Electronic Supplementary Material (ESI) for Materials Horizons. This journal is The Royal Society of Chemistry 2021

## **Supplementary Information**

## A flexible quasi-solid-state thermoelectrochemical cell with high stretchability as an energy-autonomous strain sensor

Lirong Liang,<sup>a</sup> Haicai Lv,<sup>b,</sup> Xiao-Lei Shi,<sup>c</sup> Zhuoxin Liu,<sup>\*b</sup> Guangming Chen,<sup>\*b</sup> Zhi-Gang

Chen,\*<sup>c</sup> and Guoxing Sun\*<sup>a</sup>

<sup>a</sup> Joint Key Laboratory of the Ministry of Education, Institute of Applied Physics and Materials Engineering, University of Macau, Avenida da Universidade, Taipa, SAR, Macau, China. E-mail: gxsun@um.edu.mo,

<sup>b</sup> College of Materials Science and Engineering, Shenzhen University, Shenzhen, 518055, China. Email: liuzhuoxin@szu.edu.cn, chengm@szu.edu.cn

<sup>c</sup> Centre for Future Materials, University of Southern Queensland, Springfield Central, Queensland, 4300, Australia. E-mail: zhigang.chen@usq.edu.au



**Supplementary Fig. S1.** The working principle for two heat-to-electricity conversion technologies. (a) Conventional TE materials. (b) Thermocells.<sup>[1]</sup> Copyright 2021, American Association for the Advancement of Science.

Conventional thermoelectrics, particularly semiconductor-based thermoelectrics can directly convert thermal energy into electricity via the electronic Seebeck effect (Fig. S1a), where the generated thermopower originate from the transport of electrons or holes. Its Seebeck coefficient is decided by the ratio of the open circuit potential ( $V_{oc}$ ) to the temperature difference ( $\Delta T$ ). However, these thermoelectrics show a relatively low Seebeck coefficient at room temperature and a limited output voltage that is in the order of microvolts per Kelvin, thereby hindering their effective harness of low-grade body heat.

Thermocells (TECs) can generate a large thermoelectrochemical Seebeck coefficient ( $S_e$ ) via thermogalvanic effect (Fig. S1b) resulting from the temperature-dependent electrochemical potentials of redox couples. Thus, the redox reactions are responsible for the generated thermopower, rather than the transport of electrons or holes as in conventional thermoelectrics. In a typical TEC, a redox couple-containing electrolyte is sandwiched between two electrodes that are exposed to different temperatures. The temperature dependence of redox potentials creates a potential difference across the cell, and the corresponding  $S_e$  can reach the order of millivolts per Kelvin.



**Supplementary Fig. S2.** Illustration showing the detailed preparation process of the PAAm/a-SWCNTs composite hydrogels.

First, a certain amount of a-SWCNTs were well-dispersed in SDBS solution, and then other reactants including AAm (monomer), MBA (cross-linking agent), KPS (initiator) were added to the dispersion. Subsequently, the solution was transferred into a self-made glass mold for polymerization at 50 °C for 8 h, and the flexible and uniform composite hydrogels were thus obtained. The composite hydrogels were further soaked with aqueous Sn<sup>4+</sup>/Sn<sup>2+</sup> electrolyte solutions of different concentrations for a certain time.



**Supplementary Fig. S3.** Statistical analysis of pore diameter distribution of a) pristine PAAm and b) 0.6 wt% hydrogels ( $x_c$  refers to average values,  $\omega$  refers to the standard deviation). FESEM images and pore diameters distribution of the untreated PAAm/a-SWCNTs composite hydrogels with the a-SWCNTs content of c) 0.3 wt% and d) 1.0 wt%, and their statistical analysis of pore diameters is shown

The diameter distributions of all the hydrogels are obtained by measuring at least 150 diverse sites and fitted by a Gaussian distribution in the histograms.<sup>[2-3]</sup> The resulting average values ( $x_c$ ) and standard deviations ( $\omega$ ) can be used to evaluate the statistical histograms.



Supplementary Fig. S4. Photos showing the appearance of various hydrogels after soaking in 0.05 M,

0.1 M and 0.2 M Sn<sup>4+</sup>/Sn<sup>2+</sup> aqueous electrolytes for 24 h.



**Supplementary Fig. S5.** The relative mass change of various hydrogels after soaking in 0.05 M, 0.1 M and 0.2 M Sn<sup>4+</sup>/Sn<sup>2+</sup> aqueous electrolytes for 24 h.



**Supplementary Fig. S6.** a) The electronic conductivities ( $\sigma$ ), the Seebeck coefficients (*S*), and b) the calculated power factors (*PF*) for the dried untreated PAAm/a-SWCNTs samples.



**Supplementary Fig. S7.** Nyquist plots of the a) untreated PAAm/a-SWCNTs hydrogels and b) Sn<sup>4+</sup>/Sn<sup>2+</sup>- treated PAAm/a-SWCNTs hydrogels. The amplified figures show the spectra in the high frequency range (yellow dotted box).



**Supplementary Fig. S8.** Photos showing the flexibility and stretchability of the 0.2 M Sn<sup>4+</sup>/Sn<sup>2+</sup>-treated a) the pristine PAAm hydrogel, b) 0.3%-PAAm/a-SWCNTs hydrogel, c) 0.6%-PAAm/a-SWCNTs hydrogel and d) 1.0%- PAAm/a-SWCNTs hydrogel.



**Supplementary Fig. S9.** a) Tensile stress-strain curves and b) the corresponding mechanical properties (breaking strain  $\varepsilon_b$ , breaking stress  $\sigma_b$  and Young's modulus *E*) for various untreated hydrogels.



**Supplementary Fig. S10.** The ionic conductivity variation as function of strain for the 0.2 M Sn<sup>4+</sup>/Sn<sup>2+</sup>-treated a) the pristine PAAm hydrogel, b) 0.3%-PAAm/a-SWCNTs hydrogel and c) 1.0%-PAAm/a-SWCNTs hydrogel.



**Supplementary Fig. S11.** EIS Spectra as a function of strain for the 0.2 M Sn<sup>4+</sup>/Sn<sup>2+</sup>-treated a) pristine PAAm hydrogel and b-d) PAAm/a-SWCNTs composite hydrogels.

The ionic conductivity is calculated according to the equation  $\sigma_i = L/(RA)$ . The slight decrease in resistance is attributed to the fact that sample thickness and width became thinner and smaller with the increase of stretching strain. Thus, the changed thickness and width of the sample were measured for deciding the ionic conductivity of the stretched samples.



**Supplementary Fig. S12.** Time-dependent electrical resistance variation of the 0.2 M Sn<sup>4+</sup>/Sn<sup>2+</sup>-treated 0.6 wt%-PAAm/a-SWCNTs composite hydrogel at high tensile strains (200–400%).



**Supplementary Fig. S13.** Time-dependent resistance variation of the a) 0.3%-PAAm/a-SWCNTs composite hydrogel and b) 1.0%-PAAm/a-SWCNTs composite hydrogel treated with 0.2 M Sn<sup>4+</sup>/Sn<sup>2+</sup> under various tensile strains.



**Supplementary Fig. S14.** a) The corresponding time-dependent resistance variation ( $\Delta R_i/R_{i0}$ ) of the 0.6%-PAAm/a-SWCNTs composite hydrogel treated with 0.2 M Sn<sup>4+</sup>/Sn<sup>2+</sup> as a self-powered strain sensor. b) Relative resistance change ( $\Delta R_i/R_{i0}$ ) of the self-powered strain sensor subject to strain, where  $R_{i0}$  is the resistance at zero strain.

As a self-powered strain sensor, the relative current and voltage changes ( $\Delta I/I_0$  and  $\Delta U/U_0$ ) are directly collected (Fig. 5c). The corresponding internal resistance variation ( $\Delta R_i/R_{i0}$ ) is derived from the above results, as shown in the following equations:

$$R_i = \frac{U_{open} - U}{I} = \frac{U_{open} - IR_L}{I} = \frac{U_{open}}{I} - R_L$$

Herein, the  $U_{open}$  is the the open-circuit voltage between the hot and cold side of the self-strain sensor, which can be expressed as,

$$U_{open} = S_e(T_H - T_C)$$

where  $T_H$  and  $T_C$  are the temperature of the self-strain sensor at the hot and cold end, respectively.



**Supplementary Fig. S15.** Measured current and voltage variation for the self-powered strain sensor based on the 0.6 wt%-PAAm/a-SWCNTs composite hydrogel treated with 0.2 M Sn<sup>4+</sup>/Sn<sup>2+</sup> for monitoring finger motions (the temperature difference is approximately 2K).

As shown in Fig. 5e, the thickness for the heat insulating layer is about 1mm. The length, width and thickness for the band-like shape samples are 30 mm, 6mm and  $1.5 \pm 0.2$  mm, respectively.

Table S1. Mechanical performance and the sensitivity comparison with recently reported hydrogel-

based strain sensors.

Materials	σь (KPa)	Eb	GF	Sensing range	Self- powered sensors	Ref.
HPAAm/CS/c-MWCNTs	65	2761%	1.65 (100%) 3.2 (100-500%)	200%	No	[45]
Gelatin/Na₃Cit/glycerol	2400	520%	1.5 (300%)	300%	No	[46]
MXene/PVA	5.4	1200%	0.4 (200%)	200%	No	[47]
CNT/PVA	12	800%	1.2 (200%)	200%	No	[48]
MXene/PVA	-	-	25 (40%)	40%	No	[49]
SWCNT/PVA	-	-	0.24 (200%) 1.51 (1000%)	1000%	No	[50]
PAM/CMC/NaCl	430	1100%	0.104 (300%) 0.214 (300- 800%)	800%	No	[51]
PVA/PVP+CNCs/Fe <sup>3+</sup>	2100	830%	0.48(200%)	200%	No	[52]
PAAm/a-SWCNTs + redox couple	42	600%	0.40-0.44 (40%) 0.61-0.67 (20- 100%)	100%	Yes	This work

Note: fracture strength  $\sigma_{b}$ , fracture strain  $\varepsilon_{b}$ , gauge factor GF.

## References

[1] X. Shi and J. He, Science 2021, **371**, 343-344.

[2] Y. Zhang, C. A. Fuentes, R. Koekoekx, C. Clasen, A. W. Van Vuure, J. De Coninck and D. Seveno, *Langmuir 2017*, **33**, 8447-8454.

[3] W. Deng, L. Deng, Z. Li, Y. Zhang and G. Chen, ACS Appl. Mater. Interfaces, 2021, **13**, 12131-12140.