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Supporting Information for

High-performing fiber electrodes based on gold-shelled silver nanowire framework for bioelectronics

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Experimental Section/Methods

Preparation of AgNW fibers

The primary fibers were prepared by mask spraying. First, the polyimide mask plate (aperture size: 2 mm × 10 cm) was positioned on the polyethylene terephthalate (PET) substrate and transferred onto an 85°C hot stage. Then, 5 mg mL^{-1} AgNW (stabilized with polyvinylpyrrolidone) ethanol suspension (Zhejiang Xinglong New Material Technology Co., Ltd.) was evenly sprayed on the PET substrate. The cumulative spraying amount is controlled at 4 mg cm^{-2}. Afterwards, the mask was removed, and the PET substrate loaded with the primary fibers was immersed in 1 M calcium chloride aqueous solution for chemical sintering of the AgNW network. After 20 min, they were rinsed thoroughly with deionized water. Subsequently, these chemically sintered AgNW fibers were immersed in ethanol and placed on a shaker at a speed of 20 rad min^{-1} to facilitate detachment from the PET substrate. Once all AgNW fibers detached, they were transferred onto weighing paper and rapidly dried at 90°C. Upon ethanol evaporation, self-supporting AgNW fibers were obtained.

Preparation of Au@AgNW fibers

A chemical gold plating strategy was used to *in-situ* deposit the inert shell on the AgNW fibers. Firstly, a gold seed solution was prepared by mixing 1.4 mL of tetrachloroauric acid trihydrate (Admas Co., Ltd.) aqueous solution (0.25 M), 8.4 mL of sodium hydroxide (Admas Co., Ltd.) aqueous solution (0.2 M) and 105 mL of sodium sulfite (Admas Co., Ltd.) aqueous solution (0.01 M), which was then left at room temperature for 12 h. Subsequently, the growth solution was prepared by mixing 14.0 mL sodium hydroxide aqueous solution (0.5 M), 14.0 mL L-ascorbic acid (Aladdin Biochemical Technology Co., Ltd.) aqueous solution (0.5 M), 3.5 mL sodium sulfite aqueous solution (0.1 M) and 320 mL deionized water, followed by incubation at room temperature for 2 h. Note that the pH of the growth solution could be adjusted by change the amount of sodium hydroxide.

The AgNW fibers were suspended and fixed on the glass scaffold, and then slowly immersed in the growth solution. The gold seed solution was introduced into the growth solution along the inner wall of the beaker and left undisturbed for 1 h. Throughout this process, the mixed solution maintained its transparency or exhibited with a light orange color, while the fiber surface gradually changed from gray to deep yellow. Finally, the glass scaffold was removed and soaked in deionized water for 3 times to clean the surface of the obtained Au@AgNW fibers.

Structural characterization

The macroscopic morphology of the sample was captured using a digital camera. Scanning electron microscopy (SEM, Ultra 55, Zeiss) was used to observe the microstructure at a voltage of 3 kV. High resolution transmission electron microscopy (HR-TEM, HT7700 Exalens, Hitachi) was used to observe the microstructure at a voltage of 100 kV. Energy spectroscopy was applied for elemental distribution analysis.

Mechanical performance tests

A nanoindentation tester (Ti-950, Hysitron) was used to characterize the modulus of Au@AgNW fibers and silver wires, under a maximum stress of 2 mN with a standard Berkovich probe. Three sampling points were randomly selected for each sample. A universal mechanical testing machine (Instron 3365, Instron) was used to test the bending stress of the fiber samples. The fiber samples were fixed vertically downward on the upper fixture, and a flat stainless steel plate was placed on the lower end. The fiber samples were moved downward at a speed of 2 mm min^{-1}.

Electrical and electrochemical performance tests

Electrical conductivity measurements were performed using a digital source meter (2400, Keithley) in two-point configuration. Both ends of the fiber samples were connected to conductive copper tape by conductive silver paste. An electrochemical workstation was used to test the electrochemical properties of the fibers, employing a three-electrode system. The fiber served as the working electrode, the silver/silver

chloride electrode functioned as the reference electrode and the platinum wire electrode functioned as the counter electrode. The electrolyte was 1×PBS solution (Servicebio). For the cyclic voltammetry test, the scanning range was -0.8–0.8 V, and the scanning speed was 50 mV s^{-1}. Charge injection capability was measured by applying ±0.5 V bipolar pulses with a frequency of 50 Hz.

Stability tests

The fibers were immersed directly in either hydrogen peroxide (0.5 M) or calcium chloride aqueous solution (0.5 M). Meanwhile, a sealed high-concentration ozone environment was created using an ozone cleaning machine, and the fibers were directly exposed. The bending stress change was tested after 24 h.

Simultaneously, we conducted resistance tests on each fiber sample throughout the chemical erosion process. The ends of fiber electrodes were connected to conductive copper tape using silver paste and then encapsulated with silicone rubber, leaving merely 5 mm exposed in the middle. Resistance changes at specific time points during chemical erosion were measured using a digital source meter.

Furthermore, the leakage of Ag^+ was investigated through inductively coupled plasma mass spectrometry (ICP-MS). Fiber electrodes of 5 cm were soaked into 5 mL 1×PBS solution and maintained at 37°C. The Ag^+ concentration of the solution was investigated at the 1, 4, and 7 days.

Cytotoxicity tests

The fibes were arranged closely in parallel on circular PET sheets (diameter 7.5 mm) and then sterilized by UV irradiation. The PET sheets with the sample facing up were transferred to a 48-well cell culture plate with diameter of 8 mm, followed by dropwise addition of culture medium and cell inoculation. Mouse fibroblasts (L929) were used as experimental cells. The cells were incubated at 37°C under sterile conditions with 5% CO_2, and cell counting kit-8 (CCK8) assay was performed at specified time points. The

culture medium (100 μL) was extracted from each well, and then water-soluble tetrazolium salt (WST-8, 100 μL) solution was injected into each one. The absorbance of the mixture at the wavelength of 450 nm was measured after it was incubated at 37°C for 1 h. For cell morphology characterization, iFluor™ 488-wheat germ agglutinin (WGA) conjugate was used to stain the cells. After being incubated at 37 ℃ for 30 min and washed with culture medium, the cells were observed by the optical microscopy with FITC filter (Olympus EX51).

Preparation of Au@AgNW fiber neural electrodes

Polydimethylsiloxane (PDMS) was used to insulate Au@AgNW fibers to prepare sciatic nerve stimulation electrodes. First, a 10 wt% gelatin aqueous solution was used to cover a 2 mm long area on one side of the fiber and air-dried in the dark. The end of the fiber was then connected to the conductive wire using silver paste. PDMS precursor (mixed at a ratio of 1:9) was uniformly coated over all regions of the fiber except for the gelatin-covered area. The disparate surface energies between gelatin and PDMS facilitated the avoidance of the gelatin region by PDMS, resulting in the formation of a distinct interface. After curing the PDMS insulation layer at 80°C, the nerve electrodes were immersed in 50°C water to remove the gelatin, thereby exposing the Au@AgNW fibers as electrical stimulation sites.

In vivo tests

All animal experiments were conducted in accordance with the Ethics Committee of Fudan University (certificate number: SYXK-Hu-2020-0032), and the International Ethical Guidelines and the National Institutes of Health Guide concerning the Care and Use of Laboratory Animals were strictly followed. Electrodes were tested in male mice (ICR, 6 weeks, Shanghai SLAC Laboratory Animal Co., Ltd.) housed at ordinary animal room (12 h light/dark cycle, 22 °C, food and water ad libitum). No animals were excluded from the analysis.

After strict surgical disinfection, the mice were anaesthetized with 2% isoflurane and

placed smoothly on a surgical positioning table. The mice were maintained under anesthesia by continuously inhaling 2% isoflurane through a mask.

For biocompatibility testing, the Au@AgNW fibers were subcutaneously implanted into the mice with the aid of a syringe and fixed by bio-glue (3M).

During electrodes implantation, the hair on the legs was shaved, and the exposed skin was disinfected with medical iodine. The Au@AgNW fiber electrodes were carefully wrapped around the sciatic nerve, ensuring direct contact of the exposed electrical stimulation site with the nerve. The overlapping insulation layer was then adhered together to secure the electrode position. Subsequently, the muscles and skin were sutured, and the electrode extension was further fixed by bio-glue. For leg movement, a voltage pulse with an amplitude of 100 mV was applied using the external stimulator (33210A, Keysight). The resulting undirected leg movements following stimulation were recorded.

In vivo stability tests

The subcutaneously implanted fibers were removed and washed with distilled water, and then the microscopic morphology of the electrode surface was observed using SEM.

Cut the skin fragments 5 mm in length and 3 mm in width at a distance of 1 mm parallel to the fibers. The accurately weighed fragments were then immersed in a mixed solution of 5 mL nitric acid and 5 mL hydrogen peroxide for microwave digestion. The microwave heating process was as follows: 5 min to 120 °C, hold for 5 min, 5 min to 150 °C and hold for 10 min, 5 min to 190 °C, hold for 20 min. After cooling, use distilled water to adjust the volume to 25 mL. The concentration of Ag^+ was determined using ICP-MS, enabling the calculation of Ag^+ content in the tissue.

Hematoxylin-eosin (H&E) staining

One week after the subcutaneous implantation of Au@AgNW fibers, the mice were euthanized. Relevant tissues (heart, liver, spleen, lung, kidney) were extracted and preserved in a 4% paraformaldehyde aqueous solution for 12 h. The tissues were dehydrated using the graded ethanol dehydration method and embedded in paraffin blocks. Subsequently, paraffin was sectioned into slices with a thickness of 6 μm using a microtome. For H&E staining, the tissue slices were sequentially treated with xylene, anhydrous ethanol, 75% ethanol, and distilled water. They were then immersed successively in a differentiation solution, bluing buffer and hematoxylin staining solution for 5 min each. Afterward, the slices were dehydrated, followed by a 5-min immersion in an eosin staining solution to complete the process. Prior to each change of solution, the slices were rinsed thoroughly with distilled water. H&E staining of surrounding tissues after neural electrode implantation was the same as above.

Supplementary Figures

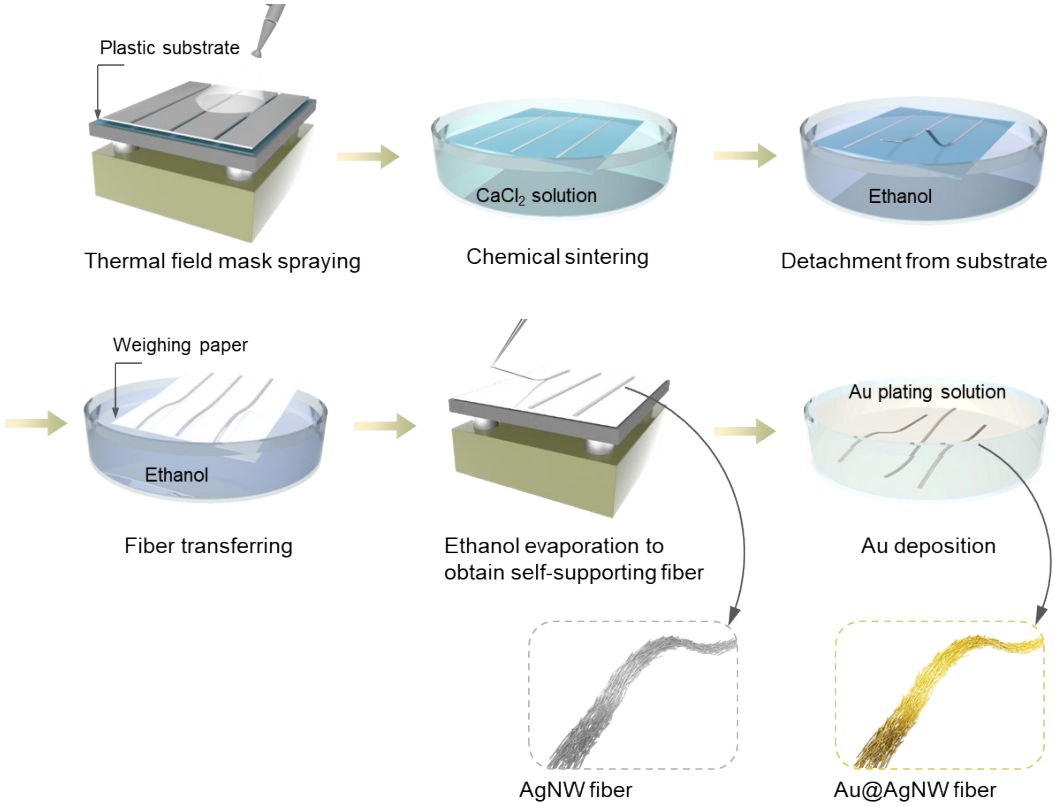

Fig. S1. The preparation process of the Au@AgNW fibers.

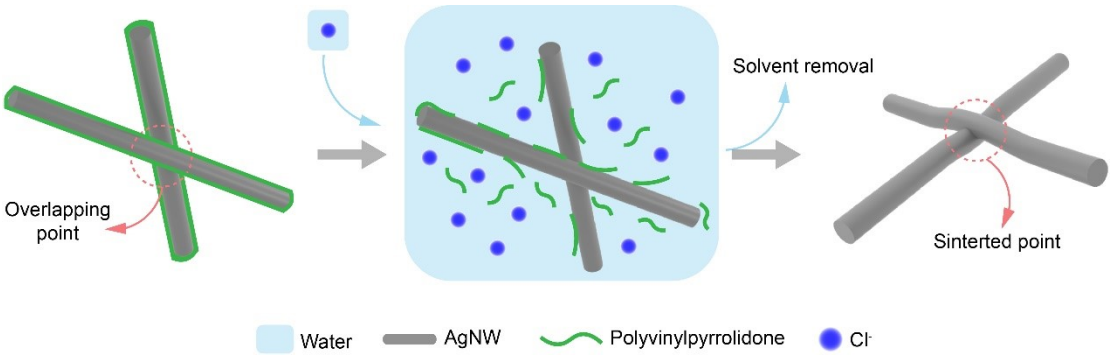

Fig. S2. The mechanism of chemical sintering of AgNW network in chloride salt solution.

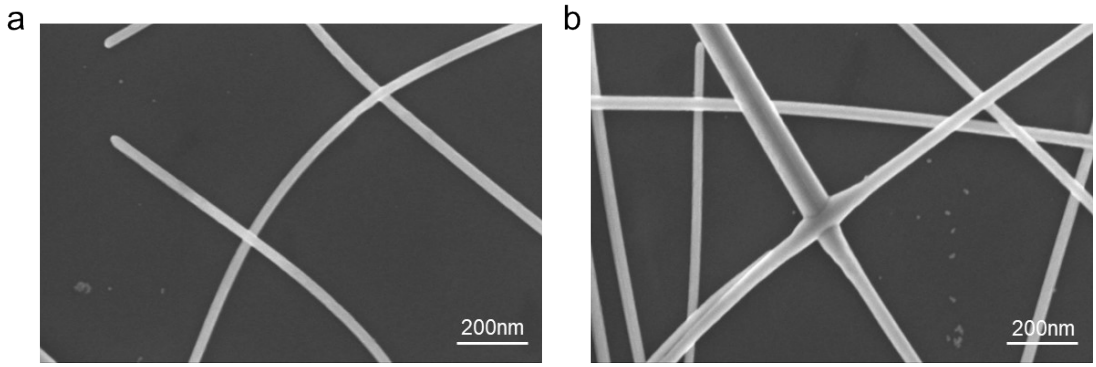

Fig. S3. Morphologies of overlapping points between AgNWs (a) before and (b) after calcium chloride solution treatment.

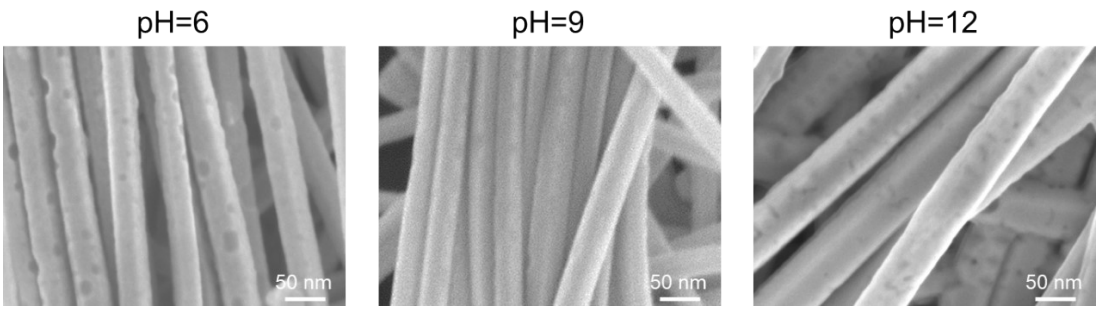

Fig. S4. SEM images of Au@AgNW fibers when the growth solution with different pH. At low pH, galvanic replacement reactions between Au^{3+} and Ag^{0} in AgNWs occur, leading to surface defects. At high pH, the gold shell was formed without galvanic replacement reactions, but the growth rate of the gold was accelerated, resulting in increased thickness and unevenness. After comparison, the optimal pH for a uniform gold shell was pH 9.

Fig. S5. Digital photos of the AgNW fiber and Au@AgNW fiber.

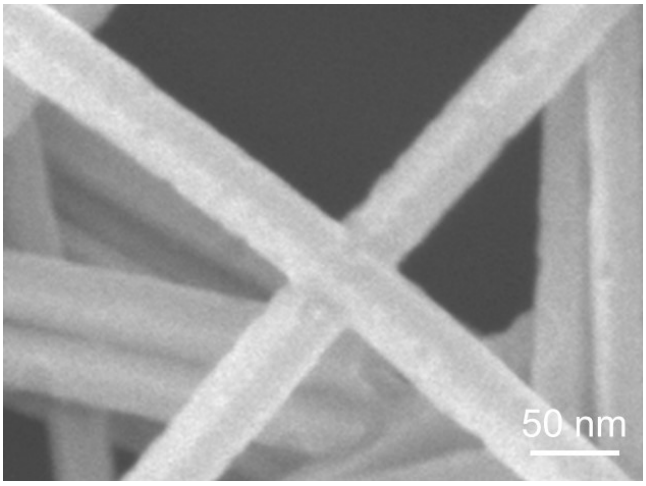

Fig. S6. High magnification SEM image of the Au@AgNW fiber.

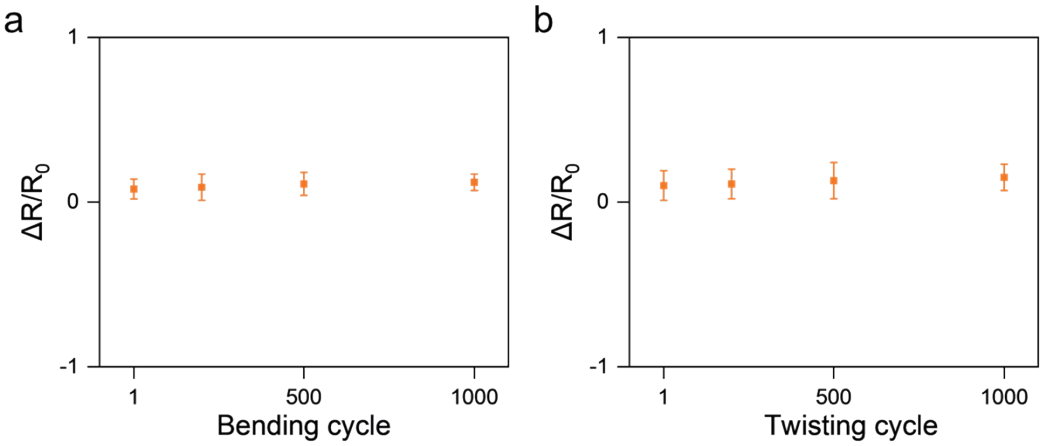

Fig. S7 Mechanical stability of the Au@AgNW fibers under (a) bending at 90° and (b) twisting at 10π rad·m^{-1}, respectively, which was reflected by the resistance change ($\Delta R/R_0$) value (N=3). Data are shown as mean ± SD.

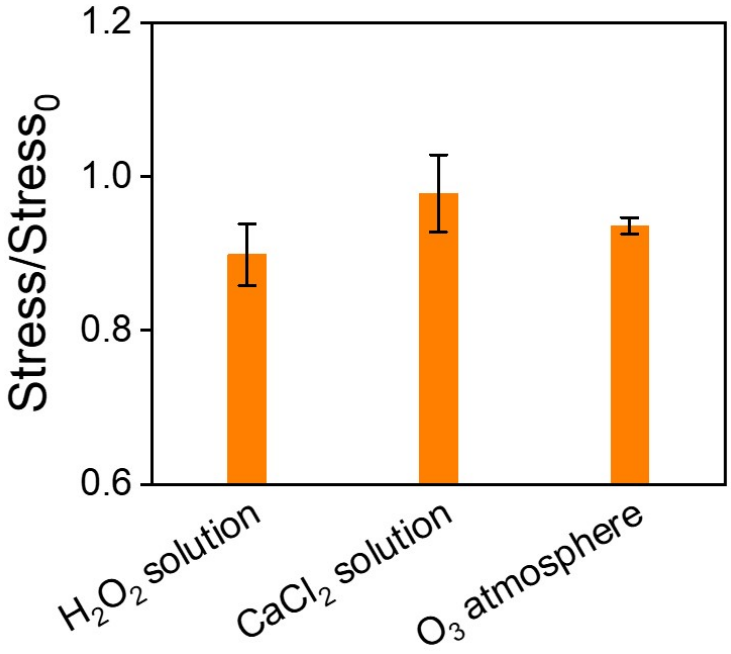

Fig. S8. Maximum bending stress changes of Au@AgNW fibers after 24 h chemical erosion in different environments (N=3). Data are shown as mean ± SD.

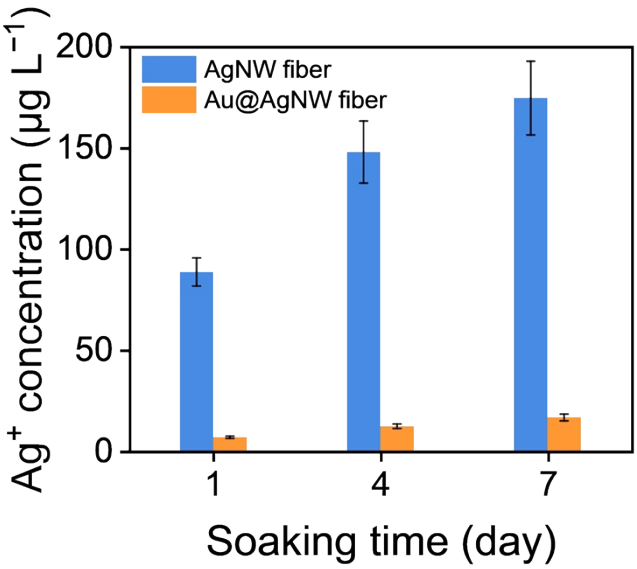

Fig. S9. The Ag^+ concentration of the solution at different time points after the fibers immersed in 1×PBS solution at 37°C (N=3). Data are shown as mean ± SD.

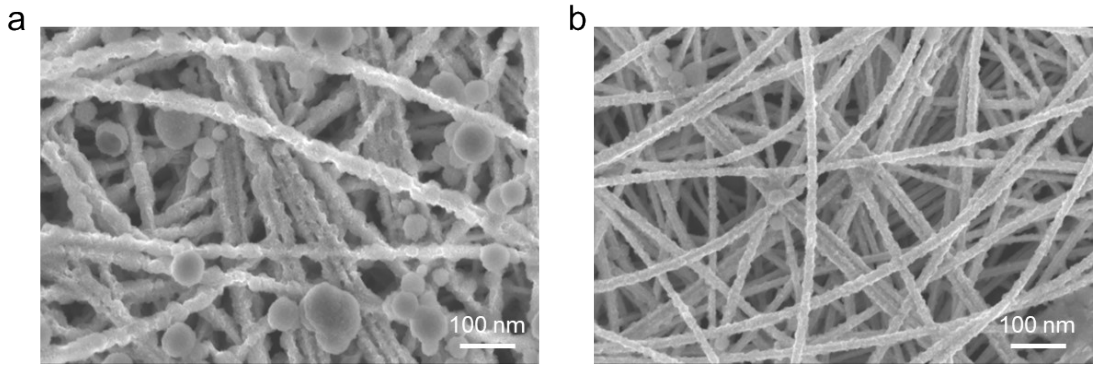

Fig. S10. SEM images of (a) AgNW fibers and (b) Au@AgNW fibers as substrates after incubation of L929 cells for 72 h.

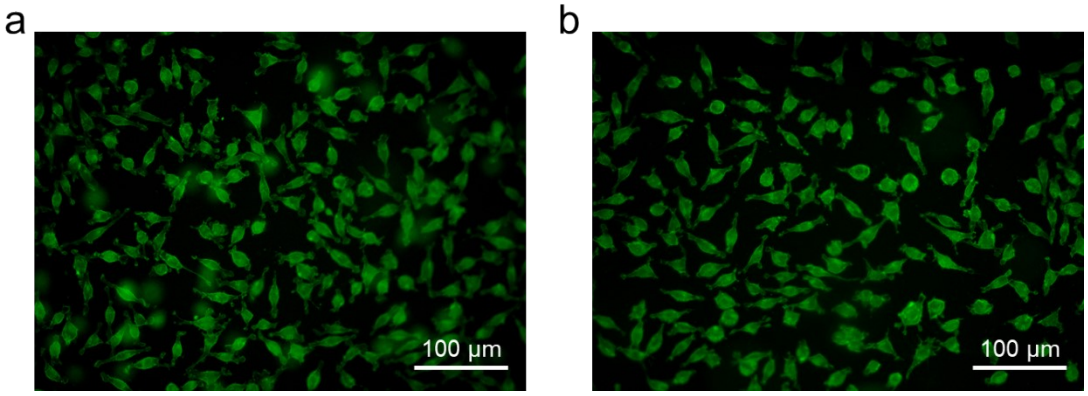

Fig. S11 Morphologies of L929 cells in (a) the Au@AgNW fiber group and (b) control group after incubation for 24 h.

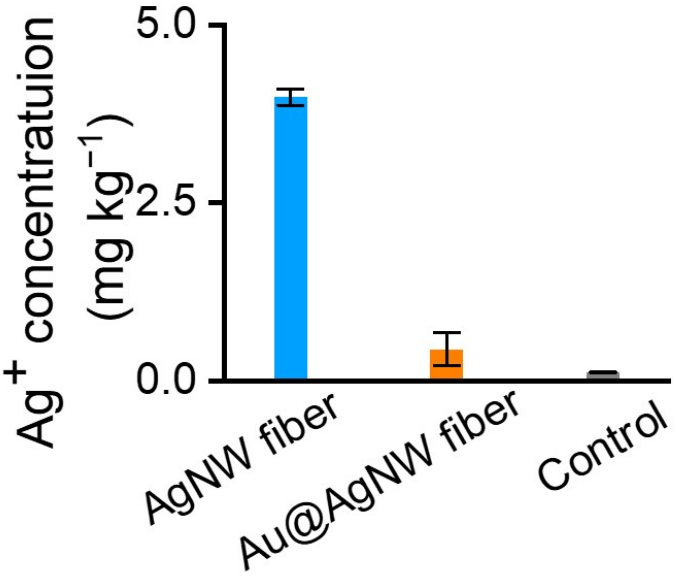

Fig. S12. The Ag^+ concentration of skin tissues after subcutaneous implantation of fibers for 7 days (N=3). Data are shown as mean ± SD.

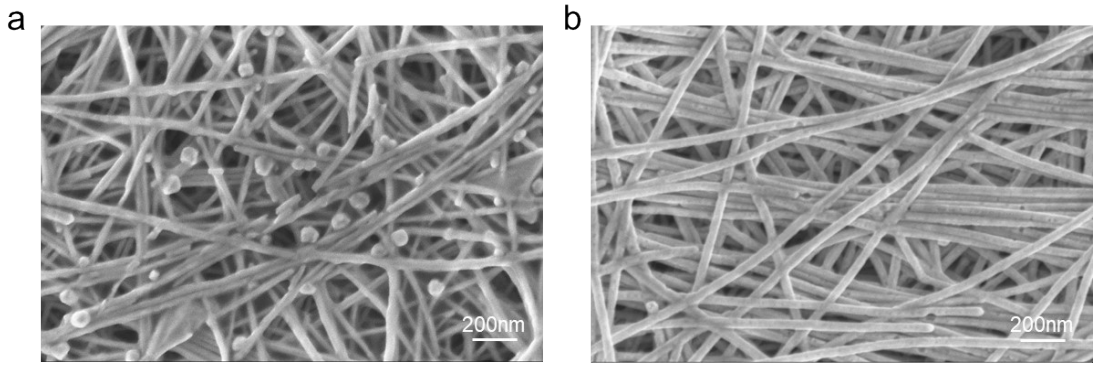

Fig. S13. Fiber morphology after 7 days of subcutaneous implantation. (a) AgNW fiber. (b) Au@AgNW fiber.

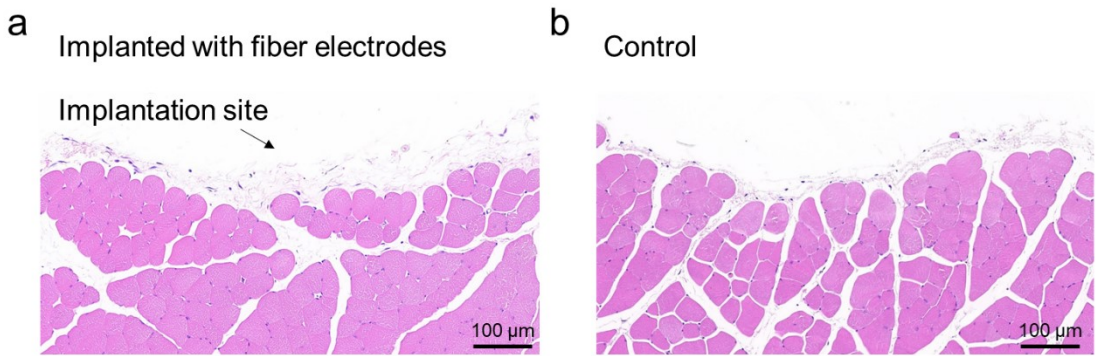

Fig. S14 The H&E staining images of surrounding tissue at the implantation site for (a) Au@AgNW fiber electrode group after implantation for 7 days and (b) control group.

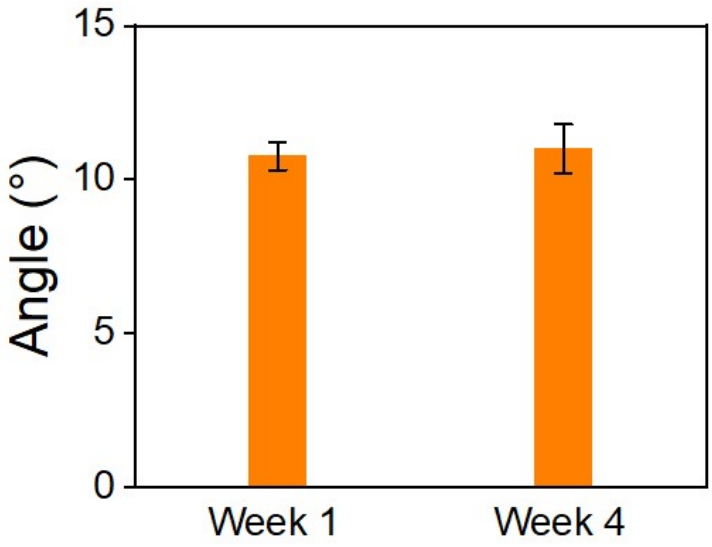

Fig. S15. Leg movement of mice induced by the electrical stimulation through Au@AgNW fiber electrodes at Week 1 and Week 4 (N=3). Data are shown as mean ± SD.