A flexible micro-thermoelectric device from carbon nanotube-epitaxially grown (Bi,Sb)₂Te₃ nanocrystal

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Article

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1 **A flexible micro-thermoelectric device from carbon nanotube-epitaxially grown**
2 **(Bi,Sb)₂Te₃ nanocrystal**

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22 **Abstract:**

23 Flexible thermoelectric (TE) materials have attracted increasing interest due to their potential
24 applications in energy harvesting and high-spatial-resolution thermal management. However, a high-
25 performance flexible micro-TE device (TED) compatible with the modern electronics fabrication
26 process has not yet been developed. Here we report a general van der Waals epitaxial growth approach
27 to fabricating a freestanding and flexible hybrid comprised of single-wall carbon nanotubes and
28 highly ordered (Bi,Sb)₂Te₃ nanocrystals. High power factors ranging from ~1,680 to ~1,020 $\mu\text{W m}^{-1}$
29 K^{-2} in the temperature range of 300-480 K, combined with a strongly depressed thermal conductivity
30 yield an average figure of merit of ~0.81. A prototype flexible micro-TED module consisting of two
31 p-n hybrids was then fabricated, which demonstrated an unprecedented open circuit voltage of ~22.7
32 mV and a power density of ~0.36 W cm^{-2} under a ~30 K temperature difference, and a net cooling
33 temperature of ~22.4 K and a heat absorption density of ~92.5 W cm^{-2} .

34 **Keywords:**

35 **flexible micro-thermoelectric generator, flexible micro-thermoelectric cooler, freestanding**
36 **thermoelectric thin film, carbon nanotube-(Bi,Sb)₂Te₃, epitaxial growth**

37 With the meteoric growth of modern electronics, there has been a significantly increased requirement
38 for energy harvesting and thermal management technologies for use in portable electronics^{1,2} and on-
39 chip integrations³⁻⁵. Recycling environmental waste heat into electrical energy using TE technology
40 based on the Seebeck effect is considered one of the most promising solutions^{6,7}. Such TE generators
41 (TEGs) complement chemical or solar batteries by extending their life or even replacing them⁸.
42 Thermal management based on the Peltier effect of TE materials is a positive cooling technology⁹,
43 and a TE cooler (TEC) enables site-specific, green, and on-demand cooling, handling a large heat
44 flux with a fast response time^{5,10}.

45 However, there are at least three deficiencies that hinder the application of conventional TEDs
46 in modern electronics. First, traditional inorganic TE materials are intrinsically rigid, and are largely
47 restricted to building planar TEDs, which yield a low TE performance owing to the poor thermal
48 contacts between the TED and curved heat source or sink. As a result, there have been tremendous
49 efforts in recent years to develop flexible TE materials¹¹⁻²³. Nevertheless, limited by the degraded
50 property of flexible TE materials and integration technology, the performance of current flexible
51 TEDs^{13-15,19,24-31} is usually far worse than that of conventional ones. Second, the micro-TEDs are
52 greatly needed in nW to mW self-powered nano-micro electronic devices without recharging⁴, and in
53 the thermal management of electronics requiring high precision, high-spatial-resolution and fast
54 temperature control^{5,10}. However, because of the natural brittleness of conventional inorganic TE
55 materials, it is very difficult to reduce their dimensions using traditional top-down processing to
56 fabricate on-chip micro-TEDs. Bottom-up approaches using thin-film technology have therefore been
57 developed^{4,5,10}, but the main drawback is their poor TE performance compared with the conventional
58 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 substrate²⁵. 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)₂Te₃ hybrids for flexible micro-TEDs. The grooves of SWCNT bundles guide the epitaxial growth of (Bi,Sb)₂Te₃ 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)₂Te₃ 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)₂Te₃ 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 performance⁸. 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 surface³². However, such heteroepitaxy can only be achieved in very limited combinations of substrates and films with similar crystal symmetries, lattice parameters, and thermal expansion coefficients³².

117 Herein, we develop a general approach to using the freestanding bundle of one-dimensional (1D)
118 SWCNTs as a deposition scaffold to guide the highly oriented growth of nanocrystalline materials to
119 form a freestanding and flexible hybrid. Our fabrication approach is applicable to many
120 semiconductors and metals with different crystal structures, such as (Bi,Sb)₂Te₃, PbTe, PbSe, Cu₂Te,
121 Ag₂Te, Pt, Au, Cu and Si (Fig. 2a; detailed characterizations of ordered microstructures in
122 Supplementary Figs. 1-7). Combined with computational simulations, an epitaxial growth mechanism
123 for such highly ordered microstructures under the driving force of minimizing free energy has been
124 shown in Supplementary Notes 1 and 2. The deposited atoms have a strong vdW interaction with the
125 SWCNTs (Fig.1 and Supplementary Figs. 8-11). Our approach may pave the way for the fabrication
126 and application of a wide variety of 1D CNT-nanocrystal hybrids with ordered microstructures.

127 In Fig. 2, we can see that the (Bi,Sb)₂Te₃ nanocrystals have a strong out-of-plane (000*l*)-texture
128 (Supplementary Note 3). The (Bi,Sb)₂Te₃ <1 $\bar{2}$ 10> orientation that is the closely packed direction on
129 the (000*l*) atomic plane, aligns well with the local SWCNT bundle axis/groove (Fig. 2b,c). From the
130 intensity profiles of two columns of atoms along <1 $\bar{1}$ 00> direction, we can deduce that there is almost
131 no growth strain in the nanocrystal directly located on the SWCNTs (Fig. 2c-e), where the vdW force
132 is dominant and there is no structural correlation or chemical bonding. With increasing deposition
133 time, the Bi-Sb-Te atoms are primarily stacked on the (000*l*) atomic plane to get a thicker deposit,
134 leaving a flat surface with an atomic height step edge (Fig. 2d and Supplementary Video 1). Such a
135 growth process is consistent with the kinetics of the layer-by-layer growth model³³. The (000*l*) atomic
136 plane/SWCNT interface with <1 $\bar{2}$ 10> orientation aligned with the SWCNT groove is the most stable
137 structure, which is consistent with the MD simulations (Fig. 2f and Supplementary Note 2). Therefore,
138 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 strength³⁴. During the growth, a high density of stacking faults and twin boundaries were thus generated along this plane³⁵, which would have a strong influence on phonon transport^{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

Fig. 3 | Thermoelectric characterization of the (000l)-textured SWCNT-Bi_xSb_{2-x}Te₃ hybrids, a (000l)-textured dense Bi_{0.5}Sb_{1.5}Te₃ film and a non-(000l)-textured SWCNT-Bi_{0.5}Sb_{1.5}Te₃ hybrid. a, Temperature-dependent in-plane electrical conductivities. **b**, Seebeck coefficients, **c**, Comparison of the ZT values of previously reported typical freestanding flexible¹¹⁻¹⁷, transferrable TEs¹⁸⁻²³ and SWCNT-Bi_{0.5}Sb_{1.5}Te₃ hybrid at ~300 K. The ratios of corresponding electrical conductivity to thermal conductivity (σ/κ) for these TE materials are also indicated.

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 ~0.5:1.5. A dense Bi_{0.5}Sb_{1.5}Te₃ film deposited on a SiO₂/Si wafer

155 with the (000*l*)-textured and a non-(000*l*)-textured hybrid were also prepared for comparison. The
 156 fitted curve of electrical conductivity (σ) as a function of $T^{-3/2}$ is compatible with the experimental
 157 results (Fig. 3a), indicating that acoustic phonon scattering is dominant over the investigated
 158 temperature range. Such a primary carrier scattering mechanism is similar to that in a pure Bi₂Te₃
 159 film³⁷ and is not obviously affected by the presence of SWCNTs (Supplementary Notes 4 and 5). The
 160 carrier mobility (μ) along the (000*l*) plane is higher than those along other orientations, due to the
 161 strong anisotropy of the carrier transport of Bi₂Te₃-based alloys³⁸. Although the hybrid contains a
 162 large number of nanopores and Bi_{0.5}Sb_{1.5}Te₃/SWCNT interfaces, its μ value is only ~20% lower than
 163 that of the (000*l*)-textured dense film. The randomly orientated GBs strongly scatter carrier transport
 164 and reduce the μ in the Bi₂Te₃ alloys^{8,39}. In contrast, low-angle tilt GBs cause little scattering when
 165 the carriers cross neighboring Bi₂Te₃-based nanocrystals^{40,41}, resulting in a relatively large σ . The
 166 well-aligned $\langle 1\bar{2}10 \rangle$ orientation with a higher μ on the (000*l*) atomic plane⁴² would also make a
 167 crucial contribution to σ . Because the Seebeck coefficient (α) is not sensitive to the crystallographic
 168 orientation and porosity, the α values of all samples are comparable. As a result, the power factor of
 169 the (000*l*)-textured hybrid is ~42% higher than that of the non-(000*l*)-textured one and ~35% lower
 170 than that of the (000*l*)-textured dense film (Supplementary Fig. 21a).

171 The in-plane thermal conductivity (κ) values of the samples are shown in Supplementary Fig.
 172 21b. We can see that the κ values of all hybrids are substantially lower than that of the dense films
 173 (Supplementary Note 6). The reduction in κ is mainly derived from a small lattice contribution (κ_l)
 174 and a bipolar effect (κ_b) (ref. ⁴³), and $\kappa_l^h + \kappa_b^h$ is as low as $\sim 0.44 \pm 0.04 \text{ W m}^{-1} \text{ K}^{-1}$ at RT
 175 (Supplementary Fig. 21b), close to the values of highly porous (Bi,Sb)₂Te₃ alloys with a weak degree
 176 of (000*l*)-texture⁴⁴. However, considering the strong anisotropy on phonon transport along with the

(000 l) atomic plane and the porosity of the hybrid is only ~one-third of the reported porous (Bi,Sb)₂Te₃ alloys, the porosity alone cannot explain the significant reduction of κ_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 κ_l . As revealed by our computational simulations (Supplementary Note 7), a low-angle tilt GB also effectively scatters the phonons and decreases κ_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)₂Te₃, 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 prepared¹¹ 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 ΔT is defined as $I_{\max}$. Both the maximum ΔT ($\Delta T_{\max}$) and $I_{\max}$ values increase with an increase of T_h (Fig. 4b), which could be caused by the increased T_h and TE performance³⁸.

201

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 ΔT ($=T_h - T_c$) as a function of applied cooling current (I_{cooling}) at different T_h values. The white dotted line indicates maximum ΔT ($\Delta T_{\max}$). **c**, Estimated cooling power density (Q_c) of the micro-TEC module as a function of applied I_{cooling} at different T_h values. The white dotted line indicates the maximum Q_c ($Q_c^{\max}$). **d**, COP of the micro-TEC module as a function of cooling power (P_c) at $\Delta T = 0$ K. **e**, The $Q_c^{\max}$ and $\Delta T_{\max}$ normalized to T_c of the micro-TEC module compared with previously reported data points of flexible macro-TECs²⁴⁻²⁷ and inflexible micro-TECs^{4,5,10,45}. **f**, Output voltage (V) and power output (P_g) of the micro-TEG module as a function of current (I) under various ΔT_g . **g**, Comparison of the maximum power density ($Q_g^{\max}$) of previously reported flexible TE modules^{13-15,19,28-31}.

210

211 In a closed system, the dependence of ΔT on applied electrical current can be attributed to three
 212 primary competing mechanisms (Supplementary Note 9), the Peltier effect, the Joule heating effect
 213 and cooling loss by thermal conduction. When the sum of Joule heating and thermal conduction
 214 effects equals the Peltier effect, the ΔT reaches its maximum value. Although, the cooling ability
 215 might have been underestimated due to the cooling loss through the suspended Pt/SiN_x bridge
 216 connected to the SiN_x/Si substrate (Fig. 4a), compared with the traditional thin-film TEC²⁵, our
 217 flexible micro-TEC achieves more efficient cooling by fully eliminating the cooling loss of the
 218 supporting substrate. Stable $\Delta T_{\max}$ values of ~14 K to ~22.4 K were obtained at 300-400 K under an
 219 applied current of less than ~1 mA. Meanwhile, the cooling power (P_c) of the micro-TEC module at
 220 different applied currents and the corresponding coefficient of performance (COP) values at $\Delta T=0$ K
 221 were calculated for different T_h , and the results are shown in Fig. 4d. The micro-TEC module
 222 delivered a maximum P_c of ~89 to ~127 μ W with a COP value of ~0.5 over the entire temperature
 223 range investigated (Fig. 4d). The cooling power density (Q_c) was estimated by dividing P_c by the
 224 total cross-sectional areas of two p-n couples along the heat flow direction. The maximum Q_c ($Q_c^{\max}$)
 225 is determined by the TE properties of the hybrid and decreases linearly with the length of the TE
 226 couples³⁸. $Q_c^{\max}$ values of ~65 to ~92.5 W cm⁻² were obtained, which are ~one order of magnitude
 227 higher than that of conventional bulk TEC (Fig. 4e). The larger the $\Delta T_{\max}$ and $Q_c^{\max}$ values, the better
 228 the cooling performance of the micro-TEC. Remarkably, the micro-TEC module achieved a large ΔT
 229 and $Q_c^{\max}$ at a micro-length scale with no forced heat removal, indicating that it may find important
 230 applications in nano-micro systems for temperature control.

231 The ability of the micro-TEG module to convert thermal energy to electric power was also tested
 232 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 (ΔT_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-TED module is negligible. When the load resistance matches the micro-TEG module internal resistance, the maximum output power ($P_g^{\max}$) is obtained, which increases with ΔT_g^2 . When the ΔT_g reaches ~30 K, the value of V increases to ~22.7 mV, accompanied by a short-circuit current of ~90 μ A. The $P_g^{\max}$ is increased to a value of ~0.49 μ W, yielding a maximum power density ($Q_g^{\max}$) 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 TEG¹⁴⁻¹⁶ 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-TED 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 transfer⁴⁶ 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-TED 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

255 using silver paint or soldering materials. For example, R_{contact} and R_{lead} account for ~50% of the R
 256 because of the use of a low-quality Pt bonding film prepared by a focused ion beam deposition
 257 technique. If R_{lead} and R_{contact} are substantially decreased, the thermal load and power load capacities
 258 of the micro-TED module could be improved by a factor of ~2 (Supplementary Note 8).

259 Flexibility of the hybrid and micro-TED module

260

261 **Fig. 5 | Flexibility of the SWCNT-Bi_{0.5}Sb_{1.5}Te₃ hybrid and micro-TED module.** **a**, Relative electrical resistance
 262 (blue) and bending radius (red) as a function of bending strain (ϵ_b) for a ~720-nm-thick (000 l)-textured SWCNT-
 263 (Bi,Sb)₂Te₃ hybrid on a polyimide substrate (open circles) and a freestanding p-n couple of the micro-TED module
 264 (filled circles). R_0 and R are the original electrical resistance in the flat state and the resistance when bent,
 265 respectively. **b**, Results of the cyclic bending test of the freestanding micro-TED module at a bending radius of ~0.3
 266 mm. Inset: SEM image of the freestanding p-n couple of the micro-TED module. Scale bar, 100 μm . The relative
 267 change of internal resistance under various bending states is normalized. Error bars, 10% (**a,b**), as determined from
 268 the measurement uncertainties in R (~5%) and R_0 (~5%). **c-e**, MD simulation of Sb₂Te₃ nanocrystals under bending
 269 with low 5° (**c**) and high 15° (**d**) tilt-angle GBs along Sb₂Te₃ $\langle 1\bar{2}10 \rangle$ direction, and low 5° (**e**) tilt-angle GBs along
 270 Sb₂Te₃ $\langle 10\bar{1}0 \rangle$ direction. The atomic shear strains for each case are shown on the Y-Z plane. **f**, MD simulation of
 271 nanocrystals in the bending cycle test along Sb₂Te₃ $\langle 1\bar{2}10 \rangle$ direction. Microstructure of the region near the GBs in
 272 Sb₂Te₃ nanocrystals with 5°, 15° and 30° tilt-angle GBs after 5 bending cycles.

273 The flexibility of the hybrid film was estimated by measuring its relative change of resistance (R/R_0)
274 at different bending radii (Fig. 5a,b). The bending strain (ε_b) can be approximately estimated from
275 the bending radius (r_b), the sample thickness and Young's modulus (Supplementary Note 10). The
276 freestanding hybrid was transferred onto a ~ 75 μm -thick polyimide substrate to increase ε_b which
277 scales linearly with thickness. Under bending, the relative electrical resistance slightly increases with
278 the decrease of r_b . When the bending radius decreased to ~ 4 mm, ε_b increased by $\sim 0.8\%$ and the
279 relative change in the electrical resistance was only $\sim 7\%$. Such excellent flexibility comes from the
280 combined effects of thinness, a nanoporous structure, a flexible SWCNT scaffold and
281 crystallographic orientation¹¹.

282 The flexibility of the micro-TED module was also evaluated. To realize bending at the microscale,
283 an AFM was used to push the suspended SiN_x membrane connected to a p-n couple. From the
284 displacement of moving end of the p-n couple, the bending radius was estimated (Supplementary Fig.
285 25). We can see that due to the freestanding structure and thickness effect, the p-n couple can be
286 freely deformed with a bending radius down to ~ 0.2 mm without any obvious increase in resistance,
287 revealing its excellent flexibility (Fig. 5a). Moreover, the p-n couple also shows good electrical
288 stability after $\sim 1,000$ bending cycles (Fig. 5b). MD simulations show the $(\text{Bi,Sb})_2\text{Te}_3$ nanocrystals in
289 the $(000l)$ orientation with a low-angle tilt GB along the $\langle 1\bar{2}10 \rangle$ direction have a much better bending
290 flexibility than others (Fig. 5c-f, Supplementary Note 11 and Supplementary Fig. 26), which is in
291 good agreement with the experimental results. Such a good flexibility may provide freedom to adapt
292 to possible displacements and internal strains caused by misfits of the material's thermal expansion
293 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)₂Te₃ 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)₂Te₃ 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 Bi₂Te₃/Sb₂Te₃ 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 Bi₂Te₃ (99.99%), Sb₂Te₃ (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.

318 **Materials characterization.** The microstructures of the samples were characterized by XRD (D8
319 Discover, Bruker), SEM (Supra 55 Zeiss) and TEM (FEI Tecnai T12, 120 kV; FEI Tecnai F20, 200
320 kV). Energy-dispersive spectra (EDS) was used to characterize the compositions of the samples. The
321 thickness of the (Bi,Sb)₂Te₃ nanocrystals deposited on the SWCNT scaffold was estimated by cross-
322 sectional TEM observations. The thicknesses of the SWCNT scaffold, (Bi,Sb)₂Te₃ thin film and
323 SWCNT-(Bi,Sb)₂Te₃ hybrids were directly measured by atomic force microscopy (AFM, Innova,
324 Bruker) and cross-sectional SEM images.

325 **Thermoelectric performance and bending flexibility measurements.** A Netzsch SBA-458 system
326 was used to simultaneously measure the in-plane σ and α with Ar (99.999%) gas protection from
327 room temperature to 480 K. The measurement errors for σ and α were less than 5% and 3%,
328 respectively. The in-plane κ values of the samples were measured using the well-developed
329 suspended thermal isolation technique. To ensure that the hybrids had good contact with the thermal
330 measurement device, a freestanding SWCNT scaffold was first transferred onto two suspended SiN_x
331 membranes with the assistance of a lab-built femtosecond laser micro-cutting system (Supplementary
332 Video 2), and (Bi,Sb)₂Te₃ was then deposited on the whole area of the scaffold using a deposition
333 mask, which ensured that the hybrid was well bonded with the SiN_x membranes. A focused ion beam
334 system (Nanolab Helios 720) was used to prepare the thermal conductivity test samples and micro-
335 TED. The uncertainty for the measurements involved in κ was ~10%. The combined uncertainty for
336 the ZT value calculation was ~20%. The Hall coefficient and carrier concentration were measured
337 with an HMS-3000 Hall system using the van der Pauw method. The bending tests were conducted
338 using a lab-built apparatus. The samples were attached to the surface of glass tubes of different radii,
339 and relative changes in electrical resistance were measured to evaluate their flexibility. The
340 measurement error for relative electrical resistance was ~10%.

341 **Fabrication and measurement of micro-TED.** A lab-built femtosecond laser micro-cutting system
342 with a beam resolution better than ~700 nm was used to tailor the hybrids with a precisely controlled
343 shape and dimensions. The freestanding p-n couples were connected in series using a SiN_x/Si
344 substrate as a heat sink and a flexible suspended Pt/SiN_x membrane as a heat source and target cooled
345 area which is analogous to the hotspots in a chip. A suspended SiN_x membrane is widely used to
346 thermally isolate sensitive thermal sensors operated at relatively low temperatures⁴⁷. Such a micro-
347 TED module has a lateral structure where the heat flow is parallel to the substrate. Pt films were

348 deposited on the SiN_x substrate to generate heat and monitor the temperature change (Fig. 4a) using
349 a focused ion beam technique. The performance of the micro-TED module was measured in a lab-
350 built vacuum instrument to minimize the influence of air convection. T_h was maintained at the range
351 of 300-400 K during the test of micro-TEC module. A series of temperature differences was produced
352 by heating one end of the micro-TEG module using a heater and the cold side of the module was
353 maintained at RT. The output voltage, current and output power under different ΔT_g values were
354 monitored by a Keithley 4200 SCS system.

355 **Methods of computational calculations.** CP2K software was used to simulate the growth of BST
356 and Pt nanocrystals deposited on SWCNT bundles. Density functional theory (DFT) calculations in
357 this work were performed to first compute the static energy. The kinetic evolution of the SWCNT-
358 nanocrystal system was simulated by the ab initio molecular dynamics (AIMD) method. DFT
359 calculations were based on the hybrid Gaussian and plane wave (GPW) scheme⁴⁸ with the Perde-
360 Burke-Enzerhof (PBE)⁴⁹ exchange correlation functional and corresponding pseudo potentials⁵⁰. A
361 plane wave density cutoff of 400 Ry and periodic boundary conditions were used. Dispersion
362 interactions were included using an empirical analytical potential, using the Grimme D3 method⁵¹,
363 within a range of 16 Å. For AIMD simulations, the temperature was from 300 K to 800 K with a time
364 step of 0.5 fs. The total number of simulation steps was up to 9,000 for each case. Details of AIMD
365 and DFT simulations are shown in Supplementary Notes 1 and 2. Classical MD simulations were also
366 performed for a Sb₂Te₃ nanocrystal with small and large tilt-angle GBs to calculate the lattice thermal
367 conductivity and the flexibility by using the Large-scale Atomic/Molecular Massively Parallel
368 Simulator (LAMMPS) package with the two-body interatomic potential. GBs were generated
369 between the neighboring nanocrystals by rotating the middle one around the surface normal by given
370 angles (Supplementary Fig. 26). In this work, the time interval was 1 ps for LAMMPS and the
371 simulation temperature was 270 to 330 K. Details of MD simulations are shown in Supplementary
372 Notes 1, 2, 7 and 11.

373 **Data availability**

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

376 **Code availability**

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

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387 **Author contributions**

388 Q.J., Y.Z., S.J., K.T. and C.L. conceived and designed the experiments. Q.J. fabricated the hybrids
389 and characterized their microstructures and thermoelectric and flexible properties. Q.J. and Y.Z.
390 performed the integration and characterization of flexible micro-TEDs. S.J. and X.L. prepared the
391 high-quality SWCNT scaffold and carried out its characterization. Y.Z. and J.T. fabricated the
392 thermal conductivity test devices and measured the thermal conductivity of the hybrids. X.L., Z.W.
393 and N.G. conducted the computational simulations. P.M., K.C., J.Q. and Y.W. contributed to the
394 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
395 the manuscript. All the authors commented on and revised the manuscript.

396 **Competing interests**

397 The authors declare no competing interests.

398 **Additional information**

399 **Supplementary information** is available for this paper at <https://XXX>.

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