Exceptional thermoelectric properties of flexible organic—inorganic hybrids with monodispersed and periodic nanophase

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Flexible organic—inorganic hybrids are promising thermoelectric materials to recycle waste heat in versatile formats. However, current organic/inorganic hybrids suffer from inferior thermoelectric properties due to aggregate nanostructures. Here we demonstrate flexible organic—inorganic hybrids where size-tunable Bi₂Te₃ nanoparticles are discontinuously monodispersed in the continuous conductive polymer phase, completely distinct from traditional bi-continuous hybrids. Periodic nanofillers significantly scatter phonons while continuous conducting polymer phase provides favored electronic transport, resulting in ultrahigh power factor of ~1350 μW m⁻¹ K⁻² and ultralow in-plane thermal conductivity of ~0.7 W m⁻¹ K⁻¹. Consequently, figure-of-merit (ZT) of 0.58 is obtained at room temperature, outperforming all reported organic materials and organic—inorganic hybrids. Thermoelectric properties of as-fabricated hybrids show negligible change for bending 100 cycles, indicating superior mechanical flexibility. These findings provide significant scientific foundation for shaping flexible thermoelectric functionality via synergistic integration of organic and inorganic components.

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Currently, more than 60% of the primary energy of fossil fuels is lost worldwide as waste heat, and the loss is around 70% in automobiles. This kind of energy loss brings a huge problem in energy utilization, and effectively recovering such waste heat is critical to overcome the energy crisis. Thermoelectrics involve conversion between heat and electricity, and thus it is extremely important for global sustainability. Integration of thermoelectric technology into industrial energy-utilization processes is of great interest and could provide an effective solution for power generation. Particularly, flexible materials are very attractive because of easy integration into various industrial processes. Flexible organic–inorganic hybrids, which can offer a huge degree of tunability because of diverse selections in both organic and inorganic components, have exhibited noteworthy promise for thermoelectric energy conversion. Owing to the fascinating interfacial transport properties caused by the possible energy filtering effect and phonon scattering at the engineered nanoscale interfaces, organic–inorganic hybrids provide a new approach to avoid suffering from the trade-offs in thermoelectric materials, display high thermal conductivity larger than 0.2 for flexible and relatively light weight. These features make them feasible to act as self-powered solid-state coolers, which are very difficult to achieve for inorganic hybrid thermoelectrics. For example, enhanced thermoelectric power factor (σS2/σT) was observed in nanowire-filled poly(3,4-ethylenedioxythiophene) (PEDOT)/SnSe nanosheets composite films and organic molecules intercalated TiSe2 single crystals, respectively. Furthermore, organic–inorganic hybrid thermoelectrics can be flexible and relatively light weight. These features make them feasible to act as self-powered wearable devices by utilizing body’s heat or other heat source to generate electricity, wearable temperature sensors, and flexible solid-state coolers, which are very difficult to achieve for inorganic thermoelectric materials since they are intrinsically brittle and rigid.

In principle, the thermoelectric parameters of organic–inorganic hybrids are highly dependent on the interfacial surface-to-volume ratio, as phonons and carriers are mainly scattered at interfaces in organic–inorganic hybrids. For example, enhanced thermoelectric power factor (σS2/σT) was observed in nanowire-filled poly(3,4-ethylenedioxythiophene) (PEDOT)/SnSe nanosheets composite films and organic molecules intercalated TiSe2 single crystals, respectively. Furthermore, organic–inorganic hybrid thermoelectrics can be flexible and relatively light weight. These features make them feasible to act as self-powered wearable devices by utilizing body’s heat or other heat source to generate electricity, wearable temperature sensors, and flexible solid-state coolers, which are very difficult to achieve for inorganic thermoelectric materials since they are intrinsically brittle and rigid.

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Bi$_2$Te$_3$(300) and PEDOT/Bi$_2$Te$_3$(600) hybrid films. Monodispersed and periodic Bi$_2$Te$_3$ nanophases in continuous PEDOT matrix were clearly observed in all PEDOT/Bi$_2$Te$_3$ hybrid films. The nanoparticle fraction was calculated according to the PS nanosphere packing model shown in Supplementary Fig. 3 (details are also provided in Supplementary Note 1), and digital photos of samples are shown in Supplementary Fig. 4. The X-ray diffraction (XRD) characterization shown in Supplementary Fig. 5 confirmed the Bi$_2$Te$_3$ crystal in the fabricated films.

**Thermoelectric properties.** The in-plane electrical conductivity, Seebeck coefficient, and power factor of PEDOT/Bi$_2$Te$_3$ hybrid films were characterized and the measurement schemes are shown in Supplementary Fig. 6 and Fig. 7 by in-house built systems. Calibration results of our systems are shown in Supplementary Fig. 8 and Fig. 9. The thermoelectric properties were investigated as a function of Bi$_2$Te$_3$ nanoparticle fraction, as shown in Fig. 3. Similar to literatures$^{30,31}$, VPP-fabricated PEDOT films displayed an extremely high electrical conductivity of ~1350 S cm$^{-1}$. With increasing Bi$_2$Te$_3$ nanoparticle fraction, the electrical conductivity of hybrid films greatly decreased while the Seebeck coefficient increased, since Bi$_2$Te$_3$ possessed a much higher Seebeck coefficient and lower electrical conductivity than PEDOT film (Supplementary Table 1). We calculated the electrical conductivity and Seebeck coefficient of hybrid films based on both parallel and series connected model$^{17,32}$,

\[
\sigma(\text{parallel}) = \sigma_{\text{Bi}_2\text{Te}_3}x + \sigma_{\text{PEDOT}}(1-x),
\]

\[
\sigma(\text{series}) = \frac{\sigma_{\text{Bi}_2\text{Te}_3} \sigma_{\text{PEDOT}}}{\sigma_{\text{Bi}_2\text{Te}_3}(1-x) + \sigma_{\text{PEDOT}}x},
\]

\[
S(\text{parallel}) = \frac{S_{\text{Bi}_2\text{Te}_3} \sigma_{\text{Bi}_2\text{Te}_3}x + S_{\text{PEDOT}} \sigma_{\text{PEDOT}}(1-x)}{\sigma_{\text{Bi}_2\text{Te}_3}x + \sigma_{\text{PEDOT}}(1-x)},
\]

\[
S(\text{series}) = \frac{S_{\text{Bi}_2\text{Te}_3} \kappa_{\text{PEDOT}}x + S_{\text{PEDOT}} \kappa_{\text{Bi}_2\text{Te}_3}(1-x)}{\kappa_{\text{PEDOT}}x + \kappa_{\text{Bi}_2\text{Te}_3}(1-x)},
\]

where \(\sigma(\text{parallel})\) and \(S(\text{parallel})\) were the calculated electrical conductivity and Seebeck coefficient of the hybrids based on the parallel connected model, \(\sigma(\text{series})\) and \(S(\text{series})\) were the calculated electrical conductivity and Seebeck coefficient of the hybrids based on the series connected model. The as-prepared hybrids containing the smallest nanoparticles exhibited the largest Seebeck coefficient and electrical conductivity were observed in PEDOT/Bi$_2$Te$_3$(100) hybrid films.

All of these results indicated that the interfacial transport also played an important role in final thermoelectric properties of hybrids apart from the simple mixed effect. Energy filtering effect has been reported to improve the Seebeck coefficient in organic—inorganic hybrids in which interfaces form energy barriers that preferentially scattered low-energy carriers$^{7,16,33}$. This can make the relaxation time strongly depend on energy and increase the asymmetry of carrier transport about the Fermi level, resulting in an enhanced Seebeck coefficient. The as-prepared hybrids containing the smallest nanoparticles exhibited the largest interfacial surface-to-volume ratio, providing the most sites to selectively scatter low-energy carriers due to the interfacial energy barrier between PEDOT and Bi$_2$Te$_3$, and thereby leading to the largest Seebeck coefficient. Additionally, saturated trend in the Seebeck coefficient was observed in PEDOT/Bi$_2$Te$_3$(100) hybrid films. Hence, a maximum power factor of ~1350 \(\mu\)W m$^{-1}$ K$^{-2}$ was achieved in PEDOT/Bi$_2$Te$_3$(100) hybrid films with ~31 vol% Bi$_2$Te$_3$ nanoparticles (Fig. 3c).

To understand the nanophase-dependent phonon transport, the in-plane thermal conductivity of fabricated films was measured by a differential 3ω method$^{17,34,35}$, which was conducted in the same direction with the measured electrical conductivity and Seebeck coefficient. We fabricated thick hybrid films with a uniform thickness of ~0.75 \(\mu\)m (as shown in Supplementary Fig. 10) for the in-plane thermal conductivity measurement since it is challenging to perform in-plane thermal conductivity measurement for thin films less than 100 nm (see
Supplementary Figs. 11, 12, and 13 and Note 4 for detailed preparation process and measurement. As-prepared neat PEDOT films (see Supplementary Note 4 in the Supplementary Information for detailed preparation process) showed a high in-plane thermal conductivity of 1.52 W m\(^{-1}\) K\(^{-1}\) at room temperature (Fig. 4a). After introduction of the monodispersed and periodic Bi\(_2\)Te\(_3\) nanoparticles into PEDOT matrix, the thermal conductivity of PEDOT/Bi\(_2\)Te\(_3\) hybrid film was greatly suppressed with Bi\(_2\)Te\(_3\) nanoparticle fraction. The thermal conductivity for PEDOT/52 vol% Bi\(_2\)Te\(_3\)(100) hybrid film was only \(\approx 0.5\) W m\(^{-1}\) K\(^{-1}\), about 300% reductions as compared to PEDOT film. More interestingly, this value was also lower than that of Bi\(_2\)Te\(_3\) film (Supplementary Table 1), going against the mixture rule in classical composites where the thermal conductivity should be between that of the two components. In addition, the thermal conductivity of hybrid films was also related to the size of Bi\(_2\)Te\(_3\) nanoparticles (Fig. 4b). With a similar volume fraction, hybrid films with smaller Bi\(_2\)Te\(_3\) nanoparticles displayed a lower thermal conductivity. These results suggested that the great reduction in thermal conductivity for PEDOT/Bi\(_2\)Te\(_3\) hybrid films should be caused by not only the relatively lower thermal conductivity of Bi\(_2\)Te\(_3\) fillers but also the interfacial effect. The unique nanostructure achieved in these hybrid films contributed to a larger interfacial surface-to-volume ratio, especially for the hybrids with smaller Bi\(_2\)Te\(_3\) nanoparticles, and thereby leading to a lower thermal conductivity due to the interfacial effect.

Taking into account the interfacial effect as well as the size and volume fraction of nanoparticles, the effective thermal conductivity (\(\kappa_{\text{eff}}\)) of hybrids composed of continuous matrix and cylindric fillers (circular cylinders oriented perpendicularly to heat flow) can be estimated by a theoretical equation:

\[
\kappa_{\text{eff}} = \kappa_m \left[ \frac{(\kappa_d / \kappa_m) - (\kappa_d / \kappa_m)}{(\kappa_d / \kappa_m + (\kappa_d / \kappa_m) + 1)} V_d + \frac{(\kappa_d / \kappa_m) + (\kappa_d / \kappa_m) + 1}{(\kappa_d / \kappa_m + (\kappa_d / \kappa_m) + 1)} \right],
\]

where \(\kappa_m\) is the thermal conductivity of the matrix (in this case PEDOT), \(\kappa_d\) is the thermal conductivity of the dispersions (in this case Bi\(_2\)Te\(_3\)), \(V_d\) is the volume fraction of dispersions, \(r_d\) is the radius of circular cylindrical dispersions, and \(h_c\) is the interfacial...
conductance. When $h = \infty$, this equation agrees with the expression of Maxwell for effective thermal conductivity of composites without considering the interfacial thermal resistance. The dash lines in Fig. 4b are theoretical values derived from Eq. (5) with an interfacial conductance of $-2.21 \times 10^5 \text{W m}^{-2} \text{K}^{-1}$ (calculated with the experimental data of PEDOT/~31 vol% Bi$_2$Te$_3$(100) hybrid film). Our experimental data were well described by this model, since all the thermal conductivities of hybrid films were relatively consistent with theoretical ones. It is noted that the interfacial thermal conductance is very low which is at least two orders of magnitude lower than lots of reported values$^{37}$. The low interfacial thermal conductance is possibly caused by the strong acoustic mismatch due to different phonon densities and velocities between polymer matrix (PEDOT) and inorganic filler (Bi$_2$Te$_3$)$.^{3,38}$ Furthermore, the phonon mean free path of PEDOT might be in $10^{-10^2}$ order of magnitude$^{39}$, which is comparable to the size of Bi$_2$Te$_3$ nanoparticles in the hybrid films. This will enhance the phonon scattering at interfaces and thereby the thermal transport can be suppressed$^{3,12}$. Regarding the electrical transport, the matrix in hybrids is continuous and highly conductive PEDOT, which provides hole transport paths. More importantly, PEDOT is in situ polymerized with the presence of Bi$_2$Te$_3$ nanoparticles. This is good for intimate contact between PEDOT and Bi$_2$Te$_3$ and thereby enhancing charge transport across the PEDOT–Bi$_2$Te$_3$ interfaces. Many works have reported in situ synthesized polymer composites with enhanced electrical transport properties$^{33,30}$. Besides, the hole mean free path of PEDOT was reported to be more than one order of magnitude smaller than the phonon mean free path$^{39}$. Thus, the hole transport is minimally affected as compared to the phonon transport. Precise experimental measurement of the interfaces at the nanoscale will be helpful to better illustrate the interfacial thermal/electrical conductance in the future work. As a result of large power factor and greatly reduced thermal conductivity, the PEDOT/Bi$_2$Te$_3$ hybrid film presented a maximum in-plane ZT value of ~0.58 at room temperature for PEDOT/31 vol% Bi$_2$Te$_3$(100) hybrid film (Fig. 4c), the highest ever shown for organic materials and organic/inorganic hybrids (Fig. 4d)$^{5,6,9,17,34,41-45}$. The effect of Bi$_2$Te$_3$ particle sizes on the power factor and ZT is also shown in Supplementary Fig. 14. Air stability tests are shown in Supplementary Fig. 15.

**Mechanical flexibility.** The mechanical flexibility of PEDOT/Bi$_2$Te$_3$ hybrid film prepared on soft substrates was also investigated, and the photos of measurements are shown in Supplementary Fig. 16. When the PEDOT/31 vol% Bi$_2$Te$_3$(100) hybrid film was attached onto the surface of glass tube with different radius, the electrical resistance only slightly changed under bending deformation, within 5% of the initial value even at a very low curve radius of 3.5 mm (Fig. 5a). In contrast, directly deposited Bi$_2$Te$_3$ film by thermal evaporation displayed significant increases in electrical resistance with decrease of curve radius, reaching 18% change at curve radius of 3.5 mm. Furthermore, the hybrid film also showed higher mechanical stability compared with Bi$_2$Te$_3$ film, demonstrating negligible change in electrical resistance upon 100 bending cycles under curve radius of 3.5 mm, as illustrated in Fig. 5b. While the resistance of Bi$_2$Te$_3$ film continually increased with the bending times because of the appearance of micro-cracks in the Bi$_2$Te$_3$ film after bending (Supplementary Fig. 17). In the hybrid films, monodispersed and periodic Bi$_2$Te$_3$ nanoparticles were homogenously surrounded by flexible PEDOT. The intimate contact between Bi$_2$Te$_3$ nanoparticles and PEDOT matrix can accommodate deformations and thereby contributes to the superior flexibility. This also can be seen in Supplementary Fig. 18, the hybrid film with the largest...
interfacial surface-to-volume ratio showed the best mechanical flexibility. In addition to the bending effect on the electrical conductivity, the bending radius effect on the Seebeck coefficient was also examined as shown in Supplementary Fig. 19. These results demonstrate the flexible hybrid thermoelectric films are possible to be tailored as new types of devices outside of the domain of conventional rigid inorganic thermoelectric materials.

**Discussion**

In summary, flexible PEDOT/Bi$_2$Te$_3$ hybrid films with monodispersed and periodic Bi$_2$Te$_3$ nanophase have been successfully fabricated, exhibiting an ultrahigh ZT value of ~0.58 at room temperature. The unique nanostructure in hybrid films supplies an optimized interfacial surface-to-volume ratio, which not only contributes to a greatly reduced thermal conductivity but also the good mechanical flexibility. These results indicate the importance
of nanostructure engineering when exploring hybrid thermoelectric materials with both high performance and mechanical flexibility. Owing to the versatility of the fabrication method, numerous organic–inorganic hybrids also can be obtained by replacing the organic or inorganic component, providing a platform for creating nanostructured hybrid materials with wide applications.

Methods

Materials. Monodisperse suspension of PS nanospheres (10 wt%, in water) with various diameters (100, 300, and 600 nm), sodium dodecyl sulfate (SDS, >99%), 3,4-ethylenedioxythiophene (EDOT, 97%), poly(ethylene glycol)-block-poly(propylene oxide)-block-poly(ethylene glycol) (PEG-PPG-PEG, Mw = 5800), dimethylylformamide (DMF), n-butanol and toluene were purchased from Sigma-Aldrich. Iron (III) tosylate (Fe(Tos)3), 40 wt%, in n-butanol (CleviosTM C-B 40 V2) were purchased from H.C. Starck. P-type Bi2Te3 powders (99.99%, ~1250 mesh) were purchased from KTD Materials. Silicon wafers (undoped, resistivity >30 Ωcm) were purchased from University Wafer. Flexible polyimide substrates were purchased from Gizmodorks. All the materials were used as received.

Preparation of PEDOT/Bi2Te3 hybrid films. Flexible hybrid films were prepared following the above procedures by using flexible polyimide substrates.

Characterizations. The obtained films were characterized by field emission scanning electron microscope (JEOL JSM-7500F), XRD (Bruker D8) with a Cu-Kα source, and optical microscopy (Olympus). The thermoelectric properties of prepared films were tested with home-built apparatus. Details of the measurements for in-plane electrical conductivity, Seebeck coefficient, and thermal conductivity were mentioned in Supplementary Notes 2–4. The mechanical flexibilility was assessed by attaching the films on glass tubes with different diameter and testing their resistances.

Data availability

The data that support the findings of this study are available from the corresponding author on request.

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**Author contributions**

S.W. conceived the research; L.W. and S.W. designed the experiments. L.W., Y.L., and B.W. prepared samples and measured the thermoelectric properties. L.W. and Z.Z. performed the other characterizations. L.W., L.F., J.Q., K.Z., and S.W. analyzed the data and wrote the manuscript with comments and inputs from all authors.

**Additional information**

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**Competing interests:** The authors declare no competing interests.

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