

Grain-boundary modulation doping for high-power-density thermoelectric generation in ZrNiSn composites

Congcong Xing^{1,2}, Na Liu², Yangtao Zhou³, Yilai Jiao⁴, Xiang Wang⁵, Kaiyang Xia¹, Huiping Hu¹, Aziz Genç⁶, Yu Liu⁷, Xiaolei Fan^{1,9}, Qingyue Wang⁸, Yu Zhang^{1,2}✉, Khak Ho Lim⁸✉, and Bed Poudel²✉

¹ Wenzhou Key Laboratory of Novel Optoelectronic and Nano Materials, Institute of Wenzhou, Zhejiang University, Wenzhou 325006, China

² Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania 16802, USA

³ Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

⁴ Center for Material Characterization, Liaoning Academy of Materials, Shenyang 110167, China

⁵ Hubei Key Laboratory of Novel Reactor and Green Chemical Technology, School of Chemical Engineering and Pharmacy, Wuhan Institute of Technology, Wuhan 430205, China

⁶ Catalan Institute of Nanoscience and Nanotechnology – ICN2 (CSIC and BIST), Campus UAB, Bellaterra, Barcelona, Catalonia 08193, Spain

⁷ Anhui Province Key Laboratory of Advanced Catalytic Materials and Reaction Engineering, School of Chemistry and Chemical Engineering, Hefei University of Technology, Hefei 230009, China

⁸ Institute of Zhejiang University–Quzhou, Quzhou 324000, China

⁹ Department of Chemical Engineering, School of Engineering, The University of Manchester, Oxford Road, Manchester M13 9PL, UK

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ABSTRACT: ZrNiSn-based half-Heusler compounds are promising thermoelectric materials for mid-to-high temperature power generation, but their widespread application is hindered by the costly reliance on hafnium (Hf) for performance optimization. Herein, we present a cost-effective, Hf-free strategy that simultaneously enhances the power factor and figure of merit (zT) in n-type ZrNiSn via grain-boundary-engineered modulation doping. Metallic tungsten (W) nanoparticles are introduced as a secondary phase, where they spontaneously segregate to grain boundaries during consolidation. This microstructure creates a network of internal heterojunctions that perform two synergistic functions: Charge injection from the low-work-function W elevates electrical conductivity, while interfacial energy-filtering barriers enhance the Seebeck coefficient. Consequently, the optimized composite achieves a peak power factor of $44 \mu\text{W}\cdot\text{cm}^{-1}\cdot\text{K}^{-2}$ and a zT of 0.76 at 910 K. Beyond intrinsic transport improvements, the practical viability of this material system is validated at the device level. When integrated into a thermoelectric unicouple, the material delivers an exceptional power density of $2.1 \text{ W}\cdot\text{cm}^{-2}$ and a conversion efficiency of 5.2% at a temperature difference of 307 K. Crucially, this approach eliminates expensive Hf, reducing material costs by over 95%. This work establishes grain-boundary modulation doping as a cost-effective route to enhance the power factor and zT of Hf-free ZrNiSn, offering a pragmatic balance between performance and economic viability for mid-temperature waste-heat recovery.

KEYWORDS: half-Heusler, modulation doping, interface engineering, thermoelectric devices, cost-effective

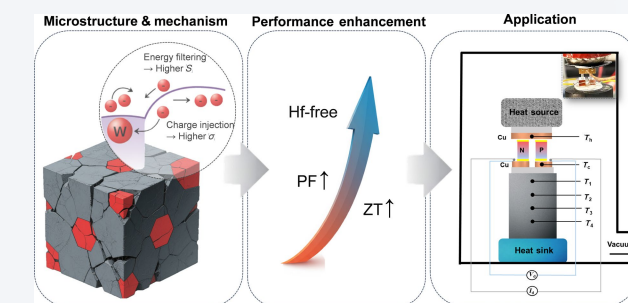
1 Introduction

Thermoelectric (TE) devices offer a robust, solid-state solution for

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✉ Address correspondence to Yu Zhang, y-zhang@zju.edu.cn; Khak Ho Lim, khl@zju.edu.cn; Bed Poudel, bup346@psu.edu



both waste-heat recovery and precise thermal management, with applications spanning consumer electronics, communications, biomedical systems, and automotive technologies [1–4]. The performance of a TE material is quantified by the dimensionless figure of merit, $zT = (S^2\sigma/\kappa)T$, where S is the Seebeck coefficient, σ the electrical conductivity, κ the total thermal conductivity, and T the absolute temperature [5]. Strategies to maximize zT focus on reducing lattice thermal conductivity (κ_l) or enhancing the power factor ($PF = S^2\sigma$), though improvements in one property invariably influence the other.

Half-Heusler compounds have emerged as a leading class of TE materials for mid- to high-temperature applications, owing to their exceptional mechanical integrity and resistance to oxidation [6–8]. Among these, n-type ZrNiSn (space group $F\bar{4}3m$) shows particular potential [9, 10], however, its simple cubic lattice yields a relatively high thermal conductivity ($7\text{--}17\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$), while its narrow band gap ($0.4\text{--}0.5\text{ eV}$) promotes bipolar conduction that degrades the S at elevated temperatures [11–13]. To address these challenges, researchers have turned to microstructural engineering (employing techniques such as melt spinning and high-energy ball milling followed by hot pressing to reduce grain size and strengthen grain-boundary phonon scattering), as well as compositional optimization [14–16], including isoelectronic alloying on the Zr site to introduce mass-/strain-fluctuation for phonon scattering to further suppress κ_L [17–19].

To date, the TE performance of ZrNiSn has been most effectively enhanced by isoelectronic substitution at the Zr site with Hf [14, 20, 21]. The large mass and size mismatch between Zr and Hf creates both mass -fluctuation and strain -field scattering centers, which strongly suppress the κ_L . For example, Liu et al. demonstrated that $\text{Zr}_{0.6}\text{Hf}_{0.4}\text{NiSn}_{0.98}\text{Sb}_{0.015}$ achieves a reduced κ_L as low as $2.55\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, approximately 70% lower than the undoped HfNiSn analogue, and achieved a peak zT of 1.0 at 970 K [20]. Similarly, Zhang et al. reported that $(\text{Hf}_{0.25}\text{Zr}_{0.75})_{0.995}\text{Nb}_{0.005}\text{NiSn}$ attains a maximum zT of 0.9 at 873 K [22]. Although a record zT of 1.4 was claimed for $\text{Hf}_{0.25}\text{Zr}_{0.25}\text{Ti}_{0.5}\text{NiSn}_{0.998}\text{Sb}_{0.002}$, its reproducibility has yet to be independently verified [23]. In practice, reliable reproduction of such high performance is often hindered by the volatility of low-melting-point elements, particularly Sn and Sb, which can lead to deviations from nominal stoichiometry during high-temperature synthesis. More critically, the dependence on hafnium imposes a severe economic constraint. In state-of-the-art (Hf,Zr)NiSn compositions, Hf accounts for approximately 99% of the total raw material cost, with market prices exceeding $\$4000/\text{kg}$ [6, 24]. This unfavorable cost structure fundamentally limits the scalability and commercial viability of half-Heusler TE modules for large-scale waste-heat recovery applications.

Herein, we propose and demonstrate a transformative, Hf-free strategy that simultaneously addresses both challenges through grain-boundary-engineered modulation doping. We introduce metallic tungsten (W) nanoparticles as a designed secondary phase, strategically segregated at the grain boundaries of a ZrNiSn matrix via controlled sintering. This microstructure creates a network of internal metal-semiconductor heterojunctions. We posit that these interfaces perform two critical, synergistic functions: (i) efficient electron injection from the low-work-function W into ZrNiSn via Fermi-level equilibration, enhancing σ without the ionized impurity scattering of substitutional doping; and (ii) the formation of nanoscale potential barriers that act as energy filters, preferentially scattering low-energy carriers to enhance S . As a result, the ZrNiSn-W nanocomposite exhibits a synergistic increase in power factor and zT . Fundamentally differing from conventional nanocomposite strategies that typically aim to introduce second phases as phonon scattering centers to minimize κ_L , this work breaks away from the conventional thermal-reduction paradigm.

2 Results and discussion

The synthesis of W-doped ZrNiSn nanocomposites was guided by a deliberate microstructural design strategy: to introduce stable, nanoscale metallic inclusions preferentially localized at grain boundaries, thereby decoupling electronic and thermal transport

pathways. This approach leverages the ultra-high melting point of W ($3422\text{ }^\circ\text{C}$) to impede grain coarsening during consolidation, while its relatively low work function compared with ZrNiSn establishes favorable band alignment for interfacial charge carrier injection.

Alloys with nominal compositions of $\text{ZrNiSn}-x\text{ wt.}\% \text{ W}$ ($x = 0, 1, 3, 5$) were synthesized via high-temperature induction melting, followed by comminution through high-energy ball milling and densification via spark plasma sintering (SPS) at 1173 K (Fig. 1(a)). The SPS conditions (5 min dwell) were optimized to retain the refined microstructure while ensuring full density. Phase purity and structural integrity were confirmed by powder X-ray diffraction (XRD, Fig. 1(b)). All major diffraction peaks correspond to the cubic half-Heusler phase (space group $F\bar{4}3m$, JCPDS 01-072-2587, Fig. 1(b)). Crucially, the lattice parameters of the ZrNiSn matrix remain unchanged with W addition, confirming the absence of substitutional doping or solid-state reaction. Concurrently, distinct diffraction peaks corresponding to elemental W (JCPDS 00-004-0806) emerge, with intensities scaling monotonically with nominal W content. This confirms the successful incorporation of W as a discrete secondary phase, a prerequisite for the intended heterogeneous modulation mechanism.

Microstructural analysis reveals the precise spatial distribution of the W phase. Backscattered-electron scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) mapping (Fig. S1 in the Electronic Supplementary Material (ESM)) indicate a uniform dispersion of W-rich regions. To gain deeper insight into the microstructure, representative scanning transmission electron microscopy (STEM) and conventional TEM (Fig. 1(d) and Fig. S2 in the ESM) were employed, which confirm the retention of the cubic hH structure (space group $F\bar{4}3m$, Fig. 1(e)), in agreement with XRD results, and reveal that W nanoparticles preferentially precipitate at grain boundaries. Significantly, STEM-EDS mapping (Fig. 1(f)) demonstrates that W nanoparticles are predominantly segregated at grain boundaries, with a minor fraction of finer inclusions dispersed intra-granularly. This targeted grain-boundary decoration is a direct consequence of the processing route: during SPS, W nanoparticles, due to their high thermal stability and limited solubility, are pinned at migrating grain boundaries, a phenomenon analogous to the Zener drag effect. Quantitative analysis of TEM micrographs yields a matrix grain size distribution of $\sim 180\text{--}700\text{ nm}$. The slightly larger grain size compared to some reported nanostructured half-Heuslers is attributed to the abbreviated (4 h) milling duration, a trade-off chosen to minimize contamination and defect formation while still achieving the critical nanostructuring necessary for phonon scattering.

X-ray photoelectron spectroscopy (XPS) was applied to investigate the surface electronic structure and oxidation behavior of ZrNiSn half-Heusler alloys following air exposure (Fig. 1(c)). As detailed in Table S1 in the ESM, the Zr 3d and Ni 2p core levels shift by $+0.1\text{--}0.3\text{ eV}$ relative to their elemental references, while the Sn 3d level shifts by -0.5 eV . These opposing chemical shifts signify electron transfer from electropositive Zr and Ni (cationic character) to electronegative Sn (anionic character), in agreement with the XYZ-type half-Heusler bonding model. High-resolution analysis of the Zr 3d spectra shows that oxidation is dominated by conversion to Zr^{4+} (ZrO_2), with a minor Zr^{2+} contribution consistent with suboxide (ZrO) formation or a Zr-rich defective interlayer [25]. This observation aligns with synchrotron studies reporting Zr^{2+} suboxide formation beneath the dioxide and prior reports of ZrO

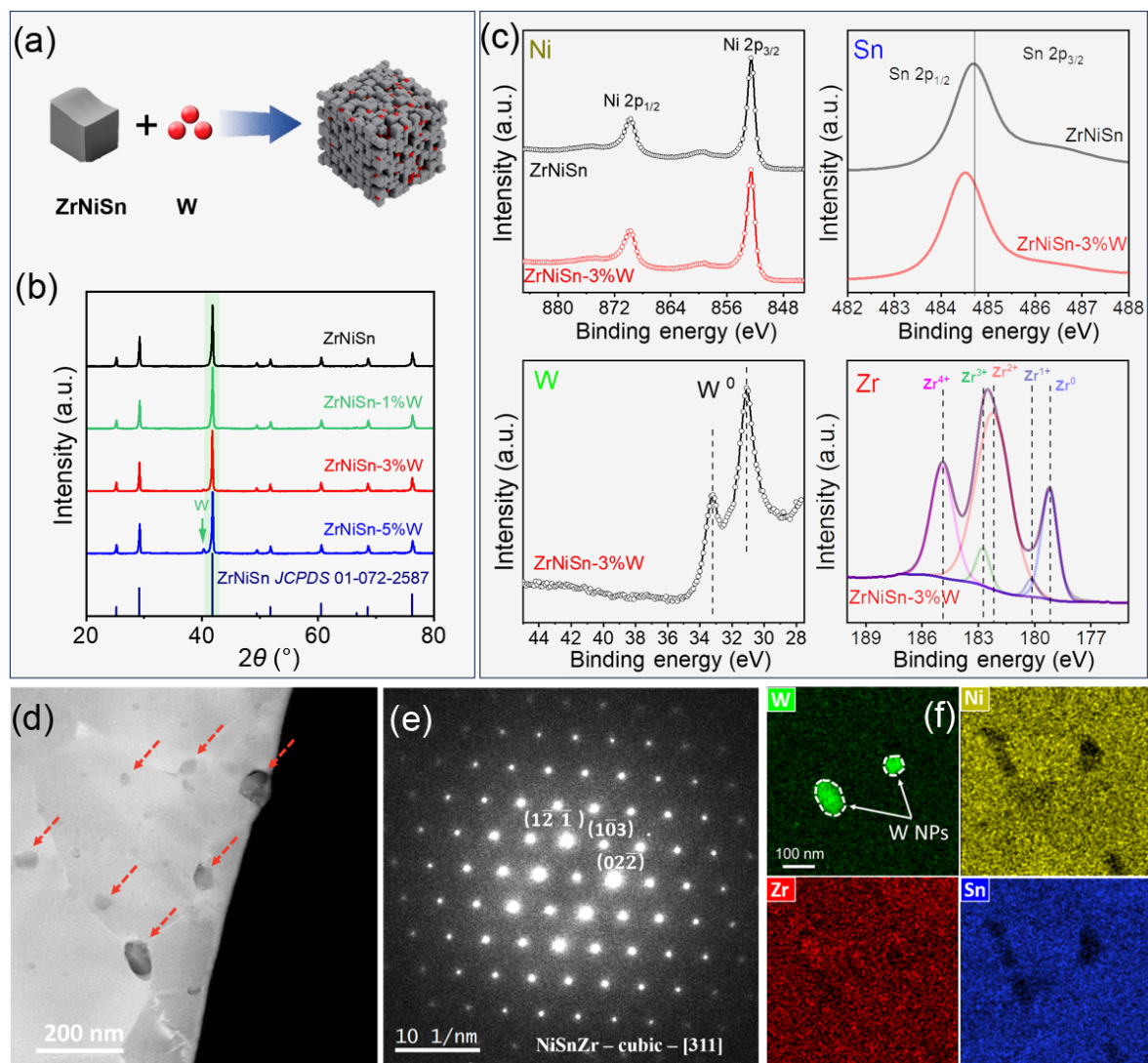
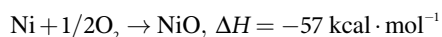
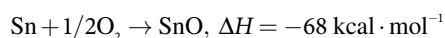
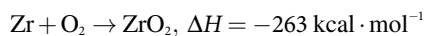


Figure 1 (a) Schematic illustration of W modulation doping in ZrNiSn matrix. (b) XRD patterns of as-synthesized ZrNiSn-W pellets. (c) High-resolution XPS spectra of ZrNiSn-3% W pellet. (d) Representative STEM image obtained for ZrNiSn-3%W, (e) selected area electron diffraction pattern, and (f) STEM-EDS mapping.

interlayers at metal-oxide interfaces. Thermodynamically, the negligible entropic contribution renders oxide formation sequential according to reaction enthalpies at ambient temperature [26–28]



The more exothermic formation enthalpy of ZrO_2 ($\Delta H \approx -263 \text{ kcal} \cdot \text{mol}^{-1}$) compared to SnO ($\Delta H \approx -68 \text{ kcal} \cdot \text{mol}^{-1}$) and NiO ($\Delta H \approx -57 \text{ kcal} \cdot \text{mol}^{-1}$) under ambient conditions indicates the preferential oxidation of Zr. In the ZrNiSn-W nanocomposite, the W 4f_{7/2} and 4f_{5/2} peaks appear at 31.2 and 33.4 eV ($\Delta E = 2.2 \text{ eV}$, intensity ratio 3:4), confirming that tungsten remains in the zero-valent metallic state after melting and sintering, consistent with XRD identification of a discrete W phase and indicative of negligible chemical interaction between W and the half-Heusler matrix.

Subsequently we employed a two-phase transport model to elucidate how the introduction of W nanoparticles, predominantly segregated at grain boundaries, modifies both electronic and thermal transport through tailored interfacial phenomena (details in the ESM). Based on the two-phase model, the additional charge barrier at grain boundaries decreases interfacial electrical resistance ($\rho_{\text{el-gb}}$) and increases electrical conductivity of the composite (Fig. 2(a)). For thermal transport, the lattice mismatch at grain boundary region may induce interfacial thermal resistance (ρ_{Kapitza}) and lead to large fractions of temperature drop across grain boundary (ΔT_{gb}), which results in higher S . Figures 2(b)–2(d) present the analysis of ZrNiSn- x wt.% W nanocomposites with and without grain boundaries. This deviation confirms that transport is governed by an energy-filtering regime responsible for the enhanced S . Quantitative analysis using the Seto grain-boundary model validates this mechanism: As presented in Fig. S3 in the ESM, the interfacial energy barrier (E_b) increases from 30 meV in pristine ZrNiSn to 45 meV in ZrNiSn-3 wt.% W. The linear correlation between the S and thermal conductivity κ (Fig. 2(b)) provides further, independent support for energy-filtered carrier transport. The increasing W content in ZrNiSn matrix decreases

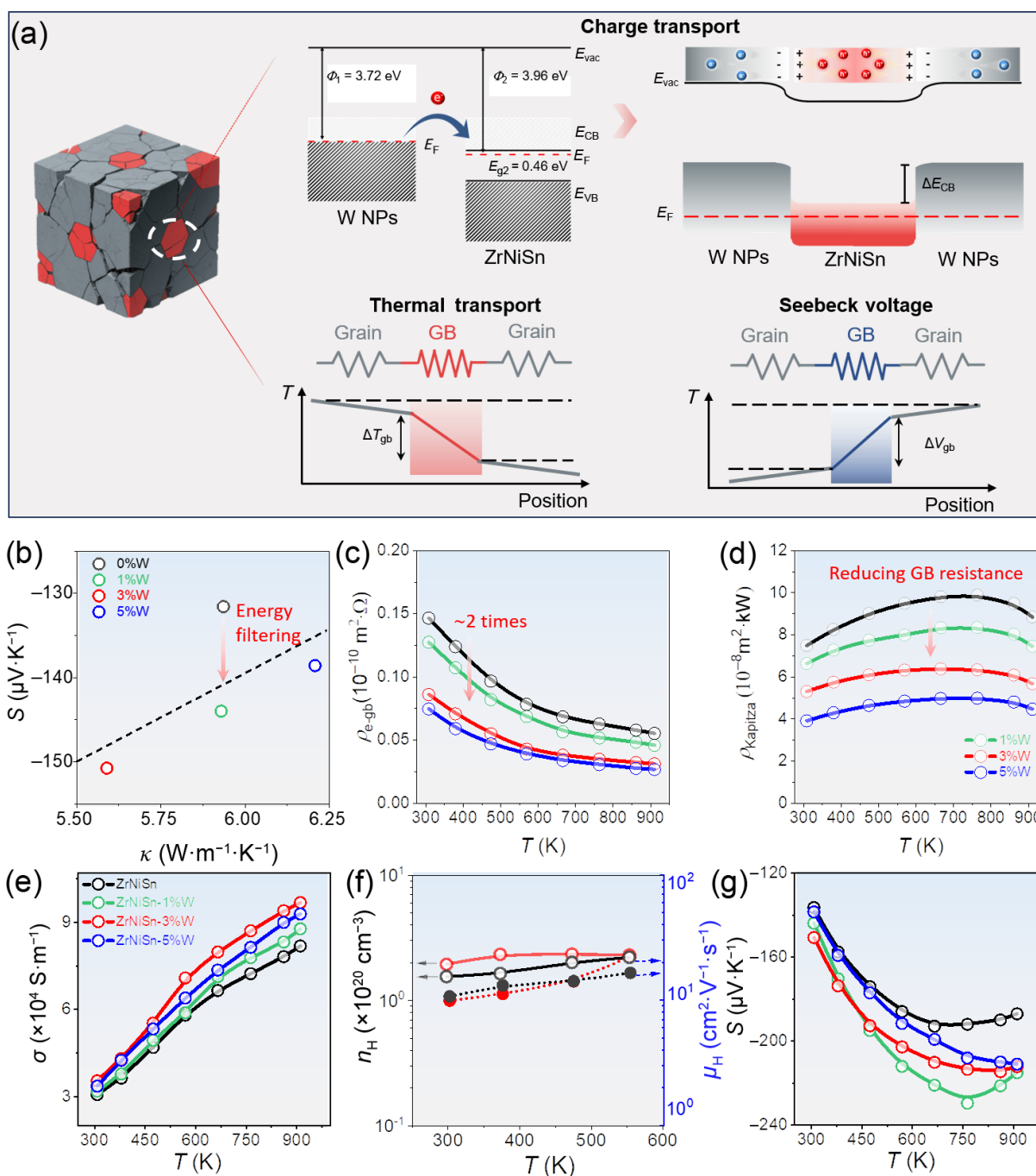


Figure 2 (a) Schematic illustration showing electron energy-band diagram, temperature drop (ΔT_{gb}), and voltage (ΔV_{gb}) at a heterojunction/ grain boundary region of W and ZrNiSn. Analysis of the grain boundary region: (b) linear correlation between Seebeck coefficient and thermal conductivity (κ); (c) interfacial electrical resistivity (ρ_{e-gb}); (d) interfacial thermal resistance ($\rho_{Kapitza}$). Temperature-dependent TE properties of ZrNiSn- x wt.%W samples: (e) electric conductivity, σ ; (f) carrier concentration, n_H and carrier mobility, μ_{H1} ; (g) Seebeck coefficient (S).

ρ_{e-gb} (Fig. 2(c)) as an indication of charge injection by W. However, the dense grain boundary network does not increase $\rho_{Kapitza}$ due to the much higher κ of W (Fig. 2(d)).

The electronic transport properties of the ZrNiSn-W nanocomposites reveal a departure from conventional doping behavior, underscoring the effect of the grain-boundary modulation doping strategy. Temperature-dependent measurements of electrical conductivity (σ) and Seebeck coefficient are presented in Figs. 2(e)–2(g). All composites exhibit n-type conduction (negative S) with σ increasing with temperature, characteristic of an intrinsic

semiconductor. The key improvement is the concurrent enhancement of both σ and S with optimal W content. At 300 K, σ rises from $3.0 \times 10^4 S \cdot m^{-1}$ for pristine ZrNiSn to $3.6 \times 10^4 S \cdot m^{-1}$ for the 3 wt.% W composite, representing a 20% improvement. Simultaneously, the magnitude of S increases modestly but systematically. This simultaneous enhancement is analyzed by two interfacial mechanisms operating in concert. First, the metallic W nanoparticles inject electrons into the ZrNiSn matrix through interfacial charge transfer, thereby significantly increasing the bulk carrier concentration (n_H). To understand the charge injection

mechanism, we performed comparative ultraviolet photoelectron spectroscopy (UPS) measurements on both the pristine ZrNiSn and the ZrNiSn-3 wt.% W nanocomposite (Fig. S4 in the ESM), with spectral analysis referenced to standard photoelectron spectroscopy handbooks [29]. Compared to the pristine phase, the addition of 3 wt.% W induces a distinct relative shift in the band features of the UPS spectra: the secondary electron cutoff (E_{cutoff}) shifts from 18.3 to 17.5 eV, and the valence band maximum (E_{VBM}) concurrently shifts from 3.2 to 2.4 eV. This clear 0.8 eV macroscopic shift in the band structure directly verifies the occurrence of pronounced interfacial band bending and charge transfer; namely, the low-work-function W acts as an electron donor, altering the local Fermi level. This observation is highly consistent with the physical picture of efficient electron injection achieved by introducing a second phase in the ZrNiSn system [30]. Furthermore, we conducted magneto transport (Hall effect) measurements to compare carrier concentration and carrier mobility between ZrNiSn and ZrNiSn-3 wt.% W samples (Table S4 in the ESM). The results confirm that the carrier concentration (n_{H}) of the 3 wt.% W sample quantitatively increases by 25%, while its carrier mobility (μ_{H}) remains well within the semiconductor characteristic range. Therefore, the moderate increase in n_{H} , corroborated by the 0.8 eV band shift observed in UPS, conclusively proves that the enhanced conductivity stems from spatially decoupled carrier injection at the pristine interfaces. Second, the W/ZrNiSn Schottky interfaces create nanoscale potential barriers that act as energy filters. Analysis of $\sigma(T)$ suggests a barrier height of approximately 5 meV, which preferentially scatters low-energy carriers while permitting higher-energy carriers to contribute to transport. This selective filtering increases the average carrier energy relative to the Fermi level, thereby enhancing S without the conductivity degradation typically associated with increased carrier concentration. Comparable interfacial energy-filtering effects have been demonstrated in a variety of metal-semiconductor TE nanocomposites, including Au nanodots-Bi₂Te₃ [31], Pt-Bi₂Te₃Se_{0.3} [32], Au-MoS₂ [33], Cu-SnSe₂ [34], and Ni_{0.05}Mo₃Sb_{5.4}Te_{1.6}-NiSb [35] composites, further supporting the generality of this mechanism.

The Pisarenko analysis in Figs. 3(a)–3(c) provides critical insight into the dominant scattering mechanisms. The experimental $S(n_{\text{H}})$ data for ZrNiSn-W nanocomposites deviate from the theoretical curve for pure acoustic phonon scattering and lie significantly below the curve for ionized impurity scattering. This positioning indicates a transport regime where energy filtering is the dominant enhancement mechanism for S . The linear correlation between S and thermal conductivity κ (Fig. 2(b)) further corroborates this, as such a relationship is a recognized signature of energy-dependent carrier scattering at interfaces. The optimal performance at 3 wt.% W represents a balance: sufficient W content to establish a percolating network for effective charge injection and filtering, but not so much as to create short-circuiting metallic paths that would degrade S .

A nuanced understanding of thermal transport is essential to evaluate the overall zT . The total thermal conductivity κ of the composites, shown in Fig. 3(f), exhibits a counterintuitive trend: κ increases with W addition, particularly above 500 K. Deconvolution of κ into its electronic (κ_{e}) and lattice (κ_{l}) components (Fig. 3(g) and Fig. S7 in the ESM) clarifies this phenomenon. The electronic contribution κ_{e} rises proportionally with the enhanced electrical conductivity, as dictated by the Wiedemann–Franz law. The more critical analysis concerns the lattice component. In typical

nanocomposites, secondary phases are introduced to scatter phonons and reduce κ_{l} . Here, however, the incorporation of high-conductivity metallic W nanoparticles creates percolative pathways for phonon transport. While some phonon scattering occurs at the mismatched W/ZrNiSn interfaces, the intrinsic thermal conductivity of tungsten ($\sim 170 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at 300 K) is an order of magnitude higher than that of ZrNiSn. Consequently, the W inclusions act as low-impedance heat flow shunts, leading to a net increase in κ_{l} . The increase in total thermal conductivity, caused by the highly thermally conductive W inclusions, is a limitation of this strategy when the sole objective is to maximize the peak thermoelectric figure of merit zT . To purely maximize zT , state-of-the-art Hf-containing half-Heusler materials conventionally rely on strong mass fluctuations to ultimately suppress lattice contribution on thermal conductivity (κ_{l}) [20, 22]. However, the goal of our strategy does not lie in breaking laboratory peak zT records, but rather in achieving macroscopic engineering cost-effectiveness through eliminating the expensive Hf (which reduces raw material costs by > 90%). Therefore, for practical and highly cost-effective waste heat recovery applications, this trade-off provides an optimized device-level solution balancing cost and output power. Furthermore, the persistence of the characteristic bipolar conduction upturn in κ at high temperatures across all samples confirms that the W inclusions do not alter the fundamental band structure of ZrNiSn, preserving its desirable semiconductor properties.

The synergistic electronic effects, charge injection and energy filtering, culminate in a dramatically enhanced PF, reaching a peak PF of $44 \mu\text{W}\cdot\text{cm}^{-1}\cdot\text{K}^{-2}$ at 910 K, surpassing values reported for Cu_{2-x}Se [36–38], PbTe [39, 40] and SnTe systems [41, 42], as well as exceeding those of commercial Bi₂Te₃-based materials [43, 44] (Figs. 3(d) and 3(e)). When combined with the moderately increased κ , this yields a peak dimensionless figure of merit (zT) of 0.76 at 910 K (Figs. 3(h) and 3(i)). Objectively, this value is moderate when compared to state-of-the-art n-type half-Heusler materials that heavily rely on expensive Hf alloying to achieve ultralow κ ($zT > 1.0$ – 1.5) [20, 22]. However, the core advantage of this work does not lie in pursuing a laboratory peak record. Instead, under the strict premise of completely eliminating Hf and drastically reducing raw material costs, the exceptional electrical performance compensates for the compromised thermal properties, thereby maintaining a highly competitive overall performance for practical engineering applications.

To translate the enhanced material performance into practical device-level metrics, we fabricated a unicouple thermoelectric generator (TEG) by integrating the optimized n-type ZrNiSn-3%W leg with a p-type AgSb_{0.94}Sn_{0.06}Te₂ leg [56] (Fig. S8 in the ESM). Under a fixed cold-side temperature ($T_{\text{c}} = 300 \text{ K}$), the open-circuit voltage (V_{oc}) exhibited a linear dependence on the applied temperature gradient (ΔT , Fig. S9 in the ESM), confirming negligible interfacial contact resistance. The output power (P_{max}) increased from 3.4 mW at $\Delta T = 58 \text{ K}$ to 170 mW at $\Delta T = 307 \text{ K}$ (Figs. 4(a) and 4(b)), achieving an exceptional power density of $2.1 \text{ W}\cdot\text{cm}^{-2}$ (Figs. 4(c), 4(d), and 4(f)). This enhancement is driven by the significantly improved PF of the nanocomposite. The unicouple demonstrated a conversion efficiency (η) of 5.2% at $\Delta T = 307 \text{ K}$ (Figs. 4(e) and 4(h)), attributed to broad-temperature zT optimization that maximizes energy conversion efficiency through balanced electrical and thermal transport. For practical operational viability, a 12 h isothermal aging test was performed on the ZrNiSn-

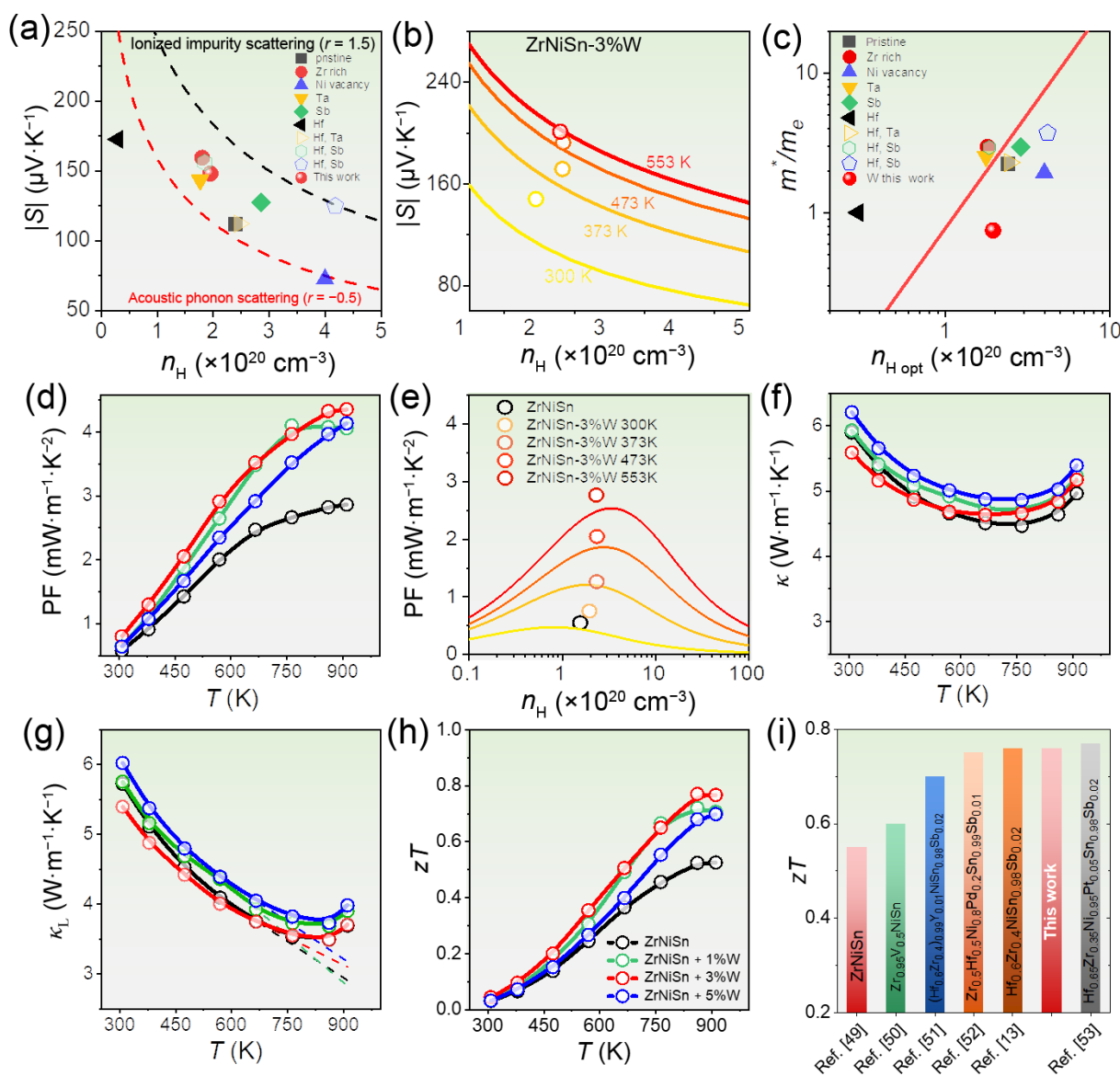


Figure 3 (a) Hall carrier concentration (n_H) dependent Pisarenko plot, showing the variation of experimental S with the predicted S , by taking into account ionized impurity and acoustic phonon scattering. (b) Pisarenko plot with increasing temperatures, based on a dominant acoustic phonon scattering mechanism. (c) Optimal carrier concentration $n_{H \text{ opt}}$ dependent density of state effective mass (m^*) for doped ZrNiSn [10, 16, 45–50]. Temperature-dependent TE properties of ZrNiSn- $x\%$ W samples: (d) power factor, PF; (e) Pisarenko plot of PF with increasing temperature; (f) thermal conductivity, κ . (g) Combination of bipolar and lattice contribution to the thermal conductivity. (h) TE figure of merit, zT . (i) Maximum zT comparison with state-of-art ZrNiSn materials [13, 51–56].

3 wt% W bulk pellet at 910 K in a protective Ar atmosphere, followed by post-aging XRD characterization. As shown in Fig. S11 in the ESM, the XRD patterns are nearly identical before and after thermal annealing, with invariant lattice parameters and no detectable secondary phases or impurity formation, confirming excellent phase stability and microstructural integrity of the ZrNiSn-3 wt.% W composite at elevated temperatures [57, 58]. More importantly, our W-based nanocomposite strategy enables a significant reduction in material cost, by over 90% compared to conventional Hf-containing systems, while maintaining competitive zT values and device-level performance (Table S2 in the ESM). Furthermore, a continuous 12 h thermal annealing test was conducted on the thermoelectric uncouple device under the maximum applied temperature difference. The open-circuit voltage V_{OC} , maximum output power P_{out} , and power density varied by less than 5% throughout the test (Fig. S12 in the ESM), while the energy

conversion efficiency (η) remained stable within 5.1%–5.3%. Collectively, these microstructural and device-level results demonstrate exceptional thermal stability and operational robustness of the present Hf-free ZrNiSn-W composite system under realistic working conditions. By entirely eliminating the use of expensive Hf, this cost-effective approach addresses a critical barrier to the large-scale manufacturing and deployment of ZrNiSn-based TE modules. Given these combined economic and performance advantages, Hf-free half-Heusler systems merit intensified attention in future thermoelectric materials research and technology development.

3 Conclusions

In summary, we have demonstrated a cost-effective, Hf-free strategy for enhancing the TE performance of n-type ZrNiSn

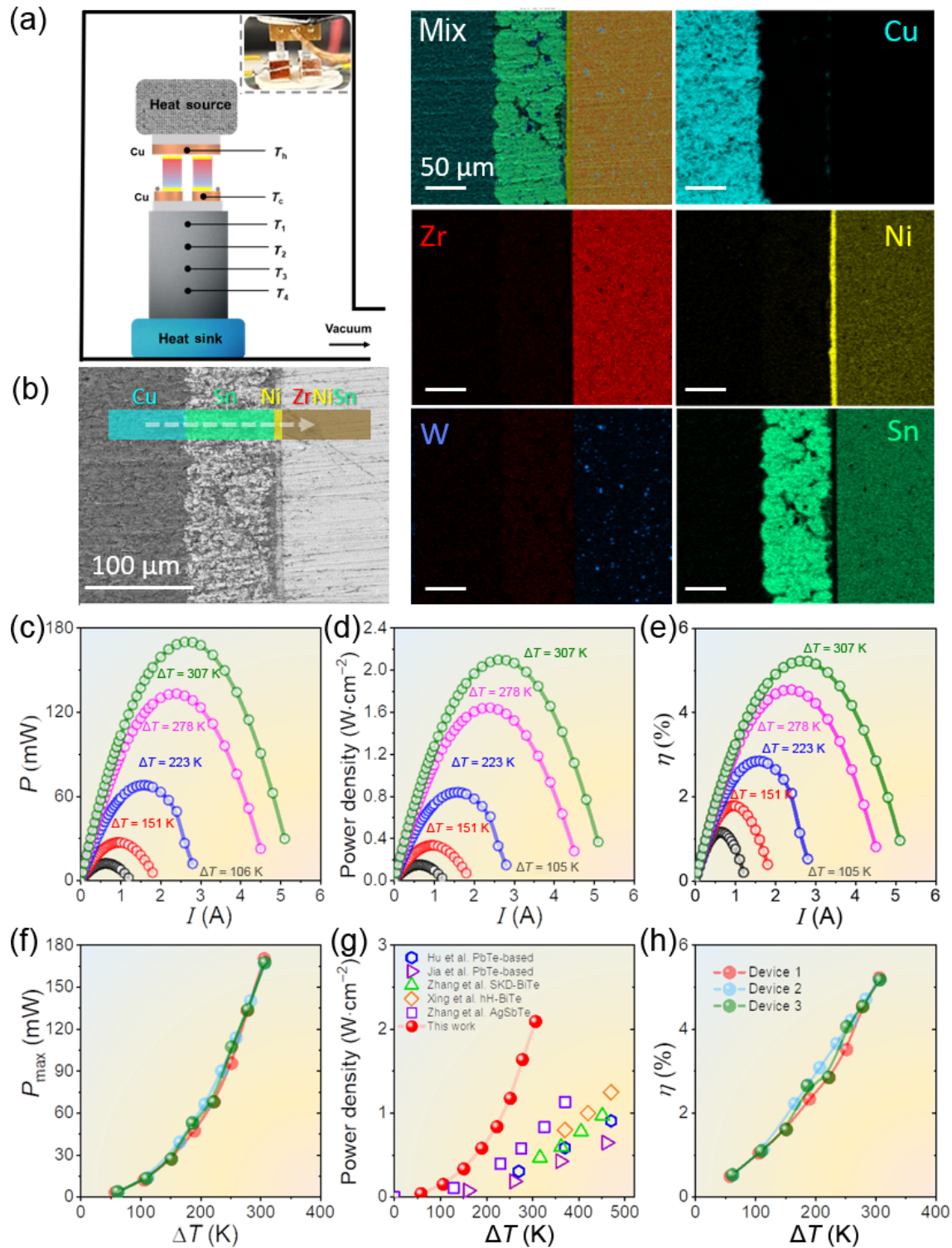


Figure 4 (a) Device-level evaluation of the optimized ZrNiSn-3%W/AgSb_{0.94}Sn_{0.06}Te₃ unicumple module. (b) Cross sectional SEM and corresponding EDX elemental mapping of the device interface. (c) Output power (P), (d) power density, and (e) conversion efficiency (η). (f) The maximum output power (P_{out}), (g) power density [56, 59–62], and (h) maximum conversion efficiency as a function of ΔT .

through grain-boundary-engineered modulation doping with W nanoparticles. By introducing a discrete W nanophase that preferentially segregates at grain boundaries, we establish a network of metal-semiconductor interfaces that perform two synergistic functions: Charge injection from the low-work-function W boosts electrical conductivity, while concurrently formed energy-filtering

barriers enhance the S . This dual mechanism yields a peak power factor of $44 \mu\text{W}\cdot\text{cm}^{-1}\cdot\text{K}^{-2}$ and a zT of 0.76 at 910 K for the optimal 3 wt.% W composite. The uniform, grain-boundary-localized W network also contributes to robust thermal and mechanical stability. A prototype unicumple module incorporating this material achieves an energy-conversion efficiency of 5.2% and a high power density

of $2.1 \text{ W}\cdot\text{cm}^{-2}$ at $\Delta T = 307 \text{ K}$. This work provides a scalable, economically viable pathway to highly cost-effective, Hf-free half-Heusler thermoelectrics and establishes a general framework for leveraging interfacial engineering in next-generation waste-heat-recovery devices.

Electronic Supplementary Material: Supplementary material (experimental details, additional structural and spectroscopic characterization, thermoelectric transport calculations, and stability testing) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909004>.

Data availability

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

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Declaration of competing interest

The authors declare no conflict of interest.

Author contribution statement

C. C. X.: Data curation, investigation, methodology, writing – original draft. N. L.: Data curation, investigation, validation. Y. T. Z.: Formal analysis, visualization. Y. L. J.: Formal analysis. X. W.: Formal analysis, visualization. K. Y. X.: Investigation, validation. H. P. H.: Data curation, validation. A. G.: Formal analysis, investigation. Y. L.: Validation. X. L. F.: Conceptualization, methodology. Q. Y. W.: Investigation, validation. Y. Z.: Conceptualization, validation, writing – review & editing. K. H. L.: Conceptualization, funding acquisition, writing – review & editing. B. P.: Conceptualization, supervision, writing – review & editing. All authors have approved the final manuscript.

Use of AI statement

None.

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