Supporting Information

Analogue Resistive Switching Memory Made of Silk Fibroin Polymer †

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Preparation of silk fibroin protein (SFP)

The cocoons of practical kind of silkworms were peeled and washed then cut them into small pieces with length of ~1 cm (practical silkworm strain LG 2). Subsequently, 2.12 g Na_2CO_3 was added into 1 L boiling water, then stirring it by glass rod until it was completely dissolved. In order to avoid water boiling, the Na_2CO_3 was added slowly. The cocoons were put into boiling 0.02 M Na_2CO_3 aqueous solution and boiled for 30 min. After degumming, the silk fibroin protein was extracted and rinsed with deionized water for three times to remove the residual of Na_2CO_3. The silk fibroin protein was dried in the fume hood. The dried silk fibroin protein was dissolved in 9.3 M lithium bromide solution, reacted at 60℃ for 3 hours, dialyzed for 48 hours, and centrifuged at 9000 rpm to obtain the precursor solution (silk fibroin protein, SFP). [1, 2, 3, 4]

Synthesis of silk fibroin protein polymer (SFPP)

The prepared silk fibroin protein solution was lyophilized in lyophilizer. After that, a 0.3 g SFP was dissolved into the 30 mL of 1 M LiCl/DMSO solution. The polymerization reaction was processed after adding the 0.3 mL 2-isocyanatoethyl methacrylate (IEM) and 10 uL dibutyltin dilaurate (DLD) into the dissolved SFP solution, respectively. This reaction was processed for 60°C for 5 hours under N_2 atmosphere. The reaction solution was extracted by the cold acetone and ethanol with the volume ratio of 1:1 to obtain white floccule. The white floccule was rinsed 3 times with the cold acetone and ethanol mixture, and washed 2 times with deionized water, then lyophilized for 2 days, yielding dried and purified SFPP. [5, 6]

Preparation of Ag/SFPP/ITO memristor device

The silk fibroin protein polymer was first dissolved in hexafluoroisopropyl alcohol to obtain an amber-colored solution. SFPP solution was spin-coated on the ITO surface at 4000 rpm for 40 s, and annealed at 60℃ for 30 min. [7] Finally, the annealed SFPP/ITO sample was covered with steel-mask, and the top electrode was prepared by magnetron sputtering. The argon gas pressure was adjusted to 0.7 Pa, the power was adjusted to 15 W, and the silver electrode was sputtered 40 s. Finally, Ag/SFPP/ITO memristor devices were prepared by the above preparation process.

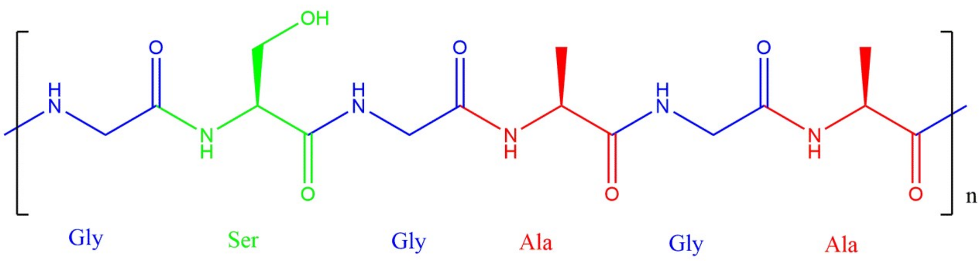

Fig. S1 The primary structure of the silk fibroin. The silk fibroin accounts for the main composition of silkworm silk (> 70 %). Its primary structure can be approximately divided into the composition of glycine (Gly), serine (Ser) and alanine (Ala). [8]

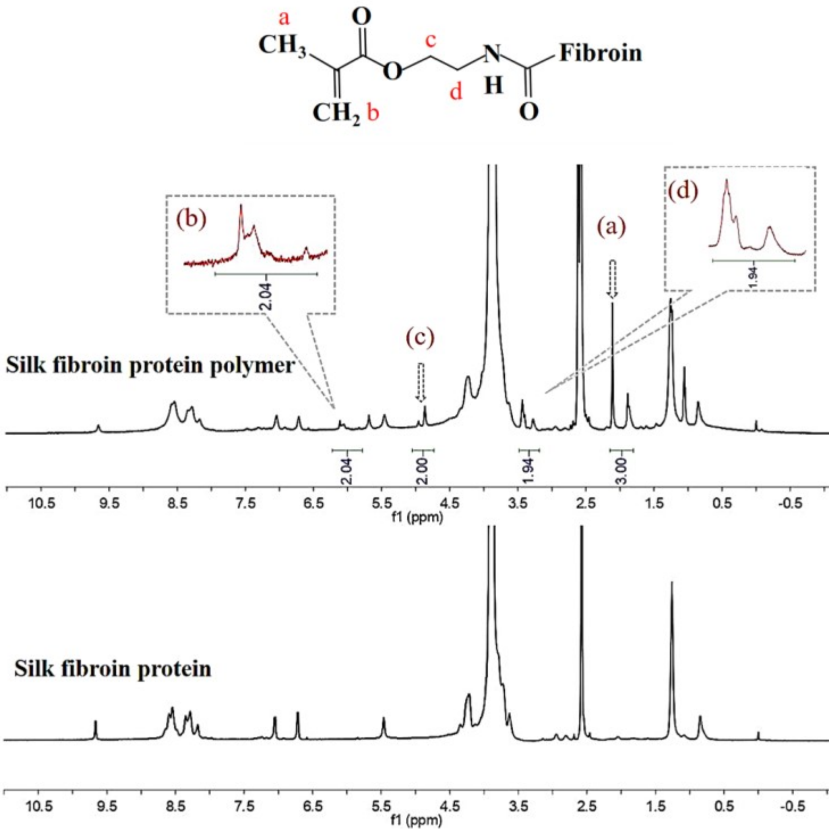

Fig. S2 Structural characterization of SFPP. ^{1}H-NMR spectra of (top) silk fibroin protein polymer and (bottom) silk fibroin protein. The peaks labeled with (a), (b), (c), and (d) correspond to the hydrogen atoms shown in the IEM.

The ^{1}H-NMR spectra are measured using silk fibroin protein (SFP) and silk fibroin protein polymer (SFPP). By comparing the ^{1}H-NMR spectra results, the methyl group (1.88 ppm), vinyl group (6.08 ppm), methylene bridge adjacent to O (4.85 ppm), and methylene bridge adjacent to N (3.26 ppm) originated from 2-isocyanatoethyl methacrylate (IEM) are detected after synthesis and the SFP structure is maintained as well. Therefore, the acrylate groups are verified in SFPP, as shown in Fig. S2. [5]

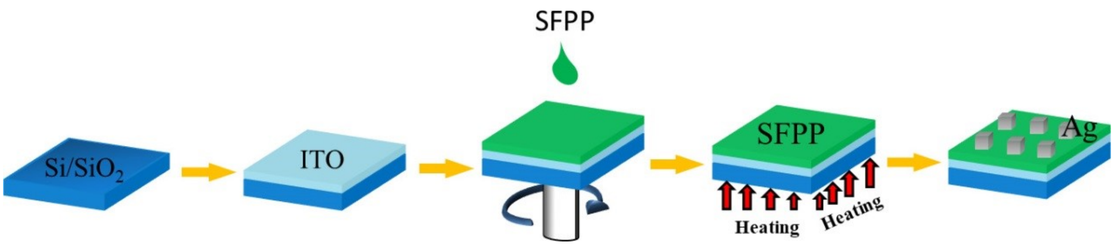

Fig. S3 The prepared process of Ag/SFPP/ITO memristor device. The functional layer of the device is silk fibroin protein polymer.

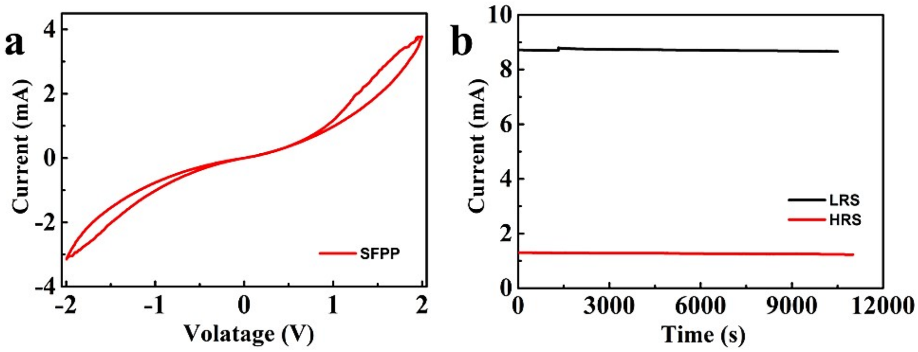

Fig. S4 a) I-V curve of the Ag/SFPP/ITO device and b) The retention measurement after the device operated several I-V scans.

The memristor-based features, such as Lissajous-like I-V curve and retention, are confirmed in our device. The Ag/SFPP/ITO devices, and the Lissajous-like I-V curve and the nonvolatility of information storage (retention) are demonstrated.

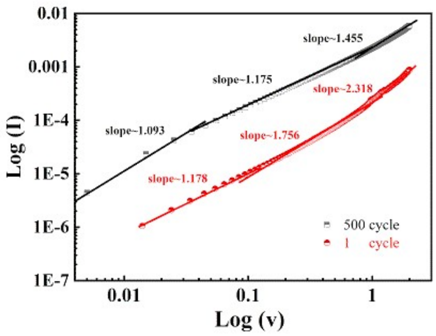

Fig. S5 Current-voltage fitted by space charge limited current mechanism. It indicate the defects center fixed by SFPP dominate the electron storage and release.

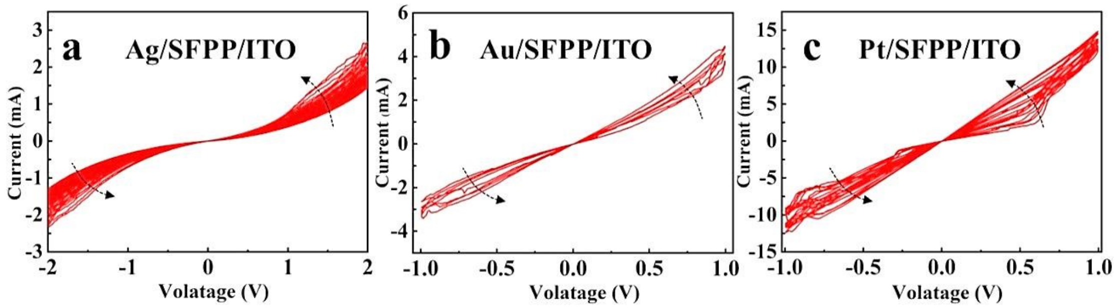

Fig. S6 To further study the RS behavior of the SFPP memristor, Ag, Pt, Au are used as the upper electrode of the device. a) the I-V curves of Ag/SFPP/ITO. b) the I-V curves of Au/SFPP/ITO. c) the I-V curves of Pt/SFPP/ITO. The RS behavior of SFPP-based memristor is independent of the formation of silver ion conducting filaments.

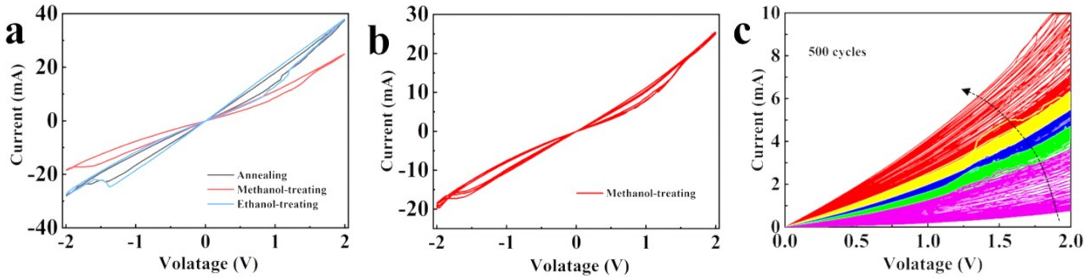

Fig. S7 a) I-V curves for the silk protein function layer-based device processed by the methanol-treating, ethanol-treating, and thermal annealing. b) The analog RS behaviors of the methanol-treating device shows narrow programming range. c) The analog RS behaviors of SFPP-based memristor shows wide programming range.

The silk protein function layers are processed by the methanol-treating, ethanol-treating, and thermal annealing, respectively. The corresponding I-V measurements have demonstrated that the analog RS are expectedly observed. By contrast, the Ag/SFPP/ITO device presents more programming conductance states, as shown in Fig. S5.

Tab. S1. A comparison RS behavior for the natural protein memristors

Functional layer	Structures	Work-	ON/OFF ratio	Retention	Capabilities	Ref
Silk fibroin	Ag|Silk-Fibroin|Au	± 1 V	10^5	10^4	Abrupt SET/RESET	1
Silk fibroin	Al|Silk fibroin |ITO	± 15 V	10	-	Abrupt SET/RESET	9
Silk fibroin	Mg|Silk fibroin|Mg	± 2 V	10^3	10^4	Abrupt SET/RESET	10
Silk fibroin	Ag|Silk fibroin|Au	-2~+4	10^7	4.5×10^3	Abrupt SET/RESET	8
Silk fibroin	Ag|Au-Silk fibroin|ITO	± 6 V	10^2	1.4×10^4	Abrupt SET/RESET	11
Silk fibroin	Ag|Ag-Silk fibroin|ITO	± 1 V	10^3	10^4	Abrupt SET/RESET	12
Silk fibroin	Au| Silk fibroin|Pt	± 4 V	10^4	5.7×10^3	Abrupt SET/RESET	13
Silk fibroin	Al|CDs- Silk fibroin|ITO	± 2 V	-	10^6	Abrupt SET/RESET	14
Silk fibroin	Al/CdSe-Silk fibroin|ITO	± 1.5 V	-	10^4	Abrupt SET/RESET	15
Silk fibroin	Ag|Silk fibroin |ITO	± 4 V	10^2	10^4	Abrupt SET/RESET	16
Silk fibroin	Ag|Silk fibroin |ITO	± 0.6V	-	10^3	Abrupt SET/RESET	17
Egg albumen	Ag|Egg albumen|ITO	± 6V	10^4	10^4	Abrupt SET/RESET	18
Natural pectin	Ag|Natural pectin|ITO	± 2V	10^2	10^4	Abrupt SET/RESET	19
Virus	Al|Virus|Al	± 6V	10^3	10^3	Abrupt SET/RESET	20
DNA	Au|CuO-DNA|Au|Si	± 1 V	50	10^3	Abrupt SET/RESET	21
Silk fibroin protein polymer (SFPP)	**Ag|SFPP|ITO**	**± 2 V**	**~5**	**10^4**	**Analog**	**This work**

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