Supplementary Information (SI) for New Journal of Chemistry.

Supporting Information

Integrated wearable electrochemical sensor based on silk protein for the detection of uric acid in sweat

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Contents

Reagents and Material

Phosphate-buffered saline (PBS) was purchased from Sangon Biotech (Shanghai) Co., Ltd. Ethanol (C_2H_5OH), $NaHCO_3$, glycerin and formic acid (CH_2O_2) were all purchased from Sinopharm Chemical Reagent Co., Ltd. $Zn(NO_3)_2 \cdot 6H_2O$, 2-methylimidazole and $CaCl_2$ was purchased from Aladdin Reagent Co., Ltd. Petroleum jelly was provided by Shanghai Macklin Biochemical Technology Co., Ltd. Ag/AgCl ink and carbon ink were purchased from Weihai Poten Technology Co., Ltd. (Wei-hai, China). The secondary distilled water required for the experiment was supplied by Milli-Q (Millipore, USA). PBS solution was used to prepare the following buffers: 1 mM PBS solution (pH 7.0) and 10 mM PBS solution (containing 100 mM NaCl, pH 7.0). The chemical reagents used are all analytical grade.

Apparatus and characterization

Sample morphology analysis was performed using a field emission scanning electron microscope (FESEM, Hitachi Regulus 8100) and a transmission electron microscope (TEM, Hitachi HT7700). Phase analysis and surface chemical characterization were performed using a powder X-ray diffractometer (PXRD, Japan Smart Lab). The crystal structure of the obtained samples was studied using a laser micro-Raman spectrometer (Raman, Thermofisher DXR2, USA). Electrochemical measurements were performed using a CHI 660E electrochemical workstation.

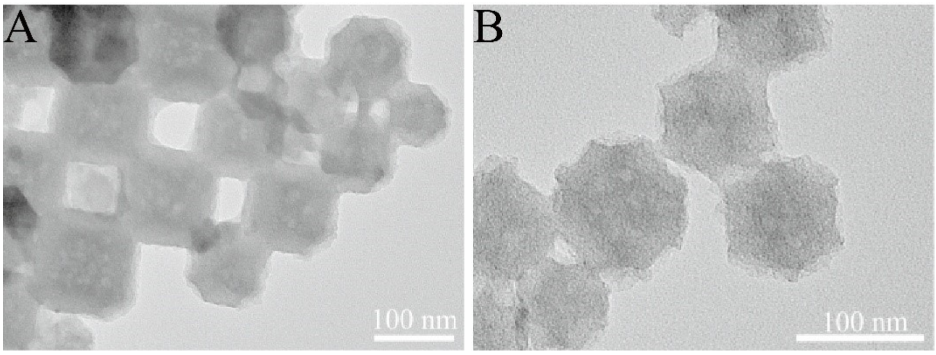

Figure S1. TEM images of (A) Z-800 and (B) Z-900.

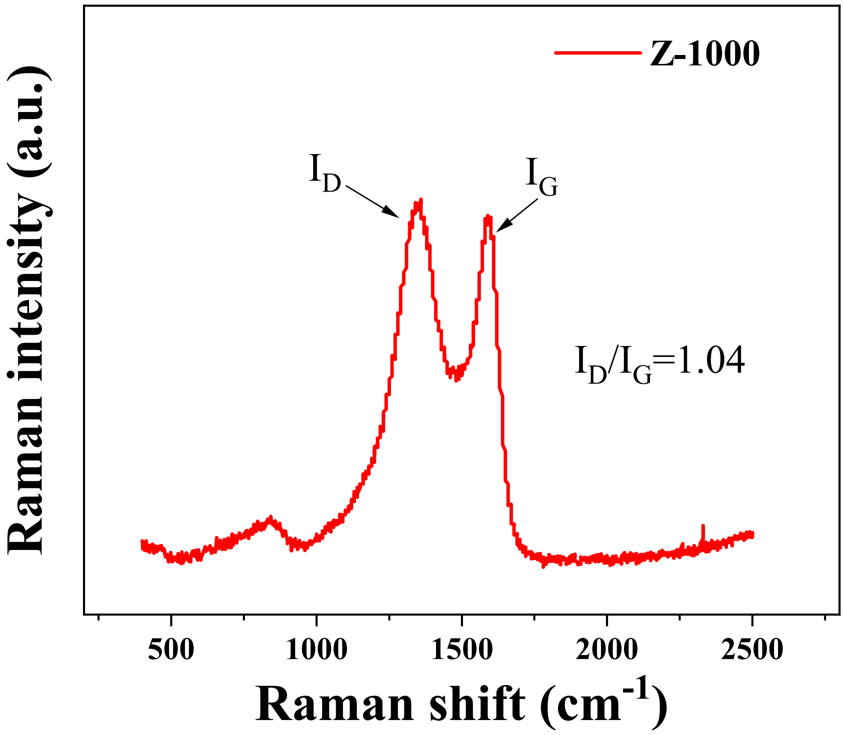

Figure S2. Raman spectrum of Z-1000.

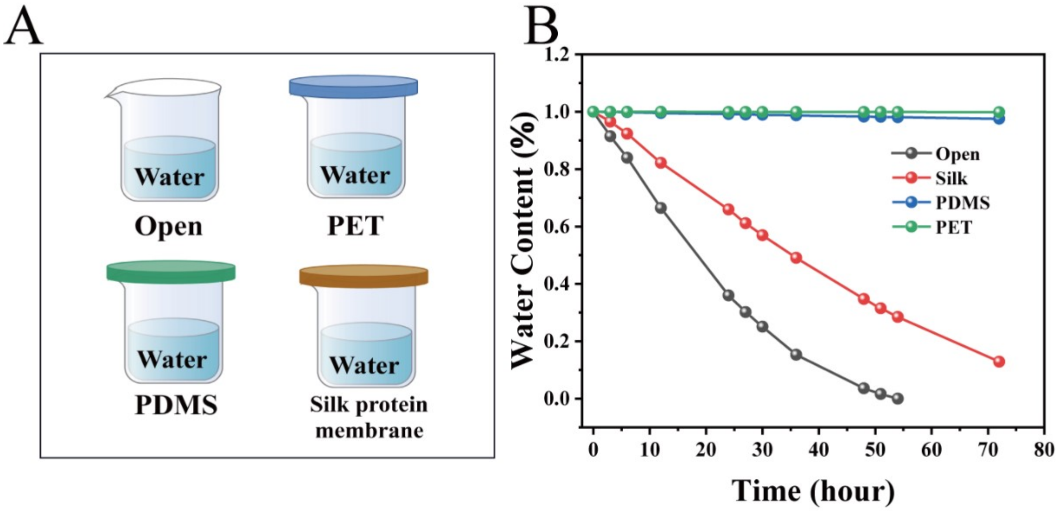

Figure S3. (A) Schematic diagram of water vapor transmission tests, (B) The mass changes of the pure water that remained in the bottles.

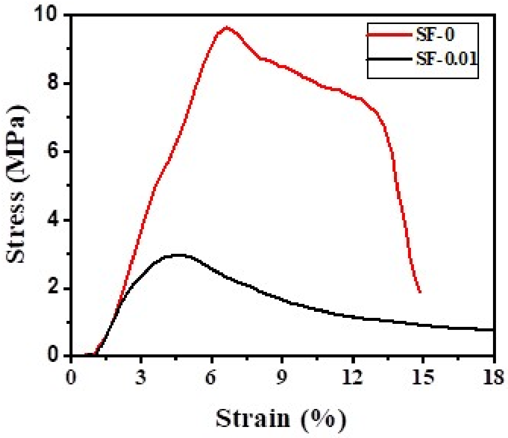

Figure S4. Stress-strain curves of silk membranes without glycerol (SF-0) and with 0.01g glycerol added (SF-0.01).

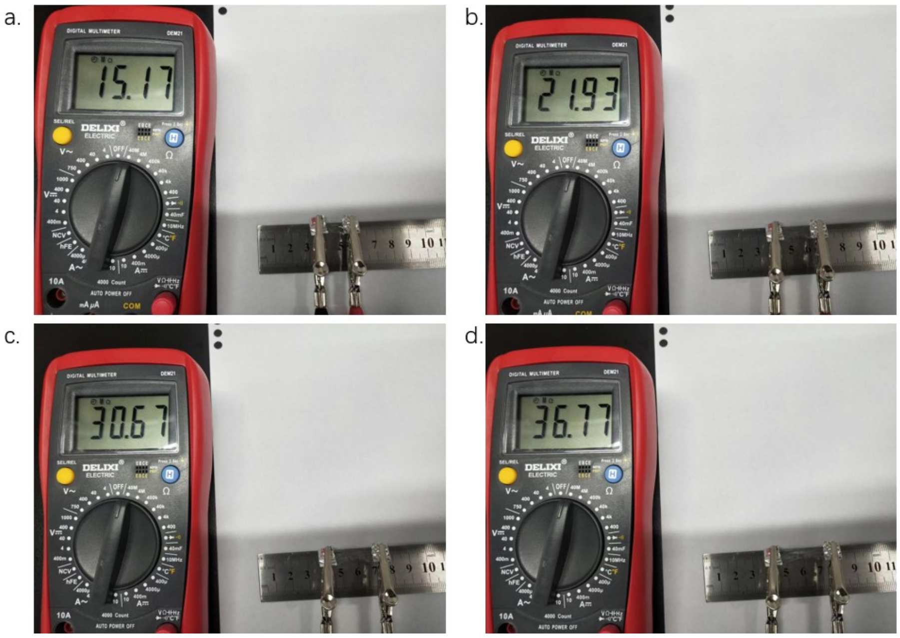

Figure S5. Multimeter measurement of silk membrane resistance at different stretched lengths.

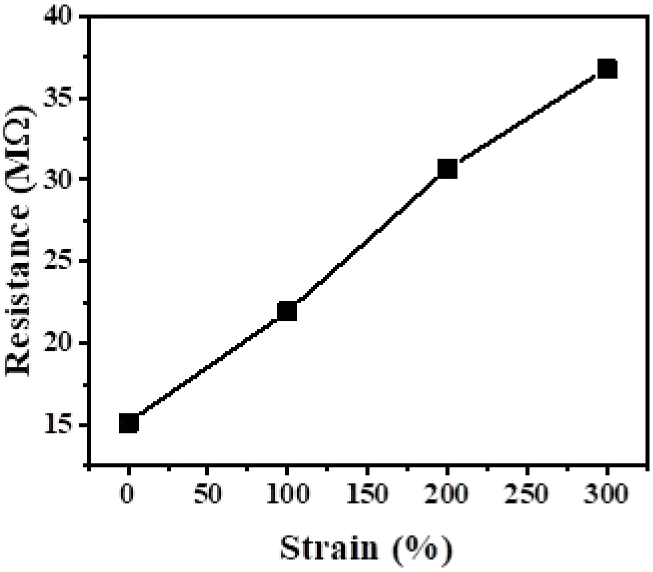

Figure S6. Resistance change of the silk membrane under different tensile strains.

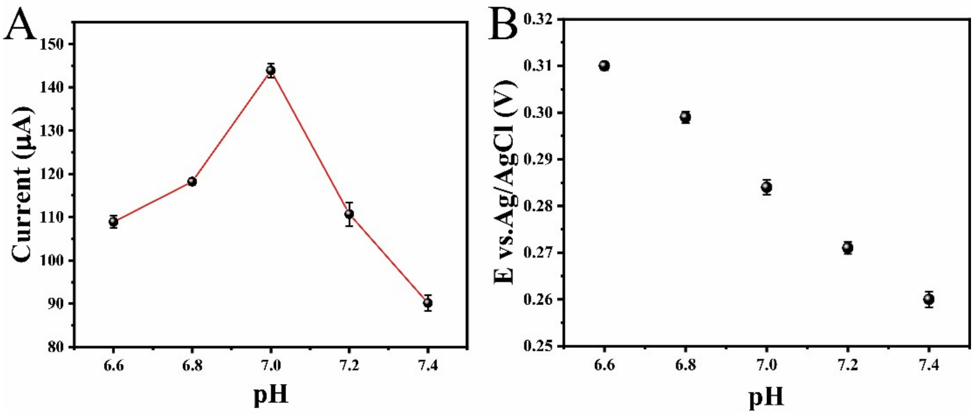

Figure S7. (A) Peak currents of 0.1 mM UA on Z-1000/SFE at different pH, (B) peak potential versus pH.

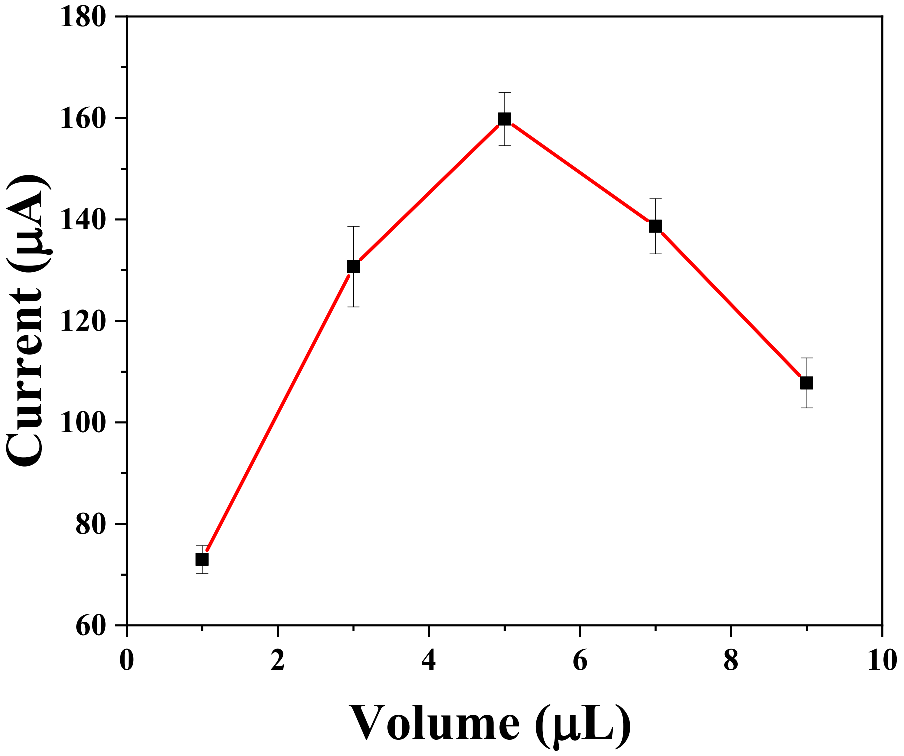

Figure S8. Peak currents of 0.1 mM UA with various Z-1000 loading.

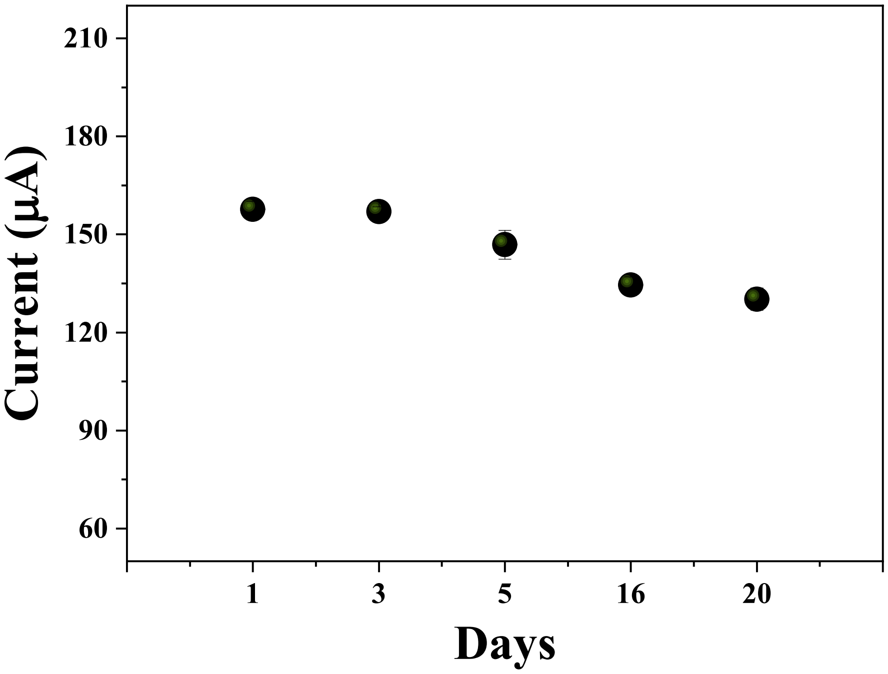

Figure S9. Current response of Z-1000/SFE in 0.1 mM UA after 20 days of storage in room temperature.

Table S1. Comparison of analytical performances of several electrochemical sensors for UA.

Sensor	Method	Linear range (M)	LOD (M)	Ref.
GO-ZnO/PGE	DPV	$1.00 \times 10^{-5} – 1.00 \times 10^{-4}$	4.76×10^{-6}	1
rGO-ZnO/GCE	DPV	$3.00 \times 10^{-6} – 3.30 \times 10^{-4}$	1.08×10^{-6}	2
PdNPs/rGO/GCE	DPV	$1.50 \times 10^{-5} – 4.20 \times 10^{-5}$	1.67×10^{-5}	3
NPGE	DPV	$6.50 \times 10^{-5} – 1.50 \times 10^{-3}$	9.00×10^{-6}	4
MWCNT-PEDOT	DPV	$1.00 \times 10^{-5} – 2.50 \times 10^{-4}$	1.00×10^{-5}	5
Z-1000/SFE	I-t	$1.00 \times 10^{-6} – 3.00 \times 10^{-4}$	4.2×10^{-7}	This work

References

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Table S2. Comparison of analytical results for UA by wearable sensor and HPLC in sweat samples.

Sample	Wearable sensor	HPLC	t_{exptl} (t_{crit}[0.05,4] = 2.78)
1	26.7 ± 0.47	27.4 ± 0.48	0.94
2	31.3 ± 0.89	30.8 ± 0.43	1.21
3	18.9 ± 0.67	18.4 ± 0.57	0.77

The t-test was performed to verify the correlation of test results between wearable electrochemical sensor (n_1, s_1, $\overline{x_1}$) and high-performance liquid chromatography (HPLC) method (n_2, s_2, $\overline{x_2}$). The combined standard deviation of two data sets was calculated according to the formula:

$$s = \sqrt{\frac{s_1^2(n_1 - 1) + s_2^2(n_2 - 1)}{(n_1 - 1) + (n_2 - 1)}}$$

then the t-value was calculated, and the formula was

$$t = \frac{|\overline{x_1} - \overline{x_2}|}{s}\sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

Table S3. Determination of UA in sweat samples for recovery using Z-1000/SFE.

Sample	**Added (μM)**	**Found (μM)**	**Recovery (%)**	**RSD (%)**
1	10	9.96 ± 0.410	99.6	2.70
2	15	15.2 ± 0.212	101	1.06
3	20	25.5 ± 0.444	102	1.02