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Interfacial energy band and phonon scattering effect in Bi₂Te₃-polypyrrole hybrid thermoelectric material

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We hybridized n-type Bi₂Te₃ with an inexpensive and abundantly available conducting polymer, polypyrrole, to obtain a bulk-structured hybrid material in which the interfacial energy band and the phonon scattering effects should occur at the interface of the two components. The obtained hybrid material inevitably exhibited a lower electrical conductivity than pristine Bi₂Te₃, which may be attributable to carrier scattering at the interfacial energy barrier. However, the hybrid material completely compensated for this loss in electrical conductivity with a significant increase in the Seebeck coefficient, and thus it retained the power factor with no loss. In addition, the hybrid material displayed a much lower thermal conductivity than pristine Bi₂Te₃ owing to the phonon scattering effect. The hybrid material exhibited significant decoupling of the electrical and thermal properties, thus affording state-of-the-art figures of merit ($ZT \sim 0.98$ at 25 °C, $ZT_{\max} \sim 1.21$ at 100 °C, and $ZT_{\text{ave}} \sim 1.18$ at 50–150 °C) that exceed those of most of the previously reported n-type Bi₂Te₃ or Bi₂(Te,Se)₃ materials. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5050089>

Bulk phases consisting of n-type or p-type Bi₂Te₃ have been primarily used for commercial thermoelectric applications at low temperatures (below 200 °C). As n-type Bi₂Te₃ generally exhibits inferior thermoelectric performance compared with its p-type counterpart, improving the performance of the former is crucial. The comprehensive thermoelectric performance is typically evaluated via the dimensionless figure of merit $ZT (= \alpha^2 \sigma T / \kappa)$, where α is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and κ is the thermal conductivity;^{1–7} thus, improvement of the thermoelectric performance can be accomplished by enhancing the electrical properties (i.e., increasing the power factor, $\alpha^2 \sigma$) or reducing the thermal conductivity. Researchers have made extensive efforts to enhance the electrical properties and/or decrease the thermal conductivity of Bi₂Te₃ via various methods, such as forming nanostructures,^{8–10} inserting nanoinclusions,^{11–13} and adding metallic or non-metallic atoms.^{14–16}

Hybridizing Bi₂Te₃ with a conducting polymer is another potential approach for improving the electrical and thermal properties of Bi₂Te₃. Conducting polymers have been evaluated as promising thermoelectric materials because they exhibit very low thermal conductivity and acceptable electrical properties.^{17–22} These organic materials are typically used as flexible thin films, which are applicable to micro-energy harvesting devices for low-temperature thermoelectric applications, rather than bulk structures. To supplement the relatively poor electrical properties of conducting polymers, researchers have investigated the addition of Bi₂Te₃;^{17–22} however, the resulting inorganic–organic composites typically exhibited rather limited electrical properties,^{18,20–22} which may be attributable to severe carrier scattering at the component interfaces

or the relatively poor charge-transport properties of the organic components. In the present study, we sought to hybridize Bi₂Te₃ with polypyrrole to obtain a bulk structure that could compensate for the possible deterioration in electrical properties. We developed an easily reproducible hybridization process, in which a small amount of polypyrrole was incorporated into n-type Bi₂Te₃ followed by spark plasma sintering compaction, thus affording a bulk-phase hybrid material. This hybrid material inevitably exhibited lower electrical conductivity than pristine Bi₂Te₃ owing to carrier scattering at the interface. However, it also displayed a significant increase in the Seebeck coefficient, because the carrier concentration was altered by the interfacial energy band, and thus retained the power factor with no loss. The hybrid material also exhibited much lower thermal conductivity due to the phonon scattering effect at the interface; thus, it induced significant decoupling of the electrical and thermal properties, which resulted in remarkable enhancement of the thermoelectric performance.

Bi₂Te₃ powder was prepared via a conventional pulverization method and suspended in aqueous Fe₂(SO₄)₃ solution. The addition of an aqueous dispersion of pyrrole led to *in situ* oxidation to afford polypyrrole, which was distributed throughout the Bi₂Te₃ powder. After filtration, the resulting powder was packed using a spark plasma sintering equipment to obtain cylindrical bulk specimens. Details of the sample preparation and characterization are provided in [supplementary materials I–III](#). The sintered specimen of the mixed powder of Bi₂Te₃ and polypyrrole (Bi₂Te₃-polypyrrole) was examined by TEM and found to consist of irregularly shaped grains of a few micrometers in size [dark contrast, Fig. 1(a)]. The specimen also contained relatively small grains of sub-micrometer size (bright contrast), which were not observed in the pristine Bi₂Te₃ specimen (Fig. S1 in the [supplementary material](#)). According to the enlarged region shown in Fig. 1(b), the dark

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FIG. 1. (a)–(c) TEM images of the Bi_2Te_3 –polypyrrole (BT-PPY) specimen: (a) low-magnification image, (b) enlarged image, and (c) HR-TEM image with the corresponding SAED patterns and schematic atomic structures of Bi_2Te_3 . (d) EDS results. (e) XRD patterns, (f) FT-IR spectra, and (g) Raman spectra of polypyrrole (PPY), Bi_2Te_3 specimen (BT), and BT-PPY. (h) Detailed analysis of the Raman spectra of BT and BT-PPY.

grains possessed distinct crystalline directions, whereas the bright grains appeared to be amorphous. Different periodic atomic arrangements were clearly observed for the dark grains [Fig. 1(c)] and the crystalline directions of Bi_2Te_3 were identified from the corresponding selected area electron diffraction (SAED) patterns [Fig. 1(c) inset]. The dark grains exhibited lattice fringes with interspaces of 3.21, 3.20, and 2.10 Å, which were indexed to (015), (105), and (110) planes, respectively, thus affording the arrangements of Bi and Te depicted in the schematic drawings. No specific atomic arrangement was evident for the bright grains [Fig. 1(c)], which was considered indicative of the amorphous phase of polypyrrole. As shown in the composition distribution obtained by energy-dispersive X-ray spectroscopy (EDS) analysis [Fig. 1(d)], the bright grains were mainly composed of C and N with no Bi and Te, whereas the dark grains mostly consisted of Bi and Te, and thus the bright and dark grains were identified as polypyrrole and Bi_2Te_3 , respectively. Both the sintered and unsintered specimens displayed the typical diffraction pattern of rhombohedral Bi_2Te_3 [Fig. 1(e)], corresponding to JCPDS Card No. 82-0358; thus, the crystalline dark grains were identified as rhombohedral Bi_2Te_3 and the stoichiometry was confirmed by the atomic composition observed by SEM/EDS (Fig. S2). No trace of polypyrrole was detected in the diffraction patterns because the bright grains possessed no specific atomic arrangement, as confirmed by the HR-TEM images, although the relatively high compositions of C and N in the Bi_2Te_3 –polypyrrole specimen were regarded as evidence for the presence of polypyrrole (Fig. S2). The typical electrical conductivity of inorganic Bi_2Te_3 (on the order of 10^3 S cm^{-1})^{6,7} is much higher than that of organic polypyrrole (on the order of 10^{-2} to 10^2 S cm^{-1}),^{23,24} which is consistent with the Bi_2Te_3 component exhibiting darker contrast than the polypyrrole component. The results therefore confirmed that the Bi_2Te_3 grains grown along the different crystalline directions were bounded by the amorphous phase of polypyrrole to form special interfaces in the Bi_2Te_3 –polypyrrole specimen.

The FT-IR spectrum of the Bi_2Te_3 –polypyrrole specimen included the characteristic IR peaks of polypyrrole (C–C stretching vibration at 775 cm^{-1} , doping state of polypyrrole at 853 cm^{-1} and 965 cm^{-1} , C–H out-of-plane bending vibration at 1039 cm^{-1} , C–C stretching vibrations at 1088 cm^{-1} and 1165 cm^{-1} , N–H deformation vibration at 1243 cm^{-1} , C–N stretching vibration at 1288 cm^{-1} , C–H in-plane stretching vibration at 1321 cm^{-1} , doping state of polypyrrole at 1384 cm^{-1} , C=C stretching vibrations at 1448 , 1543 , and 1593 cm^{-1} , and N–H in-plane bending vibration at 1630 cm^{-1})^{25–27} [Fig. 1(f)]. The FT-IR spectrum of the pristine Bi_2Te_3 specimen contained no peaks except for the signal at 1384 cm^{-1} , corresponding to the characteristic peak of Bi_2Te_3 .²⁸ This peak overlapped with the peak of the polypyrrole doping state in the spectrum of the Bi_2Te_3 –polypyrrole specimen. Polypyrrole retained its molecular structure during hybridization with Bi_2Te_3 despite the high sintering temperature of 350°C required for the compaction of Bi_2Te_3 , which is close to the degradation temperature of polypyrrole, because precise temperature control and a short sintering time were applied during the spark plasma sintering process. According to the Raman spectra [Fig. 1(g)], the characteristic peaks of Bi_2Te_3 appeared below 1000 cm^{-1} , whereas those of polypyrrole occurred above this frequency. The signals at 1370 and 1577 cm^{-1} were identified as the ring deformations of polypyrrole associated with the C–C or C–N ring-stretching modes and the C=C stretching mode, respectively,^{29–32} further indicating that the polypyrrole component had retained its molecular structure in the Bi_2Te_3 –polypyrrole specimen. The rhombohedral structure of Bi_2Te_3 is well known to consist of three quintuple layers (QLs) stacked by van der Waals forces. Each QL is alternately arranged with five atomic layers, $\text{Te}^{(1)}\text{–Bi–Te}^{(2)}\text{–Bi–Te}^{(1)}$ [Fig. 1(h)], where lattice vibrations of the atoms occur. The Bi_2Te_3 specimen exhibited both the Raman-active vibrational modes of E_g^2 (106.8 cm^{-1}) and A_{1g}^2 (137.5 cm^{-1}) and the infrared-active vibrational mode of A_{1u}^2 (120.2 cm^{-1}) [Fig. 1(h)], corresponding to the in-plane (E_g^2)

and out-of-plane (A_{1g^2} , A_{1u^2}) vibrations of $\text{Bi-Te}^{(1)}$.^{33,34} Compared with the vibrational modes of the Bi_2Te_3 specimen, those of the Bi_2Te_3 –polypyrrole specimen tended to shift to higher frequencies [Fig. 1(h)]. This phenomenon indicates that the chemical bonds between Bi and $\text{Te}^{(1)}$ are deformed by the interaction of QLs in the Bi_2Te_3 lattice structure [Fig. 1(h)] with polypyrrole molecules [Fig. 1(g)]. The detailed interaction mechanism and the underlying theory are currently under investigation to develop a reasonable model for the interaction between Bi_2Te_3 and polypyrrole molecules.

As demonstrated by the TEM analysis and FT-IR/Raman spectroscopy, Bi_2Te_3 formed interfaces with polypyrrole due to the molecular interaction, thus affording interfacial energy bands. The energy bands of Bi_2Te_3 and polypyrrole were investigated by measuring the relevant physical properties—ultraviolet photoelectron spectroscopy (UPS) was conducted to obtain the work functions (Φ) of the components, while UV–vis–NIR diffuse reflectance spectroscopy (DRS) was performed to determine their bandgaps (E_g). When He I ($h\nu = 21.2 \text{ eV}$) was used as the energy source for the UPS measurements, each component exhibited an onset energy, which is regarded as the valence band maximum (E_{VBM}), in addition to the cutoff energy (E_{cutoff}) [Figs. 2(a) and 2(b)]. The relationship between these energy levels can be expressed as shown in the following equations:^{35,36}

$$E_{\text{cutoff}} - E_{\text{VBM}} = h\nu - \Phi - (E_{\text{VBM}} - E_F), \quad (1a)$$

$$\Phi = h\nu - (E_{\text{cutoff}} - E_F), \quad (1b)$$

and thus, the work function of each component was derived [Eq. (1b)]. The Fermi level (E_F) of each component was placed below the vacuum level (E_{vac}) by the magnitude of the work function and the valence band edge (E_v) was then placed below the Fermi level by the magnitude of the valence band maximum [Fig. 2(c)]. We also used Tauc plots, which relate the optical absorbance to the incident photon energy, to determine the bandgap of each component

(Fig. S3). By using the bandgap with the valence band maximum, the conduction band edge (E_c) and the electron affinity (χ) were also derived, thus completing the band structure for each component [Fig. 2(c)]. By equilibrating the Fermi levels of the components, the equilibrium band alignment for the Bi_2Te_3 –polypyrrole specimen was obtained [Fig. 2(d)], suggesting the generation of an interfacial energy barrier with band-bending potential wells.

A wide range of values have been reported for the electrical conductivity of polypyrrole (on the order of 10^{-2} to 10^2 S cm^{-1}), depending on the fabrication method and the presence of dopants. Considering that Bi_2Te_3 generally exhibits considerably higher electrical conductivity (on the order of 10^3 S cm^{-1}), it is straightforward to understand that the electrical conductivity decreases upon the addition of polypyrrole to Bi_2Te_3 . The Bi_2Te_3 –polypyrrole specimen exhibited a 30%–38% lower electrical conductivity than the Bi_2Te_3 specimen in the measured temperature range [Fig. 3(a), Table S1]. This decrease in electrical conductivity originated from the decreases in both carrier mobility and carrier concentration upon the addition of polypyrrole [Fig. 3(a) inset]. Carrier transport would be expected to be interrupted by the interfacial energy barrier [Fig. 2(d)] and reduced physical density (Table S1), which explains the decrease in the carrier mobility for the Bi_2Te_3 –polypyrrole specimen. Owing to the band bending, the conduction band of Bi_2Te_3 may shift downward to the Fermi level, possibly resulting in electron accumulation, whereas the valence band of polypyrrole concomitantly shifts upward, thereby causing hole accumulation. These accumulated carriers should be offset at the interfaces, which explains the decrease in carrier concentration. The Seebeck coefficient (α) can be predicted using the Mott relation [Eq. (2)] and the Boltzmann formula [Eq. (3)] for degenerate and nondegenerate semiconductors, respectively,^{6,7}

$$\alpha = \frac{8\pi^2 k_B^2}{2eh^2} m^* T \left(\frac{\pi}{3n} \right)^{2/3}, \quad (2)$$

FIG. 2. (a) and (b) UPS results of the onset and cutoff energy boundaries of (a) Bi_2Te_3 and (b) polypyrrole; the full spectra are given in the insets. (c) Band diagrams of Bi_2Te_3 and polypyrrole arranged by work function (Φ), valence band maximum (E_{VBM}), bandgap (E_g), and electron affinity (χ). (d) Equilibrium band alignment for the Bi_2Te_3 –polypyrrole specimen obtained by equilibrating the Fermi levels (E_F) of the two components.

FIG. 3. Temperature dependence of thermoelectric transport properties of the Bi_2Te_3 (BT) and Bi_2Te_3 -polypyrrole (BT-PPY) specimens: (a) electrical conductivity (σ), with carrier concentration (n) and carrier mobility (μ) at 25 °C shown in the inset; (b) Seebeck coefficient (α) and power factor ($\alpha^2\sigma$); (c) thermal conductivity (κ), divided into carrier (κ_c) and lattice (κ_l) contributions; and (d) ZT .

$$\alpha = \frac{k_B}{e} \left[\left(\frac{5}{2} + r \right) + \ln \frac{2(2\pi m^* k_B T)^{3/2}}{h^3 n} \right], \quad (3)$$

where k_B , h , r , and m^* are the Boltzmann constant, the Planck constant, the scatter parameter, and the effective mass of the carrier, respectively. These equations reveal that the Seebeck coefficient is inversely proportional to the carrier concentration (n); thus, the Bi_2Te_3 -polypyrrole specimen exhibited a 23%–35% higher Seebeck coefficient than the Bi_2Te_3 specimen in the measured temperature range [Fig. 3(b), Table S1]. Therefore, although the electrical conductivity decreased upon the introduction of polypyrrole, the Seebeck coefficient increased, and the power factor was almost retained in the measured temperature range—it increased by 3%–15% depending on the measurement temperature [Fig. 3(b), Table S1]. The introduction of polypyrrole also caused a significant reduction in the thermal conductivity [Fig. 3(c)], which was primarily due to the remarkable decrease in thermal diffusivity (λ , Table S1, and Fig. S4) in addition to minor contributions from the decrease in physical density (d) and the increase in specific heat capacity (C_p) (Table S1). Owing to its lower carrier mobility and carrier concentration, the Bi_2Te_3 -polypyrrole specimen exhibited a 32%–38% lower carrier thermal conductivity (κ_c) than the Bi_2Te_3 specimen [Fig. 3(c) inset, Table S1]. The former also exhibited a 42%–69% lower lattice thermal conductivity (κ_l) than the latter as a result of vigorous phonon scattering at the interfaces of Bi_2Te_3 and polypyrrole. Consequently, the overall thermal conductivity of the Bi_2Te_3 -polypyrrole specimen was up to 50% lower than that of the Bi_2Te_3 specimen in the measured temperature range.

Upon the incorporation of polypyrrole into Bi_2Te_3 , the power factor was almost retained, while the thermal conductivity was significantly diminished; thus, a remarkable enhancement in ZT was achieved [Fig. 3(d)]—the Bi_2Te_3 -polypyrrole specimen exhibited ZT values of 0.98 at 25 °C, 1.21 at 100 °C (maximum ZT , ZT_{max}), and 1.18 at 50–150 °C (average ZT , ZT_{ave}), which were approximately double those of the Bi_2Te_3

specimen. These ZT values are not only preeminent among previously reported n-type binary Bi_2Te_3 materials, but also comparable to the excellent performance of the recently reported n-type ternary $\text{Bi}_2(\text{Te},\text{Se})_3$ material (Table S3).^{14,37–43} We are currently conducting further studies to determine the interaction mechanism, the underlying theory, and the influence of different compositions of the two components to optimize the thermoelectric transport properties.

See [supplementary material](#) for details of sample preparation, relevant characterization, TEM/SEM analyses, and electrical/thermal properties of the Bi_2Te_3 and Bi_2Te_3 -polypyrrole specimens; bandgap energies of Bi_2Te_3 and polypyrrole; and a comparison of the thermoelectric performance.

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