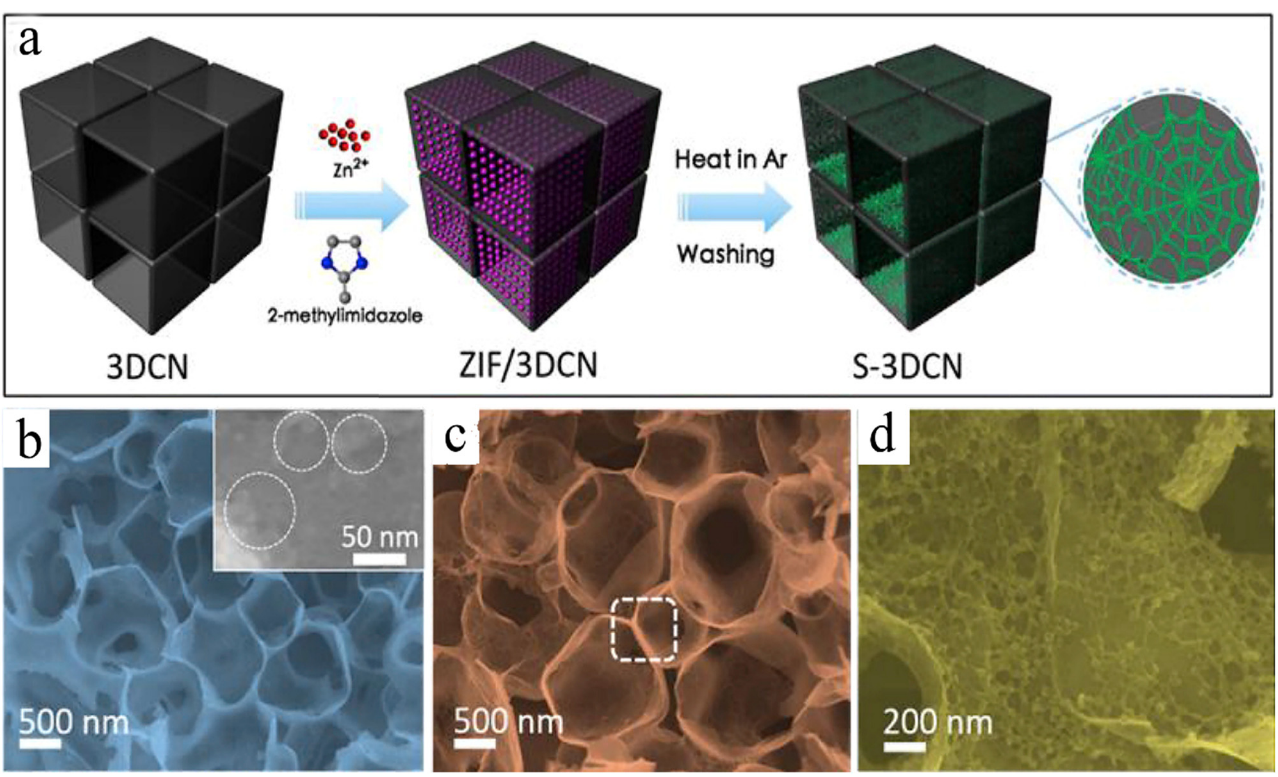

Figure 3: Product process and SEM image of S-3DCN (71). (a) Schematic diagram of the S-3DCN synthesis process. (b) SEM image of ZIF/3DCN and an enlarged image of ZIF particles on the carbon wall. (c and d) SEM image of S-3DCN. Copyright 2019, Elsevier.

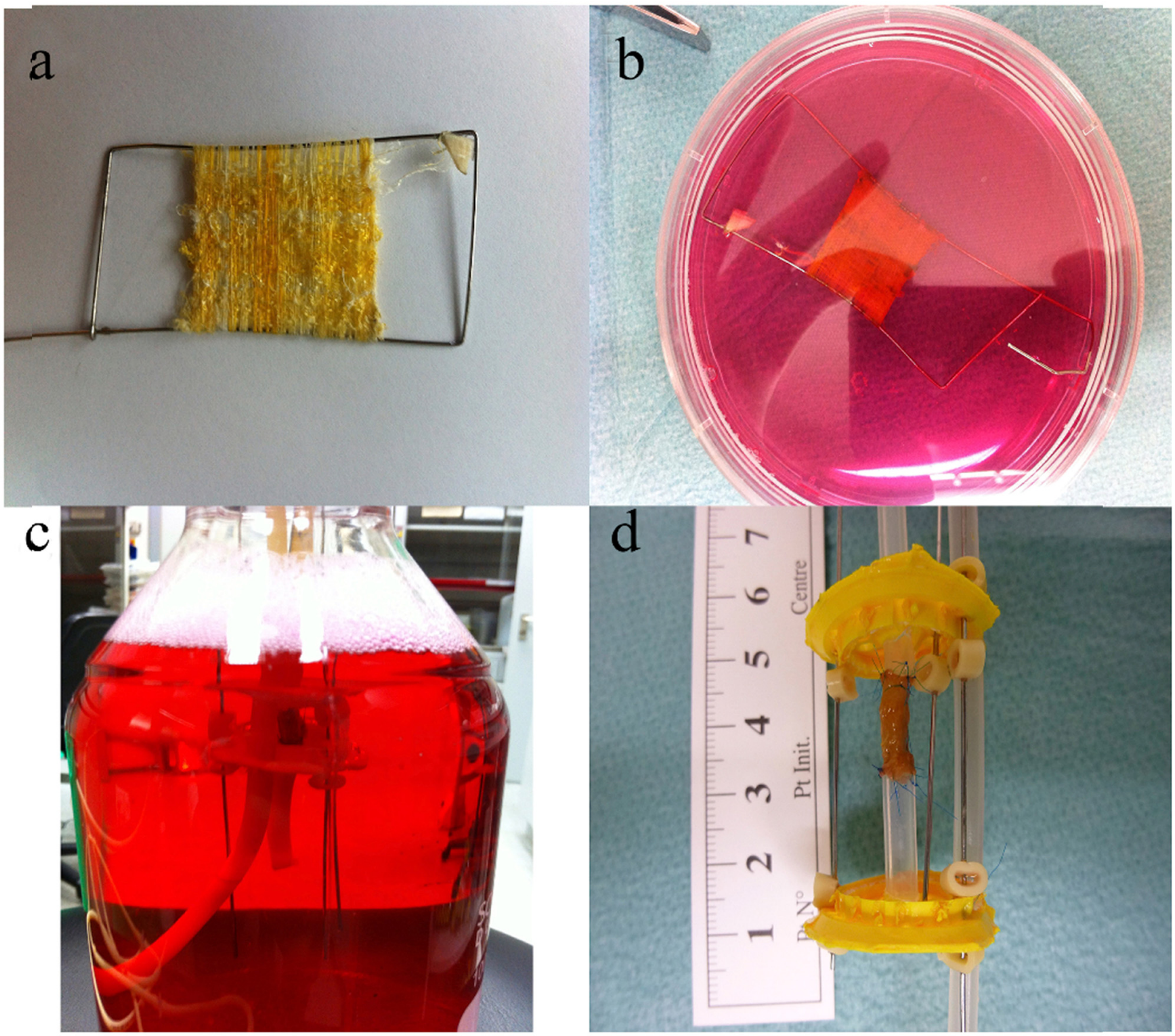

Figure 4: Artificial blood vessel preparation process (78). (a) Spider silk scaffold. (b) C2C12 and ST1.6R were cultured on both sides of the spider silk scaffolds. (c) Constructed blood vessels were induced by pulsatile flow in the bioreactor. (d) Tissue-engineered vascular graft after 3 weeks of induction. Copyright 2020, Elsevier.

4 Application analysis of spider silk bionic material

The application fields of spider silk bionic materials are very wide. Common areas such as medicine, construction, automobile industry, and aerospace have included the appearance of spider silk materials. And the application of spider silk bionic materials is constantly expanding.

4.1 Medical applications

In recent years, many biologically derived materials have gained attention in the medical field (74). Inspired by the ability of natural spider silk to stop bleeding and promote wound healing, researchers hope to develop a new vascular graft. A significant drawback of today's artificial blood vessels is their instability and lack of vascular resistance. Therefore, it is necessary to find alternative biological methods to improve the physical properties of artificial blood vessel walls. Spider silk has been proven to be degradable, flexible, and has strong mechanical properties and good biocompatibility in research (75–77). For example, Dastagir et al. (78) developed a new type of artificial blood vessel using natural spider silk as a supporting matrix. C2C12 and ST1.6R cells were seeded on the two surfaces of the spider silk scaffold, respectively, and cultivated under

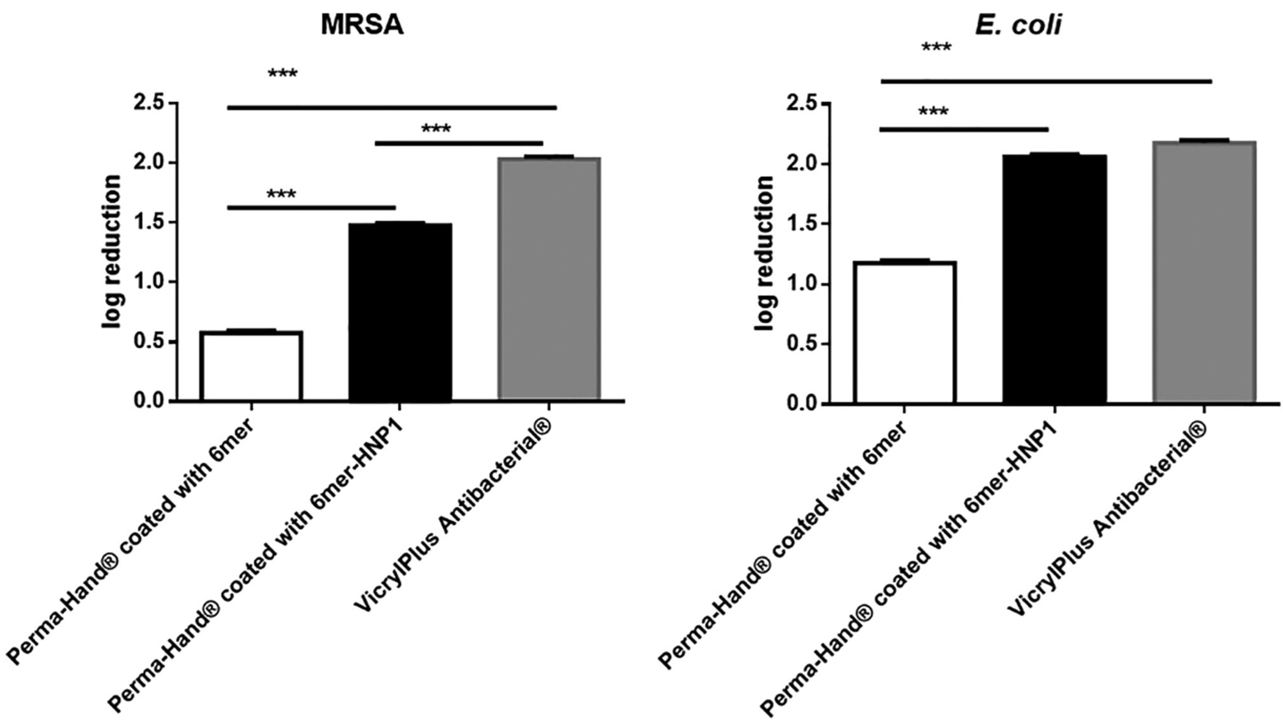

Figure 5: Comparison of the effects of Perma-Hand sutures with 6mer and 6mer-HNP1 coating on *Staphylococcus* (MRSA) and *E. coli* at 37°C (79). Copyright 2019, Elsevier.

pulsatile flow in a bioreactor, and finally induced to form a vascular prosthesis. The main processes of its preparation are shown in Figure 4. Tests show that this artificial blood vessel has extreme biocompatibility, has mechanical properties equivalent to those of natural blood vessels, and can make cells adhere, differentiate, and proliferate.

After an extensive surgery or other types of healthcare practices, doctors generally fix and connect the edges of the wound tissue with surgical sutures to promote wound healing and avoid infection. However, the suture itself is susceptible to bacteria, which easily causes infection of the biofilm and is difficult to treat. In order to prevent the formation of bacterial biofilms, an extra layer of antibiotic-based antibacterial coating is added to the sutures. However, the resistance of microorganisms is getting stronger and stronger, which has prompted researchers to find new alternatives with antibacterial capabilities. Spider silk protein solves many problems in the field of biomedicine with its unique chemical and physical properties, excellent biocompatibility, minimal immune response, and controlled biodegradability. Albina et al. (79) used recombinant DNA technology to modify chimeric spider silk proteins with antibacterial properties and developed a suture coating that can effectively avoid wound infection. First, they inserted the DNA encoding the antibacterial peptide HNP1 into the DNA of the recombinant spider silk protein 6mer and then cultivated *E. coli* to produce a more antibacterial spider silk protein 6mer-HNP1. Comparative tests on 6mer-coated, 6mer-HNP1, and uncoated sutures show that the coating has little effect on the mechanical properties of the sutures and does not affect the maximum tensile strength and breakpoint of the sutures. It does not have much effect on the degradation ability of the suture itself, and the antibacterial ability of the suture containing the coating is significantly improved. It can be seen from Figure 5 that the coating reduces the number of bacteria significantly, compared to the uncoated suture. Compared to 6mer-coated or uncoated sutures, Perma-Hand sutures coated with 6mer-HNP1 have significant inhibitory effects on *Staphylococcus aureus* and *E. coli*. The application of artificial spider protein 6mer-HNP1 as an antibacterial coating can develop a new class of drug-free sutures instead of antibiotic sutures. Not only that, the coating also has great application space in surgical instruments, biological grafts, and other fields.

Cancer is one of the major causes of death worldwide. Chemotherapy is the most common treatment, but due to the low efficiency of the targeted delivery, the anticancer drugs have toxic side effects by causing

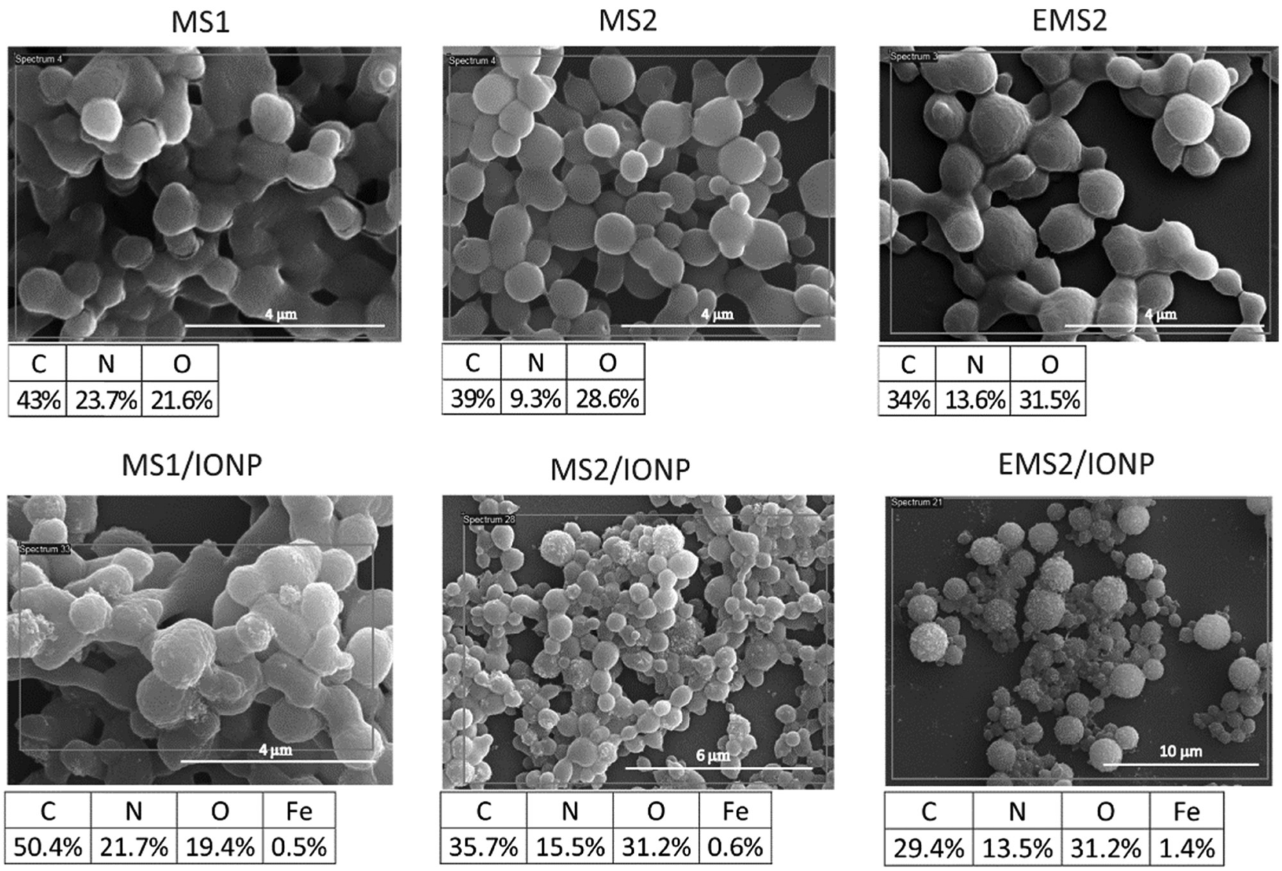

Figure 6: SEM images and EDXS quantitative results of the selected elements of MS1 and MS1/IONP spheres, MS2 and MS2/IONP spheres, and EMS2 and EMS2/IONP spheres (83). Copyright 2019, PLOS.

damage to healthy tissues. Side effects limit the effectiveness of chemotherapy (80). Iron oxide nanoparticle (IONP) is regarded as an excellent drug delivery vehicle (81), especially as its high-temperature therapy can help in cancer treatment (82), but its toxicity severely hinders its practical application. Kucharczyk et al. (83) composited bioengineered spider silk protein EMS2 with iron oxide nanoparticles into a composite sphere, which created conditions for the application of iron oxide nanoparticles. They tested three engineering spider silk protein spheres including MS1, MS2, and EMS2, mixed the spider silk protein sphere solution with iron oxide nanoparticles, and added a high-concentration potassium phosphate buffer solution to produce a new composite sphere by salting out with a potassium salt. The new composite spheres are MS1/IONP, MS2/IONP, and EMS2/IONP. It can be seen from Figure 6 that the three kinds of bioengineering spider silk proteins are spherical and still retain the spherical shape after being compounded with iron oxide particles. IONP tends to gather in tight clusters and cover the surface of the sphere in the form of small bumps. The highest IONP was detected in EMS2/IONP spheres. Through analysis, it was confirmed that iron oxide particles still existed in the sphere, and the β-sheet structure dominated the composite particles. In addition, the composite sphere has good magnetic properties, excellent biocompatibility, and non-toxicity, doubles the load efficiency of doxorubicin, and achieves a more accurate drug targeting. The results show that cytocompatible spheres made of iron oxide/spider silk composites have high magnetic properties and the ability to enhance chemotherapeutic drug loading. This composite sphere has great potential for drug delivery to cancer cells in magnetic resonance imaging and thermotherapy.

4.2 Textile applications

Natural spider silk can be used to make clothing like silk, and clothes made from spider silk have good breathability, can absorb sweat, and are more resistant to wear and tear. However, because the production efficiency of spider silk is low, spider silk clothing has

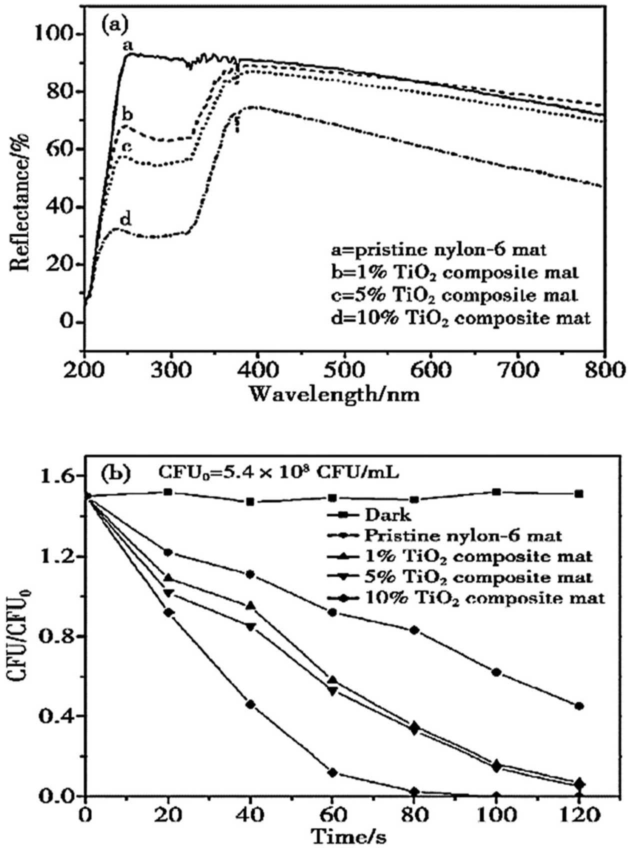

Figure 7: (a) UV-visible spectra of pristine nylon-6 and different nylon-6/TiO_2 nanocomposite mats. (b) Antimicrobial efficiency of pristine nylon-6 and different nylon-6/TiO_2 nanocomposite mats (85). Copyright 2011, Elsevier.

always been a luxury. Nanocobweb material is suitable for the manufacture of clothing, especially protective clothing. Pant et al. (84,85) obtained a composite nanocobweb fiber mat with UV and antibacterial functions by adding TIO_2 particles to PA6. Among them, TIO_2 can absorb near-ultraviolet light waves and form highly charged electrons with negative charges, while generating positively charged holes in the valence band. As shown in Figure 7(a), as the content of TIO_2 increases, the UV absorbance of the cobweb fiber mat increases and the UV reflectance decreases. Photoelectron or hole reacts with water or dissolved oxygen in the water to generate hydroxyl radicals and superoxide ions, which can biochemically react with microbial cells. Therefore, as shown in Figure 7(b), the bacterial survival rate decreases with increasing TIO_2 content. By adjusting the cobweb pore size and the number of micropores, the material's waterproof, moisture-permeable, breathable, and heat-transfer properties can be modified to meet the needs of different protective clothing.

4.3 Sensor application

Nanocobweb fiber has also been widely used in the field of sensors. The radiation on the spider web extends radially outward, supporting and transmitting signals. Liu et al. (86) inspired a unique assembly method of spiral and radiation microstructures in spider webs, proposed a new structure of electronic devices, and developed a new type of multi-resolution graphene tactile sensor. They used a highly sensitive aerogel as a sensing material and a graphene tape with high conductivity and stability as a transmission material to realize the orientation, distance, and position identification of the new tactile sensor. The electronic skin integrated by this sensor can sensitively sense various contacts, and the minimum force it can measure can reach 3.83×10^{-3} Pa. At present, the research work has attracted great attention in related fields such as robotics, wearables, and human–computer interaction.

Taking advantage of the very sensitive nature of silk fibroin to environmental humidity, Liu et al. (87) made a new type of high-sensitivity humidity sensor using spider egg-sac silk (SESS). The structure and experimental results are shown in Figure 8. Using a part of single-mode fiber and a part of SESS to make an interference cavity, changes in ambient humidity will cause a change in the diameter of the SESS, which will cause a change in the interference length. The change in the interference cavity length will cause the interference spectrum to be redshifted, and the relationship between the spectral offset and the ambient relative humidity (RH) can be obtained, thereby achieving the measurement of the ambient RH. The results show that the sensor probe has excellent stability, repeatability, and temperature resistance. The higher the ambient humidity, the higher the sensitivity. The maximum value of the sensitivity is 0.99 nm/%RH in the humidity range of 90–99%.

4.4 Acoustic applications

Spider web is composed of different radiation silk and catching silk. The ring in the center of the web can resonate at a specific frequency, which can effectively reduce and absorb the vibration of various frequencies. Based on this natural structure, Miniaci et al. (88) designed a sonic metamaterial, which consists of several square units with a Co-vibration ring, and is connected by the ligament structure to the center and surroundings of the ring. The sonic metamaterial structure model is shown in Figure 9. Five parameters can be adjusted in the structure, which is composed of two parts: hoop and traction. Under the

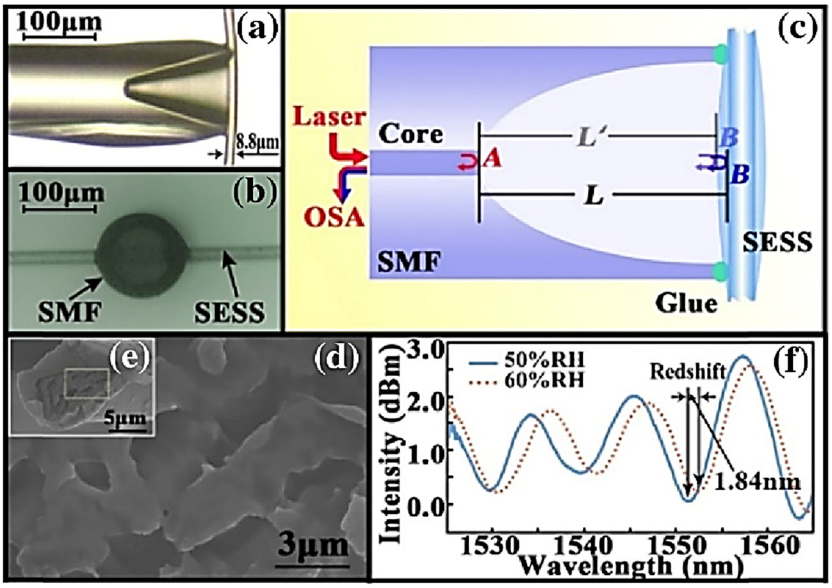

Figure 8: Structure and experimental results of a humidity sensor (87). (a) Microscopic image of a SESS-based humidity sensor probe. (b) Side view of a SESS-based humidity sensing probe. (c) Front view of a SESS-based humidity sensing probe. (d) Scanning electron microscope (SEM) photograph of the SESS profile (partially enlarged). (e) SEM photograph of the SESS data. (f) The experimental result of the redshift of interference spectrum from 50% to 60% RH at 1.8° nm at 35°C. Copyright 2019, OSA Publishing.

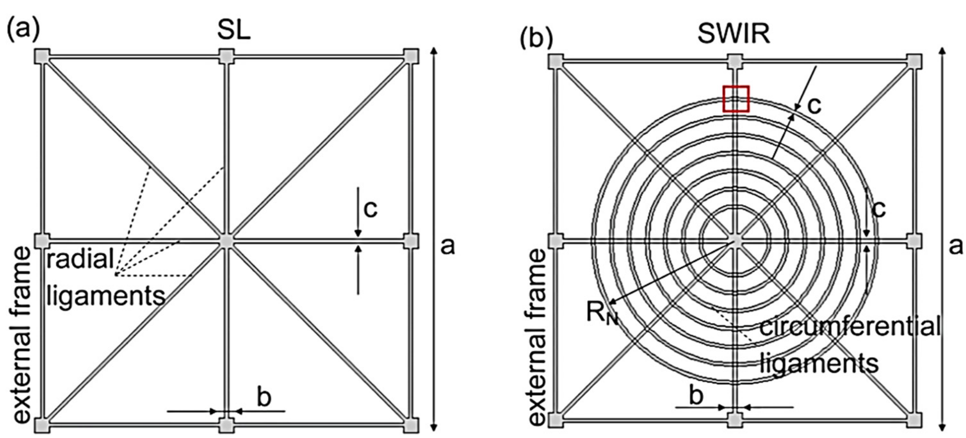

Figure 9: Structural model of a sonic metamaterial (88). (a) Traction part. (b) Hoop direction. Copyright 2016, AIP.

condition of ensuring that the material is unchanged, by adjusting these five parameters, research work on different structural parameters is realized. This metamaterial has high controllability. It can adjust five parameters to design materials that respond to different frequencies. In addition, under the condition that the structural parameters are not changed, by changing the material of the hoop and traction parts, the influence of different materials on the vibration characteristics can be tested, to find the best material, make better use of the "cobweb" structure, and achieve a better acoustic performance. Combined with the ultra-high-strength and anisotropy of spider silk, this spider silk bionic metamaterial exhibits adjustable acoustic properties and is expected to play new roles in the field of vibration, such as strengthening bridges and buildings during earthquakes, noise reduction, Yabo image technology, and sound stealth cloak and more.

5 Conclusions and outlook

In summary, based on the analysis of the research and development results of spider silk bionic materials, combined with the application needs in various fields, the research direction and application of spider silk bionic materials can be prospected. The research work on spider silk has gone through different stages from appearance, characteristics to structure and molecular composition. The application of spider silk has also experienced the development from natural spider silk to artificial spider silk, from primary to advanced applications. Today's spider silk technology involves multiple disciplines and fields, such as biology, chemistry, and polymers. In the future, the research work on spider silk should be further micronized, and the mechanical properties and biocompatibility mechanism of spider silk should be further analyzed from the perspective of molecular composition and structure, and its application should be used to improve the design of artificial fibers or enhance the performance of other materials.

With the progress and development of science and technology, people's demand for superior performance materials is getting higher and higher, which puts forward higher requirements for the research work on natural spider silk bionic materials and related science. The application of spider silk bionic material in many fields has a broad prospect:

Military field: spider silk fibers have excellent strength and toughness. The body armor and parachute made from them can not only improve performance but also greatly reduce weight. In addition, some cobweb structures can effectively absorb impact forces and help improve the strength of the material. They can be applied to the shells of equipment such as tanks, aircraft, and satellites, or the protective cover structures of military buildings.

Textile field: spider silk is similar to silk but has a better performance than silk. Cloth made from spider silk has the characteristics of light weight, non-breakability, better breathability, strong water absorption, and UV resistance. Promote the development of spider silk spinning technology, spider silk cloth will bring revolutionary changes to the field of apparel textiles.

Medical field: there is still huge room for development in the field of spider silk. With its excellent biocompatibility, it can be considered to make artificial materials such as prostheses, ligaments, and skin.

Material field: the high strength of spider silk fiber can be used to make a bionic material to replace the steel bars in concrete. It will greatly reduce the weight of the building in the construction, and the spider silk material is resistant to humidity and cold, and will not rust, which is especially suitable for building bridges and other buildings. Combining spider silk materials with the automotive industry can produce lightweight, abrasion-resistant tires, a stronger body, and bring about a significant reduction in vehicle weight.

Environmental protection: spider silk-based nanocomposites are similar to plastics and are expected to replace some common plastics. Because spider silk protein can be degraded, using it to make plastic bags will help protect the environment and reduce white pollution.

With the continuous deepening of spider silk research, the mysterious veil of spider silk is gradually opening up, and the research work on the large-scale production of artificial spider silk is also continuously deepening. A large number of superior properties of spider silk bionic materials will replace traditional materials, and spider silk bionic materials will play a huge role in the military, medical, aerospace, construction, and automotive fields.

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