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(54) **HIGH PERFORMANCE NATURAL SILK FIBER AND PREPARATION METHOD THEREOF**

(57) A high performance natural silk fiber and a preparation method thereof, wherein silk, raw silk, twisted silk or braided silk thread is used as the raw material, which then becomes a high performance silk fiber after being shrunk or stretched; more specifically, a silk swelling solution is prepared by mixing an inorganic salt, an acid and water according to a certain ratio, the silk fiber is then immersed in the swelling solution in order to be

stretched/shrunk; and finally the high performance silk fiber is obtained following rinsing with clean water, neutralizing and drying. The preparation method is simple and effective, and has a short process. The breaking strength of the silk fiber prepared by means of this method is comparable to that of spider silk. Therefore, it is well suited for application in high-tech fields, such as artificial ligaments, ophthalmic sutures, protective clothing, etc.

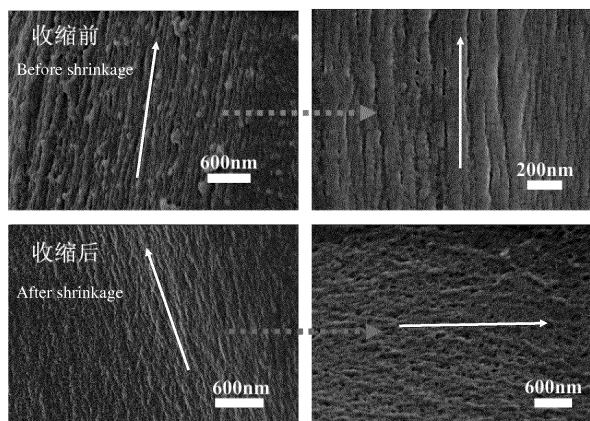


Fig. 1

Description

Technical field

- 5 **[0001]** The invention belongs to the field of natural polymer materials, and in particular relates to a high-performance natural silk fiber and a preparation method thereof.

Background technique

- 10 **[0002]** Silk is a continuous long fiber made from the coagulation of silk glands secreted from jujube when silkworm is cooked and is one of the earliest animal fibers to be used in human beings. According to different foods, silk is divided into mulberry silk, tussah silk, silk and eri silk. The strands drawn from a single silkworm cocoon are called cocoon filaments, which consist of two monofilaments that are adhesively coated with sericin. The silkworms of several silkworm cocoons were withdrawn, and the silks wrapped by silk adhesive were called raw silk. Several raw silks are processed
15 through the process of collateral, twisting, weaving, or weaving to become twisted or braided stitches. As a high-grade textile raw material, silk products are deeply loved by consumers at home and abroad.

- [0003]** In recent years, with the development of polymer science and cross-infiltration among disciplines, the application of silk materials is infiltrating from traditional textiles to high-tech fields. Among them, the research of high-performance silk fibers is one of the hot spots. As a non-physiological structural protein macromolecule, the mechanical properties
20 of silk are closely related to the aggregation structure. Spider silk has particularly excellent mechanical properties, such as high strength, high modulus, high elongation, high fracture work, and has great application value and prospects in high-tech fields such as body armor and sutures. Therefore, it has become a hot topic for material scientists today. It was found that the fiber of the best mechanical property is spider silk, which is also a non-physiologically active structural protein polymer. However, the spiders are killing to each other and cannot be mass-produced in large quantities like
25 silkworms. It has been considered that the reason why the mechanical properties of silk is far inferior to that of spider silk is that the primary structure of silk and spider silk (also known as amino acid composition and sequence distribution) is very different.

- [0004]** For this purpose, the researchers implanted genes of spider which produces spider silk into silkworm to produce silk containing spider silk protein. Compared with ordinary silk, the mechanical properties improved significantly, such
30 as the strength increase of about 20%, the elongation rate increased by about 30%. The high-performance silk fiber has broad application prospects in body armor, high-strength ultra-fine sutures, artificial ligaments, and tendons. The purpose of the transgenic technology is to transform the primary structure of silk. Although progress has been made in this area, major breakthroughs have not yet been made and industrialization cannot be achieved. NATURE magazine published in 2002 published the papers of Professor Shao Zhengzhong from Fudan University and Professor Vollrath from Oxford
35 University in the UK. They used the forced-pulling process to make the silkworm spit out the natural silk that is comparable to spider silk [Shao Z, et al. Nature 2002; 418: 741.]. This study shows that the difference in the mechanical properties of silk and spider silk is mainly caused by the structural differences of secondary structure of fibrin or above secondary structure of fibrin. This difference can be reduced or eliminated by changes in silkworm silking behavior, so as to obtain spider silk with excellent mechanical properties. However, because silkworm larvae are small and soft, have strong head
40 movements, and silk is delicate and easily broken, it is not feasible to mass-produce spider silk by altering silkworm silking behavior.

- [0005]** The difference in the speed of silk threading mainly affects the molecular orientation structure and part of the crystal structure of the silk protein, resulting in a change in the mechanical properties of the silk. Natural silk fiber, thanks to its unique multi-level structure, has excellent mechanical properties in itself. The performance improvement based
45 on this is the best way to prepare high-performance silk protein fibers. The results of strong spinning should be obtained as well theoretically by reorganization of the natural silk structure and further transformation of the silk by the stretching and setting process. However, the formed natural silk fibers are mainly anti-parallel β -sheet crystal structures, and their aggregation structure is very stable, which is difficult to change, perform physical stretching post-treatment cannot be used in the prior art. In the prior art, the natural silk is generally dissolved and then spun to obtain a product with higher
50 performance; however, due to the irreversible destruction of the multi-stage structure of the silk by the dissolving solvent and the spinning solvent, such as a decrease in the molecular weight, disintegration of the fibril structure, etc., caused the fiber structure of regenerated silk is unstable and the mechanical properties are poor. Although the mechanical properties of the regenerated silk fiber can be improved by post-stretching, the performance improvement is limited, not to mention that it is a fiber with better mechanical properties than the natural silk fiber. Therefore, the search for a method
55 for reconstructing natural silk structure to obtain high-performance natural silk fibers has important value and significance for the application of silk in high-tech fields.

Summary of the Invention

[0006] The object of the invention is to provide a high-performance natural silk fiber and a preparation method thereof. The fiber is obtained by direct treatment of natural silk and has excellent mechanical properties, and can be widely used in civilian and military protection fields.

[0007] The invention adopts the following technical solutions to achieve the purpose of the invention:

A method for preparing high-performance natural silk fiber is characterized by comprising the following steps:

(1) preparing a silk swelling liquid, the silk swelling liquid comprising acid and water;

(2) soaking the natural silk fiber in the above-mentioned silk swelling liquid for 1 second to 1 hour, and shrinking or stretching the natural silk fibers;

(3) the treated natural silk fiber are washed with water, neutralized, washed with water, and dried, to obtain high-performance natural silk fiber.

[0008] According the technical solution above, wherein in step (1), the acid is one or more of formic acid, trifluoroacetic acid, acetic acid, hydrofluoric acid, phosphoric acid, and sulfuric acid; the concentration of the acid is 10% to 99% by weight. Preferably, the acid is one of formic acid, hydrofluoric acid, phosphoric acid, and sulfuric acid; the concentration of the acid is 25% to 98% by weight.

[0009] In a preferred technical solution, wherein in step (1), the silk swelling liquid further comprises an inorganic salt; the concentration of the inorganic salt is 0.1% to 10% by weight; the inorganic salt is one or more of sodium chloride, potassium chloride, lithium bromide, calcium chloride, zinc chloride, magnesium chloride, lithium thiocyanate, sodium thiocyanate, magnesium thiocyanate, calcium nitrate, copper nitrate, calcium carbonate, and calcium phosphate. Preferably, the silk swelling liquid further comprises an inorganic salt; the inorganic salt is one of the lithium bromide, calcium chloride, magnesium chloride, and lithium thiocyanate; the concentration of the inorganic salt is 0.5% to 5% by weight.

[0010] The silk in the invention is a natural silk, which is unregenerated treatment, and it is selected from one or more of mulberry silk, tussah silk, yamamai silk, and eri silk. The natural silk fiber is one or more of silk, raw silk, twisted silk, and braided silk.

[0011] In the technical solution above, wherein in the step (2), the shrinkage during the shrinkage is 1% to 80% and the draw-ratio during the stretching is 1.1 to 5. In invention, the natural silk fiber can be stretched or shrunk while being soaked, or it can be stretched or shrunk after the natural silk fiber is soaked.

[0012] Preferably, the shrinkage during the shrinkage is 20% to 70%; and the draw-ratio during the stretching is 1.1 to 3.2; the soaking time is 5 seconds to 5 minutes.

[0013] The invention performs physical stretching/shrinkage modification on natural silk fibers (including silk, raw silk, twisted silk, braided silk, etc.), breaks through the technical problem that natural silk fibers cannot be stretched, and achieves a huge leap of the mechanical properties of natural silk fibers, to meet the application requirements of silk in special areas such as body armor, artificial ligaments, and ophthalmic sutures. Therefore, the invention also discloses a high performance natural silk fiber prepared according to the above preparation method.

The advantages of the invention

Advantages

[0014] Owing to the application of the technical solution above, compared with the prior art, this invention has the advantages as follow:

(1)The invention realizes the direct drawing treatment of natural silk fibers for the first time, thereby achieving the effect of improving the mechanical properties of natural silk, the breaking strength reaching more than 1000 MPa and the breaking elongation reaching 50% or more; overcoming the technical problem that the existing natural silk cannot stretching and achieved unexpected technical effects.

(2) The invention overcomes the defect that the prior art mainly deals with the transgene or forced wire drawing of silkworms. Compared with the prior art, the breaking strength of the natural silk obtained by the invention can be increased by a factor of 2 and can reach 1 GPa or more, and can be used for making high-performance raw silk, twisted silk, braided silk, etc., in line with production applications.

(3) The method selected suitable solvent parameters and dissolving conditions to make silkworm insolubilization and removing β -folded structure, thus providing a window for the structure modification and performance adjustment of natural silk fibers, and obtaining high performance natural silk fibers by simple method.

[0015] The processing method to improve the strength of natural fiber is simple and efficient, and can be directly

connected with the production line of the existing product to realize large-scale production of high performance natural silk fiber. Description of the drawings

FIG. 1 is a scanning electron microscopy image of a surface of a natural silk fiber before and after treatment in Example 1;

FIG. 2 is a scanning electron micrograph of the cross section of the natural silk fiber before and after the treatment in Example 1;

FIG. 3 is an infrared spectrum of a natural silk fiber before and after treatment in Example 2;

FIG. 4 is a Raman spectrum before and after treatment of natural silk fibers in Example 2.

Detailed description

[0016] The invention will be further described below with reference to the accompanying drawings and embodiments.

Example 1

[0017]

(1) Confect the natural silk swelling liquid: formic acid of 98 wt% is diluted with water to 80%, and then add lithium bromide in to get 80% formic acid solution containing 2% lithium bromide, which is the silk swelling liquid;

(2) Immerse mulberry silk in swelling liquid of the step (1) for 30 seconds, and at the same time control the silk to shrink to 60% of the original length, to obtain shrink silk;

(3) After washed with deionized water, shrink silk by the step (2) is neutralized the excess acid in aqueous sodium hydroxide solution with 1wt%, and then washed again and dried in the oven at 60°C, get high performance natural silk fiber.

[0018] Table 1 shows the mechanical tensile data of mulberry silk before and after treatment. According to the technical scheme provided by the present invention, the cocoon silk after treatment has excellent ductility, and the elongation at break reaches more than 50%.

Table 1 Mechanical tensile data of mulberry silk before and after processing

Sample	Elongation at Break (%)	Fracture work (MJ/m ³)
Original mulberry silk	21.1	64.5
Handle mulberry silk	52.3	72.8

[0019] FIG. 1, FIG. 2 and Table 1 are scanning electron microscope and mechanical tensile properties data of the above-mentioned high performance natural silk fiber before and after treatment. As can be seen from Fig. 1, the arrow of the solid line is the fiber direction. After processing, the highly ordered nanofibril orientation structure inside the silk is destroyed; as can be seen from Fig. 2, the nanofibrillar structure inside the silkworm cocoon becomes fluffy and clearly visible; the invention effectively removes the natural silk β -sheet structure, thereby greatly improving the performance of the natural silk fiber. In addition, as can be seen from Table 1, after treatment, the elongation of natural mulberry silk is significantly increased to more than 50%, and the work of fracture is improved by about 10%.

Example 2

[0020]

(1) Confect the natural silk swelling liquid: formic acid of 98 wt% is diluted with water to 80%, and then adds calcium chloride in to get 80% formic acid solution containing 2% calcium chloride, which is the silk swelling liquid;

(2) Immerse mulberry silk in swelling liquid of the step (1) for 30 seconds, and then stretch the silk to twice the original length, to obtain stretching silk;

(3) After washed with deionized water, stretching silk by the step (2) is neutralized the excess acid in the 1wt% aqueous sodium hydroxide solution, and then washed again and dried in the oven at 60°C, get high performance natural silk fiber.

[0021] Table 2 shows the mechanical tensile data of the mulberry silk before and after the treatment. According to the

technical scheme provided by the present invention, the silk has excellent strength and the breaking strength reaches 900 MPa or more.

Table 2 Mechanical tensile data before and after processing

Sample	Breaking strength (MPa)
Original mulberry silk	450
Stretching mulberry silk	920

[0022] FIG. 3, FIG. 4 and Table 2 are the infrared spectra, Raman spectra and mechanical properties of the above-mentioned high-performance natural silk fiber before and after the treatment. As can be seen from Fig. 3, after treatment, the crystallinity inside the silk was destroyed, which was significantly reduced compared with that before treatment. From Fig. 4, it can be seen that the molecular orientation degree of the silk fiber is significantly increased after stretched; this is favorable for the improvement of mechanical properties of natural silk. In addition, as can be seen from Table 2, after the stretching treatment, the breaking strength of the silk was significantly improved, and the breaking strength was 800 MPa or more.

Example 3

[0023]

- (1) Confect the natural silk swelling liquid: add lithium thiocyanate into formic acid of 98 wt% to get formic acid solution which containing 1% lithium thiocyanate, that is the silk swelling liquid;
- (2) Immerse 20-22D raw silk in swelling liquid of the step (1) for 50 seconds, and then control the raw silk to shrink to 30% of the original length, to obtain shrink raw silk;
- (3) After washed with deionized water shrink, raw silk by the step (2) is neutralized the excess acid in the 1wt% aqueous sodium hydroxide solution, and then washed again and dried in the oven at 70°C, get high performance natural silk fiber.

[0024] Table 3 shows the mechanical tensile data of the raw silk before and after the treatment. According to the technical scheme provided by the present invention, the raw silk processed has excellent ductility, the elongation at break reaches above 50%, and the work of fracture increases by about 20%.

Table 3 Mechanical tensile data of raw silk before and after treatment

Sample	Elongation at Break (%)	Fracture work (MJ/m ³)
Original raw silk	21.1	354.2
Handle raw silk	58.5	412.8

Example 4

[0025]

- (1) Confect the natural silk swelling liquid: add magnesium chloride into trifluoroacetic acid of 90 wt% to get hydrofluoric acid solution which containing 1% magnesium chloride, that is the silk swelling liquid;
- (2) Immerse 20-22D raw silk in swelling liquid of the step (1) for 50 seconds, and while stretch the raw silk to 1.5 times the original length, to obtain stretching raw silk;
- (3) After washed with deionized water stretching silk by the step (2), is neutralized the excess acid in aqueous sodium hydroxide solution of 1wt%, and then washed again and dried in the oven at 55°C, get high performance natural silk fiber.

[0026] Table 4 shows the mechanical tensile data of the raw silk before and after the treatment. According to the technical scheme provided by the present invention, the raw silk processed has excellent strength, and the breaking strength is more than 800 MPa.

Table 4 Mechanical tensile data of raw silk before and after treatment

Sample	Breaking strength (cN)
Raw silk	81.2
Stretching silk	105.6

Example 5

[0027]

(1) Confect the natural silk swelling liquid: dilute formic acid of 98 wt% to 90 wt%, which is the silk swelling liquid;
 (2) Immerse the braided silk with the diameter is about 0.22mm in swelling liquid of the step (1) for 20 seconds, and while stretch the raw silk to 1.3 times the original length, to obtain stretching braided silk;
 (3) After washed with deionized water stretching braided silk by the step (2), is neutralized the excess acid in the 1wt% aqueous sodium hydroxide solution, and then washed again and dried in the oven at 60°C, get high performance natural silk fiber. Table 5 shows the mechanical tensile data of the braided silk before and after the treatment. According to the technical solution provided by the present invention, the breaking strength of the stretched braided sutures is significantly increased and reaches over 3000 cN.

Table 5 Mechanical tensile data before and after treatment of braided silk

Sample	Breaking strength (cN)
Original braided silk (4#)	2787.8
Stretching braided silk	3875.6

Example 6

[0028]

(1) Confect the natural silk swelling liquid: dilute concentrated sulfuric acid to 30wt%, which is the silk swelling liquid;
 (2) Immerse tussah silk in swelling liquid of the step (1) for 50 seconds, and then stretch to 3 times the original length, to obtain stretching silk;
 (3) After washed with deionized water stretching silk by the step (2), is neutralized the excess acid in the 1wt% aqueous sodium hydroxide solution, and then washed again and dried in the oven at 60°C, get high performance natural silk fiber.

[0029] Table 6 shows the mechanical tensile data of the tussah silk before and after the treatment. According to the technical scheme provided by the present invention, the tensile strength of the stretched tussah silk is significantly improved and reaches above 1000 MPa.

Table 6 Mechanical tensile data of tussah silk before and after treatment

Sample	Breaking strength (MPa)
Original tussah silk	430
Stretching tussah silk	1100

Example 7

[0030]

(1) Confect the natural silk swelling liquid: dilute concentrated phosphoric acid to 25wt%, which is the silk swelling liquid;
 (2) Immerse eri silk in swelling liquid of the step (1) for 30 seconds, and then stretch to 2 times the original length, to obtain stretching eri silk;

(3) After washed with deionized water stretching eri silk by the step (2), is neutralized the excess acid in 1wt% aqueous sodium hydroxide solution, and then washed again and dried in the oven at 60°C, get high performance natural silk fiber.

[0031] Table 7 shows the mechanical tensile data of the eri silk before and after the treatment. According to the technical scheme provided by the present invention, the breaking tussah silk filament rupture strength is significantly improved and reaches 780 MPa or more.

Table 7 Mechanical tensile data of eri silk before and after treatment

Sample	Breaking strength (MPa)
Original eri silk	463
Stretching eri silk	783

[0032] The concentrations in this example are all mass concentrations. The present invention can modify the mechanical properties of existing natural silk fiber products (including silk, raw silk, twisted silk, and braided silk etc.) to construct a natural silk fiber with high performance and high elongation.

Claims

1. A method for preparing high-performance natural silk fiber is **characterized by** comprising the following steps:

- (1) Preparing a silk swelling liquid, the silk swelling liquid comprising acid and water;
- (2) Soaking the natural silk fiber in the above-mentioned silk swelling liquid for 1 second to 1 hour, and shrinking or stretching the natural silk fibers;
- (3) The treated natural silk fiber are washed with water, neutralized, washed with water, and dried, to obtain high performance natural silk fiber.

2. The method for preparing high-performance natural silk fiber according to claim 1, wherein in step (1), the acid is one or more of formic acid, trifluoroacetic acid, acetic acid, hydrofluoric acid, phosphoric acid, and sulfuric acid; the concentration of the acid is 10% to 99% by weight.

3. The method for preparing high-performance natural silk fiber according to claim 2, wherein in step (1), the acid is one of formic acid, hydrofluoric acid, phosphoric acid, and sulfuric acid; the concentration of the acid is 25% to 98% by weight.

4. The method for preparing high-performance natural silk fiber according to claim 1, wherein in step (1), the silk swelling liquid further comprises an inorganic salt; the inorganic salt is one or more of sodium chloride, potassium chloride, lithium bromide, calcium chloride, zinc chloride, magnesium chloride, lithium thiocyanate, sodium thiocyanate, magnesium thiocyanate, calcium nitrate, copper nitrate, calcium carbonate, and calcium phosphate; the concentration of the inorganic salt is 0.1% to 10% by weight.

5. The method for preparing high-performance natural silk fiber according to claim 4, wherein in step (1), the silk swelling liquid further comprises an inorganic salt; the inorganic salt is one of the lithium bromide, calcium chloride, magnesium chloride, and lithium thiocyanate; the concentration of the inorganic salt is 0.5% to 5% by weight.

6. The method for preparing high-performance natural silk fiber according to claim 1, wherein in step (2), the natural silk is one or more of mulberry silk, tussah silk, yamamai silk, and eri silk.

7. The method for preparing high-performance natural silk fiber according to claim 1, wherein in step (2), the natural silk fiber is one or more of silk, raw silk, twisted silk, and braided silk.

8. The method for preparing high-performance natural silk fiber according to claim 1, wherein in the step (2), the shrinkage during the shrinkage is 1% to 80%; and the draw-ratio during the stretching is 1.1 to 5.

9. The method for preparing high-performance natural silk fiber according to claim 8, wherein in step (2), the shrinkage

during the shrinkage is 20% to 70%; and the draw-ratio during the stretching is 1.1 to 3.2; the soaking time is 5 seconds to 5 minutes.

- 5 **10.** The high-performance natural silk fiber prepared by the preparation method for preparing high-performance natural silk fiber according to any one of claim 1 to 9.

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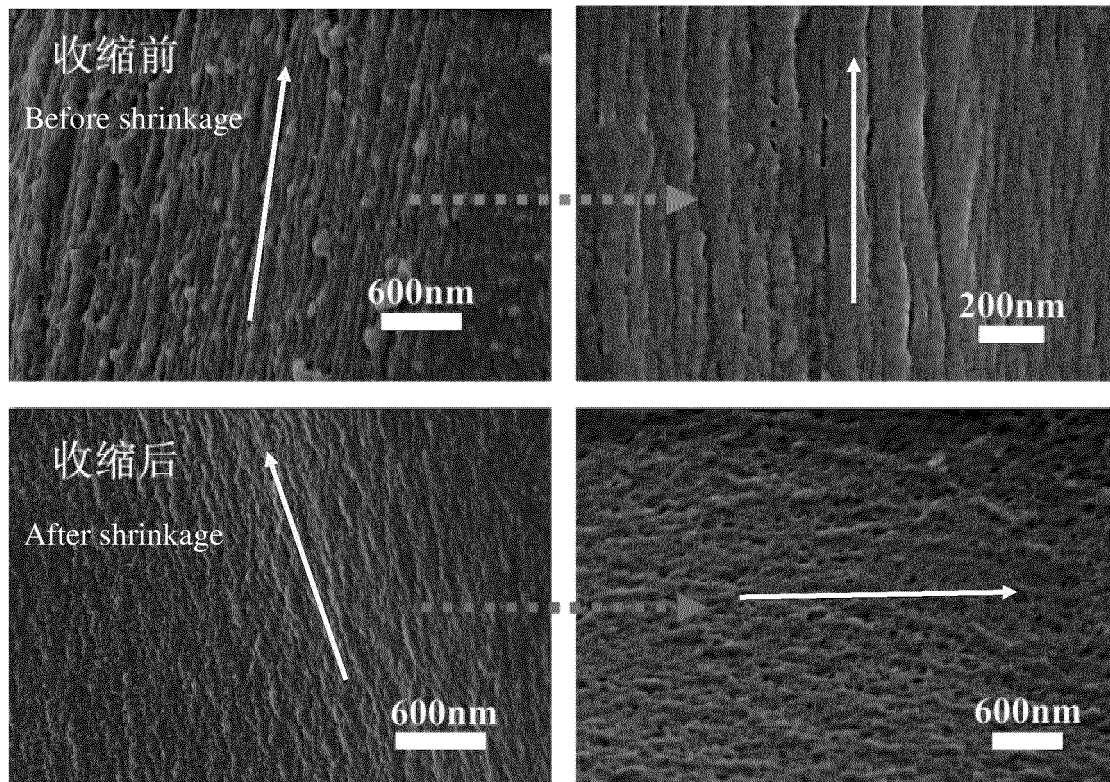


Fig. 1

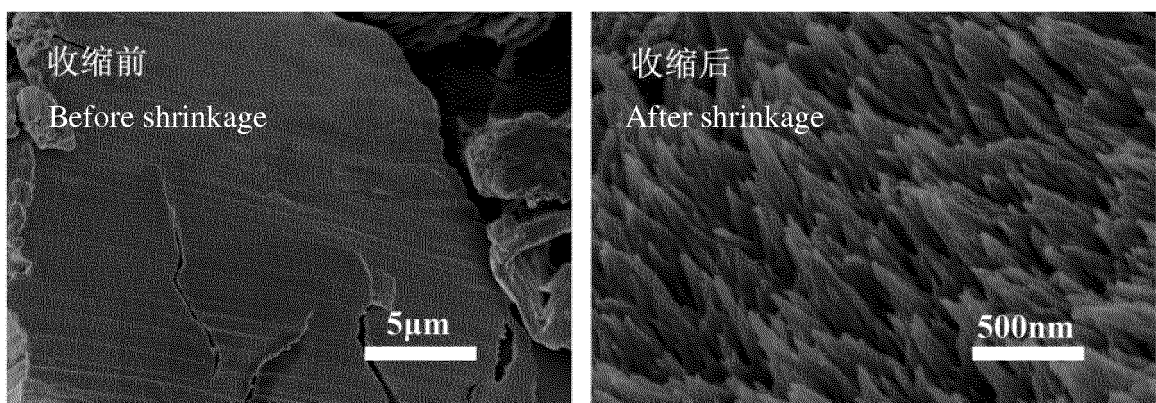


Fig. 2

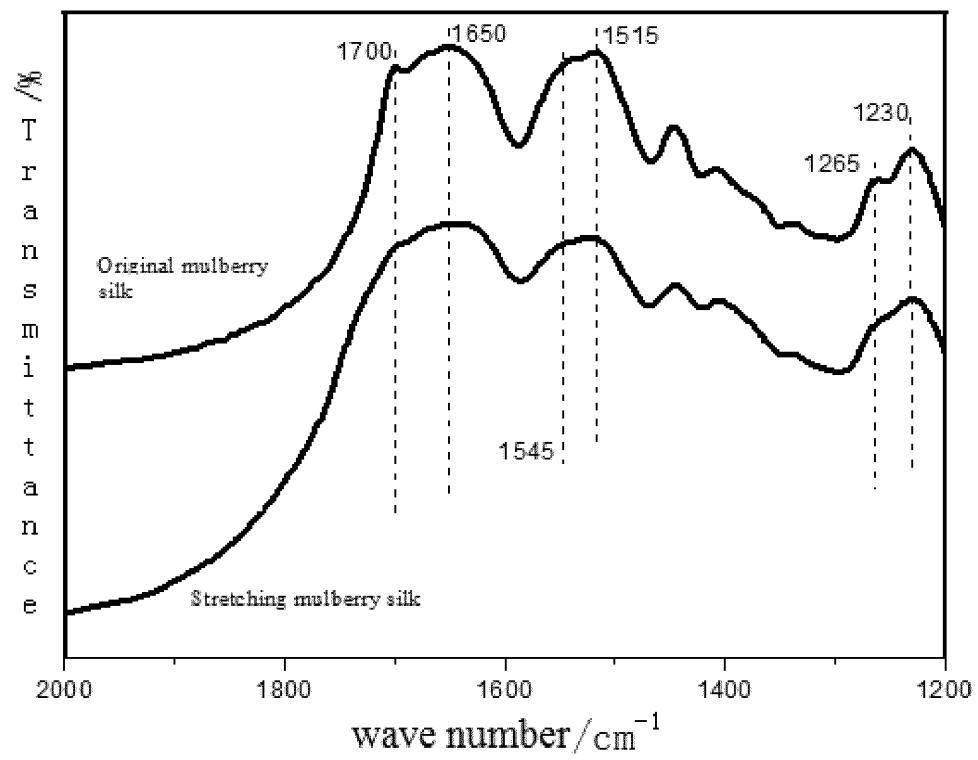


Fig. 3

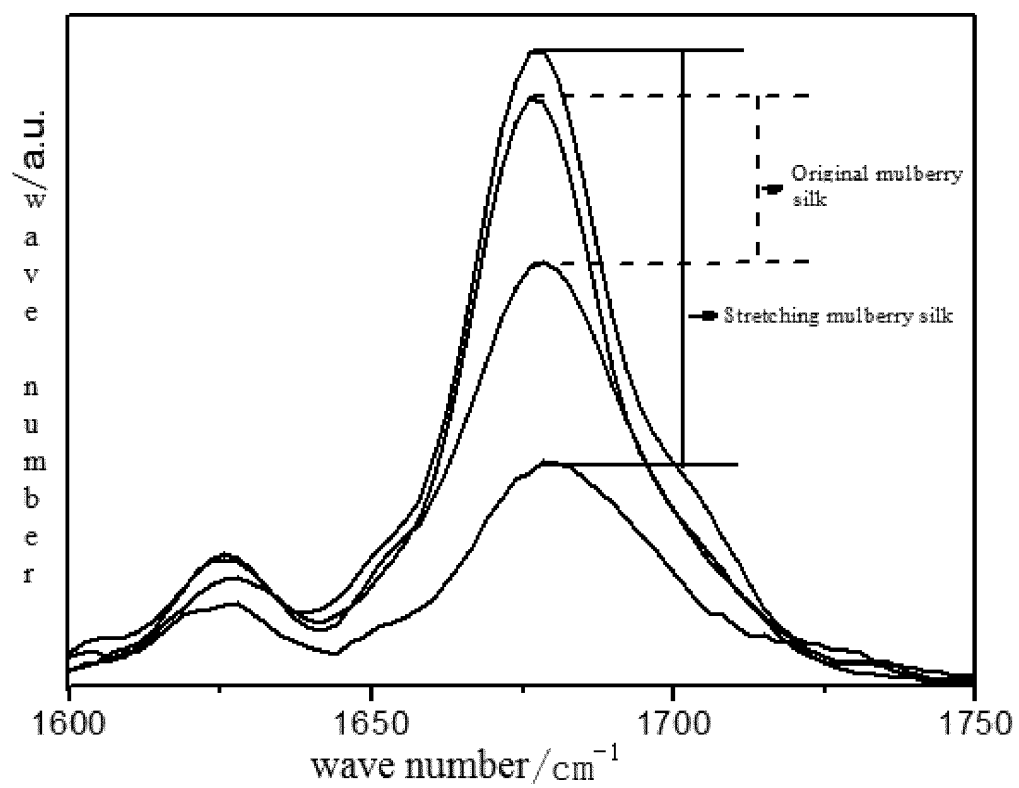


Fig. 4

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2015/093139

A. CLASSIFICATION OF SUBJECT MATTER

D06M 13/188 (2006.01) i; D06M 11/13 (2006.01) i; D01C 3/00 (2006.01) i; D02J 1/22 (2006.01) i
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

D01C, D06M, D02G

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)

WPI, EPODOC, CNPAT, CNKI: swelling, silk, acid, soak, immerse, dipping, steep, stretch, draft, draw, strength, tenacity, intension, intensity

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 101545146 A (SOUTHWEST UNIVERSITY), 30 September 2009 (30.09.2009), description, the part of invention content	1-3, 6-10
E	CN 105256544 A (NANTONG TEXTILE & SILK INDUSTRIAL TECHNOLOGY RESEARCH INSTITUTE), 20 January 2016 (20.01.2016), claims 1-10	1-10
A	CN 103469563 A (JURONG CITY HOUBAI TOWN YINGRUI PRINT WORKS), 25 December 2013 (25.12.2013), the whole document	1-10
A	JP 0141754 B2 (NORINSHO K.K.), 07 September 1989 (07.09.1989), the whole document	1-10
A	GB 485398 A (WARWICK CHEMICAL COMPANY), 19 May 1938 (19.05.1938), the whole document	1-10
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☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"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
"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	"&" document member of the same patent family

Date of the actual completion of the international search 15 July 2016 (15.07.2016)	Date of mailing of the international search report 03 August 2016 (03.08.2016)
Name and mailing address of the ISA/CN: State Intellectual Property Office of the P. R. China No. 6, Xitucheng Road, Jimenqiao Haidian District, Beijing 100088, China Facsimile No.: (86-10) 62019451	Authorized officer ZENG, Hao Telephone No.: (86-10) 62085476

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/CN2015/093139

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		JPH 0141754 B2	07 September 1989
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US 2072155 A	02 March 1937	GB 477066 A	21 December 1937

Form PCT/ISA/210 (patent family annex) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

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Non-patent literature cited in the description

- NATURE magazine, 2002 [0004]
- SHAO Z et al. Nature, 2002, vol. 418, 741 [0004]