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Modulating carrier transport by cross-dimensional compositing of Ag₂Se/MXene for high-performance flexible thermoelectrics†

Jie Qin,^{‡ab} Yao Lu,^{‡*a} Wenjing Liu,^a Zhangli Du,^c Xiang Li,^a Tianpeng Ding,^{‡c} Jianghe Feng,^{‡d} Yong Du,^{‡*b} Qinfei Ke^{*b} and Xin Wang^{‡*e}

Flexible thermoelectrics (TEs) offer immense potential for self-powering of wearable/implantable electronics. However, the trade-off between the flexibility and power factor of the materials has long been a challenge. Here, we report a nano-compositing strategy involving Ag₂Se nanowire matrix and MXene nanosheet filler to well address this issue. The as-prepared composite film has a cross-dimensional structure consisting of crystalline Ag₂Se grains and distinctive layered MXenes, which enables simultaneously rapid electron transport and high flexibility. The heterogeneous interfaces, pores and dislocations were attributed to enhanced carrier transport that favors the electrical conductivity. A film of such composite delivered a high power factor of 2125 $\mu\text{W m}^{-1} \text{K}^{-2}$ at 300 K with only a 7% decrease in electrical conductivity after 3000 bending cycles, showing remarkable merits in both power conversion and flexibility. A six-leg TE generator constructed from the composite reached a maximum power density of 24.2 W m^{-2} at a temperature difference of ~ 31 K, which is among the highest reported values in film-based TE generators. The as-assembled devices also showed sufficiently fast response to allow for solar TEs and TE sensing in addition to conventional wearable/portable energy harvesting and cooling.

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1 Introduction

The emergence of artificial intelligence and the Internet of Things has boosted the demand for portable and maintenance-free power sources, where body heat and sunlight serve as the best natural supplies.^{1,2} Thermoelectric (TE) materials can convert low-grade heat into electricity at high efficiency, and the human body and sunlight are prospective power sources for wearable electronics.^{3,4} The conversion efficiency of a TE material is evaluated using the non-dimensional figure of merit, $ZT = S^2\sigma T/\kappa$, where S , σ , T , and κ are the Seebeck coefficient, electrical conductivity, absolute temperature, and total thermal conductivity (the sum of the electronic and lattice thermal

conductivity), respectively.^{5,6} To date, most high-performance TE materials are inorganic semiconductors that are often too rigid for wearing applications. Over the past few years, researchers have dedicated their efforts to developing flexible inorganic TE materials with high efficiency ideally at room temperature (RT), yet very limited progress has been achieved in enhancing their flexibility.^{7,8} Exploring materials that offer exceptional TE performance while maintaining high flexibility continues to be the Holy Grail of wearable TE-based electronics.^{9,10}

In all inorganic TE materials, n-type β -Ag₂Se is among the most studied ones thanks to its high power factor ($\text{PF} = S^2\sigma$), low κ , and narrow energy gap ($E_g \sim 0.15$ eV) near RT.¹¹ An Ag₂Se film deposited on a rigid glass substrate was reported to have a power factor of up to 2400 $\mu\text{W m}^{-1} \text{K}^{-2}$,¹² and an Ag₂Se bulk sintered in a high-temperature quartz oven reaches 3520 $\mu\text{W m}^{-1} \text{K}^{-2}$ at RT.¹³ While these high-efficiency heat-to-electricity conversions hold huge merits in powering wearable electronics, the flexibility of Ag₂Se-based TE materials is yet to be improved to adapt to the necessary body movements. One effective strategy to improve the flexibility of Ag₂Se is to composite it with conductive polymers, such as poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS), polyaniline, and poly(3-hexylthiophene). Our group has previously prepared a Ag₂Se/Ag/PEDOT composite film with a high power factor and excellent flexibility ($\text{PF} \sim 1603 \mu\text{W m}^{-1} \text{K}^{-2}$ at

^aInternational School of Microelectronics, Dongguan University of Technology, Dongguan 523808, China. E-mail: luyao880813@126.com

^bSchool of Materials Science and Engineering, Shanghai Institute of Technology, 100 Haiquan Road, Shanghai 201418, China. E-mail: ydu@sit.edu.cn; kqf@sit.edu.cn

^cSchool of Physics, University of Electronic Science and Technology of China, Chengdu 518071, China

^dShenzhen Institute of Advanced Electronic Materials, Shenzhen Institute of Advanced Technology, Chinese Academy of Sciences, Shenzhen 518055, China

^eSongshan Lake Materials Laboratory, Dongguan 523808, China. E-mail: wangxin@sslslab.org.cn

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‡ These authors contributed equally to this work.

300 K and remaining $\sim 92\%$ after 1000 bending cycles).¹⁴ Similarly, a good power factor and superior flexibility are also simultaneously achieved on the $\text{Ag}_2\text{Se}/\text{Se}/\text{polypyrrole}$ (PPY) composite film.¹⁵ Nevertheless, the relatively poor power factor of polymers somehow compromises the overall TE performance.

In addition to compositing with polymers, compositing with inorganic nanomaterials is also an effective strategy for producing flexible Ag_2Se -based TE materials. An $\text{Ag}_2\text{Se}/\text{Ag}/\text{CuAgSe}$ composite film was reported to give an optimized power factor of $2231.5 \mu\text{W m}^{-1} \text{K}^{-2}$ at 300 K that can be maintained at 90% after 1000 bending cycles.¹⁶ Following this strategy, many other flexible high-performance nanocomposites such as $\text{SWCNTs}/\text{Ag}_2\text{Se}$ ¹⁷ and $\text{Ag}/\text{Ag}_2\text{Se}$ ¹⁸ have been prepared. In these attempts, new synthesis techniques such as impregnation have also been developed, which allow for the effortless transformation of ordinary fabrics or clothing into personalized TE devices.¹⁹

Over the vast selection of composite fillers, MXenes have gained increasing attention due to their unique properties, leading to extensive research in various domains, including energy storage, sensing, water purification, and electromagnetic interference shielding.²⁰ Nevertheless, investigations into their potential applications in the realm of TEs have been somewhat limited. The distinctive 2D layered structure of MXenes holds significant promise for enhancing TE and mechanical properties of nanocomposites. Some MXenes have been reported to exhibit good conductivity and carrier mobility. For example, the $\text{Mo}_2\text{TiC}_2\text{T}_x$ film was reported to deliver a conductivity of 1380 S cm^{-1} , a carrier mobility of $2.85 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and a power factor of $309 \mu\text{W m}^{-1} \text{K}^{-2}$ at 803 K.²¹

Despite the boosting effect of MXene in MXene/carbon,²² MXene/polymer,²³ and MXene/inorganic²⁴ TE nanocomposites, the possible synergistic effect with other dimensional materials especially one dimensional nano-fibers/wires as well as the optimal preparation strategy remain unresearched. This is very important in that cross-dimensional compositing has been shown to be promising to largely enhance the synergistic functionality, not only in the area of thermoelectrics,^{25,26} but also magnetics,²⁷ electrochemistry,²⁸ photocatalysis,²⁹ *etc.* With the aim of preparing multidimensional composites that acquire high TE performance and good flexibility, we incorporate trace 2D MXene nanosheets (NSs) into 1D Ag_2Se nanowires (NWs) matrix, where MXene acts as a bridge to connect nanowires that strengthens the linkage while regulating carrier transportation. The straightforward and cost-effective fabrication method of the composite films involves a combination of feasible vacuum filtration and a hot-pressing process. The as-prepared composite films demonstrated excellent TE performance with a power factor of $\sim 2000 \mu\text{W m}^{-1} \text{K}^{-2}$ at 300 K that goes up to $\sim 3000 \mu\text{W m}^{-1} \text{K}^{-2}$ at 400 K. Prototypes of both traditional rectangle and novel circular TE devices have been assembled using the optimized films. The power output, cooling, solar-thermoelectric, and sensing capabilities were tested systematically, unequivocally confirming the exceptionally high TE performance and enormous potential for applications of our films in waste heat recovery, cooling, and sensing fields. The

preparation of TE nanocomposites and the as-assembled devices demonstrates a promising pathway to achieve exceptional TE performance and high flexibility that makes possible potential applications in consumer products.

2 Results and discussion

The power factor of an inorganic TE material is often related to phase compositions and microstructures. This connection arises from the unique interplay between materials of distinct dimensions and the interfaces that exist between them. Therefore, a series of investigations focusing on the physical phase composition and microstructure of inorganic nanocomposites, including X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM), were conducted first.

The crystalline structure of MXene, Ag_2Se , and $\text{Ag}_2\text{Se}/\text{MXene}$ films were evaluated using XRD spectra as shown in Fig. 2a and S3.† All samples can be indexed well to the standard card of $\beta\text{-Ag}_2\text{Se}$ (JCPDF #24-1041) without obvious impurities, where the diffraction angles of 22.9° , 34.7° , 46.8° , and 48.6° correspond to the (002), (013), (004), and (014) crystal planes of $\beta\text{-Ag}_2\text{Se}$, indicating the successful synthesis of $\beta\text{-Ag}_2\text{Se}$. No peaks of MXene were detected in $\text{Ag}_2\text{Se}/\text{MXene}$ thin films with different MXene contents as no signal was found at around 6° for (002),³⁰ which is likely due to the low content ($<0.5 \text{ wt}\%$) and relatively low intensity deriving from the low structure dimensions.³¹ After hot-pressing at 340°C , the intensity of the characteristic peaks of (002), (004), (013), and (014) crystal planes increases significantly, indicating that the Ag_2Se in the thin film has oriented growth along the (00 l) and (01 l) crystal planes, which is beneficial for enhancing the TE properties of the composites.¹⁸

Compared with the sample before hot-pressing (see ESI Fig. S4a–c)†, the SEM images of MAS_0.1 show that the morphology of the composite film has significantly changed after hot-pressing (Fig. 2b and c). The Ag_2Se NWs were sintered to form a relatively dense conductive network, which will be beneficial for improving carrier transport in the nanocomposites.³² It is worth noting that unusual columnar structures are still observed. To definitively understand the composition of this columnar structure, EDS detection was performed on this marked area (Fig. S4†). The EDS mappings show that Ag and Se are evenly distributed in this region, indicating that the composition of this columnar structure is Ag_2Se . Noticeable oxygen was also detected on the surface, which may be due to the abundant $-\text{O}$ and $-\text{OH}$ in the MXene.²⁰ The Mo and Ti elements were not detected probably due to the low MXene content ($<0.5 \text{ wt}\%$). EDS detection was performed on the hot-pressed MXene film (Fig. S5†), in which distinct Mo, Ti, C, O, F, and Al can be observed, and the trace Al could come from incomplete etching. Besides, the XPS analysis of MAS_0.1 (Fig. S6†) shows significant Ag, Se, Mo, Ti, O, and C elements, where Ag and Se elements originated from Ag_2Se and Mo, Ti, C, and O primarily originated from MXene. The peaks of Mo $3d_{5/2}$, Mo $3d_{3/2}$, Ti $3d_{5/2}$, and Ti $3d_{3/2}$ can be attributed to the internal Mo–O, Mo–C, Ti–O, and Ti–C in MXene.³⁰

A cross-sectional STEM sample of MAS_0.1 was prepared by the focused ion beam (FIB) method and the internal microstructure of the sample was characterized. The STEM image shows that the film has a porous microstructure (Fig. 2d). The corresponding EDS mapping contains elements Ag, Se, O, and Ti, suggesting the existence of Ag_2Se and Mo_2TiC_2 (Fig. 2e). The STEM image of a boundary between Ag_2Se and pores illustrates edge dislocations (Fig. 2f). In addition, an HRTEM image obtained along the direction of the $[013]$ axis with a corresponding fast Fourier transform (FFT) image confirms the good crystallinity of $\beta\text{-Ag}_2\text{Se}$, as shown in Fig. 2g (FFT in the inset).

The $\text{Ag}_2\text{Se}/\text{MXene}$ composite powder shows a typical nanowire structure, as shown in the SEM images in Fig. S7,[†] confirming the successful preparation of Ag_2Se NWs (the SEM images of individual Ag_2Se NWs and MXene films as depicted in Fig. S8[†]). Noteworthily, Ag_2Se NW aggregation wraps on the surface of MXene NSS, which may produce a strong interaction between Ag_2Se and MXene. The diameter of the as-prepared Ag_2Se NWs is ~ 150 nm with a length of a few micrometers, as shown by the TEM image in Fig. 2h. The high-resolution TEM (HRTEM) confirms the interplanar spacing to be 2.58 Å and 2.56 Å, corresponding to the (121) crystal plane of Ag_2Se (Fig. 2i). The interplanar spacings, found to be 2.53 Å and 2.56 Å, correspond well to the (002) crystal plane of Mo_2TiC_2 , as shown in Fig. 2j and k, which is in agreement with those in ref. 33.

The temperature-dependence of electrical conductivity, Seebeck coefficient, and power factor for hot-pressed $\text{Ag}_2\text{Se}/\text{MXene}$ films with varying MXene content was measured and the results are illustrated in Fig. 3a–c. The optimized hot-pressing pressure, temperature, and time are 10 MPa, 340 °C, and 0.5 h, respectively (Fig. S9 and S10[†]). As MXene content increases, the

electrical conductivity of the composites initially increases and then decreases, reaching its maximum value at 0.1 wt%. The enhancement in electrical conductivity is primarily attributed to a significant increase in the carrier concentration n ($\sigma = n \times e \times \nu$, where e and ν represent the electron charge and the carrier mobility, respectively), as indicated in Fig. 3d. However, as MXene content continues to increase, the MXene with a low carrier concentration shows a dominant effect and causes a rapid decrease in electrical conductivity for the composite films. Due to the recombination effects between holes and electrons, the concentration of Ag_2Se and MXene within the composites gradually becomes the primary governing factor for the semi-conductivity. The Seebeck coefficient of the composite films introduced by MXene remains negative, indicating that electrons are the dominant charge carriers. The $|S|$ of the composite films undergoes a significant reduction following the introduction of MXene and reaches an optimal value of $109 \mu\text{V K}^{-1}$ at an MXene addition of 0.1 wt%. It can be observed that $|S|$ of MAS_0.1 is still larger than that of MAS_0.05. This phenomenon may be related to the possible energy filtering effect at the $\text{Ag}_2\text{Se}/\text{MXene}$ interface (Fig. 1), *i.e.* the low-energy electrons are blocked at the interface, while their high-energy counterparts can still effectively move, leading to some increase in $|S|$.³⁷ However, with the increasing MXene content (0.2 wt%, 0.5 wt%, *etc.*), $|S|$ exhibits an overall decreasing trend because of the dominant effect of p-type MXene.

To have an in-depth understanding of the carrier transport mechanism, we plotted the Pisarenko line based on the single-parabolic-band (SPB) model (Fig. 3e). The detailed calculation process of the SPB model is shown in ESI Note S3.1[†]. For a semiconductor, the relationship between $|S|$ and carrier

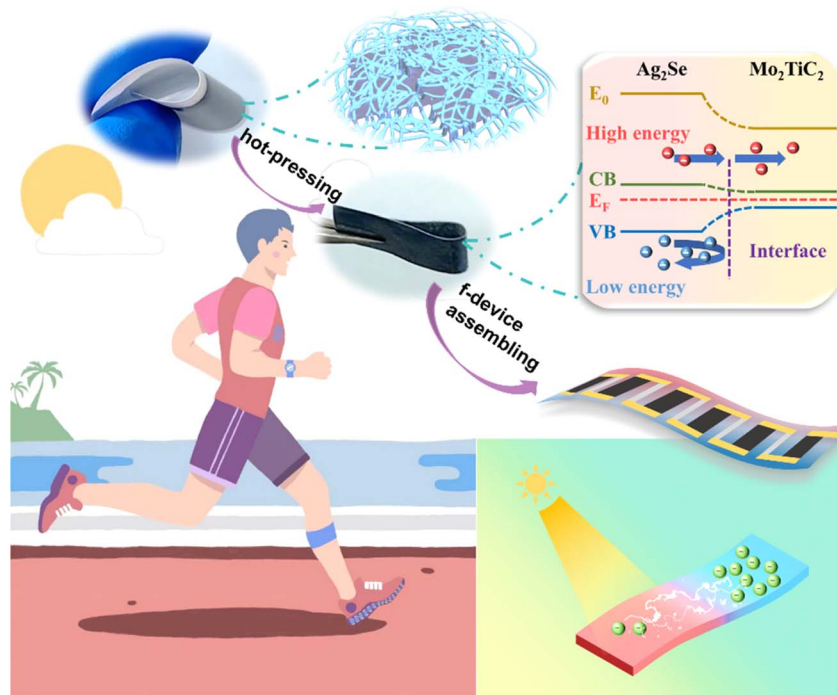


Fig. 1 Comprehensive flowchart and internal mechanism of the fabrication of $\text{Ag}_2\text{Se}/\text{MXene}$ flexible composite films and prototypical devices.

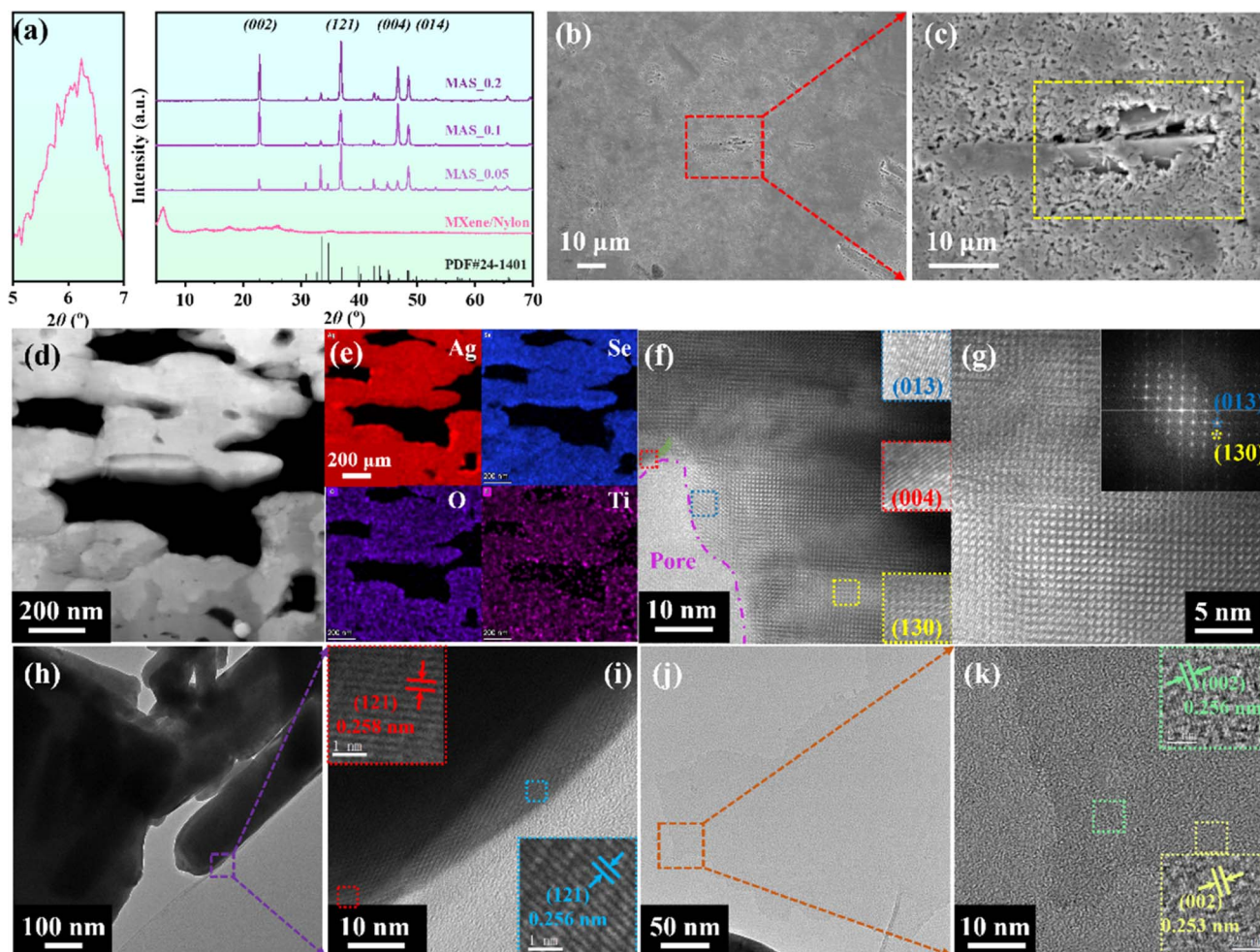


Fig. 2 (a) XRD diffractograms of the as-prepared MXene and $\text{Ag}_2\text{Se}/\text{MXene}$ films. (b and c) SEM images of the hot-pressed $\text{Ag}_2\text{Se}/\text{MXene}$ composite film. (d) An overview HAADF-STEM image, and (e) corresponding EDS-STEM elemental mapping of elements Ag, Se, O, and Ti. (f) Typical STEM image containing a boundary between Ag_2Se and pore, edge dislocations and (g) an HRTEM image (inset shows the corresponding FFT image). TEM images of (h) Ag_2Se NWs, (j) MXene nanosheets, and (i and k) corresponding HRTEM images.

concentration can be described based on the Pisarenko relation:^{38,39}

$$S = \left(\frac{8\pi^2 K_B^2}{3eh^2} \right) m^* T \left(\frac{\pi}{3n} \right)^{2/3} \quad (1)$$

where K_B represents the Boltzmann constant, e is the electron charge, h is the Planck constant, and m^* denotes the effective mass of charge carriers. As the MXene content increases, the m^* increases initially followed by a decrease (Fig. S11†) and achieved a peak value of $0.23 m_0$. Based on eqn (1), the increase in the carrier concentration has a negative effect on the $|S|$, which is offset by the significant increase in m^* from $0.16 m_0$ to $0.23 m_0$. With further increases in MXene content, the carrier concentration had a sharp drop, while no significant decrease was observed in $|S|$. This phenomenon suggests that an energy-filtering effect may exist at the $\text{Ag}_2\text{Se}/\text{MXene}$ interface in the composite films.

For the MAS_0.1 sample, the electrical conductivity is initially measured to be 1797 S cm^{-1} at 300 K, which increases to 2675 S cm^{-1} as the temperature escalates to 400 K, and the

Seebeck coefficient fluctuates slightly around $-109 \mu\text{V K}^{-1}$ within the temperature range of 300 K to 400 K. Interestingly, both electrical conductivity and the Seebeck coefficient experience a substantial plunge as the temperature increases from 400 K to 420 K. This phenomenon is attributable to the phase transition of Ag_2Se , which generally occurs near 407 K.³²

To delve into the factors contributing to the remarkable TE properties of MAS_0.1, we conducted an analysis revealing the relationship between the variable carrier concentration and carrier mobility as a function of temperature (Fig. S12†). Obviously, the carrier concentration increases by $\sim 80\%$ as the temperature increases from 300 to 420 K, while the carrier mobility initially increases before 380 K and then drops sharply as temperature further goes up. The change in the electrical conductivity and Seebeck coefficient with temperature can be explained by the Hall measurement results. The initial increase and the following drop of electrical conductivity with temperature are reflected in the expression $\sigma = nev$. Likewise, the Seebeck coefficient shows a similar trend that can be explained by eqn (1). Consequently, the power factor reaches $2125 \mu\text{W m}^{-1}$

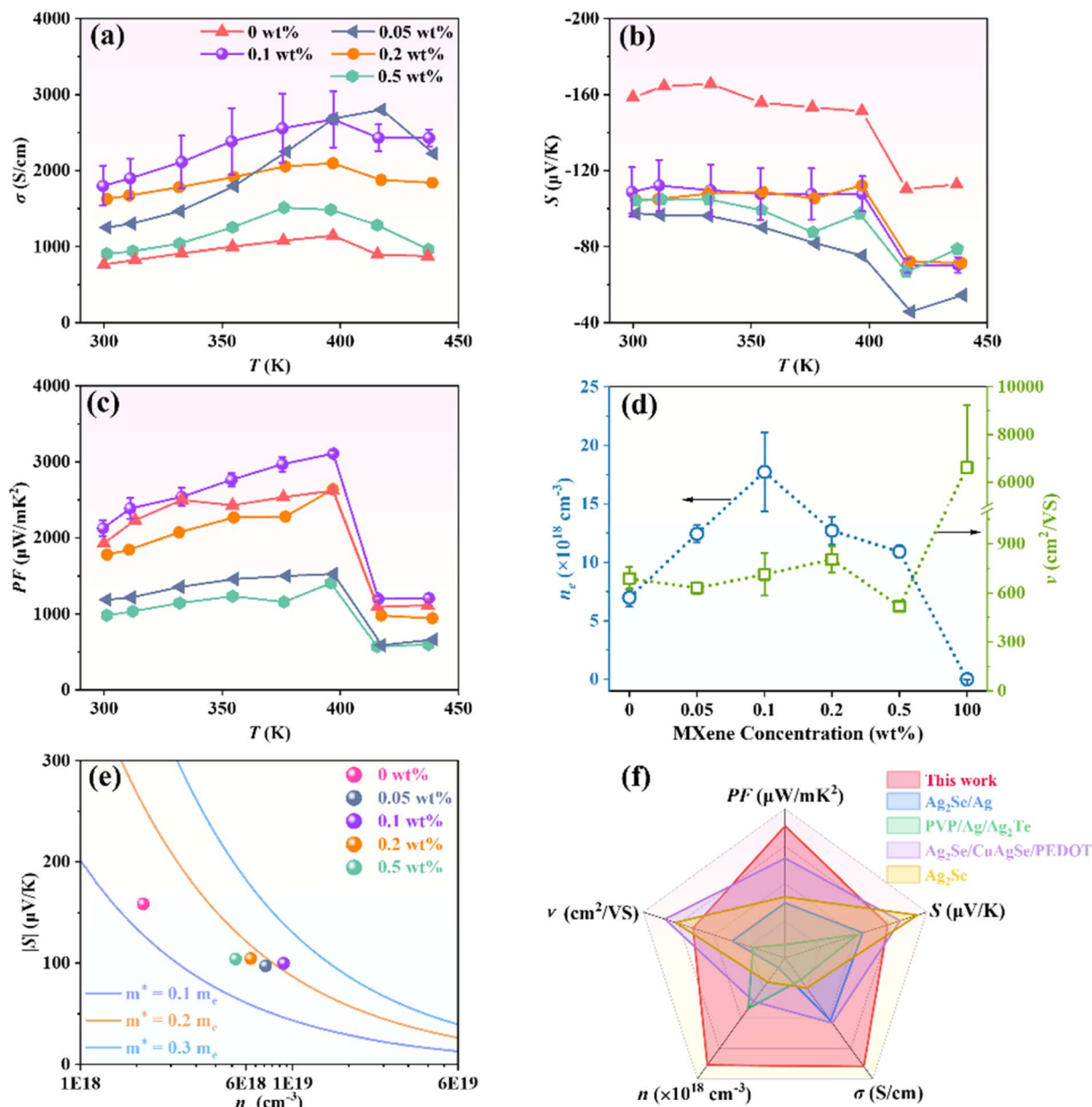


Fig. 3 Temperature dependence of the $\text{Ag}_2\text{Se}/\text{MXene}$ composites with different MXene contents: (a) electrical conductivity, (b) Seebeck coefficient, and (c) power factor. (d) Carrier concentration (n) and carrier mobility (ν) of the composites at different MXene concentrations. (e) Experimental data *versus* calculated plots of the Seebeck coefficient. The solid line connecting the scatter is predicted from a single parabolic band model, and m^* is the density of states effective mass. (f) Comparison of the power factor, $|S|$, electrical conductivity, carrier concentration, and carrier mobility between the MAS_0.1 composite in this work and other reported flexible TE materials.^{32,34–36}

K^{-2} at RT and peaks at $3109 \mu\text{W m}^{-1} \text{K}^{-2}$ at 400 K (Fig. 3c). This impressive performance is largely attributed to the distinct two-dimensional layered structure of trace MXene, which optimizes the carrier transport mechanism *via* a synergistic effect when composited with Ag_2Se NWs. The demonstrated performance remains at the forefront level within Ag_2Se -based flexible TE films and even rivals that of some Ag_2Se bulk materials (the latter however lacks sufficient flexibility).⁴⁰ Compared to other flexible TE films reported in the literature,^{32,34–36} MAS_0.1 exhibits a higher electrical conductivity, as shown in Fig. 3f. This nonetheless compensates for the negative effect of low $|S|$

on TE performance, which is mainly attributed to the optimized carrier transport.

The measurement of in-plane thermal conductivity for thin films is a challenge, especially for a composite film supported on a nylon substrate. To this end, a combined investigation involving experimental testing and simulation was adopted to mitigate potential errors. Initially, a transient photo-electro-thermal (TPET) technique⁴¹ was employed to characterize the thermal diffusivity of the MAS_0.1 composite (ESI Note 3.2 and Fig. S13b†). The resultant thermal conductivity at 300 K was as low as 0.48 W mK^{-1} , which can be attributed to the noteworthy

influence of the organic nylon substrate. Simultaneously, we conducted a thermal conductivity calculation for MAS_0.1 using a series-parallel connected model, yielding an estimated maximum value of approximately $0.92 \text{ W m}^{-1} \text{ K}^{-1}$, and a comprehensive description of the calculation is displayed in the ESI Note S3.2†. Consequently, thermal conductivity for MAS_0.1 was estimated to be within the range of 0.48 to 0.92, with a corresponding ZT value of 0.59 to 1.33 at 300 K. The achieved ZT values bear comparison to those of certain inorganic bulk TE materials^{42,43} (Na-doped Bi_2Te_3 , $1.03@300 \text{ K}$; $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$, $1.42@RT$) and establish a significant competitive advantage within the domain of flexible TE materials.^{32,44}

For practical applications, flexible TE films must exhibit not only excellent TE performance, but also robust mechanical properties and good flexibility to withstand external forces and maintain stability. The mechanical properties of pristine nylon, hot-pressed nylon (HP_Nylon), MXene, Ag_2Se , and MAS_0.1 films were evaluated and illustrated as stress-strain curves in Fig. 4a. The Ag_2Se film displays a tensile strength of 42.0 MPa at a strain of approximately 16.1%. The MAS_0.1 composite film is much stronger than the Ag_2Se film, with a tensile strength of

82.0 MPa and a strain of 22.1% (for more details see Fig. S14†). This higher mechanical performance of the MAS_0.1 film can be attributed to the reinforcing role of MXene nanosheets, which act as bridges to connect Ag_2Se NWs. Furthermore, the Seebeck coefficient *versus* tensile strain of the MAS_0.1 film was tested (Fig. 4b), where the inset shows the photograph of the sample suffering from 20% tensile strain. The Seebeck coefficient of the film remains consistent as the tensile strain increases from 5% to 20%, thus ensuring the stability of the material in practical applications. These findings will demonstrate the potential and capability of the as-prepared $\text{Ag}_2\text{Se}/\text{MXene}$ composite film for wearable TE devices.

Flexibility of TE materials for wearable applications in real-life scenarios is fundamental, and thus the variance of electrical conductivity of MAS_0.1 in response to the number of bending cycles was evaluated, as demonstrated in Fig. 4c. Remarkably, the electrical conductivity remains very steady when the film is subjected to as many as 1000 bending cycles. Even after 3000 bending cycles, the composite can preserve approximately 92.9% of its original conductivity. Moreover, the alteration of electrical conductivity after 3000 cycles shows very

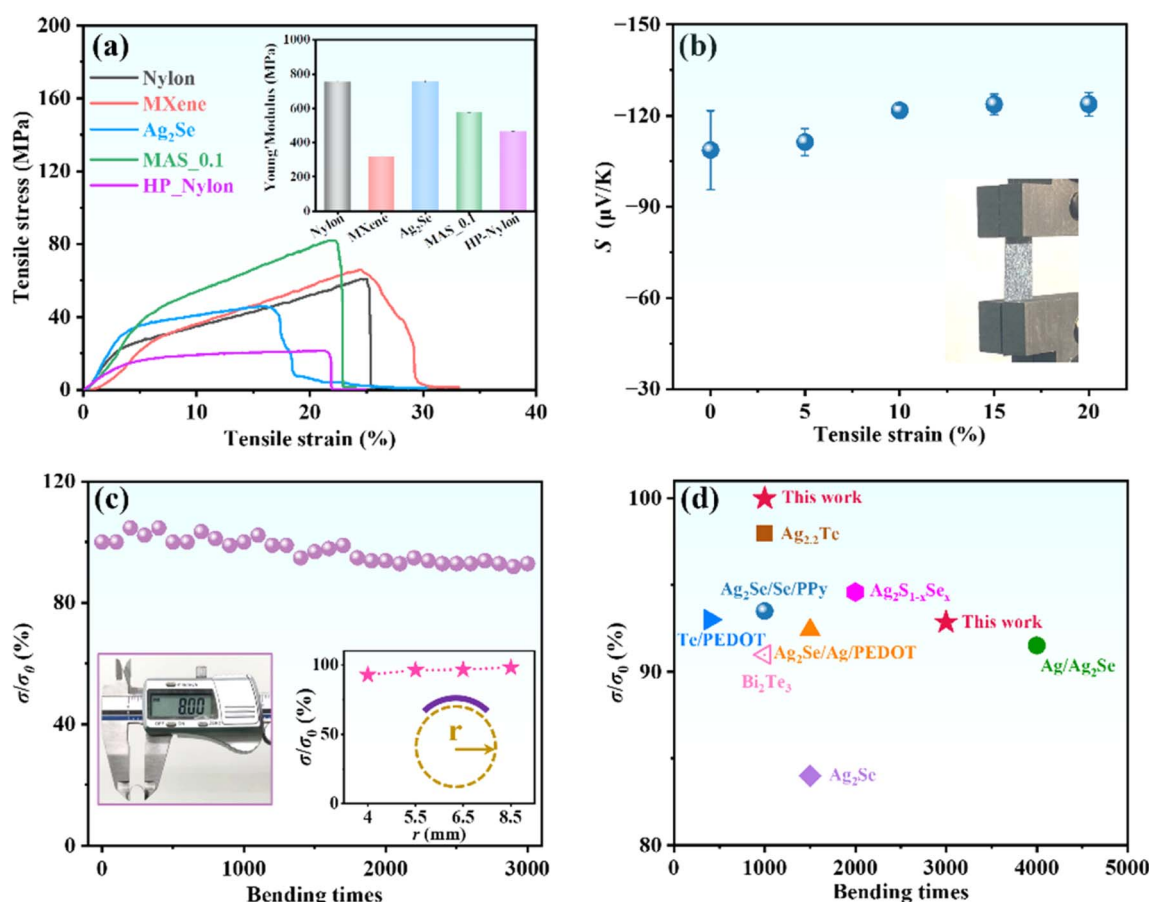


Fig. 4 (a) Stress-strain curves of a nylon membrane before and after hot-pressing, MXene, Ag_2Se , and MAS_0.1 films, with the Young's modulus shown in the inset. (b) The Seebeck coefficient of MAS_0.1 subjected to different tensile strains. The inset shows the photograph of MAS_0.1 with 20% tensile strain. (c) The σ/σ_0 of MAS_0.1 when bent at a radius of 4 mm for different times. The inset shows a photograph of a typical bending test and σ/σ_0 of MAS_0.1 after bending for 3000 cycles at different bending radii ($r = 4, 5.5, 6.5$, and 8.5 mm). (d) Comparison of flexibility between MAS_0.1 and other reported flexible TE materials.^{9,14,15,45–49}

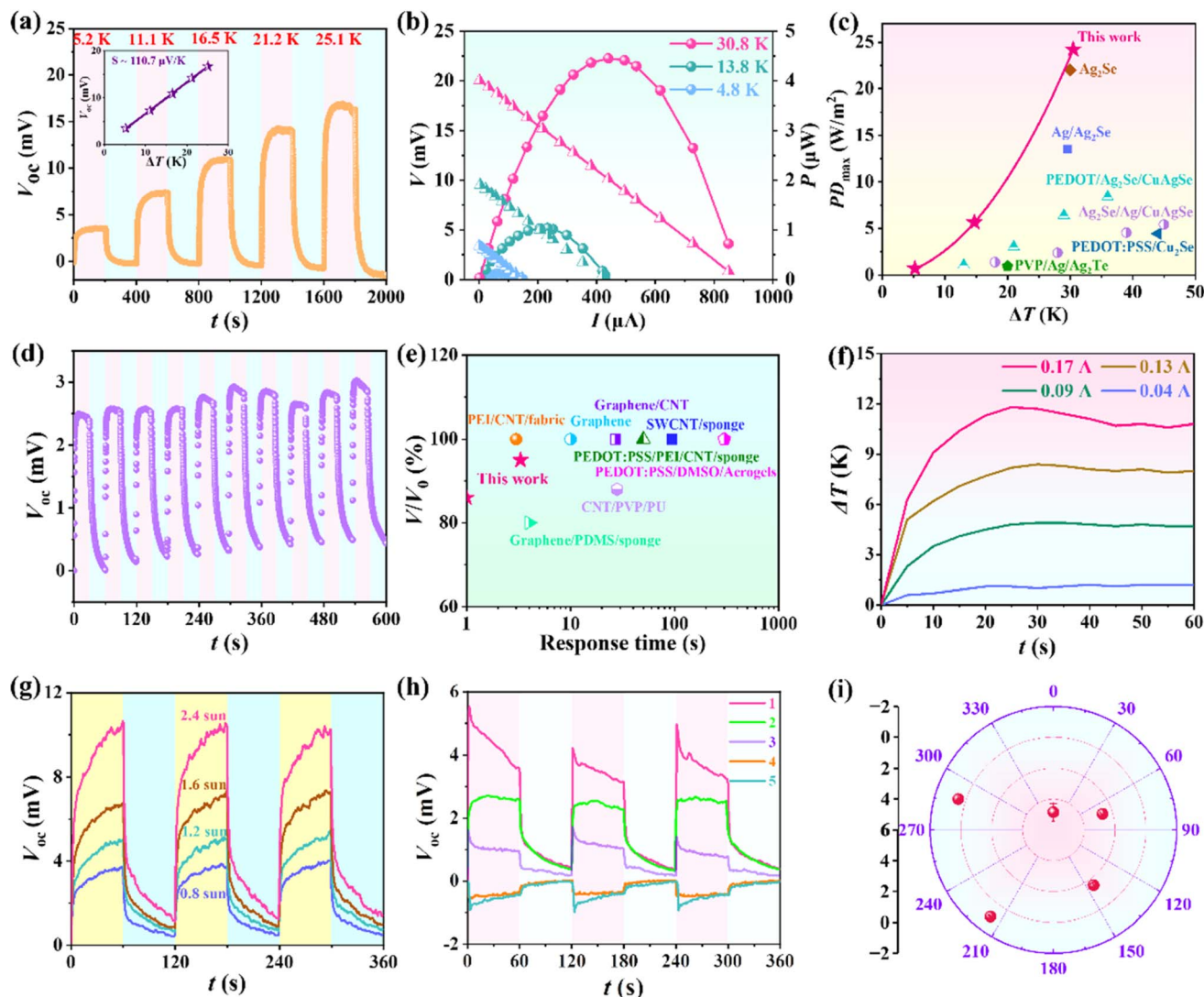


Fig. 5 (a) Variation of V_{oc} over time at different temperatures, with the inset graph depicting V_{oc} versus ΔT . (b) Output voltage and power at different ΔT for an optimized f-TEG, and (c) comparison of corresponding $P_{D,max}$ with those of other f-TEGs.^{16,18,34,35,49,50} (d) Relationship between V_{oc} and time when the device is touched with a finger, with a comparison of response levels and response times to relevant literature as shown in (e).^{30,51–57} (f) Relationship between ΔT generated by the f-TEG over time at different current intensities. (g) Variation of V_{oc} over time for the fan-shaped f-TEG at different light intensities (0.8, 1.2, 1.6, and 2.4 sun). (h) Relationship between V_{oc} over time when different positions on the fan-shaped f-TEG are touched with a finger, along with the corresponding average maximum voltage (i).

minimal change at a much larger bending radius of 8.5 mm, as displayed in the inset of Fig. 4c. These results further illustrate the excellent flexibility of the composite film, which can be attributed to a combination of factors, including the inherent flexibility of the nylon membrane, the porous network nanostructure formed by hot-pressed Ag_2Se NWs, and the synergistic interaction between the 2D MXene NSs and Ag_2Se nanograins. Such exceptional flexibility plays a critical role in ensuring stability and longevity of the flexible TE composite film even under deformations (Fig. 4d).^{9,14,15,45–49}

The MAS_0.1 film was subjected to different degrees of compression ($\Delta L/L_0$), and its σ/σ_0 was assessed (Fig. S15[†]). The test outcomes revealed a consistent σ/σ_0 within the $\Delta L/L_0$ range of 0% to 40% compression, followed by a gradual decrease. Upon returning to its uncompressed state ($\Delta L/L_0 = 0\%$), the σ/σ_0

fully recovered to 100% of its initial value. Notably, we integrated MAS_0.1 as a wire within an electrical circuit to illuminate a small LED with success even under 80% compression ($\Delta L/L_0 = 80\%$), which is mainly attributed to the outstanding flexibility of MAS_0.1.

To validate the ultrahigh TE performance and potential applications of the as-prepared nanomaterials, we assembled a six-leg f-TEG using the MAS_0.1 film (Fig. S16a and b[†]). The open-circuit voltage (V_{oc}) of the f-TEG versus temperature difference (ΔT) is shown in Fig. 5a. The $|S|$ of a TE leg is calculated to be $\sim 110.9 \mu V K^{-1}$ ($V_{oc} = N|S|\Delta T$, where N is the number of TE legs), which matches the measured value of the film with great precision ($109 \mu V K^{-1}$). The current dependence of the output voltage (V) and power (P) at different ΔT is shown in Fig. 5b, where P is expressed as:

$$P = \left(\frac{V_{oc}}{R_{ex} + R_{in}} \right)^2 \times R_{ex} \quad (2)$$

Here, R_{ex} and R_{in} represent the external variable resistance and internal resistance of the f-TEG, respectively. The maximum output power (P_{max}) is achieved when R_{ex} is the same as R_{in} . At a temperature difference of 30.8 K, the measured maximum V and P are 20 mV and 4.45 μ W, respectively, with a corresponding R_{ex} value of $\sim 22.3 \Omega$. By applying the formula $R = L/(A\sigma)$ (where L and A correspond to the length and cross-sectional area of the TE leg), the resistance of the six TE legs (R_0) was calculated to be $\sim 21.8 \Omega$. Therefore, the contact resistance of our f-TEG is $\sim 0.5 \Omega$ (resistance of Cu tape is neglected). The low contact resistance is primarily attributed to the use of contact layer Au and electrode Ag for connections,¹⁸ which is relatively lower than that of other reported f-TEGs.^{14,16,32} The maximum power density (PD_{max}) is determined as follows:

$$PD_{max} = \frac{P_{max}}{NA} \quad (3)$$

when $\Delta T = 4.8, 13.8$, and 30.8 K, the PD_{max} of our f-TEG was calculated to be $0.7, 5.64$, and 24.21 W m^{-2} based on eqn (3). We compared the PD_{max} of our assembled prototypes with that of other reported f-TEGs,^{16,18,34,35,49,50} and the value is among the highest (Fig. 5c).

By using a finger to touch one end of the six-leg f-TEG periodically, we obtained the response curve for 10 cycles (Fig. 5d). The response efficiency (V_{oc-1s}/V_{oc-max}) of the f-TEG is calculated to be 86% within 1 s (Fig. S17†). The fast response speed originated from the high carrier mobility of the MAS_0.1 film, which is mainly introduced by MXene (Fig. 3d). The response efficiency of our device is much faster compared with previous studies^{30,51–57} (Fig. 5e). The as-prepared f-TEG was further demonstrated in real-life scenarios by wearing it on the forearm, with one end in contact with the forearm as the hot end and the other end facing the ambient air as the cold end, where the two ends are separated by a layer of insulating material. The relationship between V_{oc} and time was then tested under different conditions (sitting, walking, and running), as illustrated in Fig. S18a.† The average V_{oc} values for sitting, walking, and running are 1.5, 2.3, and 4.2 mV. When the condition state changes, a noticeable increase in voltage is observed. The voltage change occurs in response to changes in body temperature as well as the present air convection.⁵⁸

Our prepared flexible TE films have prospects not only in waste heat recovery but also in cooling and sensing. The parameters of ΔT and temperature at both ends of the device are crucial parameters for evaluating the heat dissipation performance of TE devices. Fig. 5f presents the variation of ΔT with time at different currents, with corresponding infrared thermal images shown in Fig. S19.† As time increases, ΔT initially increases rapidly and then stabilizes after a slight decrease, which becomes more pronounced at higher currents. At a current of 0.17 A, the ΔT can reach a peak value of 11.8 K and eventually stabilizes at around 10.7 K at 60 s. This is primarily due to the presence of certain internal resistance in the device, which leads to delayed dissipation of Joule heat.⁵⁹

To showcase the diverse array of potential application domains and prospects for MAS_0.1, we assembled a square and a circular solar-TEG (ESI Note S1.6 and Fig. S16c and d†). By exposing the square device to light of varying intensities, we obtained the relationship between voltage and time. It is evident that with the increase in light intensity from 0.15 to 0.45 sun, the corresponding V_{oc} increases from ~ 0.3 to ~ 1.0 mV (Fig. S18b†), primarily attributed to the significant difference in light absorption efficiency between TiO_2 and MAS_0.1 (Fig. S20†). The output voltage reaches a maximum of 11 mV when radiated with 2.4 sun (Fig. 5g), having potential to power miniature sensors. The device also demonstrated excellent position-identifying capability. The time-dependent voltage curve at different finger-touching positions of the device (positions 1 to 5) was obtained and is shown in Fig. 5h and i. Different positions at the circular device show significantly different trends and magnitudes in output voltage, which allows us to identify the location of the heat source.

3 Conclusions

In this study, trace two-dimensional MXene was composited with one-dimensional Ag_2Se nanowires by a cost-effective vacuum filtration/hot-pressing approach. The synergistic effects between Ag_2Se grains with high-crystallinity and the unique 2D layered structure of MXene contributed to the high power factor and good pliability of the composite films. It was found that the MXene sheets serve as bridges that connect the Ag_2Se nanowires, facilitating charge transfer among the wires while reinforcing the combination between wires. As a result, the film showed a remarkable power factor of $2125 \mu\text{W m}^{-1} \text{K}^{-2}$ at RT and peak value of $3109 \mu\text{W m}^{-1} \text{K}^{-2}$ at 400 K. When subjected to 3000 bends at a radius of 4 mm, the electrical conductivity of the film preserves 93% of its original value. Additionally, an f-TEG comprising six legs made from the optimized film yielded a maximum power density of 24.2 W m^{-2} at a temperature difference of 31 K, validating its outstanding generating capacity. Our multi-functional f-TEGs also show great potential in applications for cooling, photo-TE conversion, and sensing. This study underscores the promise of multidimensional nano-compositing in preparing TE materials for practical utilization in wearable devices, poised to drive forward the progress of wearable TE devices.

Data availability

The data that support the findings of this study are available upon reasonable request from the authors.

Author contributions

Y. L. and J. Q. contributed equally to this work. Y. L., X. W., and J. Q. contributed to the design of the research and analysis of the experimental results. J. Q. and W. J. L. carried out the experiments and concluded the data. X. L. and J. H. F. assisted in the phase composition of samples. Z. L. D. and T. P. D. assisted in the MXene fabrication. Y. L., X. W., and J. Q. wrote

the manuscript. Y. L., Y. D. and X. W. acquired the funding and supervised the work. All authors discussed the results and revised the manuscript.

Conflicts of interest

There are no conflicts of interest to declare.

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References

- 1 Y. Jia, Q. Jiang, H. Sun, P. Liu, D. Hu, Y. Pei, W. Liu, X. Crispin, S. Fabiano, Y. Ma and Y. Cao, *Adv. Mater.*, 2021, **33**, 2102990.
- 2 I. Petsagkourakis, K. Tybrandt, X. Crispin, I. Ohkubo, N. Satoh and T. Mori, *Sci. Technol. Adv. Mater.*, 2018, **19**, 836–862.
- 3 S. A. Hashemi, S. Ramakrishna and A. G. Aberle, *Energy Environ. Sci.*, 2020, **13**, 685–743.
- 4 Y. Hou, Y. Yang, Z. Wang, Z. Li, X. Zhang, B. Bethers, R. Xiong, H. Guo and H. Yu, *Adv. Sci.*, 2022, **9**, 2103574.
- 5 P. Xu, W. Zhao, X. Liu, B. Jia, J. He, L. Fu and B. Xu, *Adv. Mater.*, 2022, **34**, 2202949.
- 6 Y. Du, J. Xu, B. Paul and P. Eklund, *Appl. Mater. Today*, 2018, **12**, 366–388.
- 7 Y. Oshima, A. Nakamura and K. Matsunaga, *Science*, 2018, **360**, 772–774.
- 8 X. Shi, H. Chen, F. Hao, R. Liu, T. Wang, P. Qiu, U. Burkhardt, Y. Grin and L. Chen, *Nat. Mater.*, 2018, **17**, 421–426.
- 9 Y. Lu, Y. Zhou, W. Wang, M. Hu, X. Huang, D. Mao, S. Huang, L. Xie, P. Lin, B. Jiang, B. Zhu, J. Feng, J. Shi, Q. Lou, Y. Huang, J. Yang, J. Li, G. Li and J. He, *Nat. Nanotechnol.*, 2023, **18**, 1281–1288.
- 10 N. Nandihalli, C.-J. Liu and T. Mori, *Nano Energy*, 2020, **78**, 105186.
- 11 Z.-Y. Yang, X.-Z. Jin, W.-Y. Wang, C.-H. Huang, Y.-Z. Lei and Y. Wang, *J. Mater. Chem. A*, 2022, **10**, 21080–21092.
- 12 S. Hou, Y. Liu, L. Yin, C. Chen, Z. Wu, J. Wang, Y. Luo, W. Xue, X. Liu, Q. Zhang and F. Cao, *Nano Energy*, 2021, **87**, 106223.
- 13 M. Ferhat and J. Nagao, *J. Appl. Phys.*, 2000, **88**, 813–816.
- 14 Z. Wang, Q. Gao, W. Wang, Y. Lu, K. Cai, Y. Li, M. Wu and J. He, *Mater. Today Phys.*, 2021, **21**, 100553.
- 15 Y. Li, Q. Lou, J. Yang, K. Cai, Y. Liu, Y. Lu, Y. Qiu, Y. Lu, Z. Wang, M. Wu, J. He and S. Shen, *Adv. Funct. Mater.*, 2021, **32**, 2106902.
- 16 Y. Lu, Y. Qiu, K. Cai, Y. Ding, M. Wang, C. Jiang, Q. Yao, C. Huang, L. Chen and J. He, *Energy Environ. Sci.*, 2020, **13**, 1240–1249.
- 17 Q.-X. Hu, W.-D. Liu, L. Zhang, W. Sun, H. Gao, X.-L. Shi, Y.-L. Yang, Q. Liu and Z.-G. Chen, *Chem. Eng. J.*, 2023, **457**, 141024.
- 18 X. Li, Y. Lu, K. Cai, M. Gao, Y. Li, Z. Wang, M. Wu, P. Wei, W. Zhao, Y. Du and S. Shen, *Chem. Eng. J.*, 2022, **434**, 134739.
- 19 Y. Liu, X. Wang, S. Hou, Z. Wu, J. Wang, J. Mao, Q. Zhang, Z. Liu and F. Cao, *Nat. Commun.*, 2023, **14**, 3058.
- 20 S. Bandaru, A. M. Jastrzębska and M. Birowska, *Appl. Mater. Today*, 2023, **34**, 101902.
- 21 H. Kim, B. Anasori, Y. Gogotsi and H. N. Alshareef, *Chem. Mater.*, 2017, **29**, 6472–6479.
- 22 J. Wei, D. Wu, C. Liu, F. Zhong, G. Cao, B. Li, C. Gao and L. Wang, *Chem. Eng. J.*, 2022, **439**, 135706.
- 23 C. Zhang, P.-A. Zong, Z. Ge, Y. Ge, J. Zhang, Y. Rao, Z. Liu and W. Huang, *Nano Energy*, 2023, **118**, 109037.
- 24 X. Lu, Q. Zhang, J. Liao, H. Chen, Y. Fan, J. Xing, S. Gu, J. Huang, J. Ma and J. Wang, *Adv. Energy Mater.*, 2020, **10**, 1902986.
- 25 T. Chiba, H. Yabuki and M. Takashiri, *Sci. Rep.*, 2023, **13**, 3010.
- 26 H. Yabuki, S. Yonezawa, R. Eguchi and M. Takashiri, *Sci. Rep.*, 2020, **10**, 17031.
- 27 S. Mourdikoudis, A. Kostopoulou and A. P. LaGrow, *Adv. Sci.*, 2021, **8**, 2004951.
- 28 D. Han, Q. Zhou, Y. Xia, D. Huang, J. Qin, L. Wang, X. Wang, X. Zheng and D. Wu, *Carbon*, 2022, **200**, 296–306.
- 29 R. Greco, L. Baxauli-Marin, F. Temerov, M. Daboczi, S. Eslava, Y. Niu, A. Zakharov, M. Zhang, T. Li and W. Cao, *Chem. Eng. J.*, 2023, **471**, 144569.
- 30 Q. Zhao, W. Zhou, M. Zhang, Y. Wang, Z. Duan, C. Tan, B. Liu, F. Ouyang, Z. Yuan, H. Tai and Y. Jiang, *Adv. Funct. Mater.*, 2022, **32**, 2270220.
- 31 C. F. Holder and R. E. Schaak, *ACS Nano*, 2019, **13**, 7359–7365.
- 32 Y. Ding, Y. Qiu, K. Cai, Q. Yao, S. Chen, L. Chen and J. He, *Nat. Commun.*, 2019, **10**, 841.
- 33 Q. Xi, F. Xie, J. Liu, X. Zhang, J. Wang, Y. Wang, Y. Wang, H. Li, Z. Yu, Z. Sun, X. Jian, X. Gao, J. Ren, C. Fan and R. Li, *Small*, 2023, **19**, 2300717.
- 34 Q. Meng, Y. Qiu, K. Cai, Y. Ding, M. Wang, H. Pu, Q. Yao, L. Chen and J. He, *ACS Appl. Mater. Interfaces*, 2019, **11**, 33254–33262.
- 35 Y. Lu, Y. Qiu, K. Cai, X. Li, M. Gao, C. Jiang and J. He, *Mater. Today Phys.*, 2020, **14**, 100223.
- 36 Y. Liu, Q. Zhang, A. Huang, K. Zhang, S. Wan, H. Chen, Y. Fu, W. Zuo, Y. Wang, X. Cao, L. Wang, U. Lemmer and W. Jiang, *Nat. Commun.*, 2024, **15**, 2141.
- 37 A. Shakouri, C. LaBounty, P. Abraham, J. Piprek and J. E. Bowers, *MRS Online Proc. Libr.*, 1998, **545**, 449.

- 38 Y. Yu, X. Xu, Y. Wang, B. Jia, S. Huang, X. Qiang, B. Zhu, P. Lin, B. Jiang, S. Liu, X. Qi, K. Pan, D. Wu, H. Lu, M. Bosman, S. J. Pennycook, L. Xie and J. He, *Nat. Commun.*, 2022, **13**, 5612.
- 39 Y. Zhu, L. Hu, S. Zhan, T. Ina, X. Gao, T. Hong and L.-D. Zhao, *Energy Environ. Sci.*, 2022, **15**, 3958–3967.
- 40 P. Jood, R. Chetty and M. Ohta, *J. Mater. Chem. A*, 2020, **8**, 13024–13037.
- 41 Y. Ling, M. Han, J. Xie, G. Qiu, G. Dong, E. Min, P. Zhang, X. Zeng, R. Liu and R. Sun, *Measurement*, 2023, **217**, 113058.
- 42 L. Y. Lou, J. Yang, Y. K. Zhu, H. Liang, Y. X. Zhang, J. Feng, J. He, Z. H. Ge and L. D. Zhao, *Adv. Sci.*, 2022, **9**, 2203250.
- 43 C. L. Chen, T. H. Wang, Z. G. Yu, Y. Hutabalian, R. K. Vankayala, C. C. Chen, W. P. Hsieh, H. T. Jeng, D. H. Wei and Y. Y. Chen, *Adv. Sci.*, 2022, **9**, 2201353.
- 44 Q. Gao, W. Wang, Y. Lu, K. Cai, Y. Li, Z. Wang, M. Wu, C. Huang and J. He, *ACS Appl. Mater. Interfaces*, 2021, **13**, 14327–14333.
- 45 P. Yu, L. Feng, W. Tang, C. Liu, J. L. Lan, Y. H. Lin and X. Yang, *ACS Appl. Mater. Interfaces*, 2023, **15**, 13144–13154.
- 46 M. Wu, J. Li, Y. Liu, Z. Wang, P. Wei, W. Zhao and K. Cai, *ACS Appl. Mater. Interfaces*, 2023, **15**, 8415–8423.
- 47 D. Ni, H. Song, Y. Chen and K. Cai, *J. Materiomics.*, 2020, **6**, 364–370.
- 48 J. Li, Y. Liu, Z. Wang, L. Chen and K. Cai, *Composites, Part B*, 2023, **265**, 110946.
- 49 C. Jiang, Y. Ding, K. Cai, L. Tong, Y. Lu, W. Zhao and P. Wei, *ACS Appl. Mater. Interfaces*, 2020, **12**, 9646–9655.
- 50 Y. Lu, Y. Ding, Y. Qiu, K. Cai, Q. Yao, H. Song, L. Tong, J. He and L. Chen, *ACS Appl. Mater. Interfaces*, 2019, **11**, 12819–12829.
- 51 X. He, J. Shi, Y. Hao, M. He, J. Cai, X. Qin, L. Wang and J. Yu, *Carbon Energy*, 2022, **4**, 621–632.
- 52 H. Cheng, Y. Du, B. Wang, Z. Mao, H. Xu, L. Zhang, Y. Zhong, W. Jiang, L. Wang and X. Sui, *Chem. Eng. J.*, 2018, **338**, 1–7.
- 53 J. Kim, E. J. Bae, Y. H. Kang, C. Lee and S. Y. Cho, *Nano Energy*, 2020, **74**, 104824.
- 54 C. Hou, H. Wang, Q. Zhang, Y. Li and M. Zhu, *Adv. Mater.*, 2014, **26**, 5018–5024.
- 55 S. Han, F. Jiao, Z. U. Khan, J. Edberg, S. Fabiano and X. Crispin, *Adv. Funct. Mater.*, 2017, **27**, 1703549.
- 56 T. T. Tung, C. Pham-Huu, I. Janowska, T. Kim, M. Castro and J. F. Feller, *Small*, 2015, **11**, 3485–3493.
- 57 Y. Zheng, H. Liu, X. Chen, Y. Qiu and K. Zhang, *Org. Electron.*, 2022, **106**, 106535.
- 58 S. Hou, Y. Liu, Y. Luo, X. Wang, L. Yin, X. Sun, Z. Wu, J. Wang, M. Li, Z. Chen, Y. Wang, J. Sui, J. Mao, X. Liu, Q. Zhang and F. Cao, *Cell Rep. Phys. Sci.*, 2022, **3**, 101146.
- 59 W. Hou, X. Nie, W. Zhao, H. Zhou, X. Mu, W. Zhu and Q. Zhang, *Nano Energy*, 2018, **50**, 766–776.