

Multistimuli Responsive and Thermoregulated Capability of Coaxial Electrospun Membranes with Core-sheath Structure and Functional Polypyrrole Layer

Meng-Hang Gao[†], Wen Feng[†], Xiao-Dong Qi^{*}, and Yong Wang^{*}

Key Laboratory of Advanced Technologies of Materials (Ministry of Education), School of Materials Science & Engineering, Southwest Jiaotong University, Chengdu 610031, China

 Electronic Supplementary Information

Abstract Developing thermal management fabrics with good energy storage and multistimuli responsive properties is important for regulating the body temperature in complex environment. Herein, the intelligent nonwoven membranes were fabricated via a coaxial electrospinning method, resulting in a core-sheath structure with poly(ethylene glycol) (PEG) as core and polyurethane (PU) as sheath. Additionally, polypyrrole (PPy) with good light absorption ability and electrical conductivity was deposited onto the surface of the PU@PEG electrospun fibers via electrochemical polymerization. The PPy layer enabled the membranes to respond quickly to sunlight and electrical stimuli. The membranes could heat up to 86 °C under simulated sunlight within 200 s or produce remarkable electrothermal effect under a low voltage input of only 1 V, exhibiting efficient energy conversion and storage performances. The photothermal and electrothermal conversion effect could be easily adjusted by controlling the polymerization time of PPy. Therefore, the multifunctional membranes with high latent heat, good mechanical properties as well as excellent photothermal/electrothermal conversion ability are promising in personal thermal management applications.

Keywords Phase change materials; Polypyrrole; Coaxial electrospinning; Photothermal conversion; Electrothermal conversion

Citation: Gao, M. H.; Feng, W.; Qi, X. D.; Wang, Y. Multistimuli responsive and thermoregulated capability of coaxial electrospun membranes with core-sheath structure and functional polypyrrole layer. *Chinese J. Polym. Sci.* 2022, 40, 1380–1388.

INTRODUCTION

As the heat exchange interface between the skin and atmosphere, the clothing fabrics play a major part in the thermal management of humans.^[1,2] Nowadays, the clothing fabrics are not only expected to ensure that the human body is in a comfortable temperature range, but also to be functional and intelligent to adapt to complex environmental conditions.^[3–5] Personal thermal management fabrics (PTMFs) can adjust the surface temperature of human body and then help the body adapt to the temperature change of the environment.^[6] Among them, the PTMFs based on phase change materials (PCMs), showing thermal buffering performance in high temperature environment as well as thermal insulation capability in low temperature environment, have attracted the attention of many researchers.^[7–9]

PCMs, a promising thermal energy storage material, can absorb and release abundant latent heat thanks to their high enthalpy value and suitable phase transition tempera-

ture.^[10,11] However, the leakage during phase change process and excessive rigidity of PCMs greatly limits their applications.^[12–15] Encapsulating PCMs into fibers is helpful to solve the leakage issue and promote the flexible deformation capacity of thermal management fabrics.^[16,17] The coaxial electrospinning method is applied to fabricate ultrafine phase change fibers (PCFs), where the polymer materials work as the “shell” to completely encapsulate the PCM “core”.^[18,19] For example, some core-shell PCFs, including octadecane/polyvinyl pyrrolidone,^[20] paraffin wax/polyacrylonitrile,^[21] and poly(tetradecyl acrylate)/poly(ethylene terephthalate),^[22] were prepared by the coaxial electrospinning technology, showing satisfied encapsulation efficiency and thermal energy performance.

Despite their excellent abilities, the lack of response to multi-stimuli seriously constrains the utilization of PCFs.^[23,24] Combining PCFs and intrinsically conductive polymers is an efficient strategy to realize the conversion and storage of different energies including solar energy and electrical energy.^[25,26] Polypyrrole (PPy) is a type of heterocyclic conjugated conductive polymer that is usually to be coated with fabrics to improve their electrical conductivity.^[27,28] PPy also exhibits excellent photothermal performance due to its wide spectrum light-absorption property.^[29] Therefore, it is expected

* Corresponding authors, E-mail: qxdjianhu@163.com (X.D.Q.)

E-mail: yongwang1976@swjtu.edu.cn (Y.W.)

[†] These authors contributed equally to this work.

Received February 19, 2022; Accepted April 21, 2022; Published online July 12, 2022

ted to combine PPy with PCFs to prepare thermal management fabrics with responsiveness to multistimuli, such as light and electric.

In this work, the thermal management fabrics with photo-thermal and electrothermal conversion functions were prepared *via* a coaxial electrospinning method and electrochemical polymerization of PPy. The thermoplastic elastomer polyurethane (PU) was chosen as the supporting shell, which was easily electrospun into fibrous fabrics with good flexibility.^[30] Poly(ethylene glycol) (PEG) with high enthalpy value and proper phase change temperature was chosen as the core to store thermal energy.^[31] Furthermore, the PPy layer was uniformly deposited onto the surface of the PU@PEG membranes through electrochemical polymerization. The PPy layer not only enhanced the interaction among microfibers and mechanical properties of membranes, but also endowed the membranes with excellent photothermal and electrothermal conversion performance. Therefore, the integrative performances of the multiresponsive PU@PEG-PPy membranes promise them great potential in thermal management under various environmental conditions.

EXPERIMENTAL

Materials

Poly(ethylene glycol) (PEG, $M_w=1500$ g/mol), pyrrole (Py) and ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were purchased from Chengdu Kelong Chemical Reagent Co., Ltd. (China). Polyurethane (PU, 1180A) was purchased from Bayer Company (Germany), and the hardness of PU was 80 shore A. *N,N*-dimethylformamide (DMF) and tetrahydrofuran (THF) were obtained from Guangzhou Chemical Reagent Factory (China). *p*-toluenesulfonic acid monohydrate (PTSA), disodium hydrogen phosphate dodecahydrate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$) and disodium dihydrogen phosphate anhydrous (NaH_2PO_4) were purchased from Aladdin Reagent Co., Ltd.

Fabrication of the PU@PEG Coaxial Electrospun Membranes

The PU@PEG membranes were prepared *via* a coaxial electrospinning method. Firstly, PU was dissolved in a blended solvent of DMF/THF ($V_{\text{DMF}}:V_{\text{THF}}=1:1$) during magnetic stirring at 60 °C with the concentration of 15 wt%. PEG was dissolved in DMF to prepare mixed solutions with different mass fractions of 50 wt%, 70 wt% and 80 wt%. Secondly, the above prepared PU solution and PEG solution were used to prepare the coaxial electrospun membranes containing “core-shell”-like PU@PEG fibers, in which PU formed the “sheath” while PEG acted as the “core”. The flow rates of PU solution and PEG solution were respectively 2 mL/h and 0.5 mL/h. The electrospinning conditions were set at room temperature (25 °C), humidity of 60%, power supply voltage of 11 kV, and the distance between the syringe and the plate collector was 13 cm. Lastly, the membranes were placed in a vacuum oven under 45 °C for 12 h. And the coaxial electrospun membranes were defined as the PU@PEG_y, where *y* represented the PEG concentration in the PEG solutions (*y*=50 wt%, 70 wt%, 80 wt%).

Electrochemical Polymerization of PPy onto the PU@PEG Membranes

The polymerization of PPy layer onto the PU@PEG membranes

by an electrochemical method is shown in Fig. 1. Firstly, an electrolyte phosphate buffer solution with a pH of 6.86 was prepared by mixing Na_2HPO_4 and NaH_2PO_4 solution. Then, 0.14 mL of Py monomer and 0.57 g of PTSA were added to 20 mL of phosphate buffer, and stirred evenly to prepare an electrolyte solution. Secondly, the two sides of the PU@PEG membranes were sprayed with ion sputtering gold to achieve the electrical conductivity. The PU@PEG membranes were sandwiched on the working electrode as the anode electrode, and Ag/AgCl was selected as the reference electrode and a platinum sheet of 5 mm × 10 mm was used as the auxiliary electrode. The three electrodes were sequentially connected to the electrochemical workstation for electrochemical polymerization with a constant current mode under 0.6 mA. The polymerization time was set as 0.5, 1, 2 and 4 h. After the reaction, the membranes were washed by using distilled water for several times and ultrasonicated for 20 min to remove dissociative PPy. The obtained membranes with different PPy polymerization time were defined as the PU@PEG-PPy_t, where *t* represented the polymerization time (*t*=0.5, 1, 2, 4 h). For comparison, the PU@PPy membrane was also prepared through the mentioned above procedures, and the polymerization time of PPy was maintained at 4 h.

Characterizations

The morphologies of the membranes were photographed through the scanning electron microscope (SEM, JSM-7800F, Japan) and the accelerating voltage is 20 kV. A transmission electron microscope (TEM, JEM-2100F, Japan) was used to observe the morphology of the PU@PEG-PPy1. Through gauging at least 100 microfibers, the average diameter of the electrospun membrane can be obtained. The fourier transform infrared spectroscope (FTIR, Thermo iS50, USA) was applied to determine the interplay among PU@PEG with PPy. The structures of the composites were observed by the wide-angle X-ray diffractometer (WAXD, Panalytical Empyrean,

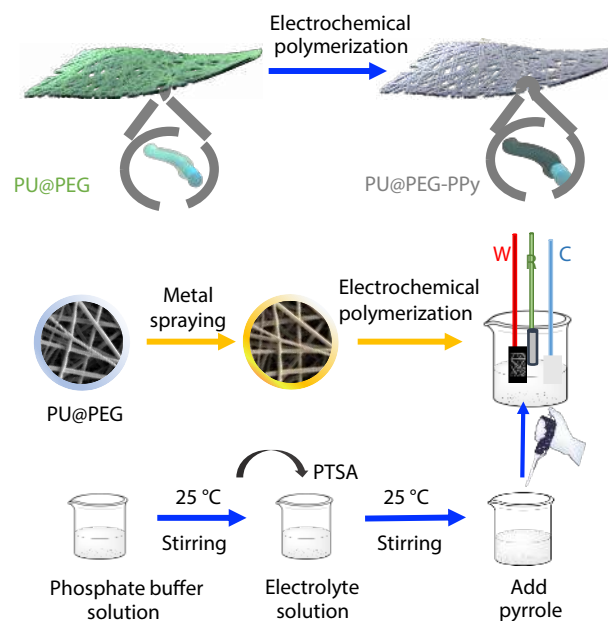


Fig. 1 Schematic diagram of the preparation procedure of the PU@PEG-PPy coaxial electrospun membranes.

Netherlands). And the differential scanning calorimeter (DSC, TA 2500, USA) was used to investigate the melting and crystallization actions of the neat PEG, PU@PEG and PU@PEG-PPy membranes. The procedure was set as firstly heating from 0 °C to 80 °C and then cooling from 80 °C to 0 °C with a constant speed of 5 °C/min. The mechanical properties of the composites were measured by the universal testing machine (AGS-J, Shimadzu, Japan) at 25 °C with an unchanging speed of 50 mm/min.

UV-Vis-NIR spectrophotometer (UV-3600i, Shimadzu, Japan) was used to measure the light absorption intensity of the PU@PEG-PPy membranes. The photothermal conversion ability of the composites was studied through using a xenon lamp (HSX-F300, China) to imitate sunlight. An infrared thermal imaging camera (FLIR T620, USA) was applied to calendar the temperature change of the PU@PEG-PPy membranes during irradiation. The four-point probe (DAQ6510, USA) could be used to measure the electrical conductivity of the PU@PEG-PPy membranes. The electrothermal energy conversion of the PU@PEG-PPy membranes was tested by the DC power supply (RXN-603D, China). Thermogravimetry analysis (TGA) tests were performed on thermogravimetry analysis instrument TGA/DSC³⁺ (Mettler Toledo, Switzerland) in the temperature range of 30–800 °C at a heating rate of 10 °C/min under nitrogen atmosphere and the mass of all samples was kept within 5–10 mg.

RESULTS AND DISCUSSION

Structure and Morphology Characterization

The PU@PEG coaxial membranes were firstly prepared through a representative coaxial electrospinning device and then the PU@PEG-PPy membranes were obtained by electrochemical polymerizing of PPy onto the PU@PEG surface. From Fig. 1, the PU@PEG microporous membranes with a "core-sheath" like structure could be acquired, in which the PU acts as a supporting sheath and the PEG works as an internal PCM core. The concentration of PEG solution has an important impact on the morphology of PU@PEG membranes. Fig. S1(a₁)–S1(c₂) (in the electronic supplementary information, ESI) show that the PU@PEG50 membrane possesses some obvious bifurcations when the PEG concentration is 50 wt% and the fiber diameter distribution is quite wide. When the PEG concentration is 80 wt%, the electrospun fibers seriously adhere to each other. On the contrary, the PU@PEG70 membrane exhibits relatively smooth electrospun fibers and a uniform fiber diameter of about 4 μm. From Fig. S2 (in ESI), the characteristic bands of PEG and PU are simultaneously observed in the FTIR spectrum, and these bands are not significantly shifted. This result confirms that it is mostly physical interaction among PEG with PU in the PU@PEG coaxial electrospun membranes.

Next, the PU@PEG70 membranes would be selected as the template to load PPy, which was *in situ* polymerized onto the membranes by an electrochemical method. TEM image (Fig. S3 in ESI) clearly shows that PPy layer homogeneously covers the surface of the PU@PEG70 coaxial electrospun microfibers. Fig. S4(a) (in ESI) shows the TGA curves of the PU@PEG-PPy membranes with different PPy polymerization time. With the increase of PPy content, the residual weight of the PU@PEG-PPy membranes increases after the temperature is raised to

800 °C. In the DTG curves (Fig. S4b, in ESI), the thermal degradation of PU@PEG mainly has two processes, namely the decomposition of PU at 280–315 °C and the decomposition of PEG at 360–420 °C. After loading PPy on the PU@PEG membranes, a new decomposition peak is observed at around 340 °C, which corresponds to the decomposition of PPy. As shown in Figs. 2(a)–2(d), the fiber diameter of PU@PEG-PPy membranes continues to increase with the polymerization time gradually extended from 0.5 h to 4 h. When the polymerization time is 4 h, the diameter of PU@PEG-PPy4 membrane is the highest, and its surface is fully wrapped with PPy protrusions, which is beneficial for the formation of electrically conductive pathways. After introducing the PPy layer, the characteristic peaks of PU and PEG are completely covered (Fig. 2e). The characteristic bands of PPy are clearly seen from Fig. 2(f), such as the bands at 1039 cm^{−1} corresponding to the out-of-plane bending vibration of C—H group. The bands at 1620, 1400 and 1261 cm^{−1} corresponding to the stretching vibration of C=C group, C—C group and C—N group, respectively.^[32] This result confirms that PPy was successfully polymerized onto the surface of the electrospun PU@PEG fibers by the electrochemical polymerization. In addition, the interaction between PPy and PU can be also confirmed through FTIR characterization as shown in Fig. S5 (in ESI). The characteristic bands at 3450, 3314 and 3309 cm^{−1} are corresponded to the stretching vibration of N—H group in PPy, PU and PU@PPy, respectively. It is known that the N—H group is sensitive to hydrogen bonding. Compared with PPy and neat PU, the N—H stretching band of the PU@PPy shifts to a lower wavenumber, suggesting the hydrogen bonding between N—H groups in PU and PPy.

Fig. 2(g) displays that the typical crystal diffraction peaks of PEG are found from the PU@PEG and PU@PEG-PPy membranes, illustrating the presence of PEG. It can be clearly noted in the PU@PEG-PPy membranes that there is a wide diffraction peak at around 22.5°, which corresponds to the amorphous region of PPy. At the same time, the diffraction peak intensity of PPy increases as the polymerization time increases, indicating that more PPy is polymerized onto the surface of the PU@PEG coaxial electrospun membranes.

Thermophysical and Mechanical Properties of the PU@PEG-PPy Membranes

For thermal management fabrics based on PCMs, the thermophysical parameters such as the enthalpy value and phase transition temperature determine their thermal regulation ability and applicable temperature. Figs. 3(a) and 3(b) display the DSC heating and cooling curves of the PU@PEG-PPy membranes with different PPy polymerization time. The thermophysical parameters are listed in Table 1. The results demonstrate that the T_m and T_c of the PU@PEG-PPy membranes are almost unchanged compared with the PU@PEG, which indicates that the introduction of PPy layer has a little impact on the crystallization behavior of PEG. With the extension of PPy polymerization time, the PPy content in the PU@PEG-PPy membranes increases, and meanwhile the relative PEG content decreases. Since the enthalpy value is related to the PEG content, the enthalpy values of the PU@PEG-PPy membranes are total lower. After the polymerization of PPy, the relative contents of PEG in the PU@PEG-PPy0.5–PU@PEG-PPy4

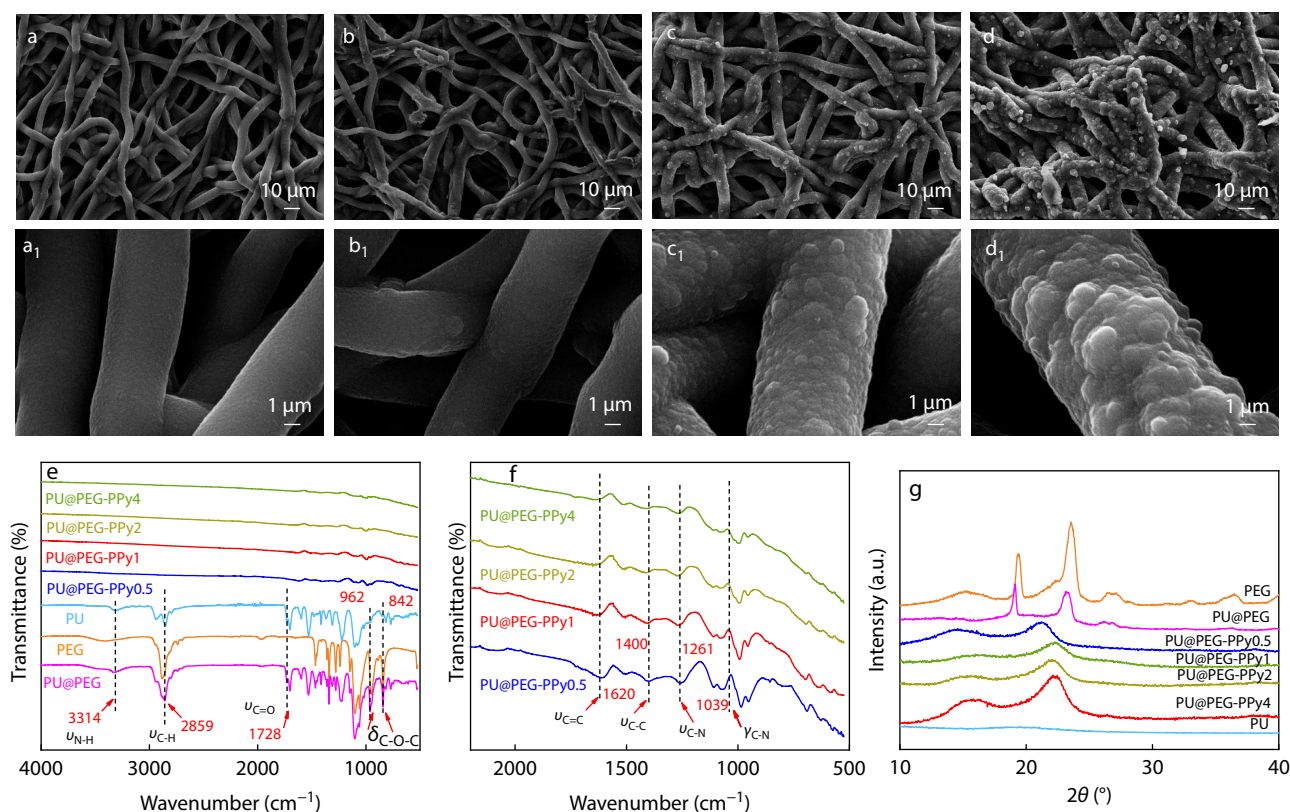


Fig. 2 SEM images of the PU@PEG-PPy membranes with dissimilar polymerization time: (a, a₁) 0.5 h, (b, b₁) 1 h, (c, c₁) 2 h, (d, d₁) 4 h; (e, f) FTIR spectra and (g) WAXD patterns of PU, PEG, PU@PEG and PU@PEG-PPy membranes.

membranes are 49.6 wt%, 44.2 wt%, 41.2 wt% and 39.2 wt%, respectively. The corresponding ΔH_m values of the PU@PEG-PPy0.5–PU@PEG-PPy4 membranes are respectively 81.0, 68.0, 64.2 and 62.8 J/g. The corresponding ΔH_c values of the PU@PEG-PPy0.5–PU@PEG-PPy4 membranes are 72.0, 59.0, 57.9 and 55.7 J/g, respectively. Although the PPy layer leads to a certain decrease in enthalpy value, the crystallization behavior of PEG is not obviously inhibited. The PU@PEG-PPy4 membrane still retains a high ΔH_m value of 62.8 J/g and ΔH_c value of 55.7 J/g, which shows great application prospects in thermal management fabrics.

Furthermore, the effect of PPy layer on the mechanical properties of the PU@PEG-PPy membranes was studied through tensile experiments. It has already been reported that PPy particles with strong rigidity can be used as a reinforcement filler to improve the strength of polymer matrix.^[33] As shown in Figs. 3(c) and 3(d), the PPy layer enhances the tensile strength of the PU@PEG-PPy membranes. The tensile strength of the PU@PEG-PPy4 reaches 14.0 MPa, which is about 3.5 times of that of the PU@PEG (3.3 MPa). Interestingly, the introduction of PPy also increases the elongation at break of the PU@PEG-PPy membranes. When the polymerization time of PPy is extended to 4 h, the elongation at break is increased from 563.8% to 784.1%. To study the reinforcing mechanism, SEM was applied to observe the fracture surfaces of PU@PEG-PPy4 membranes. The microfibers in PU@PEG-PPy4 (Fig. 3e) are bond together during stretching process, which is helpful to improve both the strength and toughness of PU@PEG-PPy membranes. PPy layer is uni-

formly polymerized onto the surface of microfibers, and the adjacent microfibers can form hydrogen interactions due to the polar groups of PPy. Therefore, the PPy layer enhances the interactions among microfibers and promotes the mechanical property improvement of the PU@PEG-PPy membranes. In addition, the elongation at break of PU@PEG-PPy4 can reach as high as 784.1% due to the elastic PU sheath. And the digital photographs of the PU@PEG-PPy4 during stretching-recovery process are shown in the Fig. S6 (in ESI) to clearly demonstrate the elasticity of the membranes. The PU@PEG-PPy4 membrane can be stretched to 200% deformation under an external force and quickly recover to its original length when the external force is removed, which illustrates the good elasticity of the PU@PEG-PPy membranes. It can be observed from Fig. 3(f) that the PU@PEG-PPy4 membrane (weight: 0.12 g) can suffer a weight of 50 g without fragile. Besides, the PU@PEG-PPy4 membrane did not show obvious leakage of PEG at 80 °C (Fig. S7 in ESI), suggesting that the “core-shell” structure plays a positive role in encapsulating molten PEG.

Photothermal Conversion Performance of the PU@PEG-PPy Membranes

The utilization of sustainable solar energy in personal thermal management fabrics is an effective energy input strategy.^[34] PPy has a molecular skeleton of a conjugated structure so that electrons stimulated by light can migrate freely along the conjugated skeleton.^[35] Then these stimulated electrons convert light energy into heat energy through non-radiative

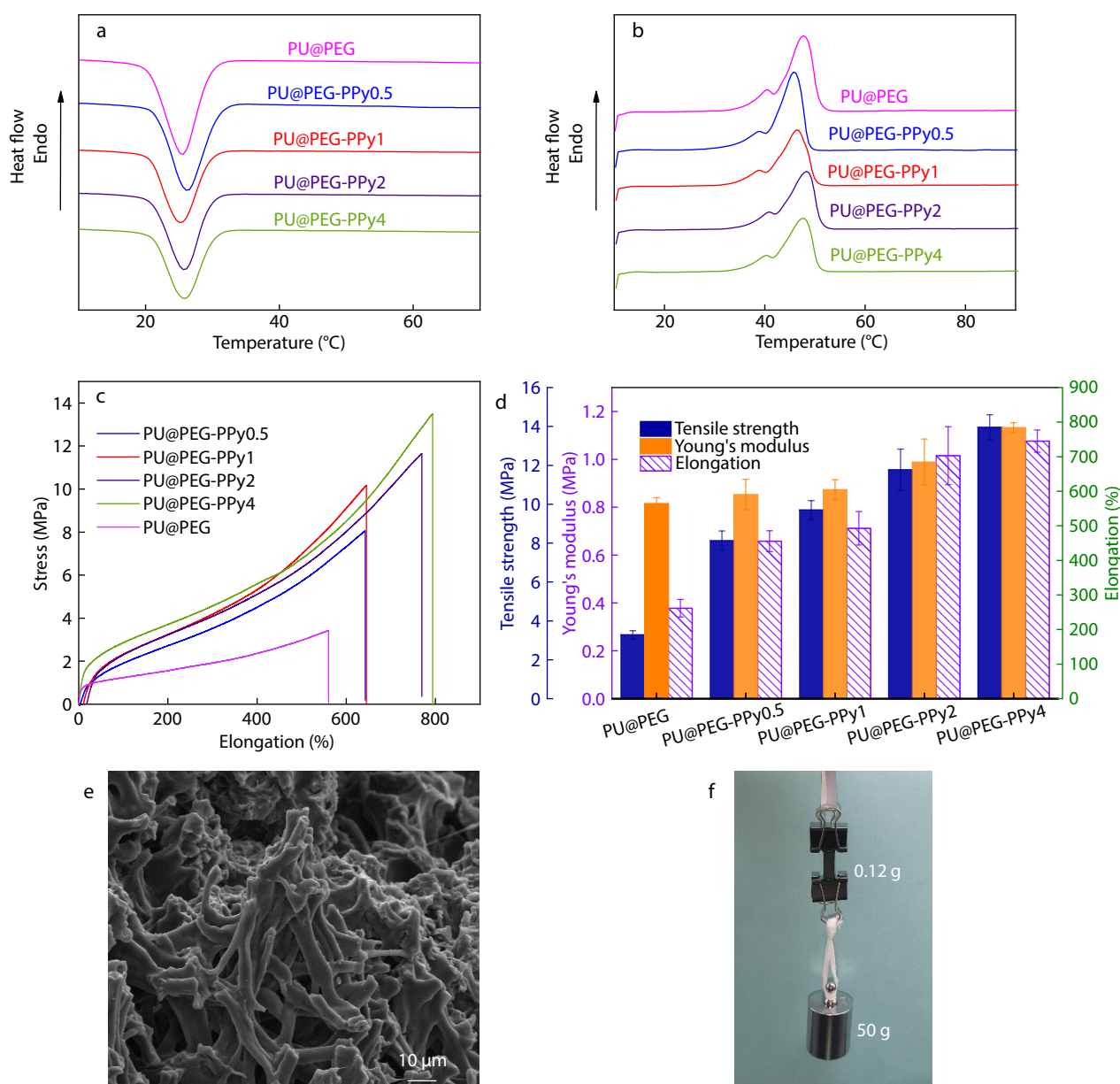


Fig. 3 DSC curves of (a) heating and (b) cooling progress of the PU@PEG and PU@PEG-PPy membranes; (c) Tensile stress-strain patterns of the PU@PEG and PU@PEG-PPy membranes; (d) Mechanical performance parameters of the PU@PEG and PU@PEG-PPy membranes; (e) SEM image of the PU@PEG-PPy4 membrane after tensile test; (f) Digital picture displaying that the PU@PEG-PPy4 membrane (0.12 g) endures a weight of 50 g.

Table 1 The melting and crystallization parameters of the PU@PEG and PU@PEG-PPy membranes received from the DSC tests.

Sample	PEG (wt%)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)
PU@PEG	53.8	48.3	84.9	27.7	83.2
PU@PEG-PPy0.5	49.6	45.9	81.0	26.2	72.0
PU@PEG-PPy1	44.2	46.5	68.0	25.9	59.0
PU@PEG-PPy2	41.2	47.7	64.2	25.8	57.9
PU@PEG-PPy4	39.2	47.5	62.8	25.7	55.7

relaxation or molecular vibration to achieve efficient energy transfer and photothermal conversion. Therefore, the introduction of PPy as photothermal layer can impart the PU@PEG membranes with a good photothermal conversion performance. The absorbance of the PU@PEG membranes

before and after depositing PPy layer was measured by UV-Vis-NIR spectrophotometer. The light absorption intensity of the PU@PEG-PPy membranes increases with the extension of polymerization time (Fig. 4a), indicating that more PPy polymerized onto the microfibers. Different from the solution samples reported in the literature,^[36] the absorbance curves of the PU@PEG-PPy membranes do not display the feature absorbance peaks of PPy, which may be due to the high absorbance ability of the membranes.

To evaluate the photothermal conversion performance of the PU@PEG-PPy membranes under sunlight, the membranes were placed inside melamine foam to avoid contact with external heat and an infrared thermal camera was used to calendar the instantaneous temperature variations of

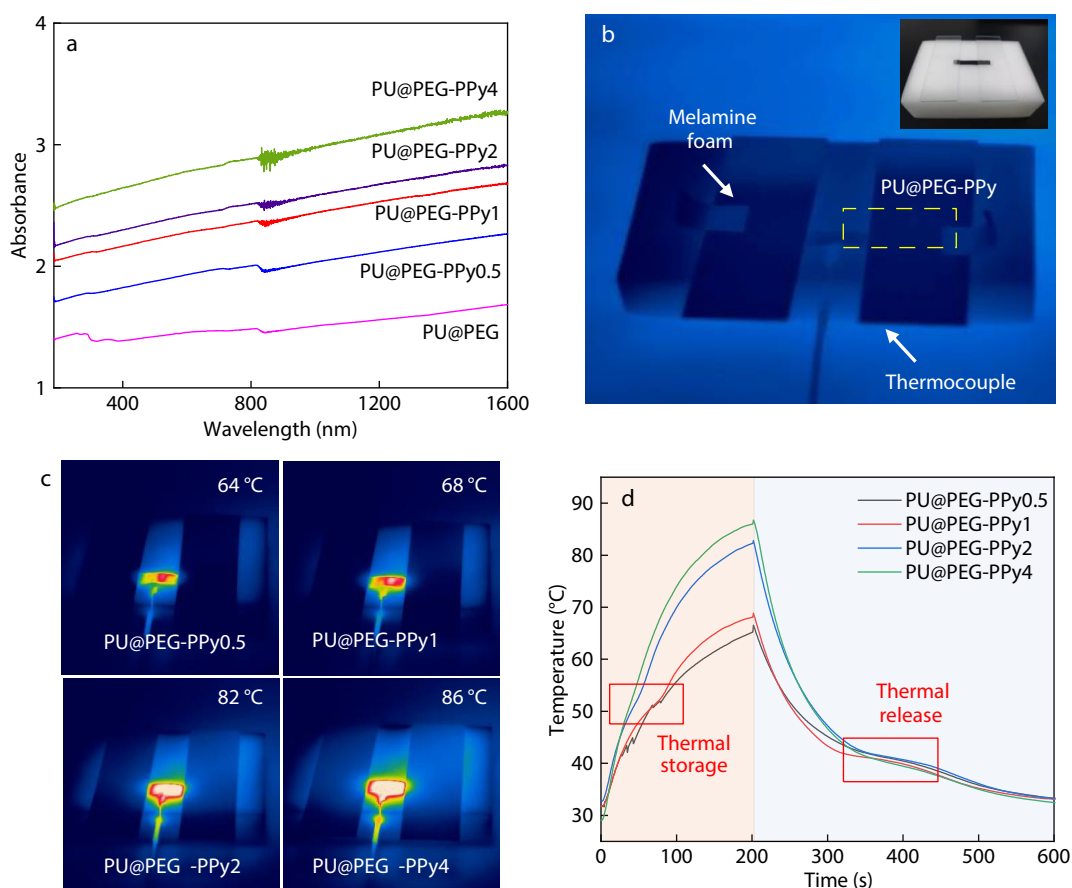


Fig. 4 (a) UV-Vis-NIR absorption spectra of the PU@PEG and PU@PEG-PPy membranes; (b) Digital photo displaying the light-to-heat conversion measurement equipment; (c) Infrared thermal photos of the PU@PEG-PPy membranes after irradiation for 200 s; (d) Temperature change curves of the PU@PEG-PPy membranes under or without the simulated sunlight.

membranes (Fig. 4b). And the PU@PEG-PPy membranes exhibit good photothermal conversion performance due to the strong light adsorption ability of PPy layer. As shown in Fig. 4(c), when the PPy polymerization time increases from 0.5 h to 4 h, the temperatures of the corresponding PU@PEG-PPy membranes after 200 s of sunlight illumination reach 64, 68, 82 and 86 °C, respectively. The temperature variation curves of the PU@PEG-PPy membranes under or without sunlight illumination are displayed in Fig. 4(d). The membranes with different PPy polymerization time exhibit different temperature rising speeds. The PU@PEG-PPy0.5 and PU@PEG-PPy1 membranes heat up rapidly under sunlight illumination. Interestingly, a temperature plateau is observed from 48 °C to 52 °C, which corresponds to the solid-to-liquid phase transition of PEG. During this period, the light energy is assimilated by the PPy shell and transformed into heat energy and then stored by PEG as latent heat. However, the phase change platform of the PU@PEG-PPy4 membrane becomes inconspicuous owing to the highest PPy loading and super photothermal conversion ability of PPy. When the sunlight source is removed, the temperature of PU@PEG-PPy membranes decreases quickly and then a heat release platform (36–42 °C) occurs in the cooling period. The occurrence of such phenomenon is attributed to the fact that the pre-stored light energy is liberated by the liquid-to-solid phase transition of PEG, exhibiting good light energy conversion and storage capability of PU@PEG-

PPy membranes. In general, the uniformly coated PPy layer can endow the PU@PEG-PPy membranes with reliable photothermal conversion ability. And by controlling the polymerization time of PPy, the light absorption and photothermal conversion capacities of the PU@PEG-PPy membranes can be easily adjusted, which provides the possibility to fabricate light-responsive thermal management fabrics.

Electrothermal Conversion Performance of the PU@PEG-PPy Membranes

Due to the successful polymerization of PPy shell, the PU@PEG-PPy membranes can not only show photothermal conversion ability, but also show good electrothermal conversion ability. It can make full use of the conductive PPy shell to input electrical energy into the PU@PEG-PPy membranes to realize thermal regulation. As shown in Fig. 5(a), the electrical conductivity of the PU@PEG-PPy membranes increases with the extension of PPy polymerization time. The PU@PEG-PPy0.5 membrane shows the electrical conductivity of about 267 S/m, and for the PU@PEG-PPy4 membrane, the electrical conductivity is dramatically increases up to 1184 S/m. The excellent electrical conductivity ensures good electric-heating performance under a low voltage input. The electric-heating effect is tested under a voltage of 3 V and the results are displayed in Fig. 5(b). The PU@PEG-PPy membranes with different PPy contents all respond quickly within 2 s and reach the temperature

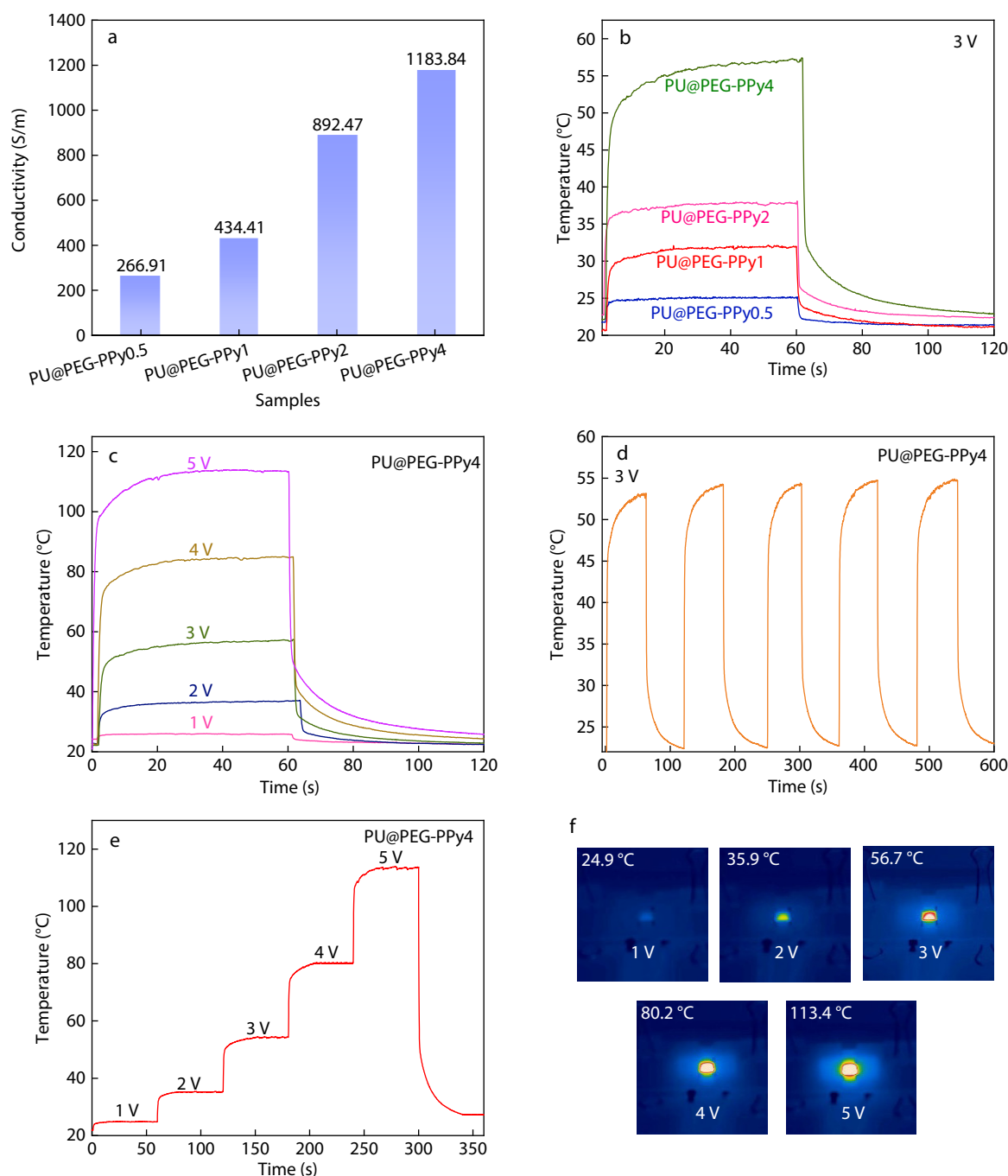


Fig. 5 (a) Electrical conductivity of the PU@PEG-PPy membranes; (b) Electric-heating temperature curves of the PU@PEG-PPy membranes at a voltage of 3 V; (c) Electric-heating temperature curves of the PU@PEG-PPy4 at different voltages (1–5 V); (d) Temperature curves of the PU@PEG-PPy4 under 3 V with five electric-heating cycles; (e) the temperature curves of the PU@PEG-PPy4 under the increasing voltages from 1 V to 5 V; (f) Infrared thermal images showing the electric-heating performance of the PU@PEG-PPy4 under different voltages.

equilibrium within 20 s. It is worth noting that the PU@PEG-PPy4 can rise from 20 °C to 57.3 °C within 2 s. When the voltage input is removed, the PU@PEG-PPy4 quickly cools down and then the cooling speed slows down within the temperature range from 30 °C to 25 °C.

The influence of input voltage on the electric-heating performance of the PU@PEG-PPy4 is shown in Fig. 5(c). The temperature correspondingly increases to 26.0, 36.8, 57.3, 85.0

and 113.5 °C, respectively, when the input voltage increases to 1, 2, 3, 4 and 5 V respectively. Benefiting from the high electrical conductivity, the PU@PEG-PPy membranes exhibit outstanding electric-heating performance even under a low voltage. From Fig. 5(d), the electric-heating stability of the PU@PEG-PPy4 was tested with or without an input voltage of 3 V. The time of controlling the heating and cooling cycle was 120 s. The equilibrium heating and cooling temperature

curves in each cycle are almost the same, suggesting a reliable stability of this Joule heater. Based on the high electrical conductivity, the electric-heating performance of PU@PEG-PPy4 was tested under continuous voltage variations (Fig. 5e). When the input voltage is increased by 1 V in every 60 s, the temperature of PU@PEG-PPy4 rapidly rises to the equilibrium temperature under this voltage. During the electric-heating period, the temperature change of the PU@PEG-PPy4 forms an obvious stepped heating stage, and the equilibrium temperature increases monotonously as a function of voltage. As shown in Fig. 5(f), the infrared thermal images visually present the electric-heating effect of the PU@PEG-PPy4 when the temperature reaches equilibrium state under different voltages. It can be seen that the electric-heating effect of PU@PEG-PPy membranes has the characteristics of high efficiency and sensitivity, which is of great significance for personal thermal management in extreme environments such as the low ambient temperature and at night. For instance, a low-voltage input button battery (3 V) can be connected with the PU@PEG-PPy membranes to realize the rapid electric-heating performance. In general, the PPy layer endows the PU@PEG-PPy membranes with excellent light responsibility and Joule heating performance, which provides multiple choice of energy utilization.

CONCLUSIONS

In this work, taking use of the excellent electrical conductivity and light absorption ability of PPy, PPy layer was uniformly deposited onto the PU@PEG coaxial electrospun membranes by electrochemical polymerization. The combination of elastic PU sheath, energy storage PEG core and effective PPy layer resulted in integrated performances, including high phase change enthalpy (81.0 J/g), improved mechanical property and remarkable photothermal/electrothermal effect. The PPy layer enhanced the interaction among microfibers, the tensile strength and the elongation at break of the PU@PEG-PPy4 reached 14.0 MPa and 784.1%, respectively. Furthermore, the PPy layer enabled the fabrics to respond quickly to different stimuli, such as sunlight and electric. The photothermal and electrothermal conversion effect could be easily adjusted by controlling the polymerization time of PPy. The PU@PEG-PPy membranes exhibit good light absorption and photothermal conversion capabilities, which can quickly reach 86 °C under simulated sunlight within 200 s. The electrical conductivity of the PU@PEG-PPy4 membrane is as high as 1184 S/m, showing rapid electric-heating effect even at a low voltage of 1 V. Considering these properties, the multistimuli responsive membranes display great application prospects in thermal management systems and wearable devices.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of

charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2773-6>.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 51803172 and 51673159), the Youth Science and Technology Innovation Team of Sichuan Province of Functional Polymer Composites (No. 2021JDTD0009) and the Key Research and Development Program of Sichuan Province (No. 2022YFG0281). SEM characterizations were supported by the Analytical and Testing Center of Southwest Jiaotong University.

REFERENCES

- Pakdel, E.; Naebe, M.; Sun, L.; Wang, X. G. Advanced functional fibrous materials for enhanced thermoregulating performance. *ACS Appl. Mater. Interfaces* **2019**, *11*, 13039–13057.
- Shi, S.; Han, Y. T.; Hu, J. L. Robust waterproof and self-adaptive breathable membrane with heat retention property for intelligent protective cloth. *Prog. Org. Coat.* **2019**, *137*, 105303.
- Li, G. Y.; Hong, G.; Dong, D. P.; Song, W. H.; Zhang, X. T. Multiresponsive graphene-aerogel-directed phase-change smart fibers. *Adv. Mater.* **2018**, *30*, 1801754.
- Zhang, K. M.; Wang, Z.; Liu, Y. T.; Zhao, H. Y.; Gao, C. H.; Wu, Y. M. Cephalopods-inspired repairable MWCNTs/PDMS conductive elastomers for sensitive strain sensor. *Chinese J. Polym. Sci.* **2022**, *40*, 384–393.
- Zuo, X. L.; Wang, S. F.; Le, X. X.; Lu, W.; Chen, T. Self-healing polymeric hydrogels: toward multifunctional soft smart materials. *Chinese J. Polym. Sci.* **2021**, *39*, 1262–1280.
- Wu, J.; Hu, R.; Zeng, S.; Xi, W.; Huang, S.; Deng, J.; Tao, G. Flexible and robust biomaterial microstructured colored textiles for personal thermoregulation. *ACS Appl. Mater. Interfaces* **2020**, *12*, 19015–19022.
- Yu, X.; Li, Y.; Yin, X.; Wang, X.; Han, Y.; Si, Y.; Yu, J.; Ding, B. Corncoblike, superhydrophobic, and phase-changeable nanofibers for intelligent thermoregulating and water-repellent fabrics. *ACS Appl. Mater. Interfaces* **2019**, *11*, 39324–39333.
- Zhang, W.; Zhang, X.; Xu, Y.; Xu, Y.; Qiao, J.; Shi, T.; Huang, Z.; Liu, Y. G.; Fang, M.; Min, X.; Wu, X. Flexible polyethylene glycol/polyvinylpyrrolidone composite phase change fibres: preparation, characterization, and thermal conductivity enhancement. *Polymer* **2021**, *214*, 123258.
- Lin, L.; Choi, Y.; Chen, T.; Kim, H.; Lee, K. S.; Kang, J. M.; Lyu, L.; Gao, J. F.; Piao, Y. Superhydrophobic and wearable TPU based nanofiber strain sensor with outstanding sensitivity for high-quality body motion monitoring. *Chem. Eng. J.* **2021**, *419*, 129513.
- Huang, X. B.; Chen, X.; Li, A.; Atinafu, D.; Gao, H. Y.; Dong, W. J.; Wang, G. Shape-stabilized phase change materials based on porous supports for thermal energy storage applications. *Chem. Eng. J.* **2019**, *356*, 641–661.
- Xia, W.; Fei, X.; Wang, Q. Q.; Lu, Y. Y.; Innocent, M. T.; Zhou, J. L.; Yu, S. L.; Xiang, H. X.; Zhu, M. F. Nano-hybridized form-stable ester@F-SiO₂ phase change materials for melt-spun PA6 fibers engineered towards smart thermal management fabrics. *Chem. Eng. J.* **2021**, *403*, 126369.
- Yang, J.; Tang, L. S.; Bai, L.; Bao, R. Y.; Liu, Z. Y.; Xie, B. H.; Yang, M. B.; Yang, W. High-performance composite phase change materials for energy conversion based on macroscopically three-dimensional structural materials. *Mater. Horiz.* **2019**, *6*, 250–273.

- 13 Shi, J. M.; Qin, M. L.; Aftab, W.; Zou, R. Q. Flexible phase change materials for thermal energy storage. *Energy Storage Mater.* **2021**, *41*, 321–342.
- 14 Hu, W. W.; Shi, X. Y.; Gao, M. H.; Huang, C. H.; Huang, T.; Zhang, N.; Yang, J. H.; Qi, X. D.; Wang, Y. Light-actuated shape memory and self-healing phase change composites supported by MXene/waterborne polyurethane aerogel for superior solar-thermal energy storage. *Compos. Commun.* **2021**, *28*, 100980.
- 15 Pantoja, M.; Alvarado, T.; Cakmak, M.; Cavicchi, K. A. Stearic acid infused polyurethane shape memory foams. *Polymer* **2018**, *153*, 131–138.
- 16 Wu, Y.; Chen, C. Z.; Jia, Y. F.; Wu, J.; Huang, Y.; Wang, L. G. Review on electrospun ultrafine phase change fibers (PCFs) for thermal energy storage. *Appl. Energy* **2018**, *210*, 167–181.
- 17 Yuan, M. J.; Hu, Z. Y.; Fang, H.; Li, S. J.; Guo, H. T.; Hu, R. B.; Jiang, S. H.; Liu, K. M.; Hou, H. Q. High performance electrospun polynaphthalimide nanofibrous membranes with excellent resistance to chemically harsh conditions. *Chinese J. Polym. Sci.* **2021**, *39*, 1634–1644.
- 18 Feng, W.; Zhang, Y. S.; Shao, Y. W.; Huang, T.; Zhang, N.; Yang, J. H.; Qi, X. D.; Wang, Y. Coaxial electrospun membranes with thermal energy storage and shape memory functions for simultaneous thermal/moisture management in personal cooling textiles. *Eur. Polym. J.* **2021**, *145*, 110245.
- 19 Lu, Y.; Xiao, X. D.; Mo, J. M.; Huan, C. M.; Qi, S.; Zhan, Y. J.; Zhu, Y. Q.; Xu, G. Green nano-encapsulation technique for preparation of phase change nanofibers mats with core-sheath structure. *Colloid Surf. A-Physicochem. Eng. Asp.* **2018**, *555*, 501–506.
- 20 McCann, J. T.; Marquez, M.; Xia, Y. N. Melt coaxial electrospinning: a versatile method for the encapsulation of solid materials and fabrication of phase change nanofibers. *Nano Lett.* **2006**, *6*, 2868–2872.
- 21 Lu, Y.; Xiao, X. D.; Fu, J.; Huan, C. M.; Qi, S.; Zhan, Y. J.; Zhu, Y. Q.; Xu, G. Novel smart textile with phase change materials encapsulated core-sheath structure fabricated by coaxial electrospinning. *Chem. Eng. J.* **2019**, *355*, 532–539.
- 22 Li, S. Q.; Wang, H. X.; Mao, H. Q.; Li, J.; Shi, H. F. Light-to-thermal conversion and thermoregulated capability of coaxial fibers with a combined influence from comb-like polymeric phase change material and carbon nanotube. *ACS Appl. Mater. Interfaces* **2019**, *11*, 14150–14158.
- 23 Niu, Z. X.; Yuan, W. Z. Smart nanocomposite nonwoven wearable fabrics embedding phase change materials for highly efficient energy conversion-storage and use as a stretchable conductor. *ACS Appl. Mater. Interfaces* **2021**, *13*, 4508–4518.
- 24 Ke, H. Z.; Ghulam, M. U. H.; Li, Y. G.; Wang, J.; Peng, B.; Cai, Y. B.; Wei, Q. F. Ag-coated polyurethane fibers membranes absorbed with quinary fatty acid eutectics solid-liquid phase change materials for storage and retrieval of thermal energy. *Renew. Energy* **2016**, *99*, 1–9.
- 25 Du, J.; Liu, D.; Zhang, Z.; Yao, X.; Wan, D.; Pu, H.; Lu, Z. Dual-responsive triple-shape memory polyolefin elastomer/stearic acid composite. *Polymer* **2017**, *126*, 206–210.
- 26 Hu, L. C.; Li, X.; Ding, L.; Chen, L. Y.; Zhu, X. Y.; Mao, Z. P.; Feng, X. L.; Sui, X. F.; Wang, B. J. Flexible textiles with polypyrrole deposited phase change microcapsules for efficient photothermal energy conversion and storage. *Sol. Energy Mater. Sol. Cells* **2021**, *224*, 110985.
- 27 Han, X. S.; Lv, L. L.; Yu, D. Y.; Wu, X. C.; Li, C. X. Conductive core-shell aramid nanofibrils: compromising conductivity with mechanical robustness for organic wearable sensing. *ACS Appl. Mater. Interfaces* **2019**, *11*, 3466–3473.
- 28 Zhang, X. Y.; Duan, C. T.; Zhao, N.; Xiao, H.; Shi, M. W.; Zhang, X. L.; Xu, J. Facile fabrication of large scale microtubes with a natural template kapok fiber. *Chinese J. Polym. Sci.* **2010**, *28*, 841–847.
- 29 Xiao, P.; Gu, J. C.; Zhang, C.; Ni, F.; Liang, Y.; He, J.; Zhang, L.; Ouyang, J. Y.; Kuo, S. W.; Chen, T. A scalable, low-cost and robust photo-thermal fabric with tunable and programmable 2D/3D structures towards environmentally adaptable liquid/solid-medium water extraction. *Nano Energy* **2019**, *65*, 104002.
- 30 Gao, Q.; Kopera, B. A. F.; Zhu, J.; Liao, X. J.; Gao, C.; Retsch, M.; Agarwal, S.; Greiner, A. Breathable and flexible polymer membranes with mechanoresponsive electric resistance. *Adv. Funct. Mater.* **2020**, *30*, 1907555.
- 31 Lai, W. C.; Chang, C. W.; Hsueh, C. Y. Shape-stabilized poly(ethylene glycol) phase change materials with self-assembled network scaffolds for thermal energy storage. *Polymer* **2021**, *213*, 123196.
- 32 Zhang, F. H.; Xia, Y. L.; Wang, L. L.; Liu, L. W.; Liu, Y. J.; Leng, J. S. Conductive shape memory microfiber membranes with core-shell structures and electroactive performance. *ACS Appl. Mater. Interfaces* **2018**, *10*, 35526–35532.
- 33 Zhang, Q.; Wang, Q.; Wang, G. Y.; Zhang, Z. L.; Xia, S.; Gao, G. H. Ultrathin and highly tough hydrogel films for multifunctional strain sensors. *ACS Appl. Mater. Interfaces* **2021**, *13*, 50411–50421.
- 34 Lin, F.; Zhang, X.; Liu, X.; Xu, Y.; Sun, Z.; Zhang, L.; Huang, Z.; Mi, R.; Min, X. Polyethylene glycol/modified carbon foam composites for efficient light-thermal conversion and storage. *Polymer* **2021**, *228*, 123894.
- 35 Wang, X.; Liu, Q. C.; Wu, S. Y.; Xu, B. X.; Xu, H. X. Multilayer polypyrrole nanosheets with self-organized surface structures for flexible and efficient solar-thermal energy conversion. *Adv. Mater.* **2019**, *31*, 1807716.
- 36 Li, J. Y.; Zhou, X.; Mu, P.; Wang, F.; Sun, H. X.; Zhu, Z. Q.; Zhang, J. W.; Li, W. W.; Li, A. Ultralight biomass porous foam with aligned hierarchical channels as salt-resistant solar steam generators. *ACS Appl. Mater. Interfaces* **2020**, *12*, 798–806.