Supporting Information

Bioinspired Leaf Vein-Architected Gold Nanowire Ecoflexible Biosensors for Ultrasensitive Occlusal Force Monitoring

*Wuxing Zhang [1, †], Heng Zhang [1, 2 †], Gangsheng Chen [1], Biao Ma[1], Yang Xia [3], Yi Chen [1, 2] **

[1] State Key Laboratory of Digital Medical Engineering, Jiangsu Key Laboratory for Biomaterials and Devices, School of Biological Science and Medical Engineering, Southeast University, Nanjing 211189, China

[2] Southeast University-Monash University Joint Graduate School, Suzhou 215123, China

[3] The Affiliated Stomatological Hospital of Nanjing Medical University, Nanjing 210029, China

[†] These authors contributed equally to this work.

* To whom correspondence should be addressed.

Email: yichen@seu.edu.cn (Y. Chen)

Table of Contents

Section 1. Materials and Methods

Chemicals and Regents: Hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4 \cdot 3H_2O$, ≥49.0% Au basis), L(+)-ascorbic acid (L-AA, ≥99%), trisodium citrate dihydrate (≥99%), (3-aminopropyl)-triethoxysilane (APTES, ≥98%), and 4-mercaptobenzoic acid (4-MBA, ≥90%) were purchased from Sigma Aldrich. NaOH was purchased from Shanghai Titan Scientific Co. Ltd. The PDMS and cross-linker (SYLGARD 184) were purchased from USA Dow Corning Co. Ltd. Silver nitrate ($AgNO_3$, ≥99%) and was purchased from Aladdin. Ethanol (analytical grade) was purchased from Greagent. Hydrochloric acid (HCl, analytical grade) was purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China).

Preparation of Leaf Vein: The Osmanthus leaves were immersed in NaOH (40g, 400 ml) solution at 100 °C for 2 h. We used the brush to remove the leaf flesh from the etched leaves, and then rinsed them with deionized water. Then the veins of the leaves were pressed flat with glass and dried in a blast drying oven (GZX-9240MBE) at 60°C.

Synthesis of Gold Nanostars: Gold nanostars were synthesized according to previously reported seed-mediated method[1], which were surfactant-free. The gold seed with a diameter of 12 nm were prepared by adding 3.75 mL citrate solution (34 mM) to 50 ml of boiling $HAuCl_4$ solution (1 mM) under vigorous stirring. The solution was boiling for 15 min, then cooled to room temperature and stored at 4°C. Then, 200 μL of the above gold seed was added to a 20 ml $HAuCl_4$ (0.25 mM) solution containing 20 μL HCl (1M) at room temperature under a stirring of 700 rpm. Quickly, 100 μL AA (0.1 M) and 200 μL $AgNO_3$ (3 mM) were added simultaneously and the solution was retaining stirring for 30s. The obtained gold nanostars were kept at 4°C until used.

Fabrication of Vein-architected AuNWs Electrode: The composite of liquid PDMS and cross-linker with a weight ratio of 20:1 was poured into the biological culture dish, then the vein of Osmanthus leaves were put into the biological culture dish. Subsequently, remove the excess PDMS from the vein of Osmanthus leaves and place them in a 60°C drying oven overnight for culturing. The vein-architected AuNWs electrode was obtained by directly growing gold nanowires on the surface of PDMS with a modified seed-mediated metho[2, 3]. Firstly, the the vein of Osmanthus leaves were attached to the microslide in order to get a flat surface. Then O_2 plasma was used to make the PDMS of the vein of Osmanthus leaves hydrophilic (treatment time, 10 min). Immediately, the vein of Osmanthus was soaked in the APTES aqueous solution (4 mM) for 2h to be functionalized with amino groups. Subsequently, APTES-modified the vein of Osmanthus leaves were immersed into the prepared gold nanostars solution for 2h in order to make gold nanostars fully adsorbed. After rinsing with deionized water three times to remove the weakly bound gold nanostars, the vein of Osmanthus leaves was transferred to another clean microslide and finally immersed into a growth solution containing 10.8 mM 4-MBA, 11.7 mM $HAuCl_4$, and 27 mM L-AA for 15 min. After rinsing (ethanol) and drying, the obtained bendable veins were used as working electrode for electrochemical properties test.

Preparation of Vein-architected AuNWs Ecoflexible Sensor: The proportional mixture of liquid PDMS and crosslinker 10:1 was poured into a 50 ml centrifuge tube, about 10 g and then vacuum in a vacuum drying tank (DZG-6050) for about 30 minutes. The vein of Osmanthus leaves was connected with wires by silver glue, followed by curing at 60 ℃ for 30 min in a drying oven. The composite of liquid PDMS and cross-linker with a weight ratio of 10:1 were poured into the biological culture dish, then the biological dish was placed in the compact homogenizer and set the rotation speed and time (200 r/min, 10s), subsequently, the The vein of Osmanthus leaves were put into the biological culture dish for encapsulation. After cured at 80℃ for 1 h in the drying oven, the synthesized Vein-PDMS film were peeled off from the biological culture dish.

Human Motion Monitoring Measurement: The experiment protocols were approved by the Ethics Committee of Southeast University. The strain tests were conducted by attaching the leaf vein-architected AuNWs ecoflexible sensor to dynamic regions of the human body, such as the finger, elbow, wrist, knee, and throat. Mechanical deformations induced by natural bending movements provided various levels of external strain. The electrical signals generated by the sensor were measured and recorded in real time using a SourceMeter.

Pressure Response Measurement: The pressure tests were conducted by placing the sensor flatly on a clean, horizontal substrate. Different levels of constant pressure were applied to the sensor, and the corresponding electrical responses were monitored using a SourceMeter.

Human Bite Force Measurement: The experiment protocols were approved by the Ethics Committee of Southeast University. A healthy male subject was recruited from Southeast University and gave written informed consent before participation in the study. Before the experiment, the oral cavity of the human subject was cleaned. Subsequently, vein-architected AuNWs ecoflexible sensors were placed flat on the occlusal surfaces of the incisors, canines, and molars of the human subject. A SourceMeter was then used to record the resistance variations during the biting process under gentle, moderate, and firm bite forces.

Characterization: The morphology of the vein-architected AuNWs electrode was investigated by field emission scanning electron microscopy (Nova NanoSEM 450). XRD patterns were recorded using a Bruker D8 Advance diffractometer using Cu Kα radiation. XPS spectra were obtained using the Thermo Fisher ESCALAB 250Xi X-ray photoelectron spectroscopy.

Section 2. Preparation of Leaf Vein Venation Skeleton

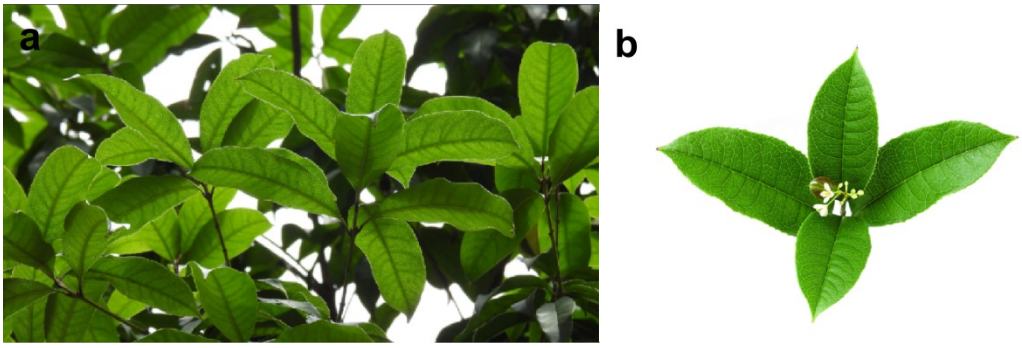


Figure S1. The picture of The Osmanthus leaves.

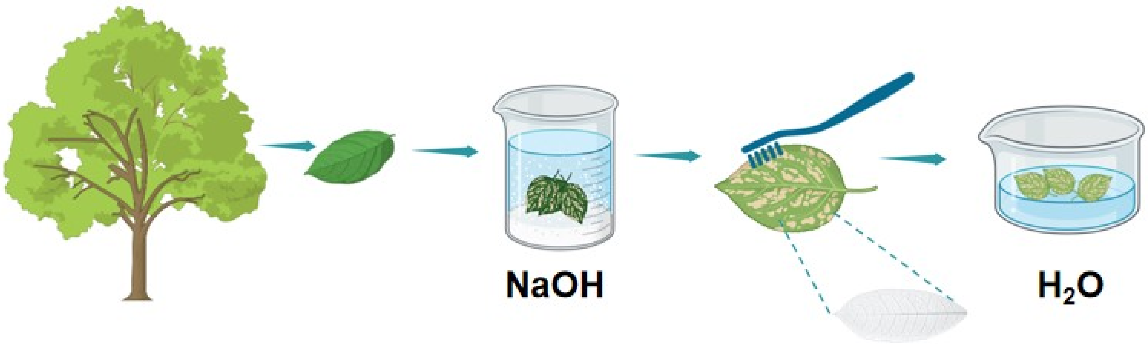
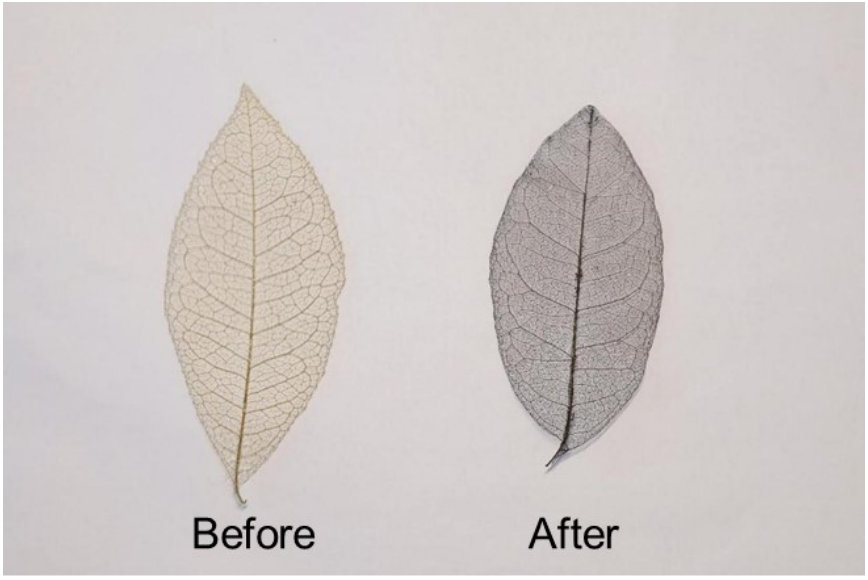


Figure S2. Schematic illustration for the preparation process of the leaf vein venation skeleton.

116 # Section 3. Leaf Vein-Architected AuNWs Electrode



117

118 **Figure S3.** Optical image of the vein-architected AuNWs electrode before and after growth of AuNWs.

119

Figure S4. Optical image of the leaf vein-architected AuNWs electrode placed under warm-toned lighting.

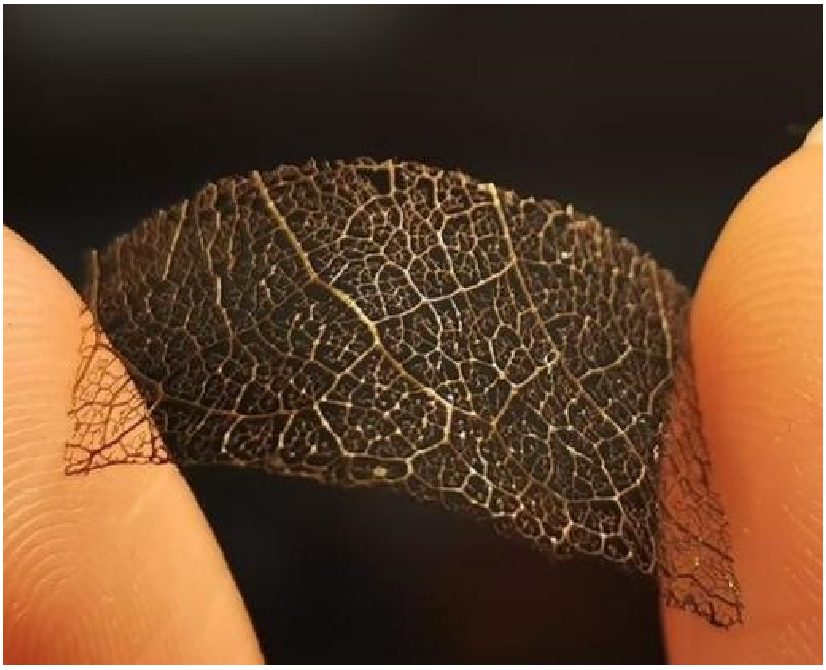
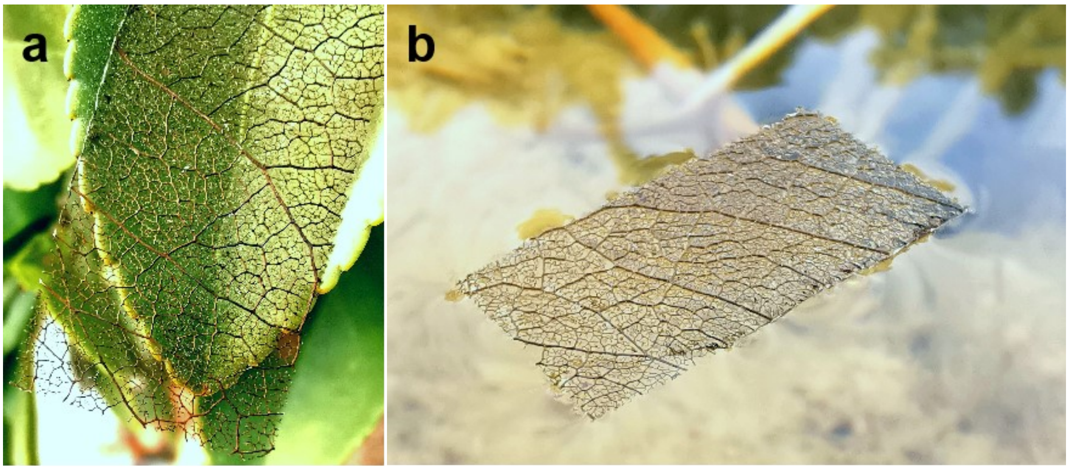


Figure S5. Optical image of the leaf vein-architected AuNWs electrode in a bent state.

126 

127 **Figure S6.** Optical images of the leaf vein-architected AuNWs electrode placed on a leaf and the surface of
128 water.
129

Section 4. Leaf Vein-Architected AuNWs Electrode Induced by 4 nm Gold Nanoparticle

Figure S7. Optical image of leaf vein-architected AuNWs electrodes induced by gold nanostars (top) and 4 nm gold nanoparticles (bottom).

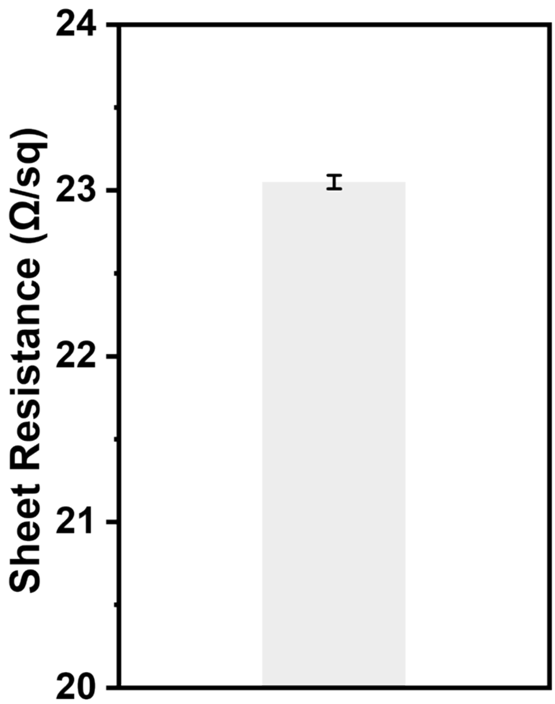


Figure S8. The sheet resistance of the leaf vein-architected AuNWs electrode induced by 4 nm gold nanoparticle.

Section 5. AuNWs Growth on Various Types of Leaf Veins

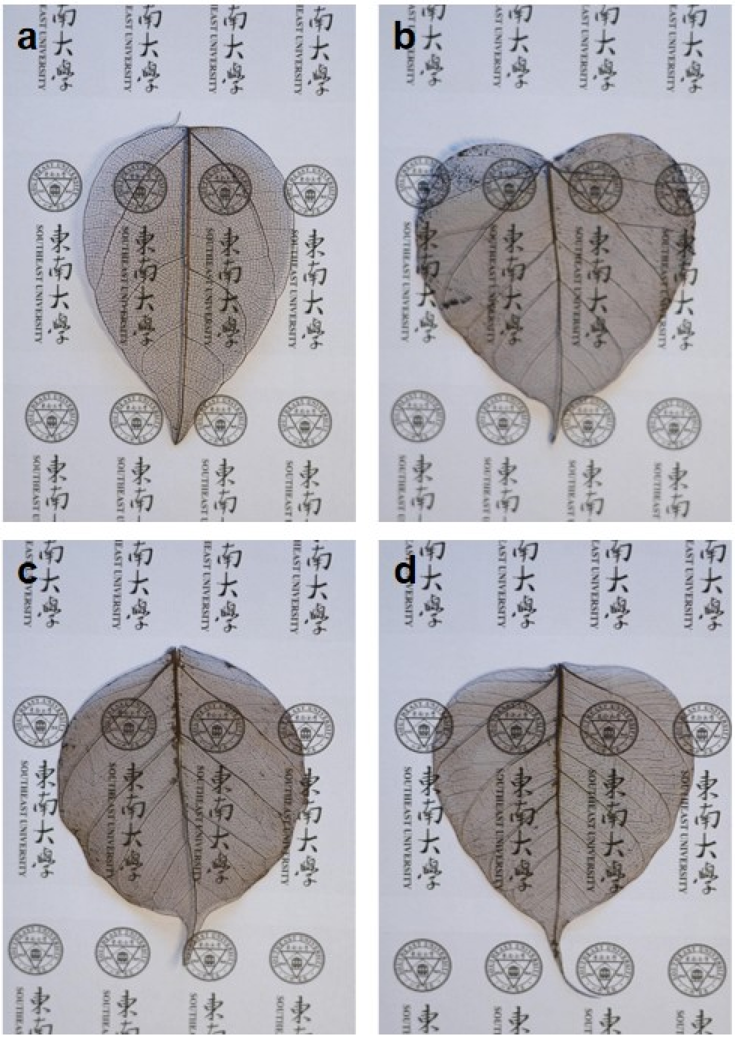


Figure S9. Optical images of leaf vein-architected AuNWs electrode using different types of leaves as substrates.

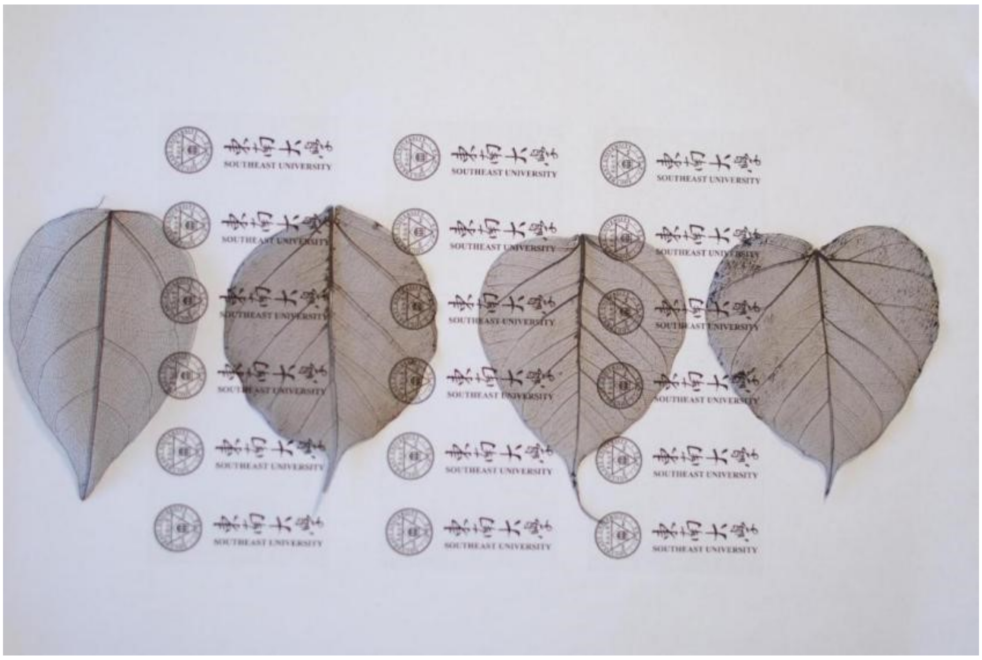


Figure S10. Optical image of different types of leaves. From left to right: ginseng leaf vein, poplar leaf vein, bodhi leaf vein, magnolia leaf vein.

Section 6. Permeability Characterization

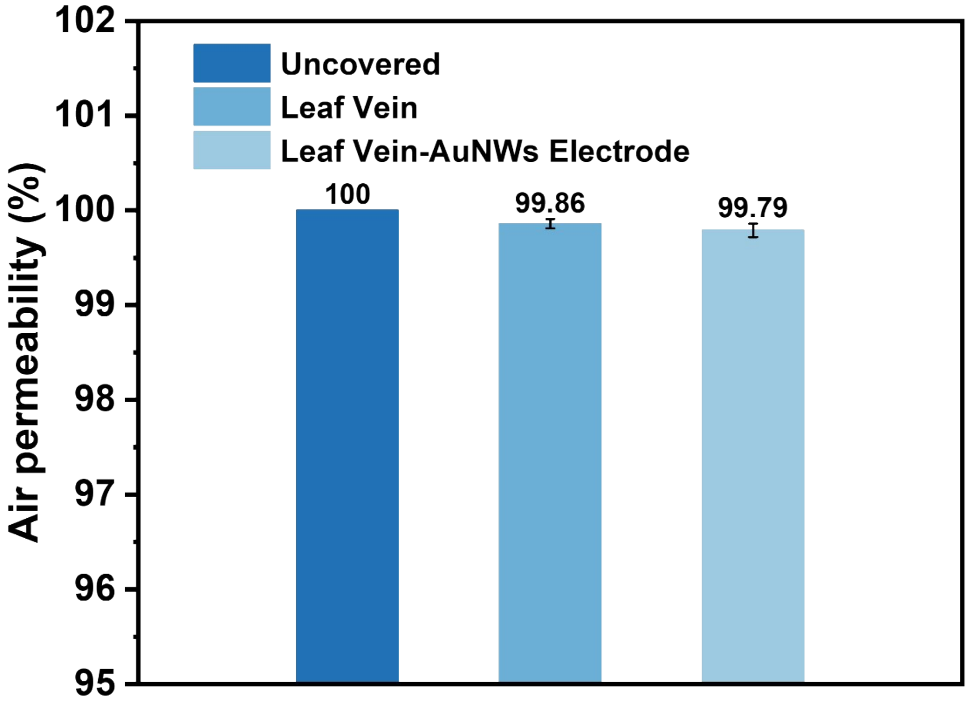


Figure S11. The Characterization of air permeability.

Section 7. Sheet Resistance of the Vein-Architected AuNWs Electrode under Different Growth Time

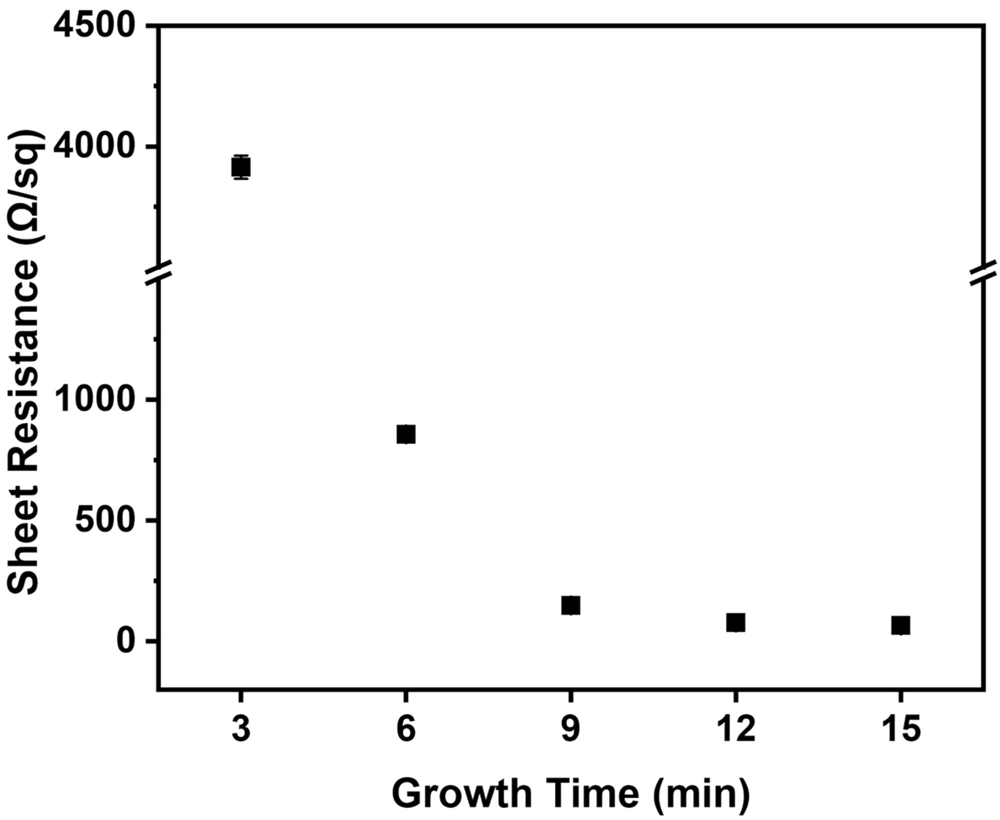


Figure S12. The sheet resistance magnitude under different growth time.

Section 8. Vein-architected AuNWs Ecoflexible Sensor

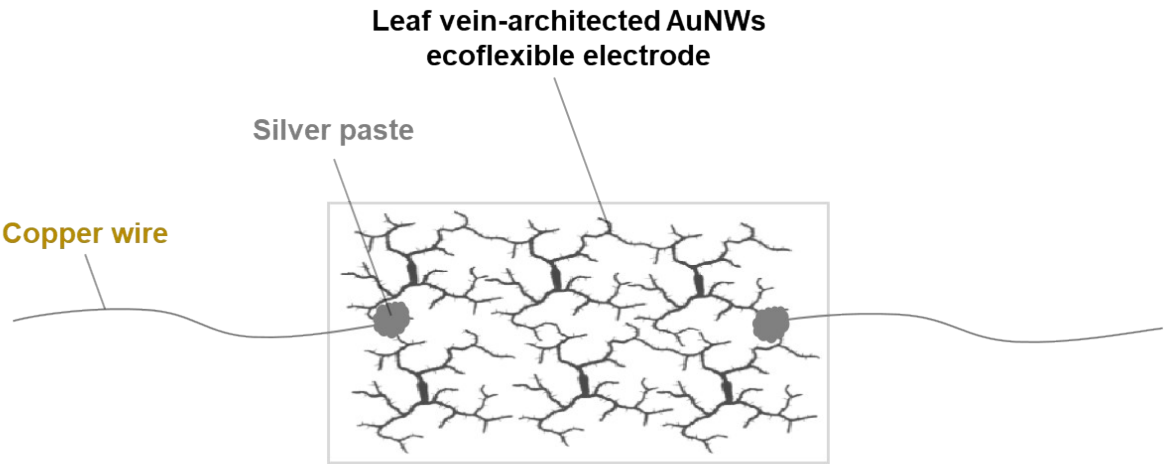


Figure S13. Electrical contacts were fabricated by connecting external copper wires to leaf vein-architected AuNWs electrode using silver paste.

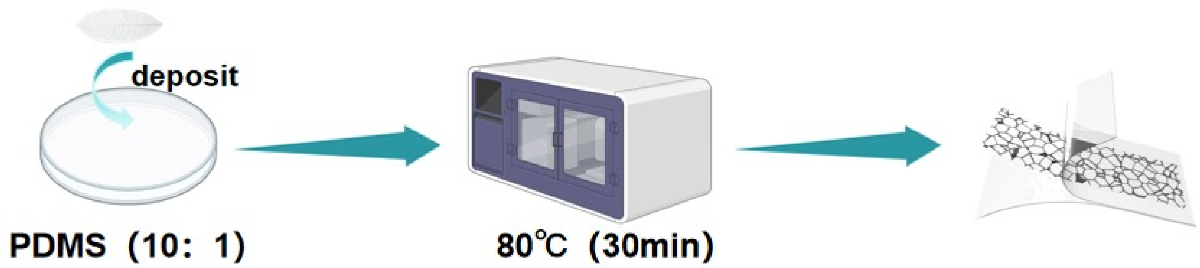


Figure S14. The Schematic of the fabrication process for the leaf vein-architected AuNWs ecoflexible sensor.

Section 9. Comparison of Mechanical Properties Between Unmodified and AuNWs-Modified Sensors

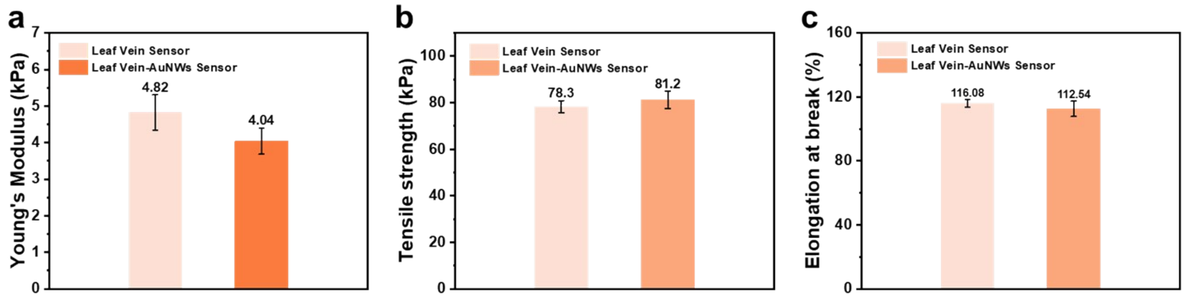


Figure S15. (a) Comparison of Young’ s Modulus (within 50% tensile strain). (b) Comparison of tensile strength. (c) Comparison of elongation at break.

Section 10. The Resistance Responses during a Stretch-Release Cycle

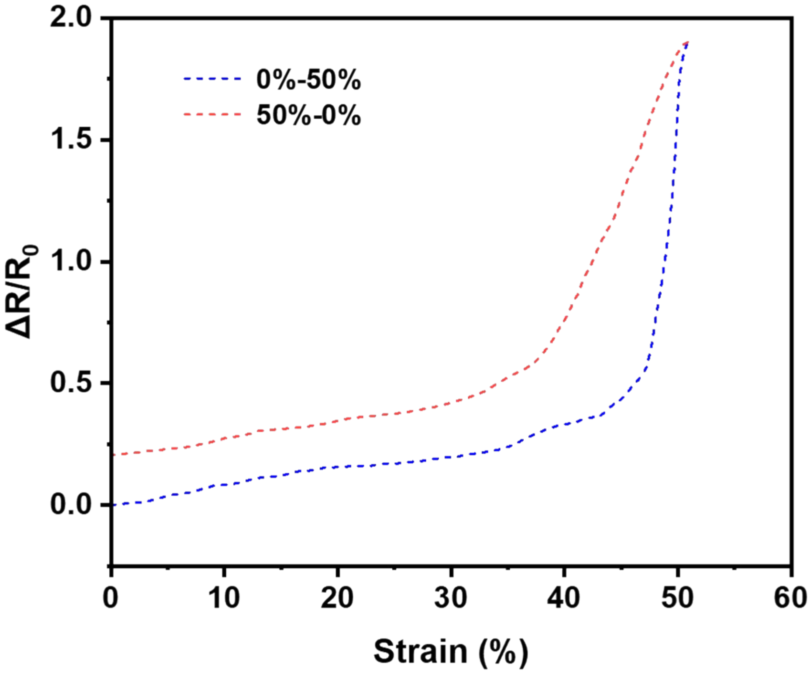


Figure S16. The resistance behavior during a complete stretch-release cycle from 0% to 50% strain and back to 0%.

Section 11. Gauge Factor (GF) Evaluation

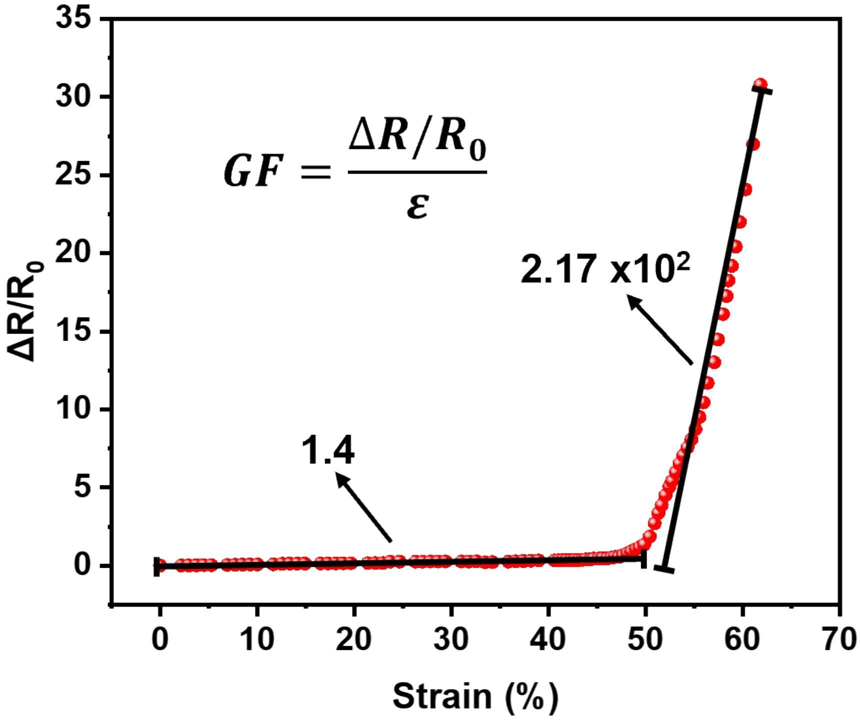


Figure S17. GF evaluation in the moderate strain range (0%-60%).

Section 12. Comparison between Leaf Vein-Architected AuNWs Ecoflexible Sensor and PDMS Film-Based AuNWs Sensor

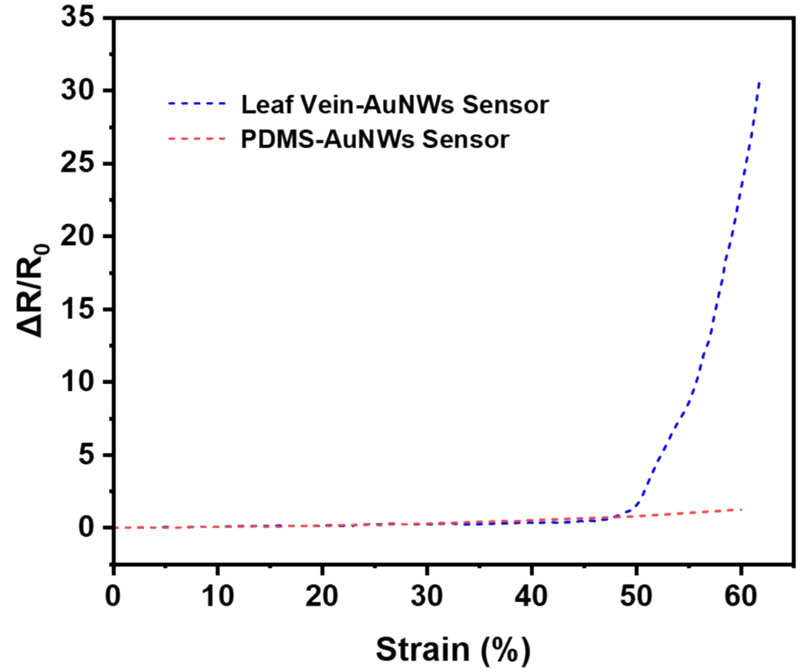


Figure S18. Comparison of strain-dependent resistance responses between leaf vein-based and PDMS film-based AuNWs sensors.

Section 13. Current-Voltage Response under Strain

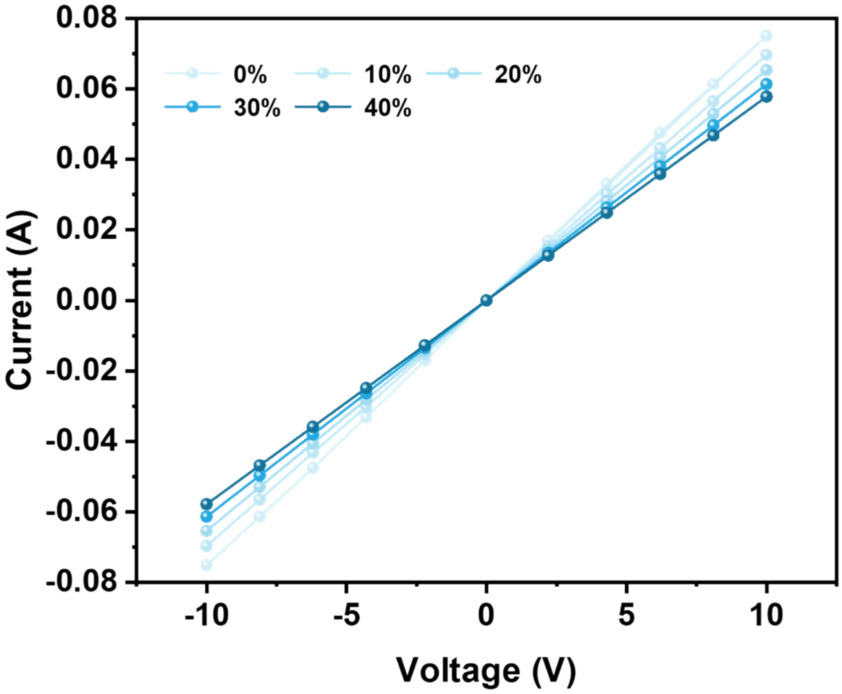


Figure S19. I-V curves of the leaf vein-architected AuNWs ecoflexible sensor under 0%, 10%, 20%, 30%, and 40% strain.

Section 14. Real Time Detection of Wrist Pulse Signals

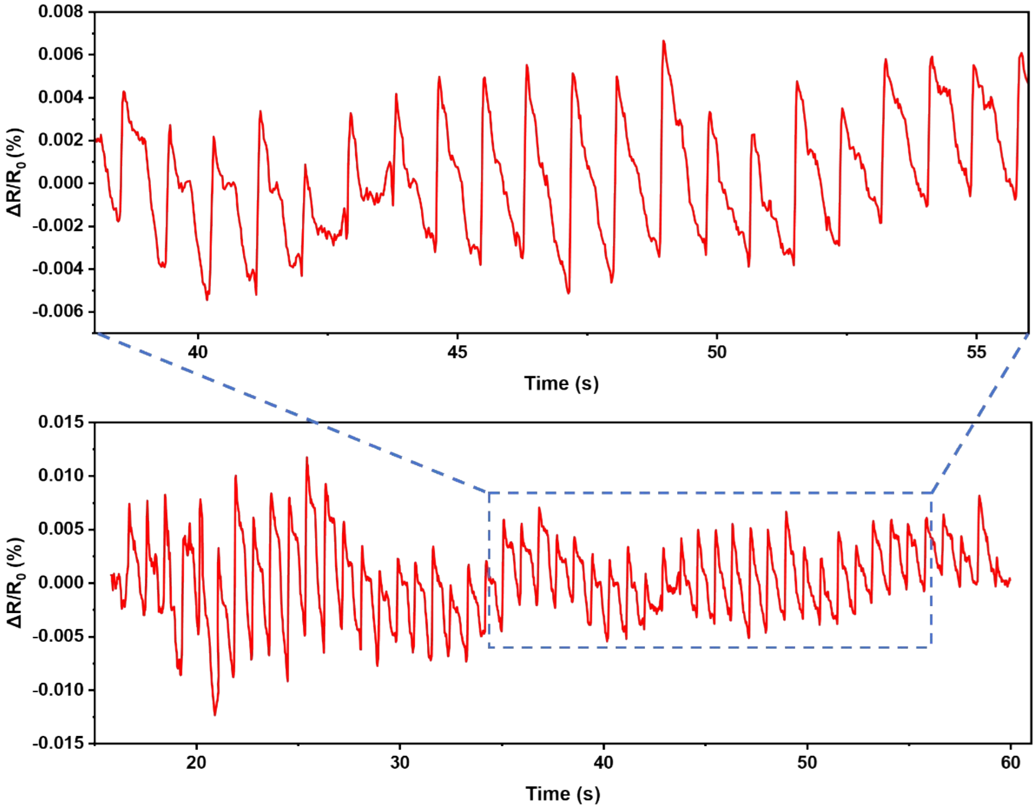


Figure S20. Real time detection of wrist pulse signals using the leaf vein-architected AuNWs ecoflexible sensor.

Section 15. Current-Voltage Response under Pressure

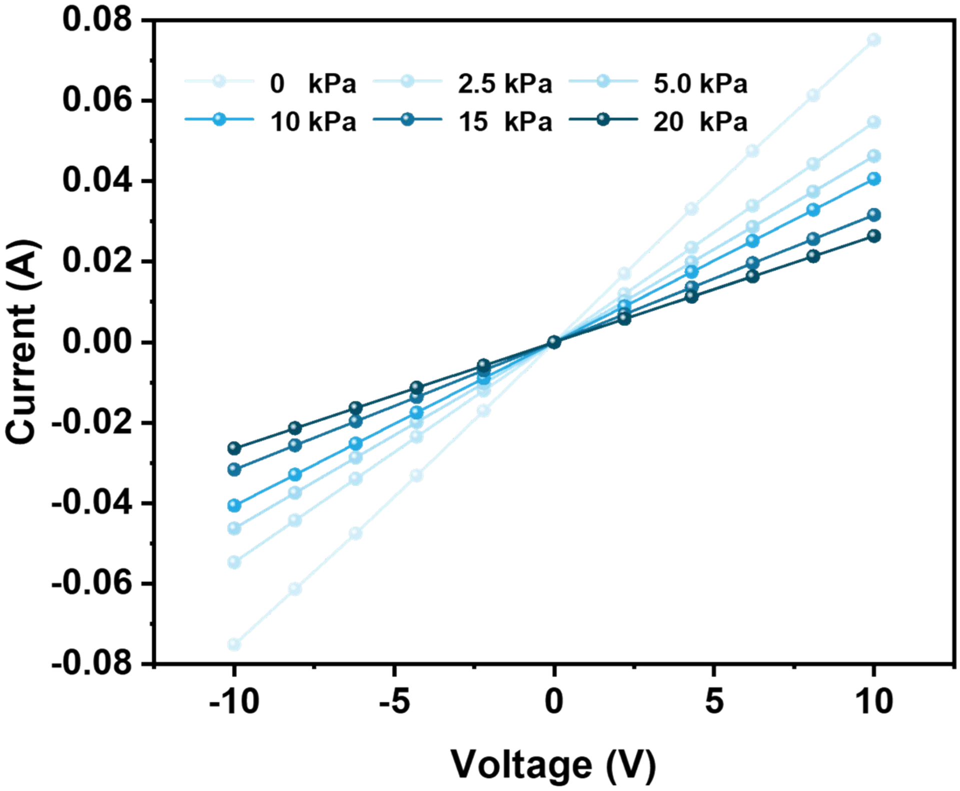


Figure S21. I-V curves of the leaf vein-architected AuNWs ecoflexible sensor under 0 kPa, 2.5 kPa, 5.0 kPa, 10 kPa, 15 kPa and 20 kPa.

Section 16. Mechanism of Resistance Variation under Mechanical Deformation

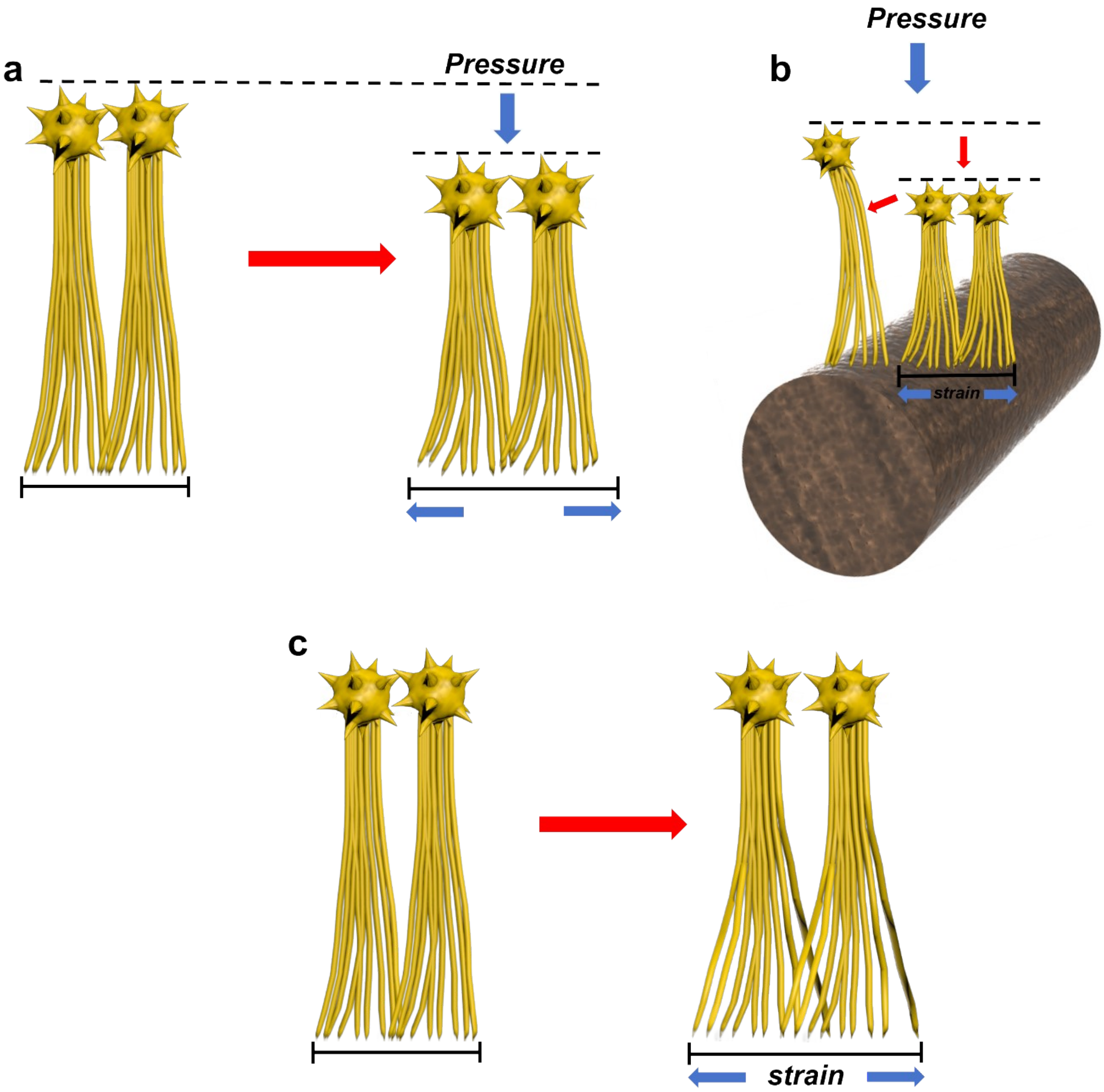


Figure S22. (a) Compressive deformation and conductive pathway dilution. (b) Structural reconfiguration guided by leaf vein structure. (c) Tensile deformation and conductive pathway dilution.

Section 17. Stepwise Pressure Response Curve of the Leaf Vein-architected AuNWs Ecoflexible Sensor

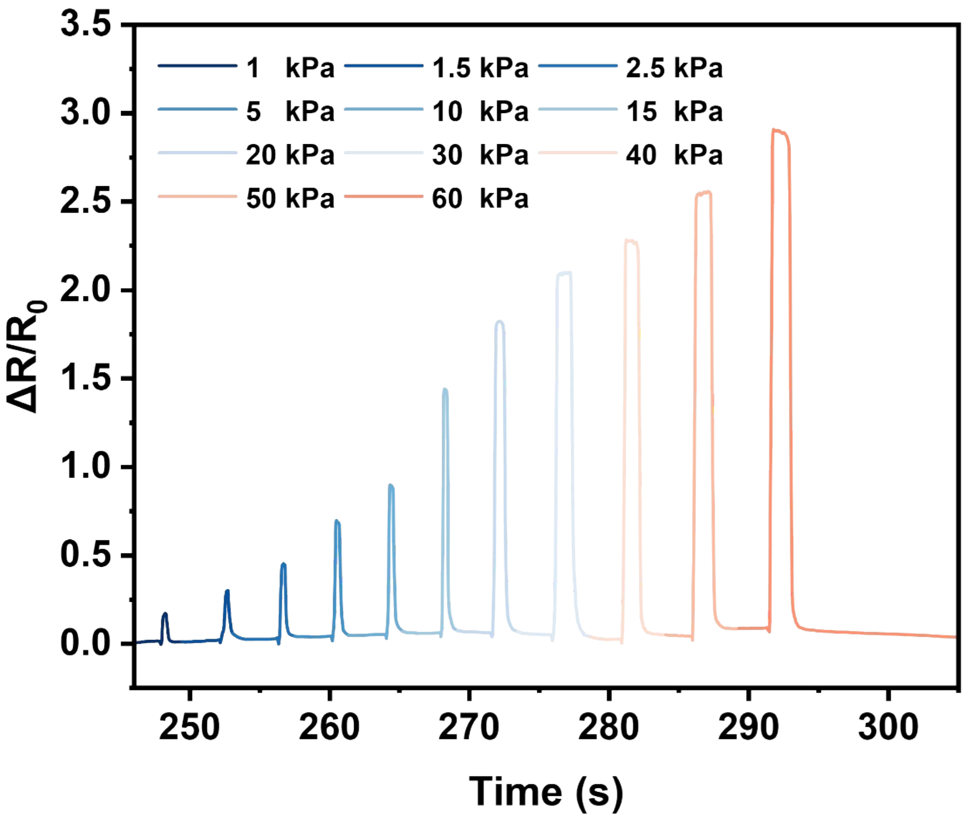


Figure S23. Multi-level pressure response curve of the leaf vein-architected AuNWs ecoflexible sensor within a 1-60 kPa range.

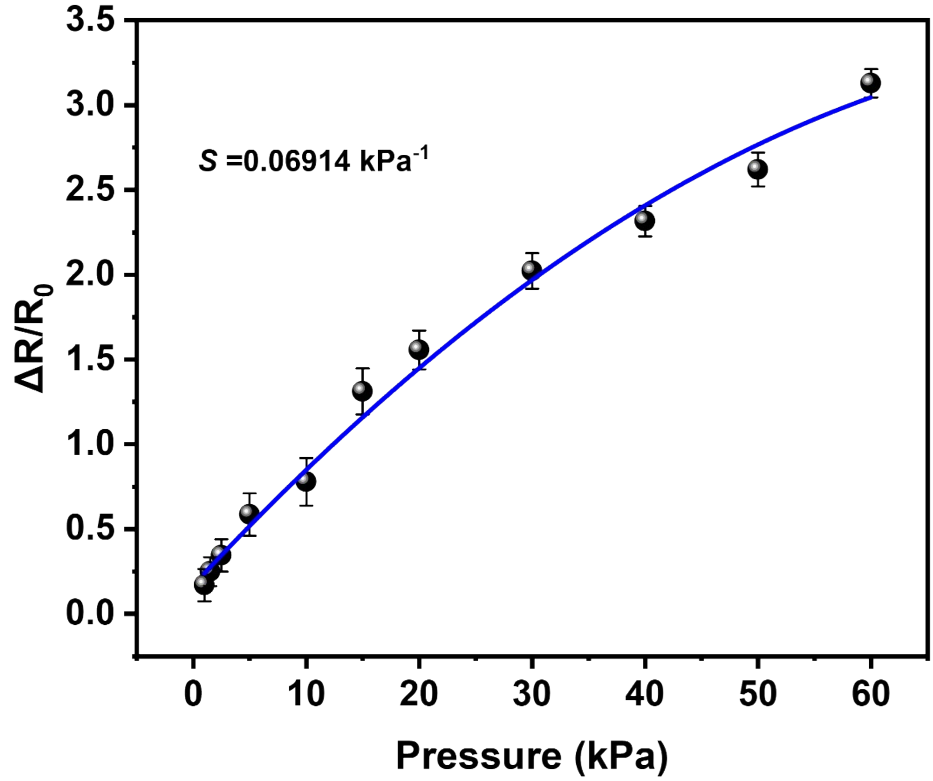


Figure S24. Sensitivity of the leaf vein-architected AuNWs ecoflexible sensor.

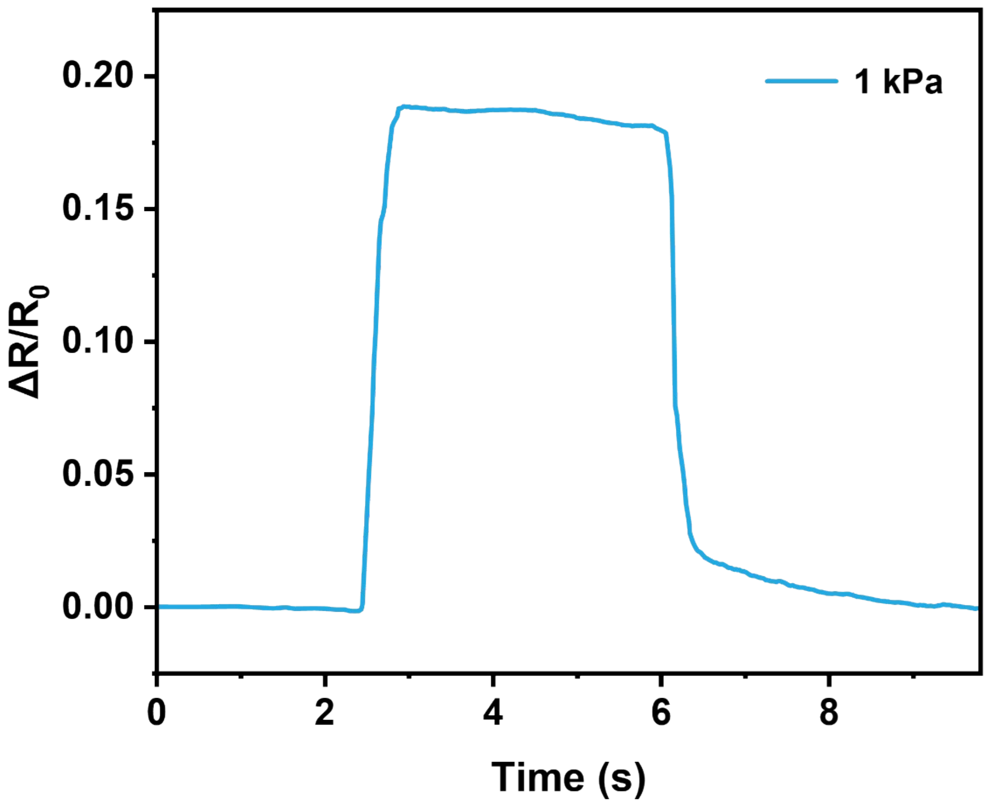


Figure S25. Hysteresis behavior of the leaf vein-architected AuNWs Ecoflexible Sensor under a loading-unloading process at 1 kPa.

References

1. H. Yuan, C. G. Khoury, H. Hwang, C. M. Wilson, G. A. Grant and T. Vo-Dinh, *Nanotechnology*, 2012, **23**, 075102.
2. Y. Wang, S. Gong, S. J. Wang, X. Yang, Y. Ling, L. W. Yap, D. Dong, G. P. Simon and W. Cheng, *ACS Nano*, 2018, **12**, 9742-9749.
3. H. Zhang, F. Lin, W. Cheng, Y. Chen and N. Gu, *Adv. Funct. Mater.*, 2022, **33**, 2209760.