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Construction and application of thermogalvanic hydrogels

Wei Liu[1], Yi Fang[1], Xiaolin Lyu[1,*], Xiangfang Peng[2,*], Zhong-Zhen Luo[1,*], Zhigang Zou[1]

[1]Key Laboratory of Advanced Materials Technologies, International (HongKong Macao and Taiwan) Joint Laboratory on Advanced Materials Technologies, College of Materials Science and Engineering, Fuzhou University, Fuzhou 350108, Fujian, China.
[2]Key Laboratory of Polymer Materials and Products of Universities in Fujian, College of Materials Science and Engineering, Fujian University of Technology, Fuzhou 350118, Fujian, China.

[*]**Correspondence to:** Prof. Xiaolin Lyu, Prof. Zhong-Zhen Luo, Key Laboratory of Advanced Materials Technologies, International (HongKong Macao and Taiwan) Joint Laboratory on Advanced Materials Technologies, College of Materials Science and Engineering, Fuzhou University, Xueyuan Road, College Town, Minhou County, Fuzhou 350108, Fujian, China. E-mail: lyuxiaolin@fzu.edu.cn, zzluo@fzu.edu.cn; Prof. Xiangfang Peng, Key Laboratory of Polymer Materials and Products of Universities in Fujian, College of Materials Science and Engineering, Fujian University of Technology, Xuefu South Road, Shangshang Town, Minhou County, Fuzhou 350118, Fujian, China. E-mail: pengxf@fjut.edu.cn

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Abstract

Low-grade heat (below 373 Kelvins) is abundant and ubiquitous, yet the lack of cost-effective recovery technologies frequently impedes its effective utilization. The advent of thermogalvanic hydrogel thermocells has garnered significant attention due to their high thermopower, inherent flexibility, low cost, and scalability. Thermogalvanic hydrogels have significantly enhanced their thermoelectric performance, resulting in the development of functional materials that exhibit flexibility, stretchability, self-healing, and frost resistance. However, there are substantial challenges in developing multifunctional thermogalvanic hydrogels that combine high power density and efficiency with practical applicability. This review discusses the synthesis of the novel redox couple, improving the performance of electrolytes to increase thermopower, creating electrodes with extensive surface areas for better current density and flexibility, and optimizing thermocell structure design to improve performance further. This comprehensive review aims to propel progress toward higher performance levels and broader applications of thermogalvanic hydrogel thermocells.

Keywords: Thermogalvanic hydrogel, thermocell, thermogalvanic effect, thermopower, energy output

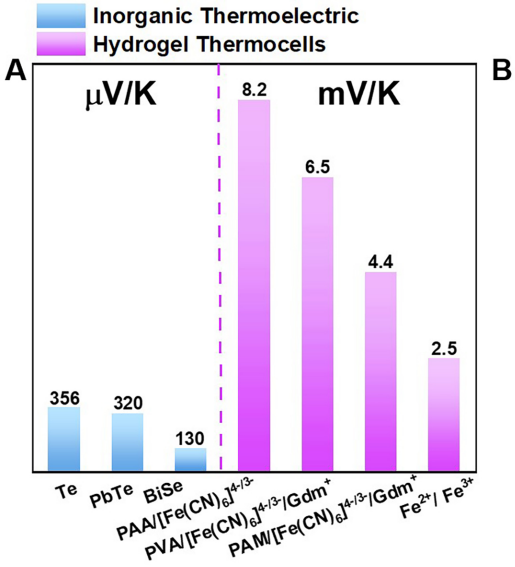
INTRODUCTION

Low-grade heat energy from natural and anthropogenic sources (such as solar radiation, industrial plants, automobiles, and the human body) is abundant but underutilized, leading to significant energy wastage[1-7]. Consequently, developing and effectively using this thermal energy has become a meaningful way to promote sustainable development[8-12]. As a critical component of green energy, thermoelectric materials can convert thermal energy into electricity[13-19]. They also play an essential role in improving energy efficiency and reducing environmental burdens[20-23]. Although inorganic solid-state thermoelectric materials have been the subject of extensive research[24-27], their constituent elements are often rare and expensive. They typically generate thermopower at the microvolt level, hindering their widespread commercialization[28]. Ionic thermoelectric materials, such as thermogalvanic hydrogels, are intriguing because their thermopower is two to three orders of magnitude higher than their inorganic counterparts[21,29-31].

Thermogalvanic hydrogel materials have significant prospects for low-grade thermal energy harvesting because of their low cost, excellent scalability, flexibility, and high thermopower[32-39]. The high thermopower implies the generation of high voltages with a slight temperature gradient, thereby simplifying device design and integration[40-43]. Regarding thermogalvanic hydrogel preparation techniques, researchers can access diverse methods. Hydrogels can be broadly categorized into physically and chemically crosslinked types based on their crosslinking methods[44-46]. The physical crosslinking method mostly uses hydrogen bonds, van der Waals forces, and other non-covalent interactions to keep the hydrogel network structure stable[47-50]. Conversely, chemical crosslinking enhances the structural integrity of hydrogels by forming covalent bonds[51-53]. Each of these crosslinking techniques possesses unique advantages and application scenarios[54,55]. Through meticulous design and optimization, thermogalvanic hydrogels are poised to emerge as pivotal components in thermal energy harvesting technologies[2,15,56,57].

The principle of thermogalvanic hydrogels converting thermal energy into electrical energy differs from traditional electronic materials[58-60]. The principle in thermogalvanic hydrogels is mainly based on the thermogalvanic effect[61]. This effect is based on the redox reaction of redox couples in ionic conductors at the electrode interface under the thermal drive[40,62]. Owing to the disparity in reaction entropy between anions and cations, the ions undergo oxidation reactions in the high-temperature region and reduction reactions in the low-temperature region. The reaction generates a thermal voltage between the two electrodes, typically reaching several millivolts per Kelvin.

In recent years, significant progress has been achieved in thermogalvanic hydrogels. For example, by adding chaotropic cations and highly soluble amide derivatives to the redox couple electrolyte, the thermopower of thermogalvanic hydrogels was as high as 6.5 $mV \cdot K^{-1}$[63]. Furthermore, efforts to improve the output performance of electrodes by utilizing a large specific surface area to promote reaction kinetics have also proven effective[64]. In addition to the significant progress in performance, functional thermogalvanic hydrogels with properties such as flexibility, stretchability, toughness, antifreeze and self-healing are crucial for practical applications. Compared to traditional solid-state thermocells, hydrogel thermocells - extensively investigated in recent years - are more competitive and practical, as illustrated in Figure 1. However, thermogalvanic hydrogels still face challenges, including low energy conversion efficiency, low power density and stability issues in integrated devices for practical applications. In recent years, some excellent reviews have been made on thermogalvanic hydrogels. This paper aims to provide new insights to guide future research toward more efficient single thermocells and higher-performance low-grade heat-harvesting devices, among other directions.



B

Merits	Inorganic Thermoelectric	Hydrogel Thermocells
Source	rare	abundant
Cost	expensive	inexpensive
Toxicity	toxic	non to low
Flexibility	inflexible	flexible
Manufacture	complex	simple
Thermopower	lower	higher

Figure 1. Comparisons of (A) thermopower and (B) merits between inorganic thermoelectric materials and hydrogel thermocells. The materials used in hydrogel thermocells are abundant, inexpensive, and low-toxic. Furthermore, hydrogel thermocells exhibit excellent flexibility and stretchability, which can meet the needs of flexible wearable electronics[33,63,65-69].

THERMOGALVANIC HYDROGEL FUNCTIONALITY AND PERFORMANCE INFLUENCING FACTORS

Working principle

Thermogalvanic hydrogels represent a new class of materials exhibiting thermoelectric properties, and their thermoelectric conversion mechanism is mainly based on the thermogalvanic effect[56,70-72]. This phenomenon refers to generating electric potential under a temperature difference. The hydrogel thermocell is mainly composed of two electrodes and an electrolyte [Figure 2]. The two electrodes are in complete contact with the electrolyte containing the redox couple, and they are connected by an external circuit[73,74]. Applying a temperature difference across the two electrodes of a thermocell causes the redox couple to undergo oxidation at the anode and reduction at the cathode[75-77]. During this process, the reduced substances return to the anode for oxidation through convection, diffusion, and migration within the electrolyte. Meanwhile, the oxidized substances migrate towards the cathode. This ensemble of reactions and migratory processes constitutes a sustained current loop[78,79]. Ideally, as long as the composition of the electrolyte does not degrade, this cyclic reaction can theoretically continue indefinitely[80]. This property endows thermogalvanic hydrogels with tremendous potential for energy conversion and storage applications, thereby presenting a novel trajectory for advancing renewable energy technologies[32,78,81-86].

Factors influencing the thermoelectric properties of thermogalvanic hydrogels

Firstly, the material itself has a significant impact on its thermoelectric performance. Hydrogel is a three-dimensional network structure polymer with high porosity and water content, and it can store a large number of ions[87,88]. With their unique structure, hydrogel thermocells act as an electrolyte to conduct ions and maintain the movement of charge carriers. Additionally, they serve as solidifying matrices for the electrodes, addressing the issue of electrolyte leakage typically associated with liquid electrolytes[89]. Therefore, the physical and chemical properties of hydrogels (such as molecular composition, crosslinking density, pore size, *etc.*) influence the conductivity, specific heat capacity, thermal expansion coefficient, and thermogalvanic effect of thermocells. These properties directly determine the energy density and power density of the redox couples. For instance, the polymer chain structure of hydrogels directly influences their

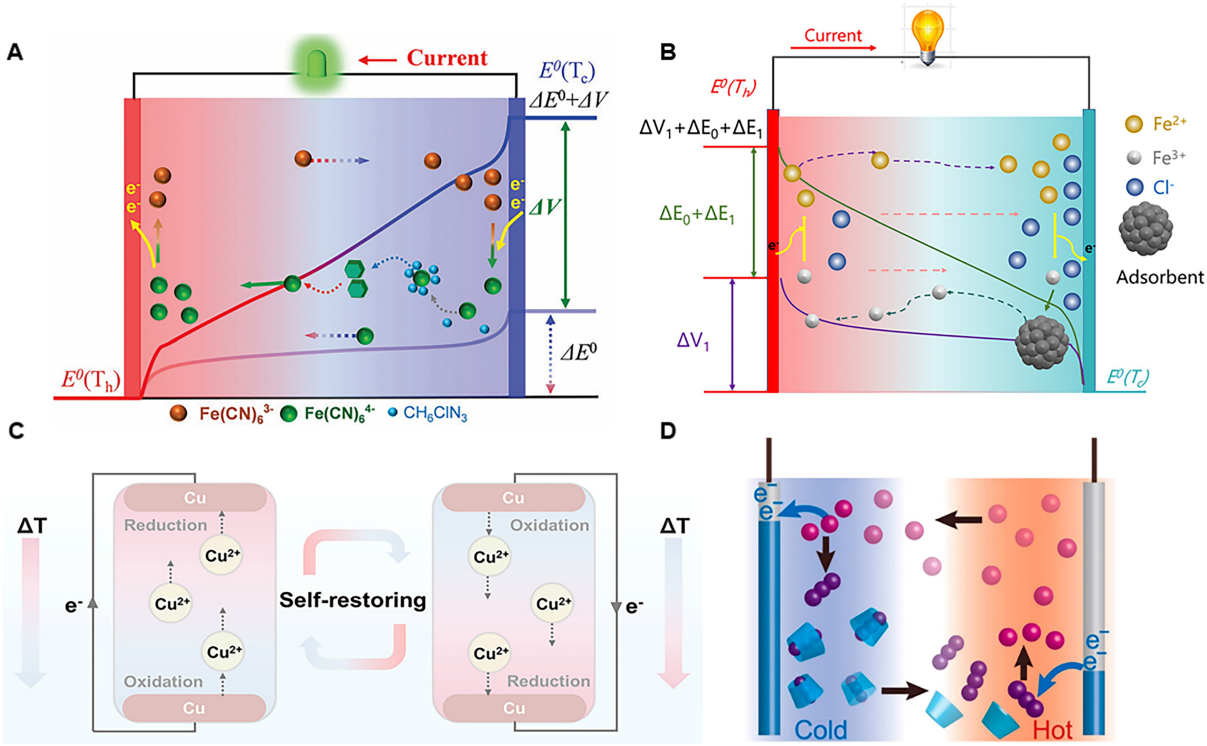


Figure 2. The thermocell working diagram (A) $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$. Reproduced with permission[33]. Copyright 2022, Royal Society of Chemistry; (B) Fe^{2+}/Fe^{3+}. Reproduced with permission[42]. Copyright 2024, Royal Society of Chemistry; (C) Cu/Cu^{2+}. Reproduced with permission[71]. Copyright 2024, Royal Society of Chemistry; (D) I^-/I_3^- Reproduced with permission[72]. Copyright 2016, American Chemical Society.

thermoelectric characteristics, including chain length, degree of branching, and copolymer composition ratio. Longer-chain polymers usually conduct heat more efficiently, while optimizing the copolymer composition ratio can enhance thermocell performance. Secondly, the crosslinking density plays a determinant role in establishing the network density of the hydrogel, thereby significantly influencing its thermoelectric properties. A high crosslinking density can enhance the mechanical strength of the thermocell but might decrease its thermal conductivity. On the other hand, a low crosslinking density can augment thermal conductivity but may compromise mechanical strength. Finally, the conductivity of hydrogels is crucial to their thermoelectric properties, as excellent conductivity is essential for converting thermal energy into electrical energy. The conductivity of hydrogels can be enhanced by adding conductive fillers or constructing conductive networks.

Hydrogel thermocells generate a potential difference at specific temperatures, which is critical in determining their output power. This potential difference is a consequence of the redox reactions occurring at that particular temperature. The potential difference directly affects the amount of energy that a redox couple can deliver, significantly influencing its power output. The redox reactions can be expressed as:

$$A + ne^- \; B \tag{1}$$

Thermopower refers to the reaction thermodynamics and is determined by the thermopower of redox species in the electrolytes. In thermocells, the thermopower parameter is also called the temperature coefficient. It is defined as the ratio of the voltage difference to the temperature change and describes the

ability to generate electromotive force unit temperature difference. This parameter is an essential factor in determining the power output of the device. Thermopower can be calculated using[90]:

$$Se = \left(\frac{\partial E}{\partial T}\right)_{t=\infty} = \left(\frac{1}{nF}\right).\left[\left(S_B + \cdot\widehat{S_B}\right) - \left(S_A + \cdot\widehat{S_A}\right) - n\bar{\bar{S}}e\right] \quad (2)$$

where n represents the number of electrons transferred in a redox reaction, F is the Faraday constant, S_A and S_B are the partial molar entropies of substances A and B, $\widehat{S_A}$ and $\widehat{S_B}$ are the Eastman entropies, and $\bar{\bar{S}}e$ is the entropy of electron transport in an external circuit. The interaction of the ions and their solvated shells with the solution influences the Eastman transport entropy. Under specific temperature differences, the output voltage of the hydrogel thermocell will increase accordingly with the thermopower. Because the internal resistance of the hydrogel thermocell is less sensitive to temperature changes, the thermocell generates significantly higher current and output power.

Thermal conductivity represents another pivotal factor that influences the performance of thermocells. If the electrolyte has good thermal conductivity, it can conduct heat more efficiently, reducing the temperature difference between the electrodes. This reduction may result in lower output power from the thermocell. It is well known that heat conduction depends on lattice vibrations. The amorphous and inhomogeneous structure of polymers makes their lattice vibrations discontinuous, resulting in generally low thermal conductivity. Hydrogel thermocells usually use polymers as matrices, leveraging the lattice vibrational discontinuities between the aggregated and entangled nanofiber networks of the polymer and the embedded ions; therefore, their thermal conductivity is generally lower.

STRATEGIES TO IMPROVE THERMOELECTRIC PROPERTIES

Enhancement of thermopower

The main factors restricting the widespread application of thermocells are their low output power, conversion efficiency, and stability[91]. To address these challenges, numerous researchers are actively working on solutions across multiple levels[92-96].

Thermopower primarily depends on the entropy change of the redox species during the reaction, and the entropy change is determined by the thermodynamics of the reaction. Specifically, the entropy change is related to the solvation structure entropy difference (ΔS) and the concentration ratio difference (ΔC) between the redox species, indicating that increasing ΔS or ΔC can effectively enhance thermopower[30]. Generally, the ΔS value of the redox species can be increased by regulating the interaction between the redox species and its solvent environment through special additives. Additives reorient and complicate the solvation structure of the redox species, thereby increasing the thermopower. Recent studies have demonstrated that the absolute value of the charge of the redox couples and the types of solvents surrounding it significantly influence the magnitude of ΔS[29]. Charge transfer leads to a change in entropy. Alterations in the charge of redox couples with large absolute charges modify the electron distribution and ionization state within the molecule, thereby increasing the complexity of the molecular internal structure. This increased complexity raises the entropy difference and the thermopower. For instance, the thermopower of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ is approximately ~ 1.3 mV·K^{-1}, much larger than that of I^-/I_3^- at ~ 0.6 mV·K^{-1}.

To amplify the entropy difference, organic solvents with different numbers of donors (DN) can be introduced to the aqueous solution[66,97,98]. The dimensions of the solvation shell are contingent upon the electron density of the surrounding solvation molecules. Meanwhile, the size of the solvation shell is inversely proportional to its entropy. Jiao *et al.*, *Lazar et al.*, *and* He *et al.* reported a series of non-liquid

electrolyte thermocells exhibiting high thermopower, with a maximum value of 2.65 mV·K^{-1}[99-101]. Li *et al.* significantly enhanced the performance of the $K_4Fe(CN)_6/K_3Fe(CN)_6$ redox couple within an organic hydrogel thermocell [Figure 3][102]. This change also influenced the structure of the solvent shell around the redox couples during the reaction, which led to a difference in the concentration of the redox anions. Consequently, the thermopower was substantially increased from 1.27 to 2.30 mV·K^{-1}. Owing to the high compressibility and inherent stretchability, these thermocells were subsequently assembled into self-powered strain sensors. These sensors could monitor the movement of the human body under various stretches and pressures in real-time with high sensitivity.

To enhance the thermopower beyond improving ΔS, an alternative approach involves increasing ΔC. However, the redox couple cannot indefinitely sustain the concentration gradient between the hot and cold ends, as this state is thermodynamically unstable and will eventually revert to a uniform state. When the electrolyte reaches a steady state, ΔC is zero. Han *et al.* reported a new concept using methylcellulose to capture I_3^- at the hot side and then release I_3^- at the cold side, creating a concentration gradient of free I_3^- in the thermocell, leading to an increase and reversal of the thermopower[31]. Zhou *et al.* successfully increased the concentration difference between the hot and cold ends by introducing α-cyclodextrin (α-CD) and potassium chloride (KCl)[72]. Due to the host-guest interaction, α-CD bound to I_3^- at the cold end, thereby reducing the relative concentration of I_3^-. Consequently, the equilibrium spontaneously shifted to the right at the cold end, where oxidation of $3I^-$ to I_3^- occurred. Concurrently, with the temperature elevation, the α-CD-I_3^- complex spontaneously dissociated, resulting in an augmented concentration of I_3^- at the hot end. This resulted in the equilibrium shifting towards the reduction of I_3^- to $3I^-$, thereby producing more I^- at the hot end. Compared to the original I^-/I_3^- system, introducing host-guest interactions created a larger concentration difference between the hot and cold ends, causing the internal cyclic reactions within the thermal thermocell to proceed more efficiently. Consequently, the thermopower increased from 0.86 to 1.97 mV·K^{-1} [Figure 4].

In addition to the methods above, introducing electrolyte additives is another advantageous strategy[2,31,33,40]. Cations with strong chaotropic properties can combine with redox ions, crystallizing redox substances. This raises the ΔS of the redox electrolyte and amplifies the ΔC, significantly improving the thermopower of the thermocell. Yu *et al.* added guanidinium ions (Gdm^+) to the electrolyte. These ions selectively caused $[Fe(CN)_6]^{4-}$ to crystallize at the cold end, which led to the formation of thermosensitive crystals [Figure 5A and B][30]. Owing to the concentration gradient, these thermosensitive crystals moved toward the hot end and dissolved there. This phenomenon generated a substantial concentration disparity between the two electrodes, resulting in higher thermopower[103]. This was attributed to the fact that $[Fe(CN)_6]^{4-}$ had a higher charge density compared to $[Fe(CN)_6]^{3-}$, and it interacted more strongly with Gdm^+. Yu *et al.* corroborated this hypothesis through comprehensive experimental and simulation analyses[30]. At the low-temperature electrode (293 K), $[Fe(CN)_6]^{4-}$ crystallized almost completely, with a concentration ratio of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ of approximately 0.02. Conversely, near the high-temperature electrode (343 K), the $[Fe(CN)_6]^{4-}$ crystals dissolved rapidly, bringing the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ concentration ratio to about 0.94. More importantly, the large concentration gradient of the redox couple significantly amplified the thermogalvanic effect. Adding Gdm^+ caused the thermopower to rise from 1.4 to 3.73 mV·K^{-1}, nearly 2.5 times than before. In addition to increasing ΔC, the crystals generated at the cold end could also inhibit thermal convection in the system, decreasing thermal conductivity [Figure 5C]. Due to the synergistic optimization of these parameters, its Carnot-relative efficiency reached 11.1%. Liu *et al.* combined stretch-induced crystallization with thermoelectric effect and proposed a high-strength quasi-solid stretchable polyvinyl alcohol thermogalvanic thermocell (SPTC) [Figure 5D][63]. Thus, the SPTC system had a large thermopower of 6.5 mV·K^{-1}, a high specific output power density of 1969 μW m^{-2} K^{-2}. The extraordinary thermoelectric and

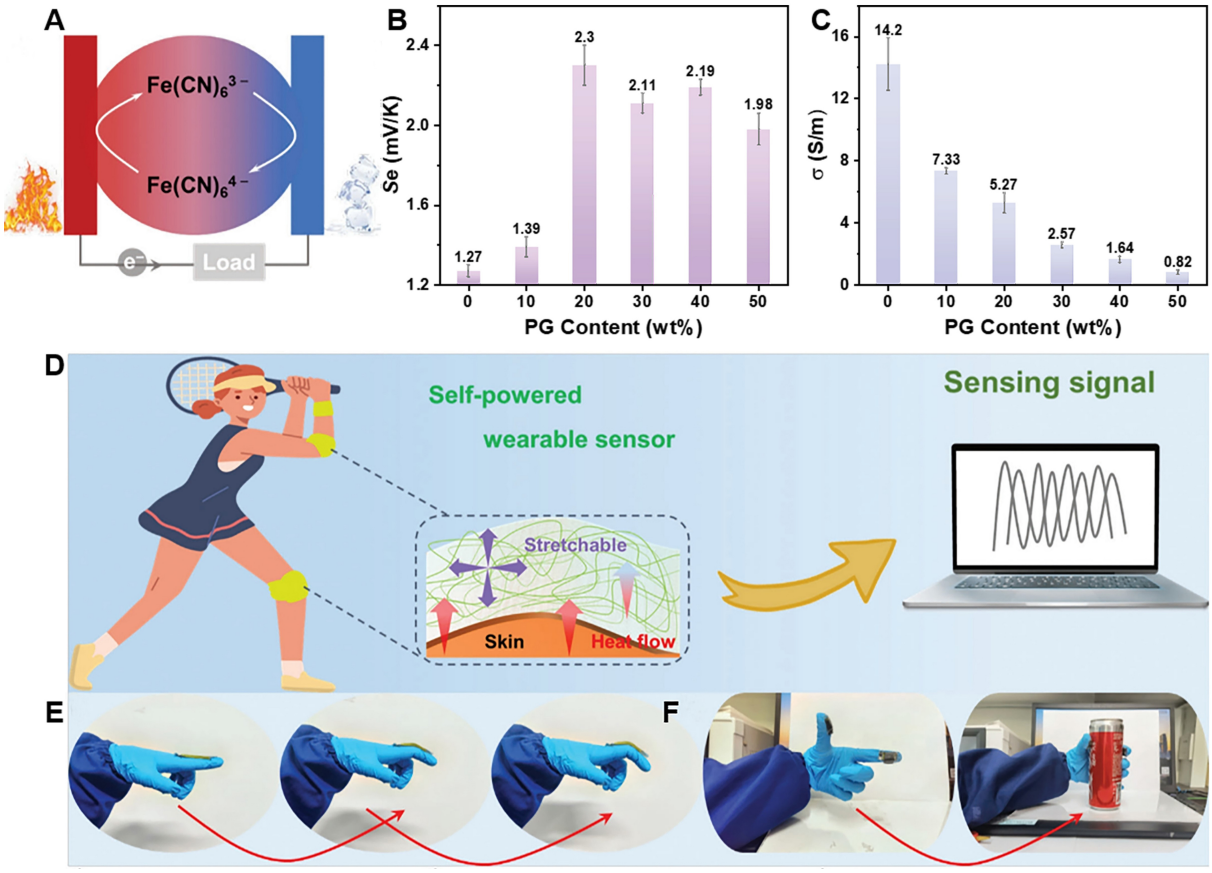


Figure 3. (A) The schematic operation mechanism for organogel-based thermocells. The thermopower (B) and conductivity (C) of thermocells. (D) Illustration showing the wearable application scenario of organized-based thermocells for self-powered strain sensing harvesting body heat. (E) The diagram of finger bending activity with a self-powered tensile sensor. (F) The thumb and index finger grasping bottle schematic with a self-powered pressure sensor. Reproduced with permission[102]. Copyright 2023, Wiley-VCH Verlag.

mechanical properties of the SPTC were superior to those of most reported quasi-solid stretchable thermogalvanic thermocells [Figure 5E].

Enhancement of ionic conductivity

The conductivity of hydrogel thermocells is generally three orders of magnitude lower than that of traditional inorganic thermoelectric materials. Consequently, research efforts have been directed towards enhancing their conductivity[104-106]. A primary approach to improving conductivity is to increase the solubility of redox couples within the electrolyte. However, this strategy could lead to an increase in the viscosity of the electrolyte, thereby intensifying mass transfer resistance and diminishing overall conductivity. Additionally, the thermopower of certain redox couples is concentration-dependent and can decline rapidly at high concentrations. For example, the thermopower could decrease by over 400% when the ion pair concentration increases from 0.01 to 2 M in I^-/I_3^- systems[107]. To solve these problems, researchers have proposed methods to optimize the properties of thermoelectric materials through electrode modification. For example, they proposed the creation of composite electrodes featuring three-dimensional pores or using copper electrodes to create three-dimensional layered electrodes through oxidation-etching-reduction processes. Im *et al.* used carbon nanotube aerogel sheets coated on the surface with Pt nanoparticles as electrodes, increasing the conversion efficiency to 3.95%[108]. Wei *et al.* used MXene as the core of the electrode structure. They put polyaniline on the carbon nanotubes to make a three-layer thin

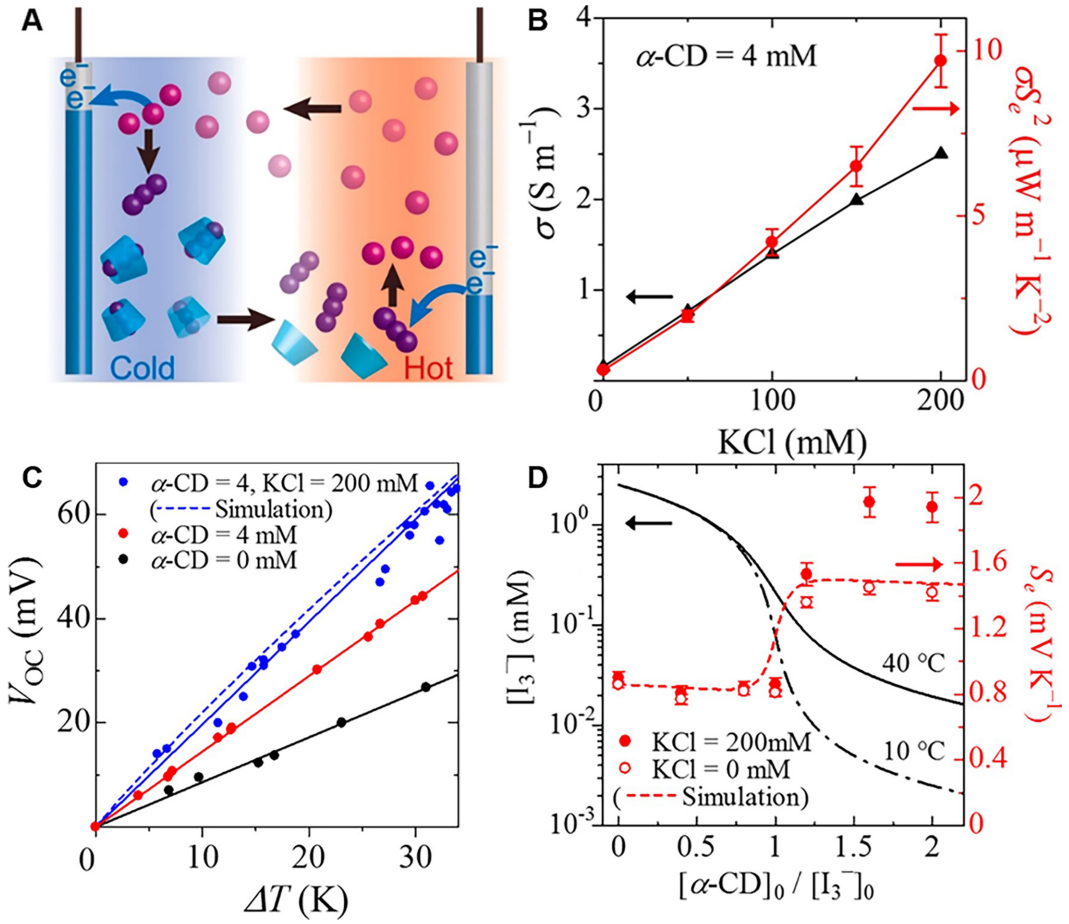


Figure 4. (A) A schematic figure of the thermocell combined with α-CD and I_3^-/I^- redox pair; (B) Increase of ionic conductivity and power factor of the thermocell with α-CD (4 mM); (C) Comparison of the thermopower values after the addition of α-CD, KCl, and (D) estimated concentration of uncomplexed I_3^- in the electrolyte solution with simulated thermopower values (Se) at 10/40 °C. Reproduced with permission[72]. Copyright 2016, American Chemical Society. α-CD: α-cyclodextrin; KCl: potassium chloride.

film with substantial electrochemically active space [Figure 6][64]. This ternary composite flexible thin film electrode demonstrated superior performance in thermoelectrochemistry due to its porous and layered architecture. The synergistic interaction between MXene and polyaniline facilitated ion and charge transport at the electrolyte-electrode interface, resulting in an output power density of up to 13.15 mW·cm^{-2} at a temperature difference of ΔT = 40 K. These methods primarily rely on increasing the specific surface area of the electrodes to reduce electron transmission resistance, thereby increasing the current density of the thermocell.

THERMOGALVANIC HYDROGEL APPLICATIONS

Thermogalvanic hydrogels, as a multifunctional advanced material, have demonstrated their unique application potential across various fields[109-118]. In the energy sector, these materials can be utilized for waste heat recovery, solar energy conversion and bioenergy conversion, potentially leading to significant energy savings and environmental benefits[65,119]. Thermogalvanic hydrogels have been proven indispensable in sensor technology, enabling temperature sensing, stress sensing, and other functions[89,120,121]. Additionally, thermogalvanic hydrogels have exhibited important application value in high-tech areas such as flexible electronics and smart nanodevices[63,122,123].

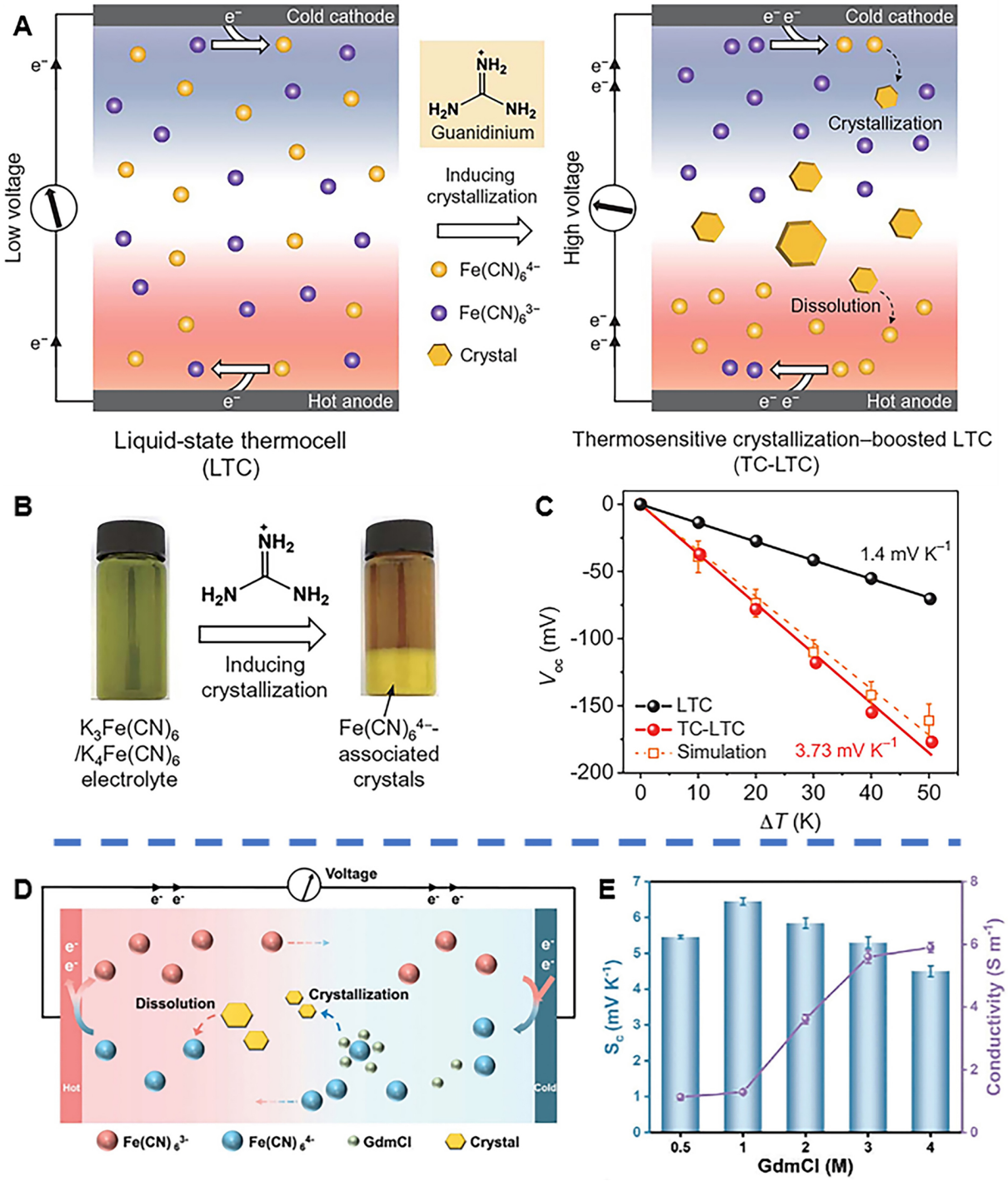


Figure 5. (A) Schematic of Gdm^+ induced $[Fe(CN)_6]^{4-}$ crystallization and enhanced Se effect in $K_4Fe(CN)_6/K_3Fe(CN)_6$ electrolyte; (B) The photo shows the 0.4 M $K_4Fe(CN)_6/K_3Fe(CN)_6$ electrolyte before and after the addition of Gdm^+; (C) The open-circuit voltage of the liquid $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ system after the addition of guanidinium chloride. Reproduced with permission[30]. Copyright 2020, American Association for the Advancement of Science; (D) A schematic illustration of the Gdm^+ contribution to the thermogalvanic effect was enhanced in the thermocell; (E) The thermopower and conductivity of thermocells. Reproduced with permission.[63] Copyright 2023, Wiley-VCH Verlag.

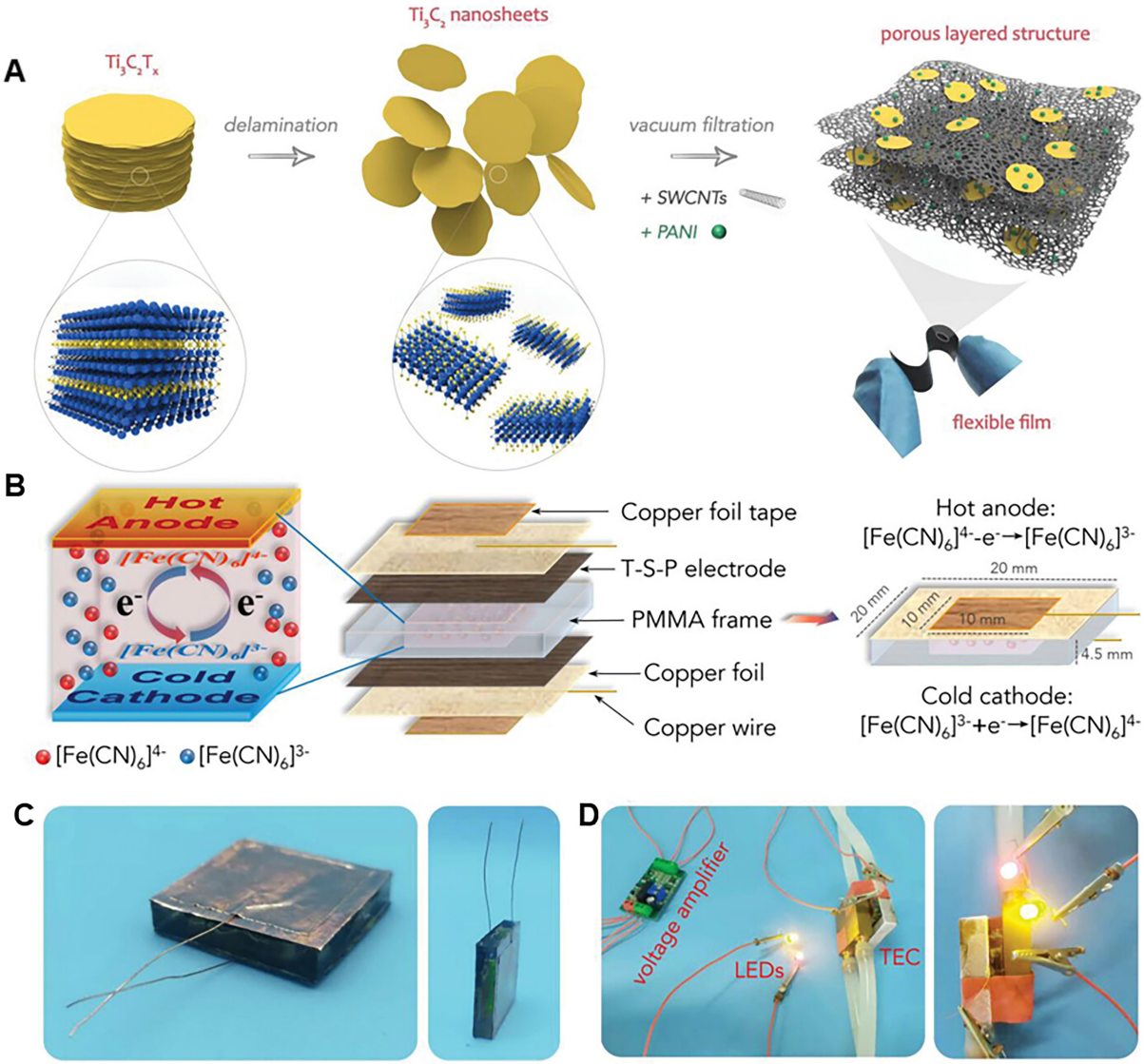


Figure 6. (A) Diagram illustrating the process of creating a flexible ternary composite thin film electrode that has a porous layer structure; (B) Schematics of the configuration and size information of the square thermocell; (C) Optical images of the as-fabricated square thermocell; (D) Demonstration of using the square thermocell to light up two LED bulbs under the temperature difference of 30 K with the assistance of a voltage amplifier. Reproduced with permission[64]. Copyright 2023, Wiley-VCH Verlag.

Energy field

As global energy demands continue to rise, finding efficient ways to reduce energy consumption and lower industrial energy usage has become a key focus for researchers[79,124]. Kong *et al.* prepared a tellurium nanowire (Te-NW)-doped poly (3,4-ethylenedioxythiophene): poly (styrenesulfonate) (PEDOT:PSS)/ polyvinyl alcohol hydrogel [Figure 7A][83]. After integration with a power management unit, the hydrogel module can drive small electronic devices such as commercial calculators and light-emitting diodes, showing good application potential in human body thermal energy harvesting. Xu *et al.* designed a PEDOT:PSS-polyacrylamide (PAAm) double network hydrogel as a high-performance interfacial photothermal material for solar steam power generation[125]. The hydrogel has good mechanical properties, long-term reliability and stability, and high-efficiency photothermal conversion performance. Meanwhile, Xu *et al.* developed a novel, cost-effective, highly porous hydrogel composite integrated with synchronous

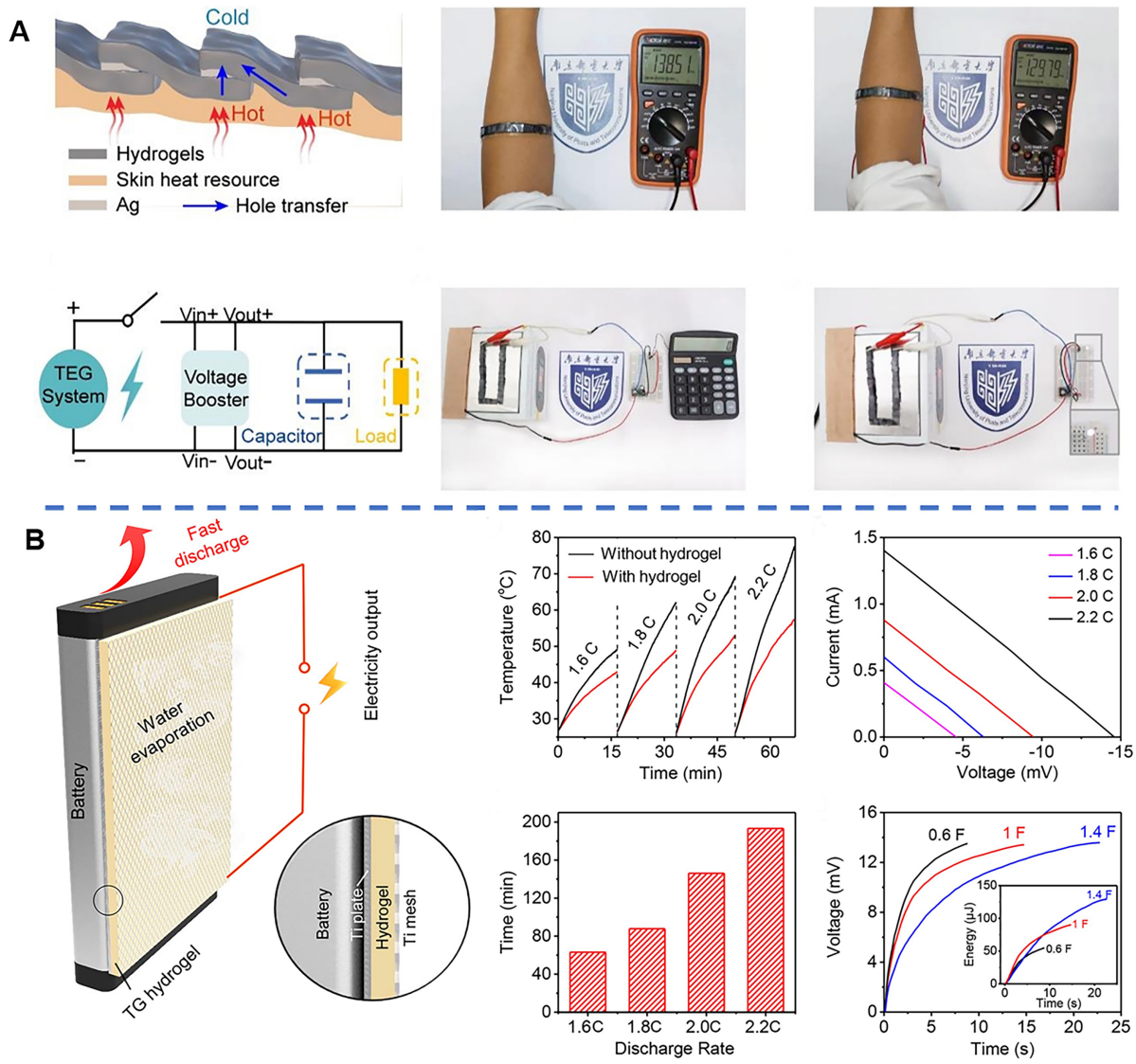


Figure 7. (A) Demonstration of thermoelectric system in powering electronic devices. Reproduced with permission[83]. Copyright 2023, Elsevier B.V; (B) A hydrogel thermocell on a mobile phone battery is demonstrated to achieve effective evaporative cooling while converting the waste heat into electrical energy. Reproduced with permission[127]. Copyright 2020, American Chemical Society. TEG: Thermoelectric generator; TG: thermogravimetric.

photothermal and photocatalytic effects by a facile two-step immobilization approach[126]. The effective recovery of waste heat generated during the production process is crucial. However, efficient heat dissipation and waste heat recovery are often contradictory and difficult to achieve simultaneously. To address this issue, Pu *et al.* designed and developed a thermogalvanic hydrogel through collaborative innovation [Figure 7B][127]. This hydrogel film was laminated onto heat-generating elements to facilitate effective evaporative cooling and convert a portion of waste heat into electricity. More uniquely, the hydrogel could absorb moisture from the surrounding air and spontaneously recycle it. The effective recovery of waste heat generated during production processes was critical for increasing energy efficiency and decreasing industrial energy consumption. Specifically, attaching the hydrogel membrane with a thickness of just 2 mm to a phone battery successfully reduced the operating temperature by 20 °C at a discharge rate of 2.2 C, while retrieving electricity of 5 μW. This method facilitated spontaneous recycling by

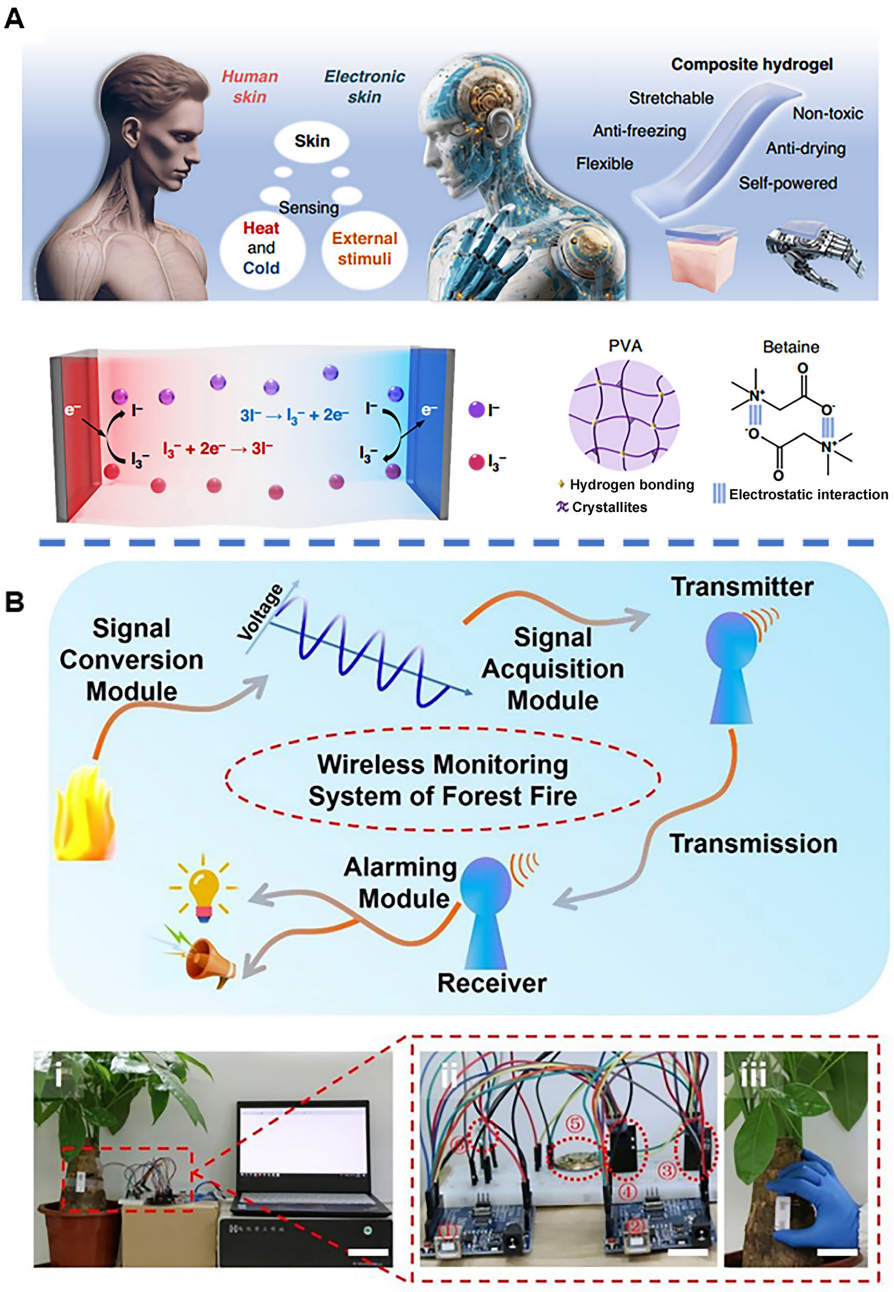


Figure 8. (A) Conceptual schematic diagram of the thermogalvanic hydrogel patch resembling skin for self-powered temperature and strain sensing. Reproduced with permission[131]. Copyright 2024, Springer Nature; (B) A wireless fire monitoring system tracks the real-time voltage change during a fire. Reproduced with permission[132]. Copyright 2020, American Chemical Society. PVA: Polyvinyl alcohol.

adsorbing water molecules from the environment when the device was unused. Thus, it provided a novel energy conservation and environmental protection solution.

Temperature sensing

As an emerging material, thermogalvanic hydrogels have demonstrated significant potential as temperature sensors[89,128-130]. Researchers can monitor temperature fluctuations by measuring voltage differences, as the open-circuit voltage of hydrogels directly relates to temperature changes. Temperature sensors based on

thermogalvanic hydrogels have gained widespread attention due to their rapid response and high precision. Wang *et al.* engineered a hydrogel-based electronic skin with dual-mode temperature and strain-sensing capabilities that harvest thermal energy from human body heat [Figure 8A][131]. They selected the iodine/triiodide (I^-/I_3^-) redox couple. By combining the thermogalvanic and piezoresistive effects, self-powered temperature and strain sensing are successfully demonstrated through encapsulation and integration of the hydrogels into human tissue. Wu *et al.* have made a significant breakthrough. By connecting ten pairs of p-n thermoelectric modules in series, they constructed a system capable of real-time fire monitoring [Figure 8B][132]. The thermogalvanic hydrogel was a self-powered electrical signal converter, transforming the temperature signal into a voltage signal. The signal acquisition module connected to the transmitter was responsible for capturing and relaying the temperature change information. The electrochemical workstation then recorded voltage changes in real-time. When the signal exceeded the threshold of the alarm circuit, the system lit up the red light-emitting diode and activated the speaker to sound the alarm.

Passive wearable sensors

Wearable sensors are another promising application area for thermogalvanic hydrogels[71,110,133-135]. Shen *et al.* reported for the first time a novel non-toxic redox couple of SO_4^{2-}/SO_3^{2-} as a high-performance, p-type thermogalvanic electrolyte ion that delivered a high Seebeck coefficient of 1.63 $mV \cdot K^{-1}$ at the redox couple concentration of 0.1 M[77]. Moreover, this PVA-$SO_{4/3}^{2-}$ hydrogel-based quasi-solid-state device showed the capacity for grabbing body heat to operate small electronics. Liu *et al.* have developed a tough and stretchable thermogalvanic hydrogel with superior thermoelectric properties [Figure 9A][63]. This hydrogel utilized the stretching-induced crystallization process and the thermogalvanic effect. With the help of freeze-thaw cycles and stretching steps, polymer chains crystallize and arrange themselves in the stretching direction, creating a layered anisotropic network. The researchers added guanidinium chloride to the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ system to change the solvent shell around the $[Fe(CN)_6]^{4-}$. The chaotropic cations promote the crystallization of $[Fe(CN)_6]^{4-}$ and enhance the reversibility of the redox reaction, thereby increasing the thermopower. The thermogalvanic hydrogel got a high thermopower of 6.5 $mV \cdot K^{-1}$ and a specific output power density of 1,969 $\mu W \cdot m^{-2} \cdot K^{-2}$. This represented a nearly fivefold increase compared to the thermopower of liquid $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ (1.4 $mV \cdot K^{-1}$) and a fourfold increase in the output power. The stretching caused the polymer chains to densify, which increased the mechanical properties. The hydrogel had a breaking strength of 19 MPa and a toughness of 163.4 $MJ \cdot m^{-3}$. The thermogalvanic hydrogels were also integrated as an array to harvest low-grade thermal energy from the environment and conduct strain sensing and health monitoring. This device generated enough electrical power to drive small medical devices, contributing to the promotion of green, sustainable, and wearable electronics in the Internet of Things era. Yang *et al.* constructed a solar thermogalvanic hydrogel[136]. The innovative system used external sunlight-induced by swinging arms to dynamically change the temperature difference of the gel during the thermoelectric conversion process [Figure 9B]. Han *et al.* developed a smart glove that integrates multiple thermal sensor arrays[121]. By monitoring all sensing nodes, the smart glove can feel the temperature and touch the position of an object, showcasing the potential application of flexible thermal sensor arrays in an intelligent environment [Figure 9C].

Coupling with catalysis

In addition to applications in energy, temperature sensing, and passive wearable sensors, thermoelectric materials can also be used in catalysis[137]. Wang *et al.* reported an in situ photocatalytically enhanced redox reaction that generates hydrogen and oxygen to realize a continuous concentration gradient of redox ions in thermogalvanic devices[65]. They used polyacrylic acid (PAA) as a hydrogel matrix, $FeCN^{4-/3-}$ as redox ions, and WO_3 (O_v-WO_3) and $ZnIn_2S_4$ as the photocatalysts (S_v-ZIS) for O_2 production and H_2 production. An O_2-evolution photocatalyst aided the forward reaction from $FeCN^{3-}$ to $FeCN^{4-}$ and facilitated H_2O to O_2 production, resulting in a high $FeCN^{4-}$ concentration on the hot side[138]. The H_2-evolution photocatalyst

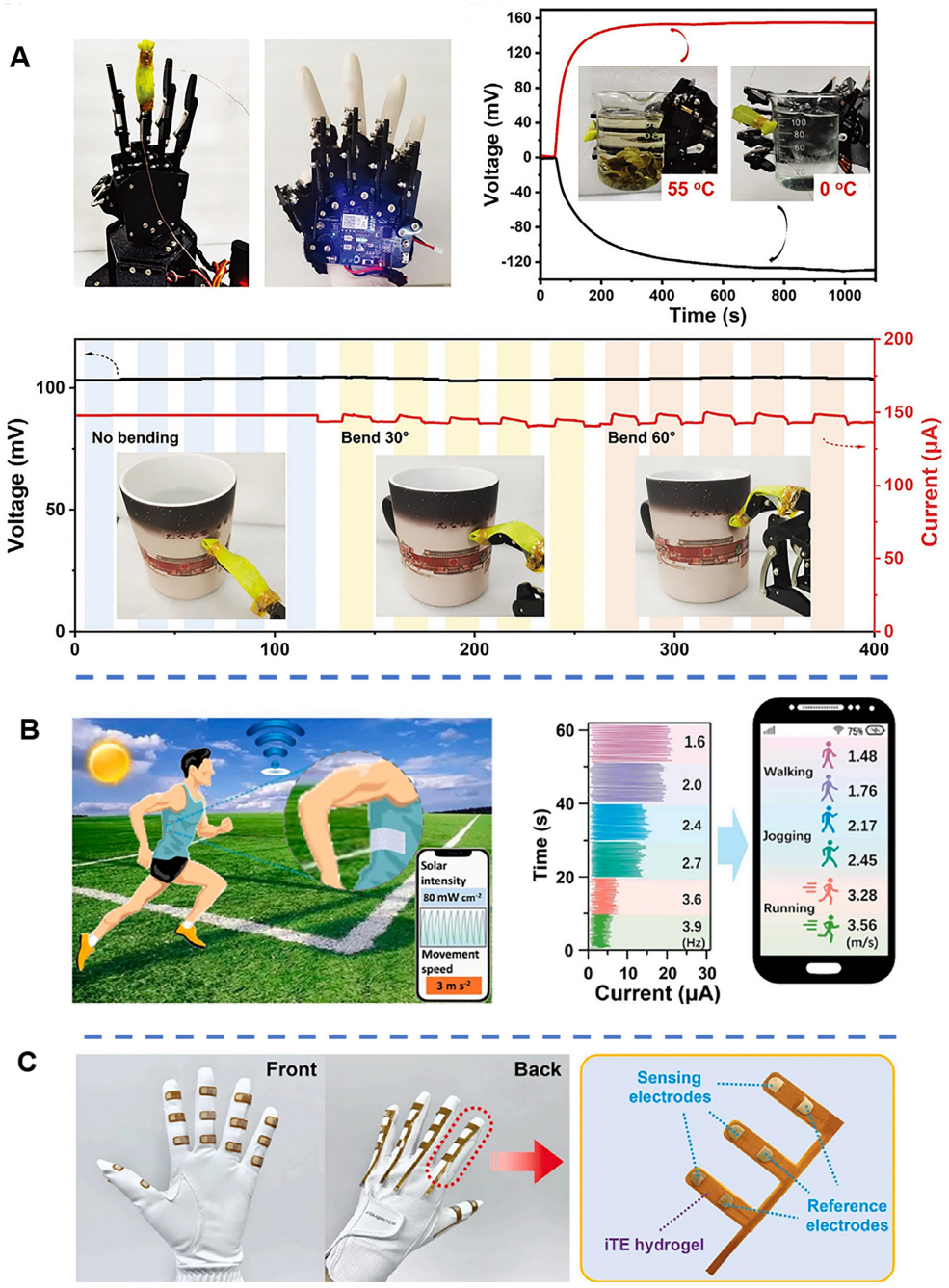


Figure 9. (A) Hydrogel thermocells are designed for wearable, flexible electronics and human health monitoring applications. Reproduced with permission[63]. Copyright 2023, Wiley-VCH Verlag; (B) Schematic illustration of the self-powered PTE patch for human motion detection, the main features of movements such as walking, jogging, and running are recognized by the PTE patch. Reproduced with permission[136]. Copyright 2023, Elsevier B.V; (C) Photographs of a smart glove integrated with multiple thermal sensor arrays. Reproduced with permission[121]. Copyright 2023, Open Access. iTE: Ionic thermoelectric.

converted the $FeCN^{4-}$ to $FeCN^{3-}$ and facilitated H_2 production from H_2O, increasing the amount of $FeCN^{3-}$ on the cold side[139]. The authors also used in-situ Raman spectroscopy to test the species distribution of the system. They found that high concentration difference distribution can indeed be achieved and can exist stably, achieving the effect of stable and efficient operation of the thermoelectric battery under light. In addition to theoretical feasibility, the system exhibited a thermopower of 8.2 $mV \cdot K^{-1}$ in actual application

tests and a solar-to-hydrogen efficiency of up to 0.4%. A large-area generator (112 square centimeters) consisting of 36 units yielded an open circuit voltage of 4.4 volts and a power of 20.1 milliwatts, as well as 0.5 millimoles of hydrogen and 0.2 millimoles of oxygen after six hours of outdoor operation.

CONCLUSION AND OUTLOOK

In summary, thermal energy conversion technology based on the thermogalvanic effect is a relatively cutting-edge form of energy conversion. In this field, various thermoelectric materials play an essential role. However, thermoelectric materials have faced challenges in their widespread application in industry, households, and other scenarios. The emerging hydrogel thermocell has the advantages of high thermopower, low cost, low thermal conductivity, excellent flexibility, and scalability, which may be an ideal choice for thermoelectric materials working at room temperature and expanding the application range of thermoelectric materials. In recent years, they have made considerable progress by optimizing electrodes, designing electrolytes, and improving device modules, but there are still some challenges.

Firstly, the underlying mechanism of hydrogel thermocells has yet to be fully understood. The associated theoretical framework has yet to be completely established. There is an urgent need for effective theoretical guidance to facilitate material optimization and design for practical applications. Consequently, the current research should focus on deepening the understanding of its mechanism and promoting the development of a comprehensive and systematic research framework.

Secondly, the efficiency of hydrogel thermocells should be improved. The three parameters of thermopower, conductivity, and thermal conductivity within the thermocell are interdependent, presenting an extreme challenge in achieving efficient improvement. For example, tuning the solvation structure of the redox couple can increase the thermopower but simultaneously decrease the conductivity. Although optimizing electrodes can accelerate reactions and enhance conductivity without lowering thermopower, thermodynamic constraints impose limits on conversion efficiency. Future research should focus on the synergistic optimization of electrolytes and electrodes to circumvent these issues. This approach aims to decouple the three parameters, thereby improving the efficiency of a single thermocell.

Finally, given the high thermopower characteristic of thermocells, their application potential in flexible sensor and refrigeration fields deserves further exploration. In the field of flexible sensor technology, hydrogel thermocells have been combined with various sensor types, such as pressure, humidity, light, and power sensors. These integrated systems are poised to find utility in various applications, such as electronic skin, monitoring human activities, personalized healthcare, and facilitating advanced human-computer interfaces.

DECLARATIONS

Authors' contributions

Literature review, data collection, data analysis and interpretation, and manuscript drafting: Liu W, Fang Y
Conceptualization and content development: Lyu X, Peng X, Luo ZZ
Critical revision of the manuscript, supervision, and project administration: Luo ZZ, Zou Z

Availability of data and materials

Not applicable.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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