

Electronic supplementary information

An ultra-thin flexible wearable sensor with multi-response capability prepared from ZIF-67 and conductive metal-organic framework composites for health signal monitoring

Youwei Zhao^{a,b}, Xiang Li^b, Tian Yuan^a, Shuhong Huang^a, Ronghui Jiang^a, Xuefei Duan^a,
Ling Li^{*a}, Xiaoting Li^{*b}, Wenming Zhang^{*a}

^a *Province-Ministry Co-construction Collaborative Innovation Center of Hebei Photovoltaic Technology, College of Physics Science and Technology, Hebei University, Baoding 071002, China.*

^b *National & Local Joint Engineering Research Center of Metrology Instrument and system, College of Quality and Technical Supervision, Hebei University, Baoding 071002, China.*

Corresponding Author:

E-mail: lilinghbu@163.com, lxt@hbu.cn and wmzhanghbu@126.com

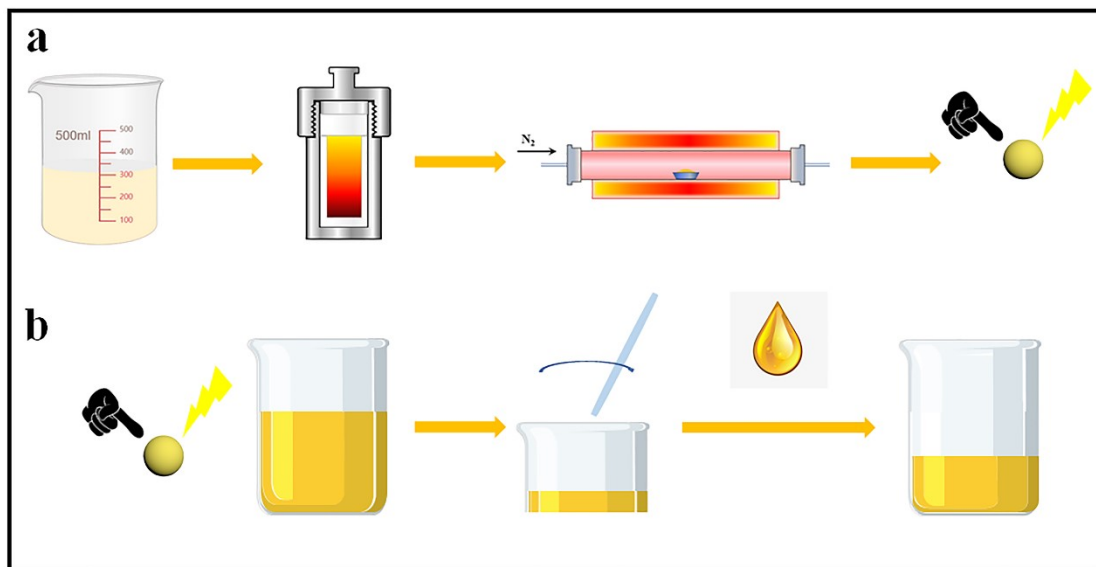
Materials

Copper nitrate, cobalt nitrate, zinc nitrate, zinc acetate dihydrate, manganese acetate, thiourea, 2-methyl imidazole methanol, 2,3,6,7,10,11-hexahydroxytriphenylene ($H_{12}C_{18}O_6$, HHTP), n-hexaoxane and ethanol purchased at Shanghai Maclean Biochemical Technology Co., Ltd. Silver conductive paint was purchased from Mechanic. Weishan Lake dried lotus leaves and ZnS:Cu were purchased at Nano New Material Technology Co., Ltd. The PDMS was purchased at Gainshine, China. Polyimide-based flexible interdigital electrode was purchased from Rigorous Technology Co., Ltd. HSV900 PVDF binder for electrodes and carbon black were purchased from advanced Materia & Laboratory Equipment. Interdigital gold electrode on polyimide substrate were purchased from interdigital electrode manufacturer.

Characterizations and Measurements.

The SEM (FEI, Nova Nano SEM 450), a transmission electron microscope ((FEI, Tecnai G220), and the Canon camera were used to examine the morphologies of the sensitive material. Field Emission TEM (FE-TEM) was performed on FEI Tecnai G2 F20 at 200 kV. The phase composition and crystal structure of the sensitive material were characterized using D8 ADVANCE (3 kW) XRD and $CuK\alpha$ irradiation ($\lambda = 1.5418 \text{ \AA}$) radiation $5^\circ \sim 35^\circ$, and the scan rate was set to $1^\circ/\text{min}$. Sensor current measurements were recorded on an Keithley (2636B) digital multimeter. The bending and pressing test of the flexible electronic sensor were characterized in tension on a universal testing machine (WDW-0.05D Jilin Guanteng Automation Technology Co. Ltd).

Figure S1 (a)The schematic diagram of zinc sulfide preparation. (b) The fabrication of



flexible micropatterned PDMS substrates.

Figure S2 The digital photo of (a) dried lotus leaves, (b) clay, (c) flexible sensor unit. (d) The size of screen-printing electrode. (e)The SEM of micropatterned PDMS film doped with ZnS:Mn. (f) The SEM of micropatterned PDMS film.

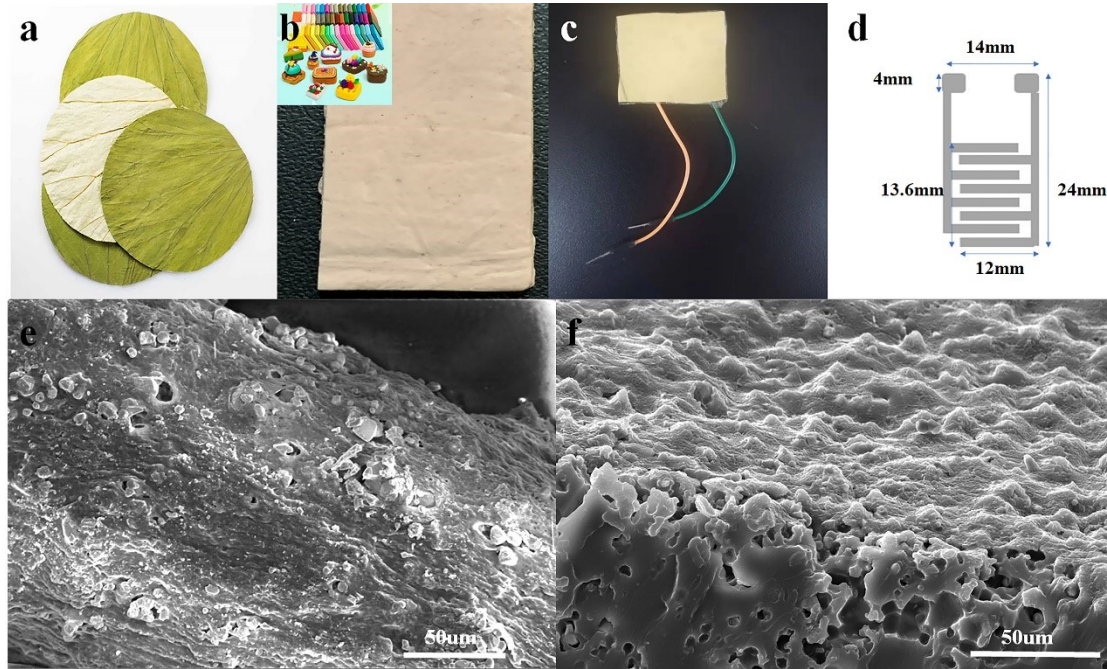
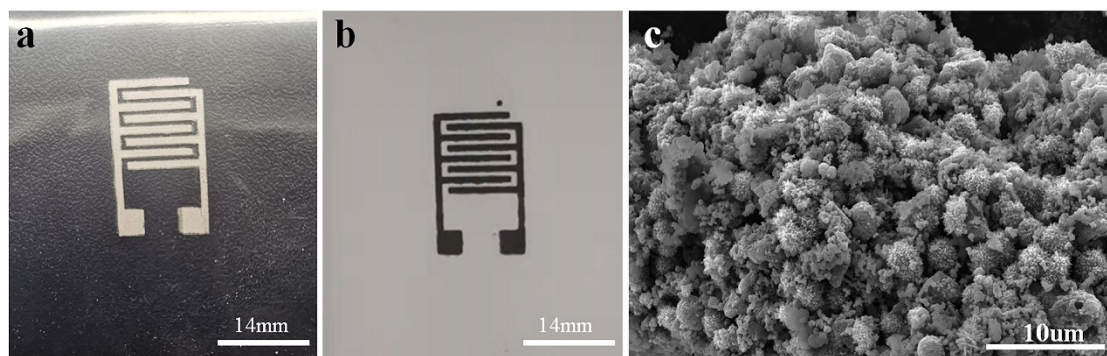


Figure S3 The digital photos of screen-printing (a) silver electrode, (b) cZIF-67@Cu-CAT electrode on different substrates. (c) The microstructure of cZIF-67@Cu-CAT



electrode.

Figure S4 The XRD of (a) ZIF-67, (b) cZIF-67, (c) ZnS prepared by hydrothermal method, (d) ZnS:Mn prepared in the laboratory.

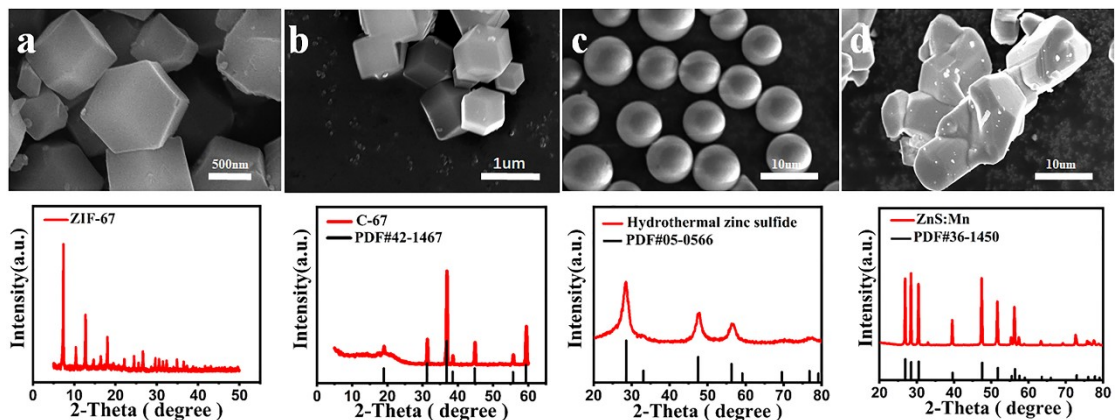


Figure S5 (a) The survey spectrum of cZIF-67@Cu-CAT.

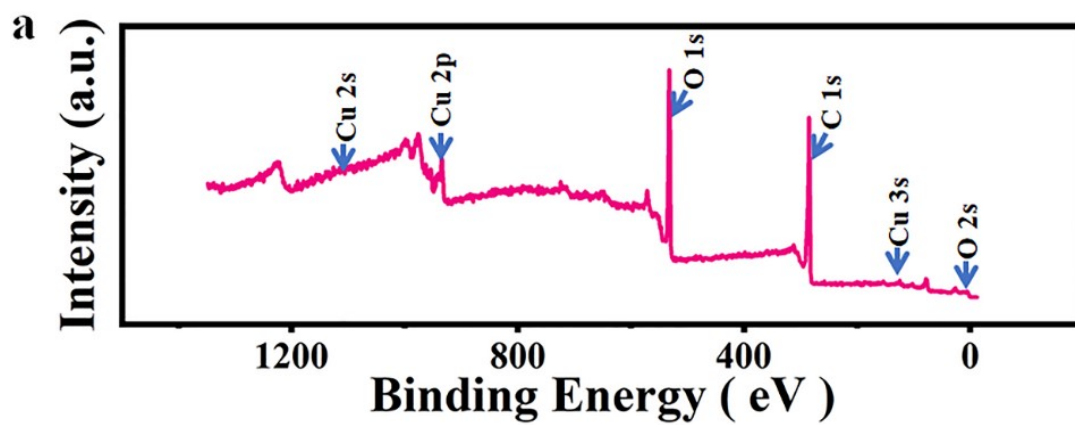
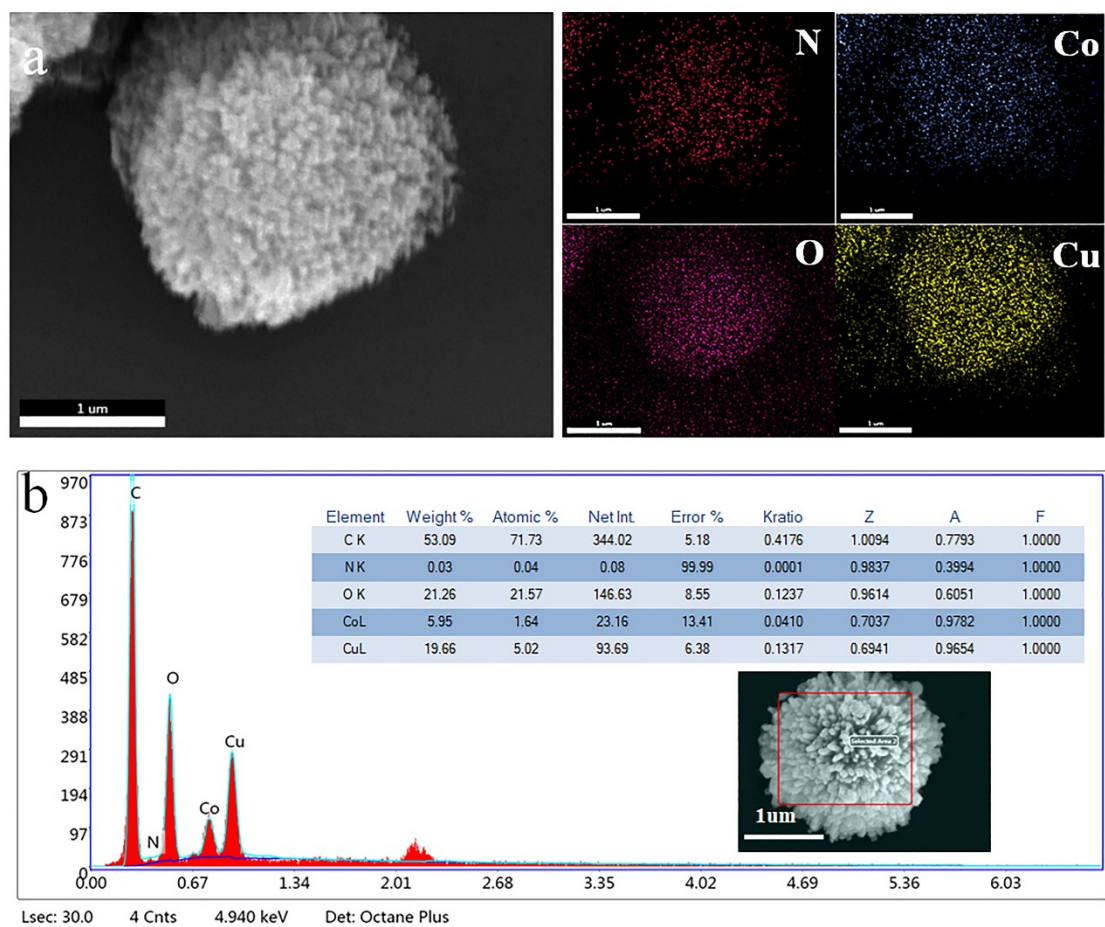
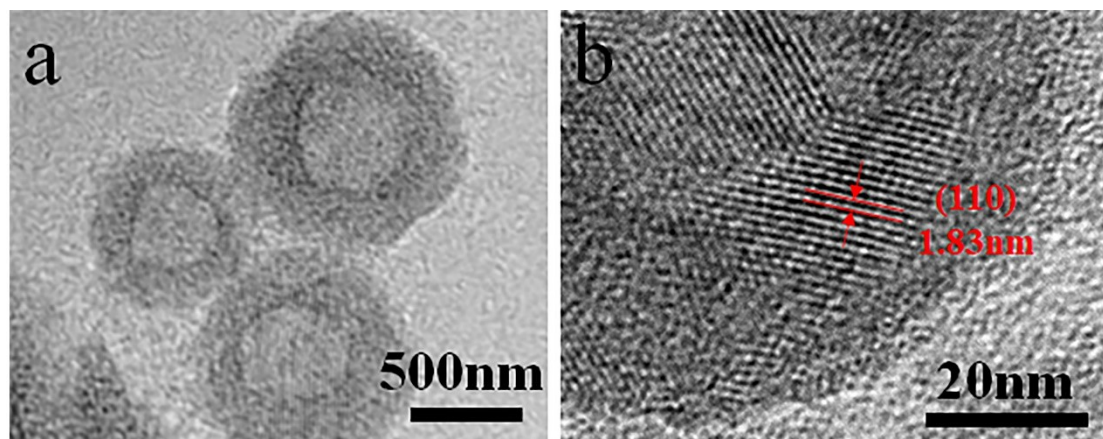


Figure S6 (a) The Energy dispersive spectroscopy (EDS) of cZIF67@Cu-CAT. (b) The



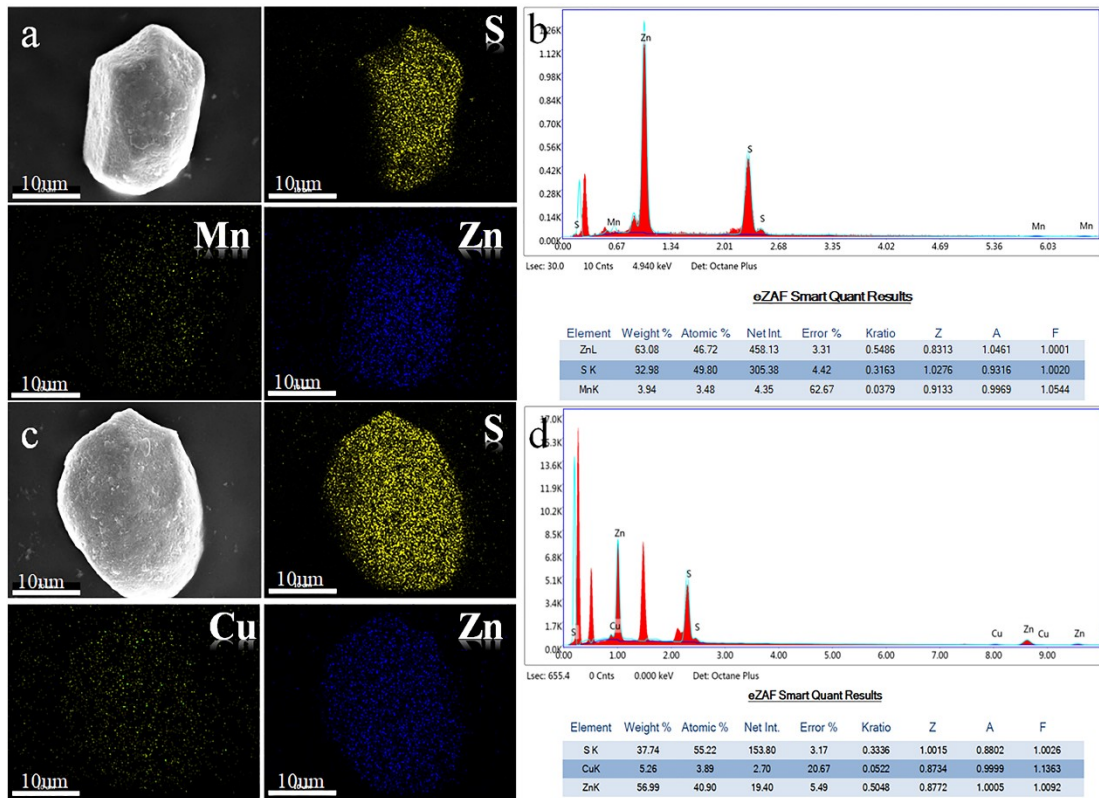
element content of N, O, Cu, Co.

Figure S7 (a) The TEM images of cZIF-67@Cu-CAT. (b) The image of the as prepared



cZIF-67@Cu-CAT.

Figure S8 (a) The EDS analysis of ZnS: Mn. (b) The element content of S, Zn, Mn. (c)



The EDS analysis of ZnS: Cu. (d) The element content of S, Zn, Cu.

Figure S9 The (a-b) sensitivity and (c) response time of the flexible wearable sensor (Carbon nanotubes ink). The (d-e) sensitivity and (f) response time of the flexible wearable sensor (cZIF-67).

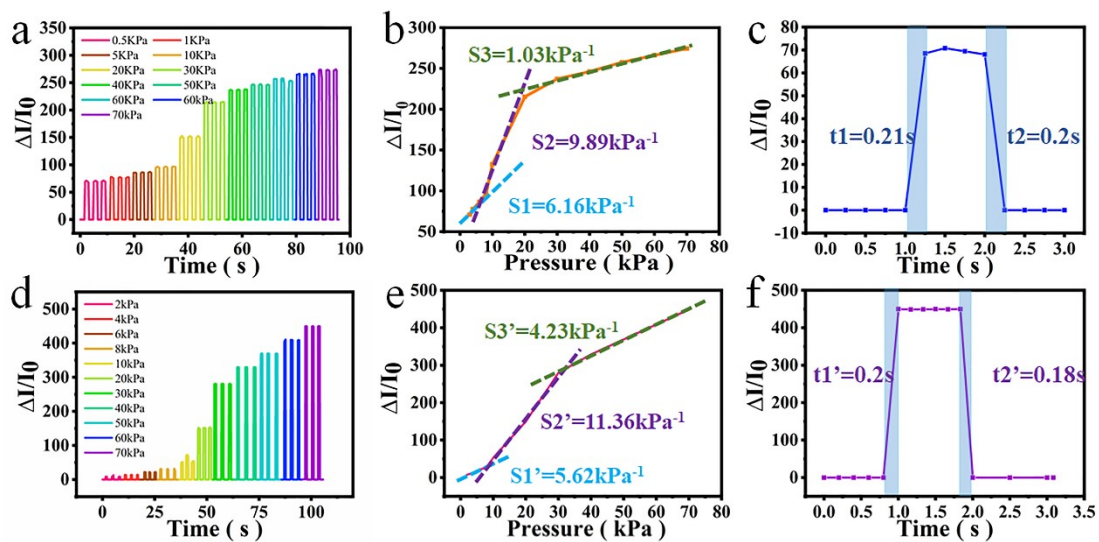
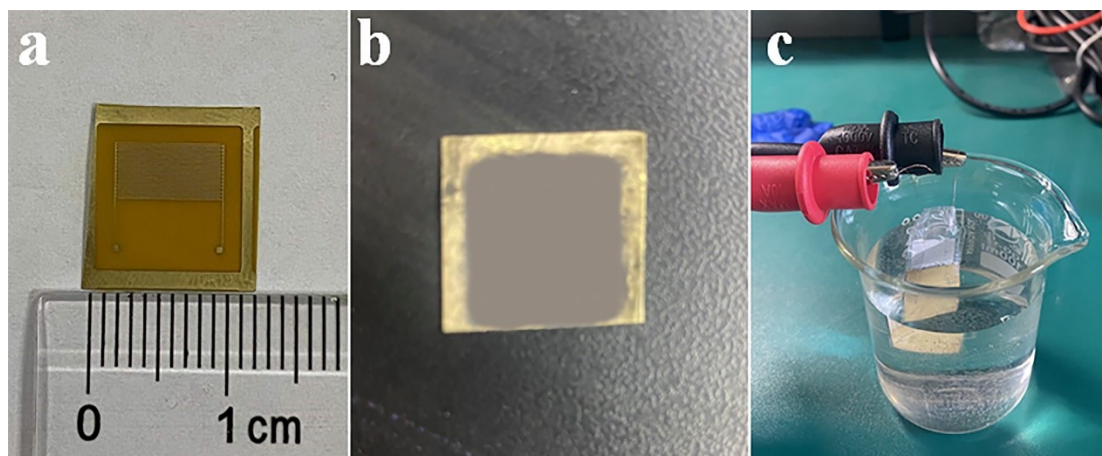


Figure S10 (a) The digital photo of golden interdigital electrode. (b) The digital photo of PDMS film sprayed with cZIF-67@Cu-CAT nanoparticles. (c) The digital photo of a



single sensor encapsulated by glue under water.

Figure S11 Schematic diagram of sensor assembly microstructure design.

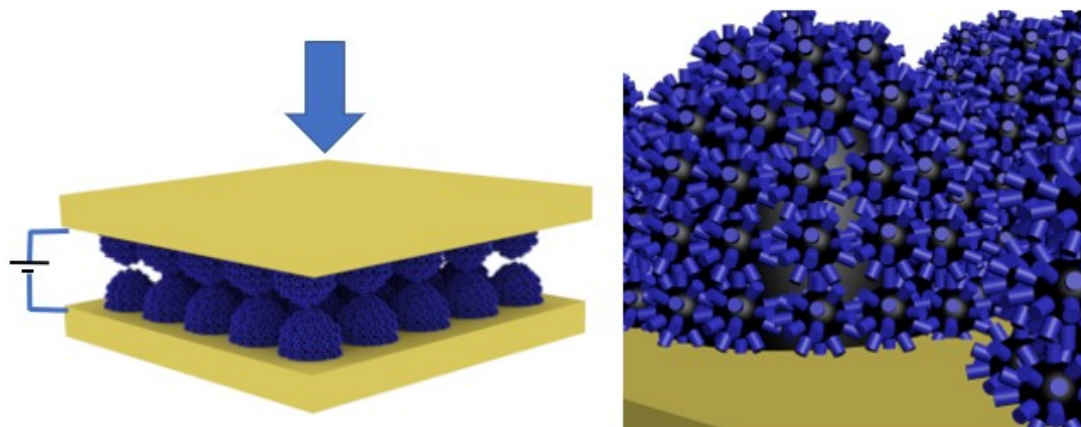


Figure S12 The adhesion of dandelion-like conductive materials on the microstructural membrane formed by PDMS (a) before and (b) after the long cycle.

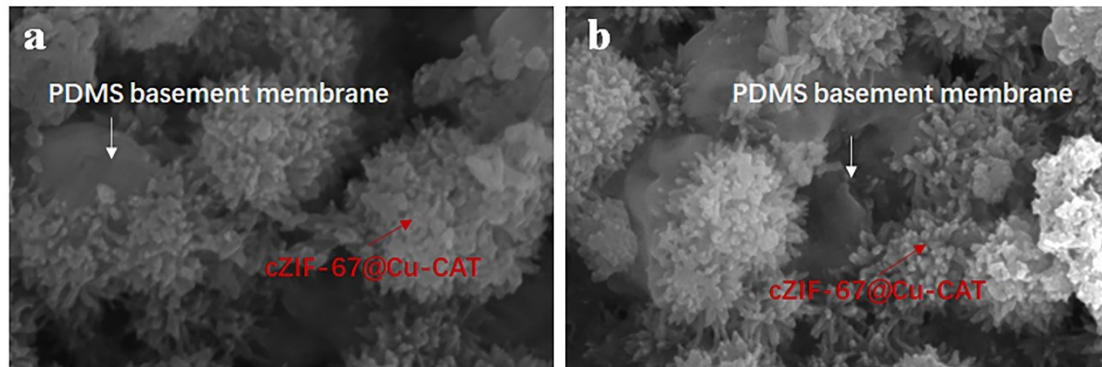


Figure S13 The sensor's sensing data is transmitted to the phone's computer port in real time via Bluetooth.

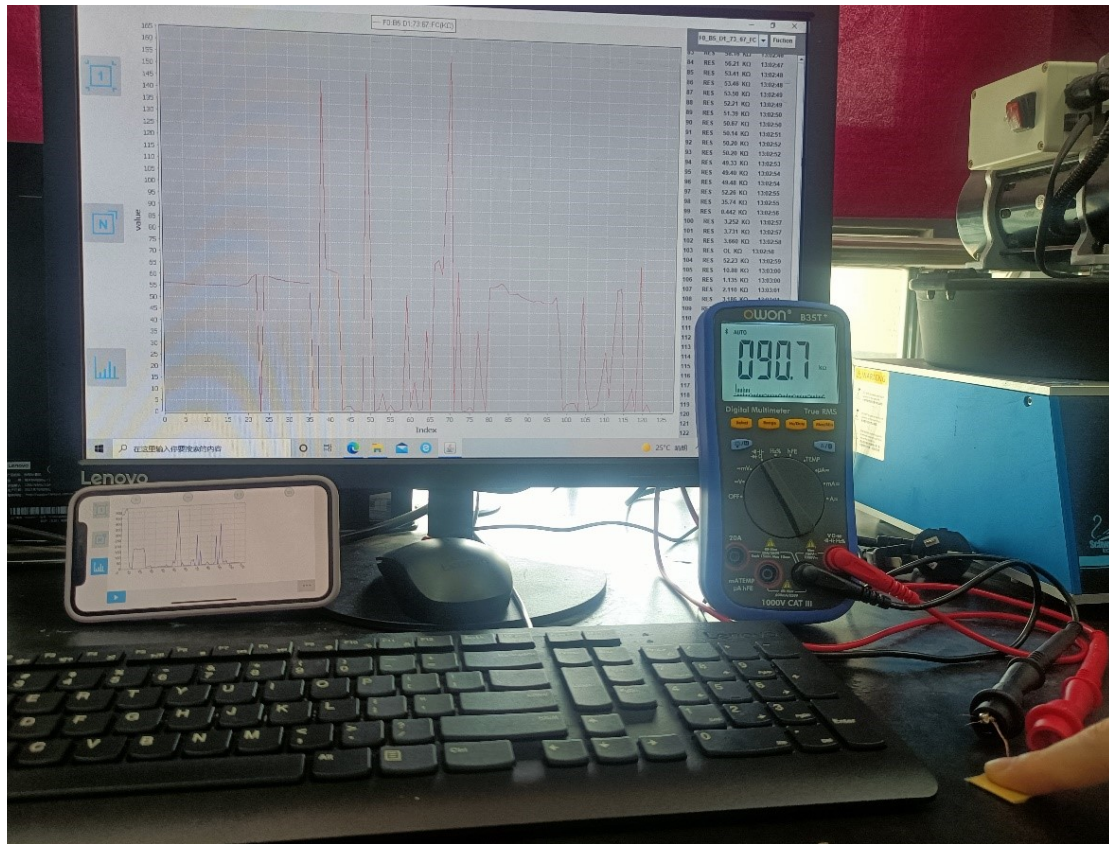


Table S1 Detailed dimensions of individual sensors

Unit	Parameter			
sensor	length	width	thickness	weight
	1cm	1cm	0.32mm	0.36g

Table S2

Device type	Pressure Sensitivity (kPa ⁻¹)	Response time(s)	Stability	Detection limit (Pa)	Ref.
All-Textile	14.4 ⁻¹	24 ms	1000	2 Pa	1
MXene/ANFs aerogel	128 kPa ⁻¹	320 ms	1000	100 Pa	2
Carbon nanotube	4.4kPa ⁻¹	10 ms	11000	0.5 Pa	3
Suspended standing nanowire membranes	4.26 kPa ⁻¹	--	--	319–1951 Hz	4
Flexible tactile sensor	3.26 kPa ⁻¹	--	--	--	5
3D porous crumpled MXene spheres	3.14 kPa ⁻¹	34 ms	5000	140 Pa	6
Microstructure -bioinspired	53 kPa ⁻¹	19 ms	50000	58.4 Pa	7
MXene/BP	77.61 kPa ⁻¹	10.9 ms	10000	0.12 kPa	8
Carbon materials with arched micro-patterns array	26.6 kPa ⁻¹	20 ms	5000	20 Pa	9

Reference

1. M. Liu, X. Pu, C. Jiang, T. Liu, X. Huang, L. Chen, C. Du, J. Sun, W. Hu and Z. L. Wang, *Adv Mater*, 2017, **29**, 1703700.
2. L. Wang, M. Zhang, B. Yang, J. Tan and X. Ding, *ACS Nano*, 2020, **14**, 10633-10647.

3. H. Xu, Y. Xie, E. Zhu, Y. Liu, Z. Shi, C. Xiong and Q. Yang, *Journal of Materials Chemistry A*, 2020, **8**, 6311-6318.
4. S. Gong, L. W. Yap, Y. Zhu, B. Zhu, Y. Wang, Y. Ling, Y. Zhao, T. An, Y. Lu and W. Cheng, *Advanced Functional Materials*, 2020, **30**, 1910717.
5. Y. Cao, T. Li, Y. Gu, H. Luo, S. Wang and T. Zhang, *Small*, 2018, **14**, e1703902.
6. Z. Yang, S. Lv, Y. Zhang, J. Wang, L. Jiang, X. Jia, C. Wang, X. Yan, P. Sun, Y. Duan, F. Liu and G. Lu, *Nanomicro Lett*, 2022, **14**, 56.
7. T. Yang, W. Deng, X. Chu, X. Wang, Y. Hu, X. Fan, J. Song, Y. Gao, B. Zhang, G. Tian, D. Xiong, S. Zhong, L. Tang, Y. Hu and W. Yang, *ACS Nano*, 2021, **15**, 11555-11563.
8. Y. Zhang, L. Wang, L. Zhao, K. Wang, Y. Zheng, Z. Yuan, D. Wang, X. Fu, G. Shen and W. Han, *Adv Mater*, 2021, **33**, e2007890.
9. M. Zhong, L. Zhang, X. Liu, Y. Zhou, M. Zhang, Y. Wang, L. Yang and D. Wei, *Chemical Engineering Journal*, 2021, **412**, 128649.