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

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The design of effective energy systems is crucial for the development of flexible and wearable electronics. Regarding the direct conversion of heat into electricity, thermoelectrochemical cells (TECs) are particularly suitable for low-grade heat harvesting to enable flexible and wearable applications, despite the fact that the electrolyte leakage and complex packaging issues of conventional liquid-based TECs await to be further addressed. Herein, a quasi-solid-state TEC is assembled using the polyacrylamide/acidified-single-walled carbon nanotube (PAAm/a-SWCNT) composite hydrogel, developed via a facile in situ free-radical polymerization route with tin(IV) chloride/tin(II) chloride (Sn4+/Sn2+) as the redox couple. The as-fabricated TEC with a 0.6 wt% a-SWCNT content presents a large thermoelectrochemical Seebeck coefficient of 1.59 ± 0.07 mV K⁻¹ and exhibits excellent stability in thermoelectrochemical performance against large mechanical stretching and deformation. Owing to this superior stretchability, the as-fabricated TEC is further assembled into an energy-autonomous strain sensor, which shows high sensitivity. The strategy of utilizing a quasi-solid-state TEC for energy-autonomous strain sensing unveils the great potential of heat-to-electricity conversion in flexible and wearable electronics.

Introduction

Given the rapid development of flexible and wearable electronics, there is an urgent need of self-powered energy supply for energy-autonomous devices. 1–3 Various energy harvesting techniques, including photovoltaics, piezoelectrics and triboelectrics, have been developed to utilize solar energy and mechanical energy from both the environment and human body movements. 4–6 Thermal energy, as another form of sustainable power source, is also widely available and holds great potential for energy harvesting and regeneration. Particularly, the human body consistently provides a surface temperature of around 35 °C for a lifetime, and hence gives thermal energy of around 100 watts to the surroundings. 7 The temperature difference between the human body and the environment may be more than ten degrees that give rise to considerable driving force for energy utilization, i.e., the operating of thermoelectric materials, thus offering a promising solution of energy supply for self-powered wearable electronics. Conventional thermoelectrics,

New concepts

The relatively low thermopower of organic thermoelectric polymers and their composites urges us to seek for techniques with higher heat-to-electricity conversion capability. Although large Seebeck coefficients originating from the Soret effect have been identified in ionic conductors, the ions cannot pass through external circuits, and the generated potential will eventually vanish. By contrast, thermoelectrochemical cells (TECs), or thermocells, can generate large and consistent thermopower via the thermogalvanic effect, which results from the temperature-dependent electrochemical potentials of redox couples, thus exhibiting large thermoelectrochemical Seebeck coefficients (Se) on the scale of millivolts per Kelvin. Current TECs still require systematic in-depth investigations to expand their applications in self-powered electronics. Herein, we developed a quasi-solid-state TEC with a large Se of 1.59 ± 0.07 mV K⁻¹ based on a polymer/carbon nanotube composite hydrogel with tin(IV) chloride/tin(II) chloride as the redox couple. The TEC exhibited high stability in thermoelectrochemical performance against large mechanical stretching and deformation. Combining the excellent heat-to-electricity conversion capability with the designed strain sensitivity, an energy-autonomous strain sensor for wearable applications was further proposed. The present study offers a practical approach to utilize quasi-solid-state TECs in flexible and stable self-powered wearable electronics.
particularly semiconductor-based thermoelectrics can directly convert thermal energy into electricity via the electronic Seebeck effect, which is based on the transport of electrons or holes, and they have shown successful applications in niche markets. However, these thermoelectrics show a relatively low Seebeck coefficient at room temperature and a limited output voltage in the order of microvolts per Kelvin, thereby hindering the effective harnessing of low-grade body heat.8 Besides, the fragility and high cost as well as the complex fabrication process of semiconductor-based thermoelectrics act as further obstacles in flexible and wearable applications.9,10 Alternatively, thermoelectrochemical cells (TECs) or thermocells are receiving increasing attention due to their capability of harvesting electricity from low-grade waste heat. TECs can generate a large thermoelectrochemical Seebeck coefficient ($S_e$) via the thermogalvanic effect resulting from the temperature-dependent electrochemical potentials of redox couples.11–13 Thus, giant thermopower can be generated via redox reactions 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. Recent studies of TECs have been focused on the exploration of high-surface-area carbon-based electrodes for higher power density, high $S_e$ redox couples with regulation strategies, and the employment of ionic liquid electrolytes for higher operating temperatures.14–18 However, the commonly-adopted liquid electrolytes in TECs impose a higher requirement on the integration and packaging of cells, thereby complicating the design and application of wearable devices. Replacing liquid electrolytes with gel electrolytes may circumvent these difficulties as gel electrolytes can be arbitrarily shaped, and can intrinsically address the liquid leakage. The solidification of gel electrolytes is also advantageous in building up an effective temperature gradient for more efficient energy harvesting, as convection is substantially weakened in solid-state gel electrolytes compared to their liquid counterparts. Although it has also been demonstrated that a separator maintains the temperature gradient in liquid-based TECs, it did not essentially eliminate liquid leakage.19 Therefore, developing quasi-solid-state TECs based on gel electrolytes is highly attractive to promote the design of power supply for energy-autonomous wearable electronics.

Hydrogels consisting of solid polymer framework and confined liquid electrolytes exhibit unique properties including high mechanical flexibility/stretchability and fast ion transport,20,21 enabling them as promising solid-state gel electrolytes for TECs. Incorporating temperature-dependent redox-active couples within hydrogels could afford TEC electrolytes with both high thermoelectrochemical performance and mechanical flexibility/stretchability.22–26 For instance, a wearable TEC was developed by incorporating aqueous ferric/ferrous chloride (FeCl$_3$/FeCl$_2$, p-type) and potassium ferri/ferrocyanide (Fe(CN)$_6^{3−}$/4−, n-type) into a polyvinyl alcohol hydrogel matrix, and the $S_e$ values of the p- and n-type hydrogel electrolytes were 1.02 and −1.21 mV K$^{-1}$, respectively.22 Alternatively, several polymer or composite matrices and ion redox couples have been developed in TECs.24–26 Very recently, we have realized the p-n conversion of iodination/triiodide (I$^−$/I$_3^−$) redox couples with an enhanced $S_e$ of $\sim$1.9 mV K$^{-1}$, and a wearable TEC device comprising alternating I$^−$/I$_3^−$ and I$^−$/I$_3^−$/PNIPAM nanogels connected in series yields an open-circuit voltage of $\sim$1 V.24 Despite these progress, hydrogel-based TECs have seldom been thoroughly studied in terms of their mechanical strength and stretchability; both are important features for wearable applications. Besides, their stability in thermochemical performance against external mechanical stress for flexible applications has not been investigated. Moreover, considering the desired mechanical properties of hydrogels and the impressive Seebeck coefficient of the thermogalvanic effect, hydrogel-based TECs seem to suit perfectly for energy-autonomous wearable strain sensing systems, while such potential is yet to be discovered.

In this work, a quasi-solid-state TEC based on composite hydrogel was facilely fabricated by using in situ free-radical polymerization of polycrylamide (PAAm) in the presence of acidified-single-walled carbon nanotubes (a-SWCNTs), followed by the incorporation of the Sn$^{4+}$/Sn$^{2+}$ redox couple via ion exchange. The a-SWCNTs were found to be beneficial to both the mechanical and thermochemical properties of the composite hydrogel. The resultant hydrogel-based TEC exhibited high flexibility and stretchability, and an excellent $S_e$ of 1.59 ± 0.07 mV K$^{-1}$ at the Sn$^{4+}$/Sn$^{2+}$ concentration of 0.2 M and a-a-SWCNT content of 0.6 wt%. When being stretched within 100% strain, it displayed a relatively constant ion conductivity and Seebeck coefficient, demonstrating its excellent thermo-electrochemical stability against large mechanical stretching and deformation. Moreover, owing to the high stretchability inherited from the PAAm hydrogel matrix and the moderate electrical conductivity brought by the a-SWCNT filler, the quasi-solid-state TEC reported here presents considerable sensitivity to strain induced by human body movements. Combining the excellent heat-to-electricity energy conversion feature based on the thermogalvanic effect with the designed strain sensing capability, a self-powered strain sensing system based on the flexible quasi-solid-state TEC was thus developed and demonstrated. The utilizing of a composite hydrogel to enable flexible and stretchable quasi-solid-state TEC for energy-autonomous wearable applications is presented in this work for the first time, and provides a feasible strategy for the development of energy supply systems for wearable electronics with low but reliable energy demand.

Results and discussion

Preparation and structure of the composite hydrogel-based TECs

A composite hydrogel electrolyte, consisting of PAAm and a-SWCNTs, was fabricated by using a convenient route via in situ free-radical polymerization followed by ion exchange in a Sn$^{4+}$/Sn$^{2+}$ redox couple-containing aqueous solution. Fig. 1a and b illustrate the network structure of the composite hydrogel, the interplay between the PAAm chains and a-SWCNTs, and...
the heat-to-electricity mechanism of the thermogalvanic effect via the Sn$^{4+}$/Sn$^{2+}$ redox reactions. The differences in working mechanisms between TECs and conventional TE materials are further discussed in Fig. S1 (ESI†), and more details of the preparation process of the hydrogel electrolyte are presented in Fig. S2 (ESI†). A self-made glass mold was employed to control the thickness and surficial smoothness of the composite hydrogel, and its shape can be further tailored to meet any dimensional need. The good dispersion of a-SWCNTs in the PAAm matrix can be guaranteed at a certain weight percentage, attributed to the non-covalent interactions between the PAAm molecular chains and a-SWCNTs. These non-covalent interactions include molecular electrostatic interactions and/or hydrogen bonding between the oxygen-containing groups from the a-SWCNTs and the amino groups from the PAAm chains. The thermogalvanic effect causes a difference in the electrochemical potential of the Sn$^{4+}$/Sn$^{2+}$ redox couple when a temperature difference is imposed on the two electrodes, yielding a temperature-dependent voltage that is characterized by the electrochemical Seebeck coefficient $S_e$. At the cathode (cold end), oxidation occurs, and electrons are transferred from electrolyte to electrode as a result of the reaction Sn$^{2+} + 2e^{-} \rightarrow$ Sn$^{4+}$; at the anode (hot end), reduction occurs and electrons are transferred from electrode to electrolyte as a result of the reaction Sn$^{4+} + 2e^{-} \rightarrow$ Sn$^{2+}$. During the entire temperature-induced electrochemical process, ions transport throughout the hydrogel electrolyte and electrons pass through the external circuit. The built-up concentration gradient of the redox couple drives a flux that returns the reduced ions to the cathode and the oxidized ions to the anode. A steady current could thus be provided if the temperature difference is maintained between the electrodes. These features reveal that TECs significantly differ from traditional solid thermoelectric materials, while they share similar advantages over other energy techniques including high reliability, easy maintenance, no moving parts, no gas emission, and no noise.

The morphology of the composite hydrogel was characterized by field-emission scanning electron microscopy (FESEM). Fig. 1c and d display the microstructures of the cross-sectional areas of freeze-dried PAAM hydrogel samples

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Fig. 1  Schematic illustration showing the (a) PAAm network (blue lines) and a-SWCNT network (black lines) within the composite hydrogel and (b) the quasi-solid-state composite hydrogel-based TEC utilizing Sn$^{4+}$/Sn$^{2+}$ temperature-dependent redox reactions. FESEM images of the untreated (c) pristine PAAm hydrogel and (d) 0.6%-PAAm/a-SWCNT composite hydrogel. (e) FTIR spectra and (f) Raman spectra of the pristine PAAm hydrogel and various PAAm/a-SWCNT composite hydrogels.
with and without a-SWCNTs prior to the incorporation of the redox couple. Under lower magnification, both samples exhibit an interconnected reticular porous structure, suggesting good ion transport when serving as the electrolyte. With increasing a-SWCNT content, the average pore size gradually decreases from 5.45 μm to 1.66 μm derived from the Gaussian distribution in the statistical histograms (Fig. S3, ESI†), possibly due to the enhanced interactions between a-SWCNTs and PAAm chains during polymerization. Notably, as indicated in the high magnification images shown in Fig. 1c and d, unique secondary surficial nanostructures can be observed on the microporous surface of the 0.6 wt% PAAm/a-SWCNT composite hydrogel, which is absent in the pristine PAAm hydrogel. This phenomenon was also confirmed in the composite hydrogels with other different a-SWCNT contents (Fig. S3, ESI†). It is thus assumed that a-SWCNTs serve as cross-linking sites or templates for the polymerization of PAAm, where acrylamide monomers tend to gather around a-SWCNTs upon molecular chain growth, resulting in a moderately decreased pore size and nanostructured pore surface of composite hydrogels. FTIR and Raman spectroscopies were employed to confirm the molecular structure of both the pristine PAAm and the PAAm/a-SWCNT composite hydrogels (Fig. 1e and f). The characteristic FTIR bands of the composite hydrogels are basically the same as those of the pristine hydrogel. The bands at 3330 cm⁻¹ and 3178 cm⁻¹ result from the symmetrical stretching modes of –NH₂ groups and the antisymmetric stretching vibration of the two –N–H bonds, respectively, and the bands at 1644 cm⁻¹ and 1591 cm⁻¹ belong to the amide I and II bonds, respectively. As for Raman spectra, the strong bands of a-SWCNTs dominate the spectra for all composite hydrogels. A typical band at 1589 cm⁻¹ (G band) is related to the vibration of sp² carbon in the 2D hexagonal lattices, and the bands at 1330 cm⁻¹ and 2640 cm⁻¹ should be attributed to the disordered or defect structures of composite hydrogels. The Seebeck coefficient $S_e$ of (a) the pristine PAAm, (b) 0.3 wt%-PAAm/a-SWCNTs, (c) 0.6 wt%-PAAm/a-SWCNTs and (d) 1.0 wt%-PAAm/a-SWCNT hydrogels as a function of Sn⁴⁺/Sn²⁺ treatment time at different Sn⁴⁺/Sn²⁺ concentrations (0.05 M, 0.1 M and 0.2 M). (e) Comparison of the $S_e$ of various samples. (f) Illustration showing the induced solvation structure of redox ions at the electrode surface that accounts for the higher $S_e$ of the 0.6 wt%-PAAm/a-SWCNT sample. (g) Ionic conductivity of the untreated and 0.2 M Sn⁴⁺/Sn²⁺-treated hydrogels as a function of a-SWCNT content. (h) Ionic conductivity and the $S_e$ of the 0.2 M Sn⁴⁺/Sn²⁺-treated hydrogels as a function of a-SWCNT content. (i) The power factor calculated for the 0.2 M Sn⁴⁺/Sn²⁺-treated hydrogels as a function of a-SWCNT content.
a-SWCNTs (D band and D’ band).\textsuperscript{31,32} FTIR and Raman spectra together with SEM images verified the presence of both PAAm and a-SWCNTs and the homogeneous microstructure of the composite hydrogels.

**Thermoelectrochemical performance**

The introduction of the Sn\textsuperscript{4+}/Sn\textsuperscript{2+} redox couple was implemented to endow the composite hydrogel with the heat-to-electricity conversion capability via the thermogalvanic effect, resulting in a quasi-solid-state TEC. Fig. S4 and S5 (ESI\textsuperscript{†}) illustrate the macroscopical appearance change and the relative mass change of all hydrogel samples after being immersing into various solutions containing different Sn\textsuperscript{4+}/Sn\textsuperscript{2+} concentrations. As can be seen, the lower the Sn\textsuperscript{4+}/Sn\textsuperscript{2+} concentration, the more obvious the swelling of hydrogel samples. This agrees well with the reduced relative mass change upon the increase of the Sn\textsuperscript{4+}/Sn\textsuperscript{2+} concentration. The reduced degree of swelling should be because the higher Sn\textsuperscript{4+}/Sn\textsuperscript{2+} concentration obviates the necessity of absorbing extra solution to decrease hydrogel internal charges.\textsuperscript{33} Fig. 2a–e demonstrate the $S_e$ of various TECs as a function of soaking time in aqueous solutions with different Sn\textsuperscript{4+}/Sn\textsuperscript{2+} concentrations (0.05 M, 0.1 M and 0.2 M). Obviously, all TECs exhibit notably increased $S_e$ with the elongation of soaking time in the initial several hours before reaching a plateau at the soaking time of around 8 h. The $S_e$ also increases with the increase of Sn\textsuperscript{4+}/Sn\textsuperscript{2+} concentration at a given treatment time. Thus, the thermopower is highly dependent on redox ion concentration and noticeably increases with the increase of the latter. Thermodynamically, the temperature-dependent thermovoltage of TECs is mainly decided by $\Delta S$ (the reaction entropy for the redox reaction): $S_e = \frac{\Delta V}{\Delta T} = \frac{\Delta S}{nF}$, where $n$ is the number of transferred electrons involved in the redox reaction and $F$ is Faraday’s constant.\textsuperscript{13,34} In an aqueous environment, the reaction entropy change stems, at least partially, from the solvation shell around the redox ions. Upon decreasing the redox couple concentration, more solvent molecules are ready to “solute” the redox ions, resulting in the change of solvation environment.\textsuperscript{8} It is believed that this solvent reorientation increases when higher concentrations of redox couples are present, which is possibly attributed to a subtle balance of self-reorientation dynamics versus solute-imposed reorientation.\textsuperscript{35} Therefore, in this case, $S_e$ increases with Sn\textsuperscript{4+}/Sn\textsuperscript{2+} concentration. It is also interesting to note that the $S_e$ of the as-prepared hydrogel-based TEC is positive, suggesting the high potential to assemble p-n connections for higher energy output considering the negative $S_e$ of the widely-investigated ferro/ferricyanide redox couple.\textsuperscript{27} The measured $S_e$ values for pristine PAAm and PAAm/a-SWCNT composite hydrogels containing 0.2 M Sn\textsuperscript{4+}/Sn\textsuperscript{2+} with the a-SWCNT contents of 0.3 wt%, 0.6 wt% and 1.0 wt% were about 1.50 ± 0.06, 1.53 ± 0.07, 1.59 ± 0.07 and 1.55 ± 0.05 mV K\textsuperscript{-1}, respectively. As revealed, the composite hydrogel with 0.6 wt% a-SWCNTs exhibited noticeably a higher thermovoltage, while the intrinsic electronic Seebeck coefficient contributed by a-SWCNTs is rather small (Fig. S6a, ESI\textsuperscript{†}), indicating that the influence of the electronic Seebeck effect brought by a-SWCNTs could not account for the increase in the overall Seebeck coefficient for the 0.6%-PAAm/a-SWCNT sample or the subsequent drop for the 1.0%-PAAm/a-SWCNT sample. The enhanced thermoelectrochemical performance upon the addition of 0.6 wt% a-SWCNTs is presumably due to the optimized interactions between the redox ions and the dissociated surficial groups on a-SWCNTs, which alters the solvation environment and thereby results in increased $\Delta S$.\textsuperscript{14} Fig. 2f illustrates this enhancement effect, in which a solvation structure change was induced via the optimized interactions between the redox Sn\textsuperscript{4+}/Sn\textsuperscript{2+} ions and the added a-SWCNTs.

The introduction of Sn\textsuperscript{4+}/Sn\textsuperscript{2+} ions also play an important role in regulating the ionic conductivity of these TECs. Electrochemical impedance spectroscopy (EIS) was employed to measure the ionic conductivity, and the corresponding EIS spectra are presented in Fig. S7 (ESI\textsuperscript{†}). Specifically, the EIS measurement was carried out on both the untreated hydrogel samples and the samples treated with 0.2 M Sn\textsuperscript{4+}/Sn\textsuperscript{2+} redox couple, and the calculated results (Fig. 2g) indicate that with the increase in a-SWCNT content, the ionic conductivity of all hydrogels increases notably and peaks at the a-SWCNT content of 0.6 wt%, and then falls when the content further increases to 1.0 wt%. At the optimum a-SWCNT content of 0.6 wt%, the incorporation of Sn\textsuperscript{4+}/Sn\textsuperscript{2+} significantly boosts the ionic conductivity to 13.47 ± 0.68 S m\textsuperscript{-1} compared to the value of 0.76 ± 0.02 S m\textsuperscript{-1} for the untreated hydrogel. This phenomenon should be attributed to the following two aspects: the fast transport dynamics of the redox ions within the porous structure of the hydrogel body, and the further improved transport capability in the presence of well-dispersed a-SWCNTs. The former can be directly evidenced by the abundant ion transport channels that can be observed in the FESEM images of Fig. 1, and the latter may originate from the surficial charges of the a-SWCNTs and the formation of extra water channels that assisted ion diffusion,\textsuperscript{36–38} which has also been discovered in energy storage systems.\textsuperscript{39,40} Thus, the presence and good dispersion of 0.6 wt% a-SWCNTs within the PAAm hydrogels make them an effective additive, which synergistically improves the ionic conductivity and the Seebeck coefficient, and in turn, optimizes the overall electrochemical performance of the resultant TEC. Fig. 2h gives the ionic conductivity and $S_e$ results of the 0.2 M Sn\textsuperscript{4+}/Sn\textsuperscript{2+}-treated hydrogels with different a-SWCNT contents. At the a-SWCNT content of 0.6 wt%, the ionic conductivity and $S_e$ reach 13.47 ± 0.68 S m\textsuperscript{-1} and 1.59 ± 0.07 mV K\textsuperscript{-1}, respectively, leading to a maximum power factor of 33.98 ± 3.81 $\mu$W m\textsuperscript{-1} K\textsuperscript{-2} (Fig. 2i). Therefore, we demonstrate that a certain amount of a-SWCNTs added to the electrolyte to interact with the redox couple is beneficial to the electrochemical performance and the heat-to-electricity conversion efficiency. Moreover, the contribution of sole a-SWCNTs to the power factor of the composite hydrogel-based TEC is also explored. As shown in Fig. S6b (ESI\textsuperscript{†}), the dried samples show an extremely low power factor in the order of 10\textsuperscript{-3} $\mu$W m\textsuperscript{-1} K\textsuperscript{-2} regardless of the a-SWCNT content, indicating that the excellent electrochemical performance of the as-prepared TEC basically originates from the thermogalvanic effect brought by
the Sn$^{4+}$/Sn$^{2+}$ redox couple, rather than the negligible electronic Seebeck effect originating from the a-SWCNTs.

Besides the thermo-electrochemical performance enhancement induced by the addition of a-SWCNTs, the mechanical properties of the resultant TECs can also be benefited. Fig. S8 (ESI†) shows the high stretchability of the as-prepared hydrogels treated with 0.2 M Sn$^{4+}$/Sn$^{2+}$, indicating that both the pristine PAAm and the PAAm/a-SWCNT composite hydrogels are flexible enough to withstand large deformations. The typical stress–strain curves and the mechanical properties of various samples are shown in Fig. 3a and b. All the hydrogels could be easily stretched up to 500–600%. Noticeably the introduction of a-SWCNTs not only substantially improves the mechanical strength of the PAAm hydrogel, but also slightly increases the elongation. The breaking strength, elongation at break and tensile modulus all reach the maxima at the a-SWCNT content of 0.6 wt% ($\sigma_b = 42.07 \pm 5.25$ KPa, $\epsilon_b = 600.83 \pm 53.78\%$, and $E = 6.97 \pm 0.55$ KPa). The superior mechanical stretchability of these hydrogels mainly stems from the covalent-crosslinking of the PAAm molecular chains, the non-covalent interactions between the amino groups of PAAm and the oxygen-containing groups of a-SWCNTs, as well as the potential hydrophobic associations within the hydrogel body.41 It was also noticed that further increasing the a-SWCNT content (1.0 wt%) may lead to possible agglomeration and hence impeded the breaking strength and mechanical stretchability.25,31,42 Similarly, for hydrogels without Sn$^{4+}$/Sn$^{2+}$ treatment, the same trend in mechanical properties can be observed (Fig. S9, ESI†). These untreated hydrogels possess even higher stretchability that exceeds 1200%. The reduced stretchability of the treated hydrogels compared to that of the untreated ones should be ascribed to the enhanced osmotic pressure and more intensive electrostatic repulsion within the porous structure as a result of the incorporation of the Sn$^{4+}$/Sn$^{2+}$ ions. Considering the intrinsic excellent flexibility and stretchability of the quasi-solid-state composite hydrogel-based TECs, it is also critical to evaluate the thermo-electrochemical performance under different strains. Fig. 3c and Fig. S10 (ESI†) reveal that the ionic conductivity of all the TECs changed very little when the tensile strain was controlled within 100%. The corresponding measured EIS spectra are presented in Fig. S11 (ESI†). The relatively constant ionic conductivity indicates that the as-fabricated quasi-solid-state TECs can operate stably under large mechanical stretching or deformation. Fig. 3d further plots the $S_e$ fluctuation ($S_e/S_{e0}$) of the 0.6 wt%-PAAm/a-SWCNT TEC as a function of tensile strain at a constant temperature gradient.
of 5 K. The change of \( S_e/S_{e0} \) is also small within the 100% strain, implying that the temperature-dependent redox reaction can be maintained during the stretching–releasing cycle. These results demonstrate the impressive stability of the quasi-solid-state TEC under severe external mechanical stress, suggesting its high potential in wearable applications.

**Externally powered strain sensor**

The highly stretchable and conductive (both ionically and electronically) TECs are particularly suitable for wearable strain sensors. Specifically, the incorporation of the a-SWCNTs endows the hydrogels with a moderate electrical conductivity that leads to electrical resistance highly sensitive to strain. The strain sensitivity of the TECs can be evaluated by the gauge factor (GF) and sensing range. To monitor various subtle or large body movements, sensors with high GF and wide sensing range are desirable.\(^{41,43}\) The GF is typically decided by the resistance change caused by strain, \( i.e., GF = \frac{AR}{R_0}/\varepsilon \), where \( R_0 \) and \( R \) are the original resistance and the resistance at the applied strain of \( \varepsilon \), respectively. Fig. 4a shows that the resistance changes of all TECs increased monotonically with the applied strain up to 100%, and a higher a-SWCNT content led to smaller resistance change, suggesting lower sensitivity to strain. Considering the optimum thermo-electrochemical performance of the composite hydrogel with 0.6 wt% a-SWCNTs, the sensing capability of the 0.6 wt%-PAAm/a-SWCNT TEC is particularly investigated. Through the fitting lines drawn in Fig. 4a, the GF values of the 0.6%-PAAm/a-SWCNT composite hydrogel were deduced to be 0.44 and 0.67, corresponding to the strain ranges of 0–20% and 20–100%, respectively. The calculated GF values for another PAAm/a-SWCNTs TEC are given in Fig. 4b. It was noted that both GF\(_1\) and GF\(_2\) values decreased with the increase in a-SWCNT content. The GF value change in the two linear regions may be ascribed to the tunnelling effect and the contact-resistance effect.\(^{43,44}\) That is, when a small strain is induced, a relatively stable conductive network can still be maintained via a-SWCNTs, although the tunnel resistance and contact resistance among a-SWCNTs are accordingly increased. However, as the strain grew larger, the a-SWCNTs became more disordered or even disconnected, thus seriously impeding the conductive pathways and resulting in a sharp increase in electrical resistance. In this study, the applied tensile strain was controlled within 100% in consideration of the thermo-electrochemical stability, as the resistance increased dramatically when the strain exceeded 100% (Fig. S12, ESI\(^\dagger\)) and an effective temperature gradient is difficult to maintain at large strains. As shown in Fig. 4c, the 0.6 wt%-PAAm/a-SWCNT TECs exhibited stable and repeatable output signals during the five successive stretching–releasing cycles with the strain being varied from 20% to 100%, revealing high and reversible strain-sensing capability. With the increase in a-SWCNT content, the compactness and stability of the conductive network formed in the composite hydrogels were further enhanced, resulting in the reduction of strain sensitivity (Fig. S13, ESI\(^\dagger\)). Owing to their excellent stretchability, high strain sensitivity and stable thermo-electrochemical performance, the quasi-solid-state composite hydrogel-based TECs were thus employed as wearable sensors to monitor human motions. As shown in the insets of

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Fig. 4  (a) Relative resistance change \( \Delta R/R_0 \) of various composite hydrogels subjected to strain, where \( R_0 \) is the resistance at zero strain. (b) Gauge factors obtained from the fitting line of \( \Delta R/R_0 \) vs. applied strain for the 0.2 M Sn\(^{4+}/\)Sn\(^{2+}\)-treated hydrogels with different a-SWCNT contents. (c) Time-dependent electrical conductivity variation of the 0.6 wt%-PAAm/a-SWCNT composite hydrogel treated with 0.2 M Sn\(^{4+}/\)Sn\(^{2+}\) under various tensile strains. (d–f) Real-time \( \Delta R/R_0 \) response of the 0.6 wt%-PAAm/a-SWCNT composite hydrogel treated with 0.2 M Sn\(^{4+}/\)Sn\(^{2+}\) for monitoring human finger, wrist, and elbow movements.
Fig. 4d–f, the 0.6 wt%-PAAm/a-SWCNT composite hydrogels were directly attached to the finger, wrist, and elbow of human body, connected, and fixed with wires and adhesive tape. When the bending angle of the finger increased to 45° and 90°, the composite hydrogel was accordingly stretched, resulting in an increase in resistance. This is consistent with the results shown in Fig. 4c. During the detection of wrist bending, the composite hydrogels are repeatedly bent and recovered, thus forming stable and repeatable electrical signals in resistance with a change in strain. Similarly, when the elbow produced different bending angles, the corresponding strain-dependent signals were generated in the composite hydrogel. These results indicate that the as-prepared composite hydrogels are particularly suitable as wearable strain sensors for human motion sensing.

Self-powered strain sensor

Given the high thermoelectrochemical performance and the desired strain-sensing capability, the as-prepared TEC based on the 0.6%-PAAm/a-SWCNT composite hydrogel can be readily used as a self-powered sensor for strain detection, where strain-dependent electrical signals can be generated from the thermogalvanic effect of the TEC itself. As shown in Fig. 5a, the two ends of the TEC were fixed on a tensile tester with a temperature difference applied between the two ends, and then connected in series with a load resistor (R_L) whose resistance equalled the internal resistance (R_i) of the TEC at zero strain. Ammeter and voltmeter were used to respectively monitor the current in the circuit and the voltage generated on the load in real-time (Fig. 5b). When the tensile strain ranged from 0% to 100% at the fixed temperature difference of 5 K, the real-time
current change ($\Delta I/I_0$) and voltage change ($\Delta U/U_0$) were recorded, as shown in Fig. 5c. As previously confirmed, the thermovoltage generated at a given temperature difference is essentially stable within a controlled strain range (as shown in Fig. 3d). Meanwhile, the internal resistance of the TEC increases with increasing applied strain (Fig. 4c), thus causing the drop in both the loop current and the voltage generated on the load resistor. As the applied strain increases from 20% to 100%, the corresponding current and voltage vary from $-3.7\%$ to $-22.5\%$. These electrical signal changes ($\Delta I/I_0$ and $\Delta U/U_0$) are highly repeatable, confirming the excellent sensitivity of the designed self-powered strain sensor. Moreover, the corresponding internal resistance variations ($\Delta R/R_{in}$) were derived based on the values of $\Delta I/I_0$ and $\Delta U/U_0$ (Fig. S14a, ESI†), which are consistent with the results of the above-mentioned external heat source-powered measurements (Fig. 4c). Fig. S14b (ESI†) shows the corresponding resistance changes of the self-powered strain sensor within 100% strain. The calculated GF can reach 0.4 below the strain of 20% and 0.61 at a strain in the range of 20–100%. It should also be noted that both GF1 and GF2 values are consistent with the sensitivity data of externally-powered sensors (Fig. 4c).

The successful application of the quasi-solid-state TEC for energy-autonomous strain sensing depicts the vision of enabling self-powered wearable electronics via effective heat-to-electricity conversion under a small temperature difference, where irregular-shaped skin surface is utilized as the heat source, as illustrated in Fig. 5d. Given the above consideration, the gel-state TEC was further rationally designed to in situ monitor human motions of finger bending, as shown in Fig. 5e. It exhibited stable and repeatable output electrical signals ($\Delta I/I_0$, $\Delta U/U_0$) and the derived $R_{in}/R_{in}$ during finger bending and releasing (Fig. 5f and Fig. S15, ESI†), which is consistent with the results of externally-heated self-powered strain sensor (Fig. 5c and Fig. S14, ESI†), indicating that the gel-state TEC possesses great potential as a wearable self-powered strain sensor. Table S1 (ESI†) presents a comparison of the mechanical properties and sensitivity of our TEC-based self-powered sensor with those of the recently reported hydrogel strain sensors. It should also be noted that a higher output energy/power can be achieved for higher energy-demanding application scenarios provided the p-type TECs are electrically connected in series with the n-type ones.

**Conclusions**

In this study, a quasi-solid-state TEC based on the PAAm/a-SWCNT composite hydrogel was developed via a facile in situ free-radical polymerization approach, followed by ion exchange with the Sn$^{4+}$/Sn$^{2+}$ redox couple-containing aqueous electrolyte. The as-prepared TEC exhibits high stretchability and stability in thermoelectrochemical performance, allowing its successful application as an energy-autonomous strain sensor for human motion detection. The concentration of the Sn$^{4+}$/Sn$^{2+}$ redox ions significantly influences the thermoelectrochemical Seebeck coefficient $S_c$ of the TEC, and the addition of a-SWCNTs further enhances its $S_c$ and ionic conductivity by regulating redox reaction entropy and ion transport dynamics. At the a-SWCNT content of 0.6 wt%, the $S_c$ and conductivity were $1.59 \pm 0.07$ mV K$^{-1}$ and $13.47 \pm 0.68$ S m$^{-1}$, respectively, leading to an optimum power factor of $33.98 \pm 3.81$ $\mu$W m$^{-1}$ K$^{-2}$. The presence of a-SWCNTs also contributed to the mechanical properties of the composite hydrogel and enabled its high sensitivity to strain. Combining the desired thermoelectrochemical performance and strain sensing capability, a self-powered TEC was subsequently designed for the first time to detect various human motions in real-time with high sensitivity. The strategy of developing a quasi-solid-state TEC for energy-autonomous strain sensors presented in this study envisions the high potential of the thermogalvanic effect-based heat-to-electricity conversion technique in wearable applications.

**Experimental section**

### Materials

SWCNTs (purity $\geq 85$ wt%, a diameter of 1–3 nm) were purchased from Shenzhen Nanotech Port Co. Ltd, China. Sodium dodecyl benzene sulfonate (SDBS), acrylamide (AAm, 99%), $N',N$-methylene diacrylamide (MBA), tin(II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), and tin(IV) chloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) were purchased from Shanghai Aladdin Reagent Chemistry Co., Ltd. Nitric acid ($\text{HNO}_3$, A.R., 65%) and sulfuric acid ($\text{H}_2\text{SO}_4$, A.R., 98%) were purchased from Shenzhen Chemical Works. Potassium persulfate (KPS) was provided by Shanghai Macklin Biochemical Technology Co., Ltd. All the chemicals were used as received without any purification or treatment. Deionized water was used in all the experiments.

### Preparation of TECs

The preparation procedure is schematically shown in Fig. S2 (ESI†). First, acidized carbon nanotubes (a-SWCNTs) were prepared via refluxing in a mixed acid solution (40 mL 98 wt% H$_2$SO$_4$ + 120 mL 65 wt% HNO$_3$) at 90 °C for 4 hours. Then, a certain amount of a-SWCNTs was dispersed in SDBS solution (1.5 mg mL$^{-1}$) under ultrasonication for 40 min. After this, AAm monomers were added into the above dispersion and stirred for 2 h, followed by the addition of a certain amount of MBA and KPS. The resultant precursor solution was poured into a glass mold and the quasi-solid-state hydrogels were obtained after polymerizing at 50 °C for 8 h. The a-SWCNT weight contents were relative to the weight content of AAm, which varied from 0.3 wt% to 1 wt%. Thus, for the preparation of the 0.6 wt% PAAm/a-SWCNT composite hydrogel, the content of each component is: 20 mL distilled water, 2 g AAm, 12 mg a-SWCNTs, 30 mg SDBS, 12 mg KPS and 2 mg MBA. The quasi-solid-state TECs were further obtained via ion exchange with aqueous Sn$^{4+}$/Sn$^{2+}$ electrolyte solutions of various concentrations at different immersing times. For comparison, pristine PAAM hydrogel was prepared under the same conditions in the absence of a-SWCNTs.
Morphology observations
The morphologies of the pristine PAAm hydrogel and the PAAm/a-SWCNT composite hydrogels were observed using a Zeiss EVO MA15 scanning electron microscope (SEM) with an acceleration voltage of 5 kV.

Structural characterizations
Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR, PerkinElmer Spectrum 3) was used to analyze the structure and components of the samples. For the ATR-FTIR process, the fresh hydrogels were cut into small pieces and scanned in the wavelength range of 4000–450 cm\(^{-1}\) with 64 scans and a nominal resolution of 4 cm\(^{-1}\) at room temperature. The Raman spectra were collected using a Raman spectrometer (LabRAM HR Evolution) equipped with a laser diode for irradiation at an excitation wavelength of 532 nm.

Mechanical property tests
The tensile stress–strain measurements were performed using a tensile tester (MTS Exceed E44) with a 50 N load cell at a deformation rate of 100 mm min\(^{-1}\) in the air at room temperature. The length, width, and thickness of the rectangular samples were 50 mm, 7 mm, and 1.5 \(\pm\) 0.2 mm, respectively. The gauge length was set to 20 mm.

Thermoelectrochemical performance measurements
The \(S_0\) of the as-fabricated TECs was determined by the fitting slope of the curve of thermoelectrochemical potential \(AV\) and temperature difference \(\Delta T\) \(\left(S = -\Delta V/\Delta T\right)\) measured on a self-established apparatus. At least five samples were measured and the average value was used. The length, width, and thickness for the measured samples were 20 mm, 6 mm, and 1.5 \(\pm\) 0.2 mm, respectively. The ionic conductivity of TECs was determined via electrochemical impedance spectroscopy (EIS) conducted on an electrochemical workstation (Chenhua 660e) at room temperature. An AC voltage of 5 mV was applied with the sweeping frequency from 0.01 Hz to 10\(^6\) Hz. The ionic conductivity \(\sigma\) was obtained from the Nyquist plot \(\sigma\) employing the following equation,

\[
\sigma = L/(R_0 \times A)
\]

where \(L\) is the sample thickness (the distance between adjacent electrodes), \(R\) is the bulk resistance, and \(A\) is the contact area between the sample and the electrode. The thickness of the sample was set to 1.5 \(\pm\) 0.2 mm. The electronic conductivities of dried samples were measured by the four-point method.

Preparation and tests of strain sensor
The as-fabricated TECs were fitted with copper electrodes on the extremities and padded using a polyimide tape to avoid short circuit. The obtained sensors were connected to a tensile tester or attached to fingers, wrist, and elbows for strain sensing test. The relative resistance changes \(\Delta R/R_0\) of the sensors were recorded using a digital multimeter (Keithley, 2700E). For the self-powered sensor test, two thermocouples were attached to the surface of the TEC near the two electrodes, and the required heating was applied to one end of the TEC through a metal ceramic heater (MCH, 220 V) connected to a power supply (Yudian, AI-719FKSOLT-25A-D1). The tensile strain was performed on a tensile tester and the corresponding external circuit voltage and current were recorded using a digital multimeter (Keithley, 2700 E).

Author contributions

Conflicts of interest
There are no conflicts to declare.

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