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Enhancing Thermoelectric Performance of Bi$_2$Te$_3$-based Nanostructures through Rational Structure Design

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Introduction

Considering the environmental pollution caused by the consumption of fossil fuels and the rising demand of energy depletion, it is necessary to develop green sustainable energy sources and energy harvesting technologies.$^1$ Thermoelectric materials, enabling the direct conversion between heat and electricity, provide an alternative solution to these crises.$^2$ The energy conversion efficiency of a thermoelectric material is gauged by the dimensionless figure of merit, $ZT = S^2T/\kappa\sigma$, where $S$, $\sigma$, $\kappa$ and $T$ are the Seebeck coefficient, electrical conductivity, thermal conductivity (including electronic component $\kappa_e$, lattice component $\kappa_l$ and bipolar component $\kappa_b$), and the working temperature, respectively.$^{3, 5}$ However, the current low $ZT$ values, especially for n-type (with free electrons) thermoelectric materials, significantly hinder the commercialization of thermoelectric devices, which demand the synergistic development of both n-type and p-type (with free holes) thermoelectric elements.$^6, 7$

Bi$_2$Te$_3$ and the family of similar compounds are the promising thermoelectric candidates at room temperature region.$^{8-10}$ Because of their six valley degeneracy, the narrow energy gap and layered crystal structure, Bi$_2$Te$_3$ potentially meets the criteria of high power factor ($S^2\sigma$) and low $\kappa$.$^{11}$ Compared with bulk counterpart, nanostructured Bi$_2$Te$_3$ can achieve much lower $\kappa$, and provides promising possibilities to manipulate the thermoelectric properties.$^{12}$ Especially, rhombohedral structured Bi$_2$Te$_3$ nanostructures, as two-dimensional nanostructures,$^{13-15}$ exhibit strengthened phonon scattering due to the dense grain boundaries after sintered into pellets.$^{16}$ To further strengthen the phonon scattering, we can assemble the randomly orientated nanoplates in the form of well-aligned hierarchical nanostructures.$^{17}$

Inspired by our previous study on epitaxial growth of T-shaped Te/Bi$_2$Te$_3$ heteronanojunctions,$^{18}$ we explored the fabrication of the hierarchical nanostructures by using the one-dimensional Te nanostructures as templates. One-dimensional Te nanostructures, including nanowires$^{19}$ and nanotubes,$^{20, 21}$ have been reported to be synthesized by the wet chemical method. Compared with nanowires, nanotubes show even lower $\kappa$ due to the existence of tube channels.$^{22}$ Because of the potential lattice match between trigonal structured Te ($a_{Te} = 4.45$ Å, $c_{Te} = 5.92$ Å)$^{23}$ and rhombohedral structured Bi$_2$Te$_3$ ($a_{Bi2Te3} = 4.38$ Å, $c_{Bi2Te3} = 30.49$ Å)$^{24}$, i.e. $a_{Te} \approx a_{Bi2Te3}$, $c_{Te} \approx 1/5$ $c_{Bi2Te3}$, it is anticipated a small lattice mismatch of (110) plane for Te and Bi$_2$Te$_3$ ($< 2\%$),$^{25}$ so that [110] planes of Te nanotubes can serve as templates for the epitaxial growth of Bi$_2$Te$_3$ nanotubes, as demonstrated in the atomic models of Te/Bi$_2$Te$_3$ heteronanojunctions (refer to Fig. 1a and b). Using this crystallographic relationship, Te/Bi$_2$Te$_3$ hierarchical nanostructures can be formed on Te nanostructures. For layered Bi$_2$Te$_3$ single crystals, $\kappa$ is anisotropic and its value along the c-axis is only $\sim 50\%$ of that on the a-b plane,$^{26}$ so that massive studies have explored the advantage of well-aligned Bi$_2$Te$_3$ layered nanostructures to reduce $\kappa$.$^{7, 15, 27}$ Therefore, this hierarchical nanostructures is expected to result in significantly

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enhanced phonon scattering, as schematically illustrated in Fig. 1c. On the other hand, the crystalline nature of Te nanotube walls may enhance $\sigma$.22,28

In this study, we employed a microwave-assisted solvothermal method to synthesize Te/Bi$_2$Te$_3$ hierarchical nanostructures using Te nanotubes as templates. To confirm the superiority of Te/Bi$_2$Te$_3$ hierarchical nanostructures in enhancing thermoelectric efficiency, highly uniform Bi$_2$Te$_3$ nanoplates were also investigated as a reference. Through the comparison of the morphology-dependent thermoelectric performance, we fundamentally studied the structural effects on tuning thermoelectric properties.

Experimental

Materials Synthesis and Processing

In this study, analytical grade Bi(NO$_3$)$_3$·5H$_2$O, Na$_3$TeO$_3$, ethylene glycol, poly(N-vinyl-2-pyrrolidone) (PVP, $M_w = 4000$), and NaOH solution were used as precursors.

The synthesis of the Te/Bi$_2$Te$_3$ hierarchical nanostructures was carried out in two steps. The first step is to synthesize Te nanotubes as the precursors, following by the second step - synthesis of Te/Bi$_2$Te$_3$ hierarchical nanostructures. In the first step, we added 332.4 mg Na$_3$TeO$_3$ and 0.2 g PVP into 40 mL ethylene glycol. The solutions were stirred vigorously for 30 min at room temperature. Subsequently, the obtained clear solutions were sealed in a 100 mL teflon vessel, which was heated in a CEM Mars-6 microwave oven at 230 °C for 5 min. After naturally cooled to room temperature, the as-synthesized Te nanotubes were collected by a high-speed centrifugation, washed six times with distilled water and absolute ethanol, and finally dried at 60 °C for at least 12 h in a vacuum oven.

Materials Characterizations

The phase purities of the as-synthesized products were examined by the X-ray diffractometer (XRD) equipped with graphite monochromatized, Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). The morphological, structural, and compositional characteristics of the synthesized products were investigated by scanning electron microscopy (SEM, JEOL 7800) and transmission electron microscopy (TEM, FEI F20), equipped with EDS for compositional analysis.

Fabrication of Pellets

The as-synthesized Te/Bi$_2$Te$_3$ hierarchical nanostructures and Bi$_2$Te$_3$ nanoplates were compressed by the spark plasma sintering (SPS) under 40 MPa and at 250 °C for 5 min in vacuum into pellets with a diameter of 12.5 mm and a thickness of 2 mm. The densities ($\rho$) of sintered pellets were measured by an Archimedes method, and confirmed to be over 90%.
Thermoelectric Performance Measurement

Thermal diffusivity \( (D) \) of sintered pellets was measured by a laser flash method (LFA 457, NETZSCH), and \( \kappa \) was calculated through \( \kappa=DC/\alpha d \), where \( C_p \) is the specific heat capacity. \( C_p \) is obtained from empirical formulas \( C_p=108.06+5.53 \times 10^{-2}T \) JK\(^{-1}\)mol\(^{-1}\) for Bi\(_2\)Te\(_3\). \( \sigma \) and \( D \) were measured simultaneously on a ZEM-3, ULVAC. The uncertainties of the thermoelectric performance measurements \( (S, \sigma \) and \( D \) \) were estimated as \( \sim 5\% \) for each.

Results and discussion

Fig. 2a is the X-ray diffraction (XRD) pattern collected from the as-synthesized Te/Bi\(_2\)Te\(_3\) nanopowders with the inset showing its enlarged view of 20 in the range of 34° – 43°. As can be seen, the diffraction peaks can be indexed as the rhombohedral structured Bi\(_2\)Te\(_3\) phase with lattice parameters of \( a=4.38 \) Å and \( c=30.49 \) Å (JCPDS No. 89-2009)\(^{24} \) and the trigonal structured Te phase with lattice parameters of \( a=4.45 \) Å and \( c=5.92 \) Å (JCPDS No. 36-1452).\(^{23} \) It should be noted that no Bi contamination was detected in the as-prepared samples, although our samples contain excessive Bi\(^{3+}\) (dissolved from Bi(NO\(_3\))\(_3\)5H\(_2\)O). We believe that the excessive Bi\(^{3+}\) was still in the solvent after the synthesis that was washed away during the post-synthesis process. Fig. 2b is a SEM image, and shows that the majority (> 90%) of synthesized products are rod-like nanostructures. Fig. 2c is a TEM image of a typical rod-like nanostructure, in which the feature of a hierarchical nanostructure is seen — many parallel nanoplates are linked by a nanotube (as a stem). Their crystallographic relationship was further analyzed using selected area electron diffraction (SAED) and high resolution TEM (HRTEM). Fig. 2d is a SAED pattern taken from the circled area of such hierarchical nanostructure showing superimposed \([1 \bar{1} 0 0]\) zone-axis diffraction patterns of a trigonal structured Te phase and a rhombohedral structured Bi\(_2\)Te\(_3\) phase, from which the crystallographic relationship between the Te nanotube and the Bi\(_2\)Te\(_3\) nanotube stem can be determined as \([0001]_{\text{Te}} // [001]_{\text{Bi2Te3}} \) and \([11\bar{2} 0]_{\text{Te}} // [11\bar{2} 0]_{\text{Bi2Te3}} \). Fig. 2e and f are the corresponding HRTEM images taken from the arrowed nanotube body and the nanoplate edge, respectively, which further suggests the coexistence of a high-crystalline trigonal structured Te nanotube stem and rhombohedral structured Bi\(_2\)Te\(_3\) nanoplate. EDS was applied to examine the compositions of the nanotube and nanoplates. Fig. 2g shows the EDS profiles collected respectively from the labeled areas in Fig. 2c, suggesting that the nanotube is indeed Te, while the nanoplates are composed of Bi and Te with a mole ratio of approximately 2:3. To understand the structural characteristics of Te/Bi\(_2\)Te\(_3\) hierarchical nanostructures, we examined structures of Te nanotubes after first step synthesis (an example is shown in the ESI), which demonstrated that the
obtained nanotubes have their lengths of 2 - 6 μm and diameters of 100 - 200 nm. Our extensive electronic microscopy investigations of Te/Bi₂Te₃ hierarchical nanostructures indicate that the lateral size and thickness of the epitaxially grown Bi₂Te₃ nanoplates are relatively independent to the diameters of Te nanotubes.

As a comparison, Bi₂Te₃ nanoplates were also synthesized and characterized. Fig. 3a is a XRD pattern of as-prepared Bi₂Te₃ nanoplates, confirming Bi₂Te₃ nanoplates are highly pure rhombohedral structured Bi₂Te₃ phase. Fig. 3b is the low-magnification SEM image of as-synthesized Bi₂Te₃ hexagonal-shaped nanoplates that have uniform morphology with their lateral size of ~1μm. The inset of Fig. 3b is the high-magnification SEM image showing the side-view of several nanoplates, from which the nanoplate thickness of ~20 nm can be revealed. Fig. 3c is the TEM image of a typical nanoplate with lateral size of ~1μm, in accordance with the size determined by SEM (refer to Fig. 3b). Fig. 3d is the [0001] zone-axis SAED pattern and Fig. 3e is the corresponding HRTEM image with a lattice spacing of 0.22 nm, which matches well with the d value of the (11̅20) planes of rhombohedral structured Bi₂Te₃. Fig. 3f shows the EDS profile, indicating that the elemental ratio of Bi and Te is approximately 2:3 (note that Cu and C peaks are caused by the TEM Cu grid with C supporting films).

In order to evaluate their thermoelectric performance, we examined sintered pellets made from Te/Bi₂Te₃ hierarchical nanostructures and Bi₂Te₃ nanoplates. Fig. 4a presents σ and S as a function of temperature, indicated by the left-hand side of the graph, and the right-hand side y-axis, respectively. As can be seen, σ declines from ~8×10⁻⁴ Sm⁻¹ to ~5×10⁻⁴ Sm⁻¹ with increasing the temperature for both Bi₂Te₃ and Te/Bi₂Te₃ based pellets; however the declining trend in Te/Bi₂Te₃ is mitigated. In the case of S, its negative sign for both Bi₂Te₃ and Te/Bi₂Te₃ cases indicates their n-type feature. Specifically, S for Bi₂Te₃ ranges from -150 μVK⁻¹ to -170 μVK⁻¹, while that for Te/Bi₂Te₃ fluctuates between -165 μVK⁻¹ and -182 μVK⁻¹ in the studied temperature range. Moreover, the absolute value of S increases first and then decreases with increasing the temperature. The decrease in |S| should be caused by the bipolar conduction, and the peak of |S| for Te/Bi₂Te₃ shifts towards the higher temperature, suggesting that the bipolar conduction is suppressed at the higher temperature. Based on the measured σ and S, we can calculate S′σ, and plotted in Fig. 4b as a function of temperature. As can be seen, the peak S′σ of 19.2×10⁻⁴ Wm⁻¹K⁻² for Te/Bi₂Te₃ is larger than that of 18×10⁻⁴ Wm⁻¹K⁻² for Bi₂Te₃, and the peak S′σ for Te/Bi₂Te₃ shifts to higher temperature. This is due to the suppressed bipolar conduction and the mitigated declining trend in σ with increasing the temperature in Te/Bi₂Te₃ (refer to Fig. 4a).

To understand the enhanced S′σ, we calculated the reduced Fermi level (η=E/Fₜ, with Fₜ representing the Fermi level and kₜ the Boltzmann constant) based on the measured S by using the following equation,

$$ S = -\frac{k_B}{e} \left[ \frac{2F(\eta)}{F'_r(\eta)} \right] \eta, $$

with the generalized Fermi integral

$$ F_r(\eta) = \int_0^\infty \frac{e^{\xi/a}}{1+e^{\xi/a}}d\xi; $$

where e is the elementary charge. The inset of Fig. 4b plots the variation of η with temperature for both Bi₂Te₃ and Te/Bi₂Te₃.
in which \( \eta \) for Te/Bi\(_2\)Te\(_3\) is smaller than that for Bi\(_2\)Te\(_3\).

According to our previous study,\(^{34} \) to maximize \( S' \sigma \), the Fermi level should locate near the conduction band edge for n-type thermoelectric materials. Compared with Bi\(_2\)Te\(_3\), \( \eta \) for Te/Bi\(_2\)Te\(_3\) is closer to its conduction band edge, so that an enhanced \( S' \sigma \) for Te/Bi\(_2\)Te\(_3\) can be anticipated. The \( \eta \) decline for Te/Bi\(_2\)Te\(_3\) nanostructures can be ascribed to the excessive Te (provided by Te nanotube stems), which might suppress the Te vacancies in epitaxially grown Bi\(_2\)Te\(_3\) nanoplates. Te vacancies in Bi\(_2\)Te\(_3\) are generally unavoidable (giving n-type transport feature), and the Te vacancies lead to the Fermi level residing deep in the conduction band. Favourably, by adding more Te, Te vacancies in in Bi\(_2\)Te\(_3\) can be suppressed; resulting in the shift of the Fermi level towards the valance band in our Te/Bi\(_2\)Te\(_3\) nanostructures. Fig. 4c plots \( \kappa \) versus temperature, from which \( \kappa \) in Te/Bi\(_2\)Te\(_3\) shows \(~20\%\) reduction than that for Bi\(_2\)Te\(_3\). Due to the enlarged \( S' \sigma \) and simultaneously decreased \( \kappa \) \( ZT \) for Te/Bi\(_2\)Te\(_3\) is enhanced, as shown in Fig. 4d. \( ZT \) for Te/Bi\(_2\)Te\(_3\) reaches \(~1\) much larger than that of \(~0.75\) for Bi\(_2\)Te\(_3\).

From above discussion, one of the critical reasons for enhanced \( ZT \) is the significantly decreased \( \kappa \). To clarify the underlying principle, we studied the contributions of \( \kappa \) from electrons, phonons and bipolar conduction. According to the Wiedemann-Franz law,\(^{35} \) \( \kappa \) can be expressed as

\[
\kappa = L e T,
\]

where \( L \) is the Lorenz number. Employing the single Kane band model, \( L \) can be determined by\(^{36} \)

\[
L = \left( \frac{k_B}{\epsilon} \right)^2 \frac{3E_F(\eta)}{E_F(\eta)} \left( \frac{2E_F(\eta)}{3E_F(\eta)} \right)^{1/3} \left( \frac{2E_F(\eta)}{3E_F(\eta)} \right)^{1/3}
\]

(4)

Through inputting the determined \( \eta \) (refer to the inset of Fig. 4b) into Equation (4), we can calculate \( L \). The results are shown in Fig. 5a, in which \( L \) fluctuates around \(1.6 \times 10^{-8} \) \( V^2 K^{-2} \) for both samples, matching with reported values for nanostructured thermoelectric systems.\(^{37} \) On this basis, Fig. 5b plots the calculated \( \kappa \), over the studied temperature, where \( \kappa_\text{e} \) is reduced in Te/Bi\(_2\)Te\(_3\) due to its smaller \( \sigma \) and \( L \) over Bi\(_2\)Te\(_3\). By subtracting \( \kappa_\text{e} \) from \( \kappa \), we can study the variation of \( \kappa_\text{th} \) although there is a \( \kappa_\text{th} \) contribution at high temperature. Fig. 4b shows the obtained temperature dependent \( \kappa_\text{th} \), which suggests that \( \kappa_\text{th} \) in Te/Bi\(_2\)Te\(_3\) is significantly decreased. This is because Te/Bi\(_2\)Te\(_3\) hierarchical nanostructures have the well-aligned nanoplates attached on the body surface, which lead to stronger phonon scattering compared with the randomly oriented Bi\(_2\)Te\(_3\) nanoplates.\(^{38} \) Moreover, \( \kappa_\text{th} \) is calculated using the reference-outlined method.\(^{39} \) Specifically, by extrapolating the linear relationship between \( \kappa_\text{th} \) and \( 1/T \) demonstrated in the insert of Fig. 5c, we can obtain \( \kappa_\text{th} \) in the entire studied temperature range, and finally, though subtracting \( \kappa_\text{e} \) from \( \kappa - \kappa_\text{th} \), we can obtain \( \kappa_\text{th} \), Fig. 5d shows the determined \( \kappa_\text{th} \) as a function of temperature. As can be seen, \( \kappa_\text{th} \) for Te/Bi\(_2\)Te\(_3\) is reduced; suggesting that the bipolar conduction in Te/Bi\(_2\)Te\(_3\) has been indeed suppressed, which is consistent with the peak of \( S \) for Te/Bi\(_2\)Te\(_3\) shifting to the high temperature (refer to Fig. 4a). To understand this, we note that the band gap difference between Te (0.33 eV)\(^{40} \) and Bi\(_2\)Te\(_3\) (0.15 eV)\(^{41} \) may lead to an extra energy offset between the conduction and valance bands for the Te/Bi\(_2\)Te\(_3\) nanostructures. In addition, our Bi\(_2\)Te\(_3\) nanoplates in Te/Bi\(_2\)Te\(_3\) are generally thinner than the normal Bi\(_2\)Te\(_3\) nanoplates, leading to the enlargement of band gap in our thinner Bi\(_2\)Te\(_3\) nanoplates.\(^{42} \) As a consequence, the bipolar conduction can be suppressed in our Te/Bi\(_2\)Te\(_3\) nanostructures.

**Conclusion**

We successfully fabricated Te/Bi\(_2\)Te\(_3\) hierarchical nanostructures using Te nanotubes as templates by the facile microwave-assisted solvothermal method. Through systematic morphological, structural and compositional characterizations, structural quality and the epitaxial growth of well-aligned Bi\(_2\)Te\(_3\) nanoplates on Te nanotube stems are verified. The thermoelectric properties measured from their sintered pellets indicate an increased \( ZT \approx 1 \) when compared with their pure Bi\(_2\)Te\(_3\) nanoplates with \( ZT \approx 0.75 \). Our modelling studies suggest that the enhanced \( ZT \) of our Te/Bi\(_2\)Te\(_3\) hierarchical nanostructures is caused by the optimized reduced Fermi level, the strengthened phonon scatterings, and the suppressed bipolar conduction. This study provides an effective approach to enhance thermoelectric efficiency by designing rational nanostructures.

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Notes and references

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Enhanced thermoelectric performance in Te/Bi$_2$Te$_3$ hierarchical nanostructures caused by strengthened phonon scattering, optimized Fermi level, and suppressed bipolar conduction.