Preparation of silk fibroin and graphene composite membrane and its response driving performance test

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Abstract. With the development of materials, intelligent materials have the functions of sensing, controlling and driving objects, self-adaptive repair and so on, so they have been widely used. Silk fibroin fiber is a kind of natural protein, which is formed by silk degumming, insoluble in water, and can be decomposed gradually in alkaline solution without irritation and side effects, so it has a good prospect of biological application. The silk fibroin film was mixed with graphene composites, and the intelligent materials for functional response were prepared by means of the excellent optical and thermal properties of graphene. The biaxially oriented polypropylene film (BOPP) / silk fibroin bilayer composite film was prepared by the simple composite method, which showed good thermal response bending deformation properties. The graphene solution was dripped on one side of the fibroin film by a dripping method. After low-temperature drying, the final BOPP/SF/RGO/PEDOT:PSS composite film was prepared by adding a layer of poly (3meme 4-ethylenedioxythiophene / polystyrene sulfonate) (PEDOT:PSS). The flexible film driver was prepared, which can respond to multiple stimuli under light, heat and humidity.

1. Introduction

With the development of artificial intelligence system, especially in the field of bionic and intelligent robot [1-2], people pay more and more attention to intelligent devices with the ability of perception, processing and response.

Silk is the lightest, softest and thinnest natural fiber in nature, which can be easily restored after the external force is removed. Silk fibroin fiber is a kind of natural protein, which is formed by silk degumming. It can be decomposed step by step in alkaline solution without irritation and side effects, so it has a good prospect of biological application [3-4].

Graphene is very hard and thin, with a complete lattice structure, almost no defects, and even lower conductivity than silver. It is a high-quality material for the preparation of electronic devices. The unique spin characteristics, thermal properties, optical properties and chemical activity of graphene also require attention. Graphene has high thermal conductivity and the best thermal conductivity, which is higher than carbon nanotubes and diamonds. The excellent physical and chemical properties of graphene make graphene a good two-dimensional material. With people's exploration of smart materials and continuous innovation in research and development technology, graphene composite materials have received great attention [5-6].

High-performance multi-response stimulus deformation material is a kind of material that triggers its rapid change of size and shape through the stimulus source without any external mechanical action. It is a hot topic to use green energy in nature to drive intelligent systems. Stimulus response actuators are particularly prominent because they can convert external energy into dynamic driving behavior in
response to the stimuli of the external environment, such as light stimulus response, thermal stimulus response, humidity stimulus response, electrical stimulus response and so on. With the development of artificial intelligence system, people pay more and more attention to intelligent devices with the ability of perception, processing and response. Smart or smart materials that respond to a variety of environmental stimuli by changing shapes or internal characteristics have aroused great interest. Among them, electronic skin, artificial muscle and intelligent sensing device have broad application prospects. It is widely used in multi-function intelligent system, artificial intelligence and medical rehabilitation.

There are many flexible drivers about stimulus response, which have many limitations, such as single response, poor biological prospect and so on. In this paper, through continuous exploration and innovation, composite thin film drivers that can respond to multiple stimuli, including thermal stimulation, humidity stimulation and light stimulation, have been prepared by using materials such as graphene and silk fibroin, and the performance of stimulus response is much better than before to achieve low cost, fast response, no pollution, and a high degree of bending.

2. Experimental part

2.1 Materials
Biaxially oriented polypropylene film is provided by Deli Group Co., Ltd., poly (3jn4-ethylene dioxythiophene)-poly (styrene sulfonate) provided by Suzhou Grey Co., Ltd., Bombyx mori raw silk, sodium bicarbonate (0.01m) pH 9.5), lithium bromide solution (9.3 mol/L), concentrated sulfuric acid, distilled water, hydrogen peroxide, sodium nitrate, dilute hydrochloric acid (volume fraction 5%), potassium permanganate. Graphene powder, polyethylene glycol and SnCl2/EtOH solution are provided by Suzhou Baino Biotechnology Co., Ltd.

2.2 Preparation of graphene oxide aqueous solution
The process of preparing graphene oxide by Hummers method, the GO powder was added to deionized water, stirred for 1 hour, and then sonicated for half an hour. Repeated 5 times, and after stirring evenly, centrifuged for 15 minutes (5000 rpm) with a centrifuge to filter out the unoxidized graphite and some impurities, and configured it as a 10 mg/ml graphene oxide aqueous solution.

2.3 Preparation of silk fibroin membrane
80g raw silk of silkworm was weighed by precision balance, and the solution of sodium bicarbonate/sodium carbonate with a mass fraction of 0.01 M pH 9.5 was slightly boiled for 30 minutes. The silk was removed and washed with deionized water. Repeat the above steps three times. Finally, the silk with complete removal of sericin was dried in an oven at 60 °C to get pure silk fibroin fiber. The pure silk fibroin fiber was dissolved in lithium bromide solution with a concentration of 9.3 mol/L at 65 ±2°C, the bath ratio was 15/100, and the dissolution time was about 1 hour. After cooling, the fibroin fiber was removed into a dialysis bag and dialyzed in deionized water for 3-4 days. The pure silk fibroin solution was filtered with skimmed cotton. The silk fibroin solution was concentrated to 6% by polyethylene glycol, poured into a petri dish and placed in an oven, and the temperature was controlled at 60 °C to prepare a membrane.

2.4 Preparation of BOPP / SF / RGO / PEDOT: PSS composite film
The self-adhesive BOPP film was cut into 75×12mm size, and then the silk fibroin film of the same size was compounded on the BOPP film. The graphene oxide aqueous solution prepared by 10mg/ml was dripped on the composite BOPP/SF composite film by drip coating. The graphene oxide was reduced by SnCl2/EtOH solution, and then dried in a 30°C blast drying oven for 3 hours. Then the BOPP/SF/RGO composite film was dripped with PEDOT:PSS solution, and then dried in a blast drying oven for 3 hours, and then the BOPP/SF/RGO/ PEDOT :PSS composite film was obtained. Figure 1 shows the preparation process of BOPP/SF/RGO/PEDOT:PSS composite membrane.
3. Results and discussion

3.1 Scanning electron microscope analysis of BOPP / SF / RGO / PEDOT: PSS composite film

The cross-section scanning electron microscope image of the BOPP / SF / RGO / PEDOT: PSS composite membrane driver is shown in Figure 2. The four-layer membrane structure can be clearly observed in the picture. The thickness of the silk fibroin film (SF) is about 150μm, the thickness of the remaining layers is about 325μm, and the total thickness is about 1125μm.

![Fig 2 scanning electron microscopy (SEM) of the cross section of BOPP/SF/RGO /PEDOT: PSS film.](image)

3.2 Thermal response test

The BOPP / SF / RGO / PEDOT: PSS composite film was placed in a blast drying oven at 50°C, placed horizontally on a copy paper, and photographed and recorded at regular intervals to obtain the following figure. From Figure 3 (a-d) It can be seen that with the continuous growth of time, the BOPP / SF / RGO / PEDOT: PSS composite membrane continuously bends upwards to overcome gravity.
3.3 Mechanical properties test

The bending deformation performance of BOPP / SF / RGO / PEDOT: PSS composite film was tested. As shown in Fig. 4 (a), the curve of the bending angle of the composite film over time is shown as the temperature is controlled at 50 °C. It can be seen from the figure that when the response time is about 20s, the maximum bending angle can be about 250℃. And the bending angle increases almost linearly with time. After the composite film was taken out of the baking box after 20s, the composite film would gradually return to the initial state with the increase of time, indicating that the bending deformation of the composite film was reversible. Figure 4 (b) shows the curve of the curvature of the composite film over time when the temperature is controlled at 50℃.

4. Application

The main advantages of stimulus-triggered actuators: they can be driven wirelessly and remotely, without any external energy supply system, and can be driven with changes in temperature, humidity or light in the environment. Figure 5 is an example of the cooperation of three BOPP / SF / RGO / PEDOT: PSS high-performance multi-response composite membrane flexible actuators. The weight is about 0.2g. It can be seen from the figure that the driver is flat without the stimulation of external temperature. When
the temperature rises to 40℃, the flexible driver slightly lifts the object. When the temperature rises to 50℃, the driver completely lifts the heavy object. The driver can maintain this state well until the external conditions are stimulated, and then the original state can be restored.

Figure 5  (a-c) Fabrication of BOPP/SF/RGO/PEDOT:PSS high performance multi response composite membrane. (d-e) Cooperative actuation of three actuator legs triggered by a change in temperature.

5. Conclusion

We replace the paper base in the previously reported BOPP/A4 paper / RGO/PEDOT:PSS driver with silk fibroin substrate. The high-performance multi-stimulus response flexible actuator film BOPP/SF/RGO/PEDOT:PSS can achieve bending deformation under the stimulation of light, heat and humidity, and has a certain degree of reversibility, and the advantage of this kind of actuator is that the silk fibroin film base in the programmable actuator is foldable. It is also biodegradable in organisms. Secondly, through experiments, the bending deformation ability of silk protein film-based actuators is also better than that of paper-based actuators. We expect that this polymer composite will contribute to future research on the mechanical basis of self-folding structures, as well as applications in biomedical devices (such as flexible medical stents) and spatially expandable structures (such as deployable space antennas). Promising applications include microfluidic devices, self-assembled devices, and four-dimensional printing.

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