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A flexible micro-thermoelectric device from carbon nanotube-epitaxially grown (Bi,Sb)$_2$Te$_3$ nanocrystal

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Abstract:
Flexible thermoelectric (TE) materials have attracted increasing interest due to their potential applications in energy harvesting and high-spatial-resolution thermal management. However, a high-performance flexible micro-TE device (TED) compatible with the modern electronics fabrication process has not yet been developed. Here we report a general van der Waals epitaxial growth approach to fabricating a freestanding and flexible hybrid comprised of single-wall carbon nanotubes and highly ordered (Bi,Sb)$_2$Te$_3$ nanocrystals. High power factors ranging from ~1,680 to ~1,020 µW m$^{-1}$K$^{-2}$ in the temperature range of 300-480 K, combined with a strongly depressed thermal conductivity yield an average figure of merit of ~0.81. A prototype flexible micro-TED module consisting of two p-n hybrids was then fabricated, which demonstrated an unprecedented open circuit voltage of ~22.7 mV and a power density of ~0.36 W cm$^{-2}$ under a ~30 K temperature difference, and a net cooling temperature of ~22.4 K and a heat absorption density of ~92.5 W cm$^{-2}$.

Keywords:
flexible micro-thermoelectric generator, flexible micro-thermoelectric cooler, freestanding thermoelectric thin film, carbon nanotube-(Bi,Sb)$_2$Te$_3$, epitaxial growth
With the meteoric growth of modern electronics, there has been a significantly increased requirement for energy harvesting and thermal management technologies for use in portable electronics\(^1,2\) and on-chip integrations\(^3-5\). Recycling environmental waste heat into electrical energy using TE technology based on the Seebeck effect is considered one of the most promising solutions\(^6,7\). Such TE generators (TEGs) complement chemical or solar batteries by extending their life or even replacing them\(^8\). Thermal management based on the Peltier effect of TE materials is a positive cooling technology\(^9\), and a TE cooler (TEC) enables site-specific, green, and on-demand cooling, handling a large heat flux with a fast response time\(^5,10\).

However, there are at least three deficiencies that hinder the application of conventional TEDs in modern electronics. First, traditional inorganic TE materials are intrinsically rigid, and are largely restricted to building planar TEDs, which yield a low TE performance owing to the poor thermal contacts between the TED and curved heat source or sink. As a result, there have been tremendous efforts in recent years to develop flexible TE materials\(^11-23\). Nevertheless, limited by the degraded property of flexible TE materials and integration technology, the performance of current flexible TEDs\(^13-15,19,24-31\) is usually far worse than that of conventional ones. Second, the micro-TEDs are greatly needed in nW to mW self-powered nano-micro electronic devices without recharging\(^4\), and in the thermal management of electronics requiring high precision, high-spatial-resolution and fast temperature control\(^5,10\). However, because of the natural brittleness of conventional inorganic TE materials, it is very difficult to reduce their dimensions using traditional top-down processing to fabricate on-chip micro-TEDs. Bottom-up approaches using thin-film technology have therefore been developed\(^4,5,10\), but the main drawback is their poor TE performance compared with the conventional bulk TEDs. Third, in micro-TEDs where the heat flow is perpendicular to the device plane\(^4,5,10\),
difficulties in the fabrication and maintenance of the temperature gradient are very challenging. In contrast, micro-TEDs with a lateral structure where the heat flow is parallel to the device plane, can be more easily fabricated by integrated circuit (IC) compatible technologies, which allows the TEDs to fit various complex packaged electronic devices. But such a micro-TED has poor performance because of the heat loss/short circuit through the substrate. Consequently, freestanding thin-film TE materials are highly desired for micro-TED integration. The fabrication of high-performance flexible micro-TEDs is very important for the development of modern electronics, but it currently remains a big challenge.

Fig. 1 | Illustration of the structure and fabrication process of freestanding SWCNT-(Bi,Sb)$_2$Te$_3$ hybrids for flexible micro-TEDs. The grooves of SWCNT bundles guide the epitaxial growth of (Bi,Sb)$_2$Te$_3$ nanocrystals with highly aligned crystallographic orientations. The deposited nanocrystals have a strong van der Waals (vdW) interaction with the SWCNTs. The hybrid can be tailored by a femtosecond laser and transferred to any substrate for micro-TED integration.

Here we show a general epitaxial growth approach to preparing freestanding and flexible hybrids of single-wall carbon nanotube (SWCNT)-nanocrystal materials, which does not require a small lattice mismatch and allows fine dopant tuning for property optimization. P-type SWCNT-
(Bi,Sb)$_2$Te$_3$ hybrid TE films with well-aligned crystallographic orientations were fabricated using a layer-by-layer growth process, as illustrated in Fig. 1. This hybrid TE material has an average figure of merit ($ZT$) of ~0.81 in the temperature range of 300-370 K, because of its highly ordered microstructure and optimized composition. Our experimental and computational evidence show that the low-angle tilt grain boundary (GB) is important in determining the carrier and phonon transport properties as well as mechanical flexibility. We designed and fabricated a prototype micro-TEC/TEG module consisting of two p-n couples of the freestanding and flexible SWCNT-(Bi,Sb)$_2$Te$_3$ hybrid, which has a record-high power generation and cooling ability and excellent flexibility. This work demonstrates a promising strategy to fabricate flexible micro-TEDs with high performance.

**Epitaxial growth of a SWCNT-nanocrystal hybrid**

Since different crystallographic orientations mean different surface/interface atomic and electronic structures, microstructure control is crucial for designing novel structural and functional materials with desirable physical and chemical properties. This is especially true for materials that have anisotropic TE properties, where obtaining a high anisotropy in the polycrystalline material similar to that in the single-crystal is an effective approach to achieving a high TE performance$^8$. The conventional epitaxial growth of films with ordered nanostructures by vapor-phase deposition inevitably requires single-crystal substrates with a small lattice mismatch and an atomically flat surface$^{32}$. However, such heteroepitaxy can only be achieved in very limited combinations of substrates and films with similar crystal symmetries, lattice parameters, and thermal expansion coefficients$^{32}$. 

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**Fig. 2** | Microstructural characterization of highly-ordered SWCNT-nanocrystal hybrids. 

**a**, SEM images of the SWCNT-(Bi,Sb)$_2$Te$_3$, SWCNT-PbTe hybrids and bright-field TEM images of the SWCNT-Ag$_2$Te and SWCNT-Pt hybrids showing their well-ordered microstructures. Scale bars, 500 nm, 300 nm, 100 nm and 50 nm, respectively.

**b**, High-resolution TEM image of the SWCNT-(Bi,Sb)$_2$Te$_3$ hybrid. Inset: corresponding fast Fourier transform (FFT) pattern of the (Bi,Sb)$_2$Te$_3$ close to the [000l] zone axis.

**b-1**, Close-up of the yellow square area in **b** and a corresponding schematic of the hybrid. Scale bar, 10 nm.

**c, d**, HRTEM images of a (Bi,Sb)$_2$Te$_3$ nanocrystal from the part directly located on the SWCNT and the freestanding part, which are respectively marked by the turquoise and pink squares in **b**. Scale bars, 1 nm (**c, d**).

**e**, Intensity traces for atomic columns along <1̅100> direction from the turquoise line-1 in **c** and the pink line-2 in **d**, showing similar interatomic distances.

**f**, Calculated energy of a (000l)-orientated (Bi,Sb)$_2$Te$_3$ nanocrystal/SWCNT with different rotation angles (θ) along the <000l> direction after full relaxation. The energy of the hybrid has a minimum value when the <12̅10> direction is parallel to the SWCNT bundle groove.

**f-1**, Corresponding schematic of the calculation model.

**g**, Bright-field TEM image of two neighboring (Bi,Sb)$_2$Te$_3$ nanocrystals. Scale bar, 100 nm.

**h**, Selected area electron diffraction (SAED) pattern of the crystals in **g**, which is close to the [000l] zone axis. Inset is the intensity distribution of diffraction spots marked by red line-3.

**i**, ASTAR orientation map of the two neighboring nanocrystals in **g**. Scale bar, 100 nm. Inset is the corresponding inverse pole figure. The GB and SWCNT direction are respectively marked by the turquoise and yellow dotted lines.

**j**, Line scan of the misorientation angle along the direction marked by the blue line-4 in **i**. **j-1**, Corresponding schematic of distance (L) dependent misorientation angle (φ). Note that there is a low-angle tilt GB between the neighboring (Bi,Sb)$_2$Te$_3$ nanocrystals, because the (000l) atomic plane has six-fold rotational symmetry and is symmetric after a 60º rotation.
Herein, we develop a general approach to using the freestanding bundle of one-dimensional (1D) SWCNTs as a deposition scaffold to guide the highly oriented growth of nanocrystalline materials to form a freestanding and flexible hybrid. Our fabrication approach is applicable to many semiconductors and metals with different crystal structures, such as (Bi,Sb)$_2$Te$_3$, PbTe, PbSe, Cu$_2$Te, Ag$_2$Te, Pt, Au, Cu and Si (Fig. 2a; detailed characterizations of ordered microstructures in Supplementary Figs. 1-7). Combined with computational simulations, an epitaxial growth mechanism for such highly ordered microstructures under the driving force of minimizing free energy has been shown in Supplementary Notes 1 and 2. The deposited atoms have a strong vdW interaction with the SWCNTs (Fig.1 and Supplementary Figs. 8-11). Our approach may pave the way for the fabrication and application of a wide variety of 1D CNT-nanocrystal hybrids with ordered microstructures.

In Fig. 2, we can see that the (Bi,Sb)$_2$Te$_3$ nanocrystals have a strong out-of-plane (000$l$)-texture (Supplementary Note 3). The (Bi,Sb)$_2$Te$_3$ $<$1210$>$ orientation that is the closely packed direction on the (000$l$) atomic plane, aligns well with the local SWCNT bundle axis/groove (Fig. 2b,c). From the intensity profiles of two columns of atoms along $<$1$\bar{1}$00$>$ direction, we can deduce that there is almost no growth strain in the nanocrystal directly located on the SWCNTs (Fig. 2c-e), where the vdW force is dominant and there is no structural correlation or chemical bonding. With increasing deposition time, the Bi-Sb-Te atoms are primarily stacked on the (000$l$) atomic plane to get a thicker deposit, leaving a flat surface with an atomic height step edge (Fig. 2d and Supplementary Video 1). Such a growth process is consistent with the kinetics of the layer-by-layer growth model$^{33}$. The (000$l$) atomic plane/SWCNT interface with $<$1$\bar{2}$10$>$ orientation aligned with the SWCNT groove is the most stable structure, which is consistent with the MD simulations (Fig. 2f and Supplementary Note 2). Therefore, low-angle tilt GBs are formed between neighboring nanocrystals, as shown in Fig. 2g-j. The (000$l$)
quintuple layers are interconnected by vdW bonding, leading to a low inter-plane shear strength\textsuperscript{34}. During the growth, a high density of stacking faults and twin boundaries were thus generated along this plane\textsuperscript{35}, which would have a strong influence on phonon transport\textsuperscript{8,36}. Samples with different Bi:Sb chemical compositions were prepared, all of which have almost the same microstructural characteristics (Supplementary Fig. 1), indicating that the dopant concentration can be finely controlled to optimize the TE performance.

**Thermoelectric performance**

![Thermoelectric characterization of the (000l)-textured SWCNT-Bi\textsubscript{0.5}Sb\textsubscript{1.5}Te\textsubscript{3} hybrids, a (000l)-textured dense Bi\textsubscript{0.5}Sb\textsubscript{1.5}Te\textsubscript{3} film and a non-(000l)-textured SWCNT-Bi\textsubscript{0.5}Sb\textsubscript{1.5}Te\textsubscript{3} hybrid. a, Temperature-dependent in-plane electrical conductivities. b, Seebeck coefficients, c, Comparison of the $ZT$ values of previously reported typical freestanding flexible\textsuperscript{11-17}, transferrable TE\textsuberscript{s}\textsuperscript{18-23} and SWCNT-Bi\textsubscript{0.5}Sb\textsubscript{1.5}Te\textsubscript{3} hybrid at $\sim$300 K. The ratios of corresponding electrical conductivity to thermal conductivity ($\sigma/\kappa$) for these TE materials are also indicated.](image)

The temperature-dependent in-plane TE properties of the samples are shown in Fig. 3. The Bi:Sb ratio is finely controlled to optimize the TE performance (Supplementary Note 4) and the optimum is achieved when the Bi:Sb ratio is $\sim$0.5:1.5. A dense Bi\textsubscript{0.5}Sb\textsubscript{1.5}Te\textsubscript{3} film deposited on a SiO\textsubscript{2}/Si wafer
with the (000l)-textured and a non-(000l)-textured hybrid were also prepared for comparison. The fitted curve of electrical conductivity ($\sigma$) as a function of $T^{-3/2}$ is compatible with the experimental results (Fig. 3a), indicating that acoustic phonon scattering is dominant over the investigated temperature range. Such a primary carrier scattering mechanism is similar to that in a pure Bi$_2$Te$_3$ film$^{37}$ and is not obviously affected by the presence of SWCNTs (Supplementary Notes 4 and 5). The carrier mobility ($\mu$) along the (000l) plane is higher than those along other orientations, due to the strong anisotropy of the carrier transport of Bi$_2$Te$_3$-based alloys$^{38}$. Although the hybrid contains a large number of nanopores and Bi$_{0.5}$Sb$_{1.5}$Te$_3$/SWCNT interfaces, its $\mu$ value is only ~20% lower than that of the (000l)-textured dense film. The randomly orientated GBs strongly scatter carrier transport and reduce the $\mu$ in the Bi$_2$Te$_3$ alloys$^{8,39}$. In contrast, low-angle tilt GBs cause little scattering when the carriers cross neighboring Bi$_2$Te$_3$-based nanocrystals$^{40,41}$, resulting in a relatively large $\sigma$. The well-aligned <1210> orientation with a higher $\mu$ on the (000l) atomic plane$^{42}$ would also make a crucial contribution to $\sigma$. Because the Seebeck coefficient ($\alpha$) is not sensitive to the crystallographic orientation and porosity, the $\alpha$ values of all samples are comparable. As a result, the power factor of the (000l)-textured hybrid is ~42% higher than that of the non-(000l)-textured one and ~35% lower than that of the (000l)-textured dense film (Supplementary Fig. 21a).

The in-plane thermal conductivity ($\kappa$) values of the samples are shown in Supplementary Fig. 21b. We can see that the $\kappa$ values of all hybrids are substantially lower than that of the dense films (Supplementary Note 6). The reduction in $\kappa$ is mainly derived from a small lattice contribution ($\kappa_l$) and a bipolar effect ($\kappa_b$) (ref. $^{43}$), and $\kappa_l^h+\kappa_b^h$ is as low as ~0.44 ± 0.04 W m$^{-1}$ K$^{-1}$ at RT (Supplementary Fig. 21b), close to the values of highly porous (Bi,Sb)$_2$Te$_3$ alloys with a weak degree of (000l)-texture$^{44}$. However, considering the strong anisotropy on phonon transport along with the
atomic plane and the porosity of the hybrid is only ~one-third of the reported porous (Bi,Sb)\(_2\)Te\(_3\) alloys, the porosity alone cannot explain the significant reduction of \(\kappa_l\). The phonons in the hybrid have a wide range of wavelengths and are strongly scattered by many different defects (Supplementary Note 6), such as GBs, interfaces, nanopore boundaries, twin boundaries, stacking fault, dislocations and point defects, significantly reducing \(\kappa_l\). As revealed by our computational simulations (Supplementary Note 7), a low-angle tilt GB also effectively scatters the phonons and decreases \(\kappa_l\) (Supplementary Fig. 22). Consequently, the average in-plane \(ZT\) of the hybrid is as high as ~0.81 from 300 to 370 K (Supplementary Fig. 21c), which is comparable to the n-type counterpart and the state-of-the-art bulk (Bi,Sb)\(_2\)Te\(_3\), and higher than previously reported flexible TE materials (Fig. 3c).

**A micro-TED module for cooling and energy harvesting**

An n-type hybrid with compatible TE properties was prepared\(^{11}\) and its detailed characteristics are shown in Supplementary Fig. 23. Two hybrid p-n couples were tailored by a lab-built femtosecond laser microfabrication system (Supplementary Video 2) and transferred onto a micro-chip (Fig. 4a) to integrate a prototype micro-TEC and TEG module to evaluate their cooling and power conversion abilities (Fig. 4 and Supplementary Note 8). The p-n couples were bonded on the surface of a micro-chip using a Pt film (see Methods and Supplementary Note 8). The cooling performance of the micro-TEC module is shown in Fig. 4b,c. The heat sink temperature (surrounding temperature, \(T_h\)) was kept constant in the range of 300-400 K, and the temperature of the target cooled area (\(T_c\)) was monitored as a function of the current supplied to the micro-TEC module (Fig. 4a). With increasing electrical current, the \(T_c\) driven by the net cooling of the p-n couples first gradually decreased to a minimum
value and then increased when the current was further increased. The current producing the maximum net cooling temperature $\Delta T$ is defined as $I_{\text{max}}$. Both the maximum $\Delta T$ ($\Delta T_{\text{max}}$) and $I_{\text{max}}$ values increase with an increase of $T_h$ (Fig. 4b), which could be caused by the increased $T_h$ and TE performance.

Fig. 4 | Cooling and power generation performance of the micro-TED. a, SEM image and schematic of the micro-TEC module. Scale bar, 100 μm. b, Measured cooling temperature $\Delta T$ ($\approx T_h-T_c$) as a function of applied cooling current ($I_{\text{cooling}}$) at different $T_h$ values. The white dotted line indicates maximum $\Delta T$ ($\Delta T_{\text{max}}$). c, Estimated cooling power density ($Q_c$) of the micro-TEC module as a function of applied $I_{\text{cooling}}$ at different $T_h$ values. The white dotted line indicates the maximum $Q_c$ ($Q_{c\text{max}}$). d, COP of the micro-TEC module as a function of cooling power ($P_c$) at $\Delta T=0$ K. e, The $Q_{c\text{max}}$ and $\Delta T_{\text{max}}$ normalized to $T_c$ of the micro-TEC module compared with previously reported data points of flexible macro-TECs and inflexible micro-TECs. f, Output voltage ($V$) and power output ($P_g$) of the micro-TEG module as a function of current ($I$) under various $\Delta T_g$. g, Comparison of the maximum power density ($Q_{g\text{max}}$) of previously reported flexible TE modules.
In a closed system, the dependence of $\Delta T$ on applied electrical current can be attributed to three primary competing mechanisms (Supplementary Note 9), the Peltier effect, the Joule heating effect and cooling loss by thermal conduction. When the sum of Joule heating and thermal conduction effects equals the Peltier effect, the $\Delta T$ reaches its maximum value. Although, the cooling ability might have been underestimated due to the cooling loss through the suspended Pt/SiN$_x$ bridge connected to the SiN$_x$/Si substrate (Fig. 4a), compared with the traditional thin-film TEC$^{25}$, our flexible micro-TEC achieves more efficient cooling by fully eliminating the cooling loss of the supporting substrate. Stable $\Delta T_{\text{max}}$ values of ~14 K to ~22.4 K were obtained at 300-400 K under an applied current of less than ~1 mA. Meanwhile, the cooling power ($P_c$) of the micro-TEC module at different applied currents and the corresponding coefficient of performance ($COP$) values at $\Delta T=0$ K were calculated for different $T_h$, and the results are shown in Fig. 4d. The micro-TEC module delivered a maximum $P_c$ of ~89 to ~127 $\mu$W with a $COP$ value of ~0.5 over the entire temperature range investigated (Fig. 4d). The cooling power density ($Q_c$) was estimated by dividing $P_c$ by the total cross-sectional areas of two p-n couples along the heat flow direction. The maximum $Q_c$ ($Q_c^{\text{max}}$) is determined by the TE properties of the hybrid and decreases linearly with the length of the TE couples$^{38}$. $Q_c^{\text{max}}$ values of ~65 to ~92.5 W cm$^{-2}$ were obtained, which are ~one order of magnitude higher than that of conventional bulk TEC (Fig. 4e). The larger the $\Delta T_{\text{max}}$ and $Q_c^{\text{max}}$ values, the better the cooling performance of the micro-TEC. Remarkably, the micro-TEC module achieved a large $\Delta T$ and $Q_c^{\text{max}}$ at a micro-length scale with no forced heat removal, indicating that it may find important applications in nano-micro systems for temperature control.

The ability of the micro-TEG module to convert thermal energy to electric power was also tested with the cold-side temperature maintained at RT (Fig. 4f,g and Supplementary Note 8). The output
TE voltage increased linearly with the temperature gradient ($\Delta T_g$) and the calculated total $|\alpha|$ value of a p-n couple is close to the sum of measured $|\alpha|$ values of p- and n-type hybrids (Fig. 3b and Supplementary Fig. 23), indicating that the contact thermal resistance in the micro-TEG module is negligible. When the load resistance matches the micro-TEG module internal resistance, the maximum output power ($P_{g\text{max}}$) is obtained, which increases with $\Delta T_g^2$. When the $\Delta T_g$ reaches ~30 K, the value of $V$ increases to ~22.7 mV, accompanied by a short-circuit current of ~90 µA. The $P_{g\text{max}}$ is increased to a value of ~0.49 µW, yielding a maximum power density ($Q_{g\text{max}}$) of ~0.36 W cm$^{-2}$ across the micro-TEG module (Supplementary Note 8). Such an ultrahigh power density is several orders of magnitude higher than the values for bulk TEG$^{14-16}$ and flexible TEG reported in literature$^{13-15,19,28-31}$ due to the micro size of p-n couples and the high-density integration (Fig. 4g). Such a micro-TEG is expected to have important applications in nano-micro electronics.

The outstanding cooling and power conversion abilities of the module primarily result from the high $ZT$ value of the hybrid, the freestanding structure and the microscale dimensions of the device. Our TE hybrids with highly ordered microstructures have a comparable performance to the state-of-the-art bulk TE materials and can be arbitrarily tailored for integration with surfaces of any heat source and sink (Fig. 1). The freestanding p-n couples effectively avoid heat and cooling loss via the underlying substrate, resulting in good energy conversion performance. Moreover, the in-plane structured TED also reduces direct radiative and convective heat transfer$^{46}$ between the heat source and heat sink for improved energy conversion efficiency in a specially confined space (Supplementary Fig. 24). The performance of the micro-TEG module might be enhanced by optimizing the couple configuration, dimensions and thickness, using better TE materials and other techniques to give low electrical and thermal resistances of the contact and lead materials, such as
using silver paint or soldering materials. For example, $R_{\text{contact}}$ and $R_{\text{lead}}$ account for $\sim 50\%$ of the $R$
 because of the use of a low-quality Pt bonding film prepared by a focused ion beam deposition
 technique. If $R_{\text{lead}}$ and $R_{\text{contact}}$ are substantially decreased, the thermal load and power load capacities
 of the micro-TED module could be improved by a factor of $\sim 2$ (Supplementary Note 8).

**Flexibility of the hybrid and micro-TED module**

Fig. 5 | Flexibility of the SWCNT-Bi$_{0.5}$Sb$_{1.5}$Te$_3$ hybrid and micro-TED module. **a.** Relative electrical resistance
(blue) and bending radius (red) as a function of bending strain ($\varepsilon_b$) for a $\sim 720$-nm-thick (000l)-textured SWCNT-
(Bi,Sb)$_2$Te$_3$ hybrid on a polyimide substrate (open circles) and a freestanding p-n couple of the micro-TED module
(filled circles). $R_0$ and $R$ are the original electrical resistance in the flat state and the resistance when bent,
respectively. **b.** Results of the cyclic bending test of the freestanding micro-TED module at a bending radius of $\sim 0.3$
mm. Inset: SEM image of the freestanding p-n couple of the micro-TED module. Scale bar, 100 $\mu$m. The relative
change of internal resistance under various bending states is normalized. Error bars, 10% (a,b), as determined from
the measurement uncertainties in $R$ ($\sim 5\%$) and $R_0$ ($\sim 5\%$). **c-e.** MD simulation of Sb$_2$Te$_3$ nanocrystals under bending
with low $5^\circ$ (c) and high $15^\circ$ (d) tilt-angle GBs along Sb$_2$Te$_3$ $\langle1\bar{2}10\rangle$ direction, and low $5^\circ$ (e) tilt-angle GBs along
Sb$_2$Te$_3$ $\langle10\bar{1}0\rangle$ direction. The atomic shear strains for each case are shown on the Y-Z plane. **f.** MD simulation of
nanocrystals in the bending cycle test along Sb$_2$Te$_3$ $\langle1\bar{2}10\rangle$ direction. Microstructure of the region near the GBs in
Sb$_2$Te$_3$ nanocrystals with $5^\circ$, $15^\circ$ and $30^\circ$ tilt-angle GBs after 5 bending cycles.
The flexibility of the hybrid film was estimated by measuring its relative change of resistance \( \frac{R}{R_0} \) at different bending radii (Fig. 5a,b). The bending strain \( \varepsilon_b \) can be approximately estimated from the bending radius \( r_b \), the sample thickness and Young’s modulus (Supplementary Note 10). The freestanding hybrid was transferred onto a \( \sim 75 \) μm-thick polyimide substrate to increase \( \varepsilon_b \) which scales linearly with thickness. Under bending, the relative electrical resistance slightly increases with the decrease of \( r_b \). When the bending radius decreased to \( \sim 4 \) mm, \( \varepsilon_b \) increased by \( \sim 0.8\% \) and the relative change in the electrical resistance was only \( \sim 7\% \). Such excellent flexibility comes from the combined effects of thinness, a nanoporous structure, a flexible SWCNT scaffold and crystallographic orientation.\(^\text{11}\)

The flexibility of the micro-TED module was also evaluated. To realize bending at the microscale, an AFM was used to push the suspended SiN\(_x\) membrane connected to a p-n couple. From the displacement of moving end of the p-n couple, the bending radius was estimated (Supplementary Fig. 25). We can see that due to the freestanding structure and thickness effect, the p-n couple can be freely deformed with a bending radius down to \( \sim 0.2 \) mm without any obvious increase in resistance, revealing its excellent flexibility (Fig. 5a). Moreover, the p-n couple also shows good electrical stability after \( \sim 1,000 \) bending cycles (Fig. 5b). MD simulations show the \((\text{Bi,Sb})_2\text{Te}_3\) nanocrystals in the (000l) orientation with a low-angle tilt GB along the <1\(\bar{2}\)10> direction have a much better bending flexibility than others (Fig. 5c-f, Supplementary Note 11 and Supplementary Fig. 26), which is in good agreement with the experimental results. Such a good flexibility may provide freedom to adapt to possible displacements and internal strains caused by misfits of the material’s thermal expansion coefficients and improve reliability and stability. This freestanding and flexible hybrid has good
scalability and can be simply tailored into any shapes and dimensions for integration with arbitrary substrates (Supplementary Video 2).

Conclusion

We have reported the fabrication of highly ordered SWCNT-nanocrystal hybrid films with unique microstructures by epitaxial growth guided by the grooves of SWCNT bundles. Flexible and high-performance p-type TE hybrids consisting of a SWCNT scaffold and (Bi,Sb)$_2$Te$_3$ nanocrystals were obtained. Because of their freestanding structure, the hybrids can be arbitrarily tailored and bonded to any surfaces of the heat source and sink. A prototype flexible micro-TED module using two p-n hybrid couples was assembled, and a record-high output power density of ~0.36 W cm$^{-2}$ under a ~30 K temperature difference and a cooling power density of ~92.5 W cm$^{-2}$ at ~400 K were demonstrated. These hybrids and the micro-TED can be easily scaled by current IC compatible techniques for various applications, such as flexible and portable electronics and on-chip thermal management. Our work sheds light on the development of flexible micro-TEDs in modern electronics.

Methods

Fabrication of SWCNT-(Bi,Sb)$_2$Te$_3$ hybrid. High-purity, high-quality and freestanding SWCNT films prepared by a floating catalyst chemical vapor deposition method were used as a deposition scaffold. The film was composed of randomly distributed SWCNT bundles with an average diameter of ~10 nm. Using magnetron sputtering, (000$l$)-textured hybrids with different Bi$_2$Te$_3$/Sb$_2$Te$_3$ ratios and a (000$l$)-textured dense film were fabricated at ~600 K and a non-(000$l$)-textured hybrid was fabricated at ~550 K. Commercial 4-inch Bi$_2$Te$_3$ (99.99%), Sb$_2$Te$_3$ (99.99%) and Te (99.99%) targets were used for co-sputtering so that the composition and doping carrier concentrations could be tuned. During the deposition, the base pressure of the deposition chamber was ~5.0×10$^{-5}$ Pa and the operating Ar pressure was maintained at ~1 Pa. By changing the deposition time, temperature, chamber vacuum pressure and target used, the structure of the hybrid obtained was controlled.
Materials characterization. The microstructures of the samples were characterized by XRD (D8 Discover, Bruker), SEM (Supra 55 Zeiss) and TEM (FEI Tecnai T12, 120 kV; FEI Tecnai F20, 200 kV). Energy-dispersive spectra (EDS) was used to characterize the compositions of the samples. The thickness of the (Bi,Sb)$_2$Te$_3$ nanocrystals deposited on the SWCNT scaffold was estimated by cross-sectional TEM observations. The thicknesses of the SWCNT scaffold, (Bi,Sb)$_2$Te$_3$ thin film and SWCNT-(Bi,Sb)$_2$Te$_3$ hybrids were directly measured by atomic force microscopy (AFM, Innova, Bruker) and cross-sectional SEM images.

Thermoelectric performance and bending flexibility measurements. A Netzsch SBA-458 system was used to simultaneously measure the in-plane $\sigma$ and $\alpha$ with Ar (99.999%) gas protection from room temperature to 480 K. The measurement errors for $\sigma$ and $\alpha$ were less than 5% and 3%, respectively. The in-plane $\kappa$ values of the samples were measured using the well-developed suspended thermal isolation technique. To ensure that the hybrids had good contact with the thermal measurement device, a freestanding SWCNT scaffold was first transferred onto two suspended SiN$_x$ membranes with the assistance of a lab-built femtosecond laser micro-cutting system (Supplementary Video 2), and (Bi,Sb)$_2$Te$_3$ was then deposited on the whole area of the scaffold using a deposition mask, which ensured that the hybrid was well bonded with the SiN$_x$ membranes. A focused ion beam system (Nanolab Helios 720) was used to prepare the thermal conductivity test samples and micro-TED. The uncertainty for the measurements involved in $\kappa$ was ~10%. The combined uncertainty for the $ZT$ value calculation was ~20%. The Hall coefficient and carrier concentration were measured with an HMS-3000 Hall system using the van der Pauw method. The bending tests were conducted using a lab-built apparatus. The samples were attached to the surface of glass tubes of different radii, and relative changes in electrical resistance were measured to evaluate their flexibility. The measurement error for relative electrical resistance was ~10%.

Fabrication and measurement of micro-TED. A lab-built femtosecond laser micro-cutting system with a beam resolution better than ~700 nm was used to tailor the hybrids with a precisely controlled shape and dimensions. The freestanding p-n couples were connected in series using a SiN$_x$/Si substrate as a heat sink and a flexible suspended Pt/SiN$_x$ membrane as a heat source and target cooled area which is analogous to the hotspots in a chip. A suspended SiN$_x$ membrane is widely used to thermally isolate sensitive thermal sensors operated at relatively low temperatures$^{47}$. Such a micro-TED module has a lateral structure where the heat flow is parallel to the substrate. Pt films were
deposited on the SiN$_x$ substrate to generate heat and monitor the temperature change (Fig. 4a) using a focused ion beam technique. The performance of the micro-TED module was measured in a lab-built vacuum instrument to minimize the influence of air convection. $T_h$ was maintained at the range of 300-400 K during the test of micro-TEC module. A series of temperature differences was produced by heating one end of the micro-TEG module using a heater and the cold side of the module was maintained at RT. The output voltage, current and output power under different $\Delta T_g$ values were monitored by a Keithley 4200 SCS system.

**Methods of computational calculations.** CP2K software was used to simulate the growth of BST and Pt nanocrystals deposited on SWCNT bundles. Density functional theory (DFT) calculations in this work were performed to first compute the static energy. The kinetic evolution of the SWCNT-nanocrystal system was simulated by the ab initio molecular dynamics (AIMD) method. DFT calculations were based on the hybrid Gaussian and plane wave (GPW) scheme$^{48}$ with the Perdew-Burke-Enzerhof (PBE)$^{49}$ exchange correlation functional and corresponding pseudo potentials$^{50}$. A plane wave density cutoff of 400 Ry and periodic boundary conditions were used. Dispersion interactions were included using an empirical analytical potential, using the Grimme D3 method$^{51}$, within a range of 16 Å. For AIMD simulations, the temperature was from 300 K to 800 K with a time step of 0.5 fs. The total number of simulation steps was up to 9,000 for each case. Details of AIMD and DFT simulations are shown in Supplementary Notes 1 and 2. Classical MD simulations were also performed for a Sb$_2$Te$_3$ nanocrystal with small and large tilt-angle GBs to calculate the lattice thermal conductivity and the flexibility by using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package with the two-body interatomic potential. GBs were generated between the neighboring nanocrystals by rotating the middle one around the surface normal by given angles (Supplementary Fig. 26). In this work, the time interval was 1 ps for LAMMPS and the simulation temperature was 270 to 330 K. Details of MD simulations are shown in Supplementary Notes 1, 2, 7 and 11.

**Data availability**

The data supporting the findings of this study are provided in the Supplementary Information. Additional relevant data are available from the corresponding authors upon reasonable request.
Code availability

The code or subroutines that support the findings of this study are available from the corresponding author, upon reasonable request. The parameters used for the present work are available in the Supplementary Information.

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Author contributions

Q.J., Y.Z., S.J., K.T. and C.L. conceived and designed the experiments. Q.J. fabricated the hybrids and characterized their microstructures and thermoelectric and flexible properties. Q.J. and Y.Z. performed the integration and characterization of flexible micro-TEDs. S.J. and X.L. prepared the high-quality SWCNT scaffold and carried out its characterization. Y.Z. and J.T. fabricated the thermal conductivity test devices and measured the thermal conductivity of the hybrids. X.L., Z.W. and N.G. conducted the computational simulations. P.M., K.C., J.Q. and Y.W. contributed to the discussion of the results. Q.J., Y.Z., X.L., N.G., K.T., C.L. and H.M.C. analyzed the data and wrote the manuscript. All the authors commented on and revised the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information is available for this paper at https://XXX.
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