

Nanostructured Semiconductors for Enhanced Waste Heat-to-Electricity Conversion [†]

Pabina Rani Boro ¹, Rupam Deka ¹, Pranjal Sarmah ¹, Partha Protim Borthakur ^{1,*} and Nayan Medhi ²

¹ Department of Mechanical Engineering, Dibrugarh University, Dibrugarh 786004, India; pabinaboro2602@gmail.com (P.R.B.); rupamdeka@dibru.ac.in (R.D.); pksnit07@dibru.ac.in (P.S.)

² Department of Petroleum Engineering, Dibrugarh University, Dibrugarh 786004, India; nmedhi.duiet@dibru.ac.in

* Correspondence: partha@dibru.ac.in

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Abstract

Nanostructured semiconductors have emerged as transformative materials for enhancing the efficiency of waste heat-to-electricity conversion through thermoelectric (TE) processes. By altering structural features at the nanoscale, these materials can simultaneously reduce lattice thermal conductivity and optimize electronic transport properties, thereby significantly improving the thermoelectric figure of merit (ZT). Recent studies have demonstrated that introducing periodic twin planes in III–V semiconductor nanowires can achieve a tenfold reduction in thermal conductivity while maintaining excellent electrical performance. Similarly, $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$ alloys, through controlled spinodal decomposition, form stable nanostructures that maintain low thermal conductivity even after thermal cycling, crucial for high-temperature applications. Enhancing electrical properties is another key advantage of nanostructuring. PbTe-based materials, when heavily doped and engineered with nanoscale inclusions, have achieved a ZT of approximately 1.9 and a thermoelectric efficiency of around 12% over a 590 K temperature difference. Single-walled carbon nanotubes (SWCNTs) also show strong correlations between their electronic structure and thermoelectric conductivity, highlighting their potential for next-generation devices. Two-dimensional silicon–germanium (Si_xGe_y) compounds offer ultra-low lattice thermal conductivity and high Seebeck coefficients, providing a promising pathway for future TE applications. Despite these advancements, challenges remain, particularly regarding scalability and integration into existing energy recovery systems. Techniques such as focused ion beam milling and solution-based synthesis of porous nanostructures are being developed to fabricate high-performance materials on a commercial scale. Moreover, integrating nanostructured semiconductors into real-world systems, such as automotive exhaust heat recovery units, requires improvements in material durability, fabrication efficiency, and device compatibility. In conclusion, nanostructured semiconductors offer a powerful route for enhancing waste heat-to-electricity conversion. Their ability to decouple electrical and thermal transport at the nanoscale opens new opportunities for high-efficiency, sustainable energy harvesting technologies. Continued research into scalable manufacturing techniques, material stability, and system integration is essential to fully unlock their potential for commercial thermoelectric applications.

Keywords: nanostructured semiconductors; thermoelectric materials; waste heat recovery; thermal conductivity reduction; silicon–germanium nanostructures



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1. Introduction

Nanostructured semiconductors are one of the most exciting areas in materials science today. They are changing how we think about energy, electronics, lighting, and even medicine. These materials are very small—on the nanoscale—and that makes them behave differently from larger, bulk materials. Because of their size, they show unique electrical, chemical, and optical properties. This includes tunable band gaps, high surface area, and better charge movement, which make them great for advanced technologies [1]. There are many types of nanostructured semiconductors. These include 2D materials, quantum dots, and nanowires. For example, MoS₂ and WS₂ are 2D materials known for their fast charge movement and strong light interactions. They are ideal for future electronic and optoelectronic devices [1]. Quantum dots—tiny particles made from materials like CdSe or ZnS—can change their color or energy based on their size. This makes them useful in LEDs, solar cells, and even medical imaging [2,3]. Nanowires, especially when combined with quantum dots, help improve how light and electricity move through a device, leading to better performance in sensors and lasers [4]. These materials have many uses. In solar energy, they help improve the performance of dye-sensitized and quantum dot-sensitized solar cells. Materials like TiO₂ and ZnO allow more light to be absorbed and reduce energy loss, which boosts power output [5,6]. In electronics, nanostructures are used in things like high-speed lasers, signal processors, and optical amplifiers [3]. Environmental monitoring is another area where they shine. They can detect small changes in water quality—such as pH levels, metal ions, or oxygen content—which is useful for pollution tracking [1,7]. In medicine, their small size and reactive surface make them excellent for biosensors and imaging tools. They can even help with targeted drug delivery and cell-level tracking [8–10]. Making these nanostructures requires special techniques. Some common methods include lithography, etching, and self-assembly. Newer methods like core-shell engineering and hybrid materials are also becoming popular. For instance, ZnO-carbon quantum dot combinations improve energy transfer in optoelectronic devices [11]. Similarly, core-shell structures like CdSe@Au and ZnS@Pt are being used for solar energy and catalysis. These pair different materials together to obtain the best performance from both [12].

2. Nanostructured Semiconductors in Energy Harvesting

Nanostructured semiconductors have unique physical and electronic properties. These come from their tiny size and large surface-to-volume ratio. This makes them ideal for energy storage and conversion technologies. By adjusting their bandgaps and using quantum effects, these materials can be engineered for better performance. That is why they are at the heart of many sustainable energy solutions [13]. One major way to improve thermoelectric materials is by lowering their lattice thermal conductivity. Nanostructuring helps with this. It includes creating nanowires, nanocomposites, and superlattices. These features block the flow of heat without affecting electricity. For example, PbTe thermoelectrics with Ge nanostructures reached a high ZT of 1.9 at 805 K. This was possible because nanoscale precipitates scattered heat-carrying phonons without harming electrical mobility [14]. Other materials like III–V semiconductor nanowires, with crystal twin planes, showed a 10× drop in thermal conductivity. This was thanks to better phonon scattering [15]. Embedding semiconducting particles inside PbTe further improved both electrical performance and reduced thermal vibrations [16]. Researchers also boost thermoelectric performance by tweaking the material's makeup. Adding extra sodium (Na) to PbTe raised the charge carrier count and improved power output at high temperatures [14]. Doping with bismuth and mixing in SiC nanoparticles helped fine-tune the Seebeck coefficient and increased electrical conductivity [17]. Quantum confinement also helps. For example, arranging Si nanowires in chains modified how electrons and phonons moved. This lowered thermal conductivity

and raised ZT scores [18]. Long-term stability is another concern. But alloys like PbTe-GeTe hold up well during repeated heating. Their nanoscale phase separation remains stable, helping retain low thermal conductivity over time [19]. Similarly, Ba-Cu-Si clathrates with SiC particles show good thermoelectric performance even under operating conditions [20]. These improvements make nanostructured thermoelectrics ready for real-world use. For instance, combining Bi₂Te₃ with nanostructured PbTe has led to modules reaching up to 12% efficiency at a 590 K temperature difference [14]. Other compositions, like PbSe_{0.5}Te_{0.5}, offer stable ZT values at room temperature—perfect for wearable, low-power electronics [21]. In solar energy, nanostructures also shine. Quantum dots, nanowires, and porous films improve light capture and carrier movement. GaAs solar cells with built-in nanostructures lose less light and move electrons more efficiently. This helps lower costs and raise power output [22,23]. New materials like perovskite nanostructures are flexible, light, and cheaper, offering great potential for solar power [24]. These semiconductors are also excellent for turning heat into electricity. When engineered with small grains and special interfaces, they block heat flow while keeping electrical pathways open. This helps develop solid-state devices that can recover waste heat from factories or electronics [25]. Energy storage is another area where nanostructures help. In lithium-ion batteries, nanostructured electrodes with neat layouts speed up ion flow and improve charging cycles [26]. Metal nanosponges with pores boost conductivity and durability in both batteries and supercapacitors [27]. Oriented nanostructures push energy performance even further [28]. For flexible and wearable tech, these materials are game-changers. When used in piezoelectric and triboelectric devices, they convert body movement or vibration into electricity. ZnO-based nanocomposites are often used in these applications to power sensors and small gadgets [29,30]. Finally, in solar-to-chemical systems, nanostructured semiconductors like TiO₂, ZnO, and CdS drive photocatalysis. They help with hydrogen production and breaking down pollutants [25]. These materials solve energy problems while also helping the environment. Still, there are challenges. Making these materials at scale, ensuring they stay stable over time, and lowering production costs are key to bringing them to market [13,22,30].

Silicon (Si) and germanium (Ge) are among the most widely studied semiconductors for thermoelectric applications due to their favorable electronic properties and high-temperature stability. Numerous reviews have explored their thermoelectric behavior, particularly when used as silicon-germanium (Si-Ge) alloys. These alloys are well-suited for energy harvesting in extreme environments such as outer space, as demonstrated by their successful application in NASA's radioisotope thermoelectric generators [31]. One of the most critical indicators of thermoelectric performance, the ZT, has reached impressive values in Si-Ge systems. For example, superlattice-structured Si-Ge nanowires have achieved ZT values up to 4.7 for n-type and 2.74 for p-type configurations [32]. The thermoelectric efficiency of these materials is also driven by high Seebeck coefficients, with Si₅₀Ge₅₀ alloys reporting values as high as 588 $\mu\text{V}/\text{K}$ at 50 °C [33]. In addition to high electrical conductivity, nanostructuring plays a vital role in reducing thermal conductivity through enhanced phonon scattering. Strategies such as thin films, nanowires, and superlattices have been employed to enhance thermoelectric behavior [34]. Pressure-induced phase transitions offer another method to tune electrical transport properties and optimize performance [35]. Despite their potential, challenges remain in the form of complex fabrication processes and limited geometric flexibility. Advances in manufacturing techniques, such as laser powder bed fusion, are currently being explored to enable more adaptable device designs [33]. Recent research also focuses on doping, microstructural tuning, and exploring new Ge-based alloys to further boost thermoelectric efficiency [36,37].

Nanostructured semiconductors have greatly advanced the thermoelectric field. By using quantum confinement, interface engineering, and phonon scattering, they significantly

boost energy conversion efficiency. One of the most important effects at the nanoscale is quantum confinement. This changes the electronic density of states near the Fermi level. As a result, the Seebeck coefficient and electrical conductivity are both enhanced—especially in one-dimensional materials like nanowires and nanotubes [38,39]. In these tiny systems, electrons are confined in narrow spaces, creating discrete energy levels. This helps charge carriers move more efficiently, which improves thermoelectric performance [38]. Similarly, quantum dots and layered heterostructures show better power factors because of this confinement effect [39]. Interface engineering is another key technique. Interfaces within nanomaterials scatter phonons effectively, which reduces thermal conductivity without hurting electrical performance [40–44]. Using hierarchical nanostructures, which include scattering centers of different sizes, targets phonons with a range of mean free paths. This strategy further improves thermal insulation [41,42]. Another useful method is isotope doping, especially in silicon-based nanomaterials. It slows down heat transfer by scattering phonons while maintaining electronic properties [45]. This kind of tuning—lowering heat flow without reducing electrical current—is crucial to improving the ZT, a key measure of thermoelectric efficiency. Phonon scattering remains central to controlling thermal transport in nanostructures. Researchers have designed materials with tiny boundaries and embedded heterostructures to cut down lattice thermal conductivity [43]. For instance, modulated-width silicon nanowires and nanoparticle chains show impressive reductions in thermal conductivity, yet they still support good electrical conduction [46]. This balance—stopping heat while letting electricity flow—is essential for high-performance thermoelectrics. In addition, phonon confinement in materials like ZnO nanowires and silicon nanocrystals reduces vibrational energy transfer across the material, further lowering thermal conductivity [42]. Innovations in material design have introduced new hybrid and composite architectures. Embedding nanoparticles or metals into semiconductors helps scatter phonons and raise the Seebeck coefficient [44,47]. Core-shell designs, such as Ge-coated Si nanoparticles, use mismatched lattices to reduce heat flow even more. Other materials, like Fe₂O₃-dispersed Cu₁₂Sb₄S₁₃, use earth-abundant elements to achieve strong thermoelectric performance in a sustainable way [43]. These strategies have improved both the ZT value and power factor. In many cases, hierarchical and interface-engineered materials reach ZT values above 1.0, which is more than double what traditional bulk materials offer [41,43,48,49]. Even more impressively, researchers have found ways to decouple electrical conductivity from the Seebeck coefficient, allowing both to be optimized for better power output [40,41].

Figure 1 illustrates how thermoelectric performance is enhanced through nanostructuring by decoupling thermal and electrical transport mechanisms. Figure 1 visually emphasized the differences in transport behavior between bulk and nanostructured materials. In bulk materials, phonons and electrons are allowed to travel relatively unimpeded due to the limited presence of scattering interfaces. As a result, thermal conductivity remains high, and any attempt to increase electrical conductivity often leads to a corresponding rise in heat transport, limiting the ZT. In nanostructured materials, significant phonon scattering is introduced through the inclusion of grain boundaries, twin planes, nanoinclusions, and other interface features [50,51]. These structures are strategically engineered to disrupt phonon transport while allowing electron pathways to remain largely unaffected or even enhanced [52,53]. Through this process, lattice thermal conductivity is suppressed by multiscale scattering mechanisms, as has been observed in nanostructured systems such as PbSe and ultrathin silicon membranes [50,52]. Simultaneously, electronic conductivity is preserved or improved via mechanisms such as quantum confinement, energy filtering, and semi-coherent interfaces ([54,55]). As a result, the intrinsic coupling between electrical and thermal transport properties is mitigated, allowing a higher ZT to be achieved [56,57].

Table 1 presents the properties of nanostructured semiconductors and their influence on waste heat-to-electricity conversion efficiency.

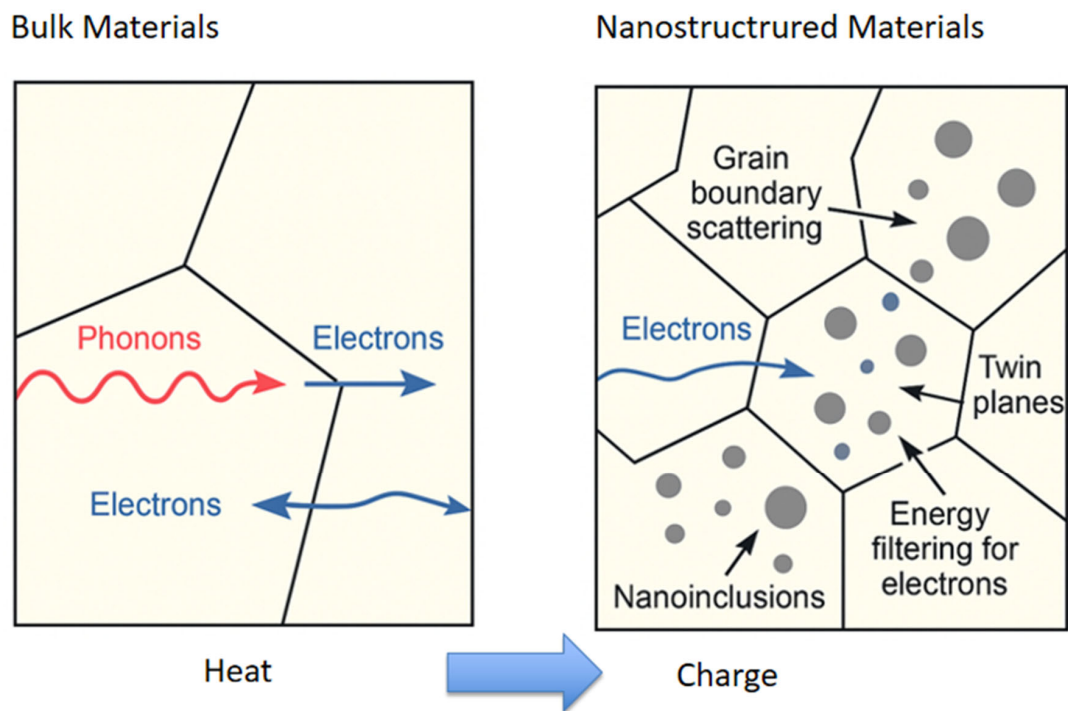


Figure 1. Decoupling mechanism of phonon engineering and electron transport in nanostructures.

Table 1. Properties of nanostructured semiconductors on waste heat-to-electricity conversion efficiency.

Property	Material	Thermal Conductivity	Electrical Conductivity	Seebeck Coefficient	Figure of Merit (ZT)
Low Thermal Conductivity	III–V Semiconductor Nanowires	Drastically reduced due to twinning superlattice [15]	Unaltered	Unaltered	Tenfold enhancement
High ZT	PbTe-based Thermoelectrics	Reduced by Ge nanoprecipitates [14]	Enhanced by Na doping	High	1.9 at 805 K
Low Thermal Conductivity	SiGe Nanocomposites	Reduced due to phonon scattering [58]	Comparable to bulk	Enhanced	High
Low Thermal Conductivity	PbTe–GeTe Alloys	Reduced by spinodal decomposition [19]	Comparable to bulk	Enhanced	High
High ZT	PbTe _{0.5} Se _{0.5}	Low due to nanostructures [21]	Low	High	0.7 (400–600 K)
Low Thermal Conductivity	Nanostructured Bulk Si	Reduced by nanostructuring [59]	Limited degradation	Enhanced	3.5× higher
High ZT	Bi ₂ Sb _x Te ₃ Alloys	Reduced by nanostructuring [60]	Enhanced by Zintl ions	High	High
Low Thermal Conductivity	Nanostructured SiGe	Reduced due to grain boundary scattering [61]	Lower	Higher	High
High ZT	Metal Selenides and Tellurides	Reduced by nanostructuring [62]	Enhanced by doping/alloying	High	High
Low Thermal Conductivity	Nanostructured Ceramics	Reduced by grain growth prevention [19]	Comparable to bulk	Enhanced	High

3. Thermoelectric Efficiency and ZT Evolution of Representative Materials Across Temperature Ranges

Figure 2 provides a comprehensive overview of thermoelectric material performance and efficiency trends. In panel (a), the graph illustrates thermoelectric conversion efficiency (η) as a function of the hot side temperature (T_H) while keeping the cold side temperature (T_C) constant at 300 K. The efficiency curves are plotted for different average ZT values (ZT_{avg}), demonstrating that as ZT_{avg} increases, the efficiency improves significantly. At $ZT_{avg} = 1$, the maximum achievable efficiency remains below 15% even at 1000 K. To reach the practical efficiency threshold of 20–30%—considered necessary for thermoelectrics to be competitive with fossil fuels—a material must achieve a ZT_{avg} of at least 2 to 3. This emphasizes how important it is to develop materials with higher ZT values for real, practical thermoelectric applications. Panel (b) of the figure shows how the ZT value changes with temperature for various high-performance thermoelectric materials. These materials are grouped by generations of technological advancement. First-generation materials—like bismuth telluride (Bi_2Te_3) and silicon–germanium (SiGe) alloys—have ZT values around 1. They are still widely used in commercial thermoelectric modules for low- and high-temperature applications. Second-generation materials, such as $\text{AgPb}_{18}\text{SbTe}_{20}$ and those based on GeTe, achieve ZT values close to 1.5. These improvements are mainly due to nanostructuring and doping techniques, which help optimize thermal and electrical transport. Third-generation materials have made even more impressive gains. One of the standout examples is p-type SnSe, which reaches ZT values above 3 at high temperatures (~800–900 K). This puts it among the most promising materials currently being studied for thermoelectric power generation. In the figure, colored bands clearly show the different generations. These bands serve as visual benchmarks to highlight how far the technology has come. Despite this progress, the comparison shows that more work is needed. To truly enable widespread adoption of thermoelectrics for energy harvesting and power generation, we must keep developing materials that deliver high and stable ZT values across a broad range of temperatures [63].

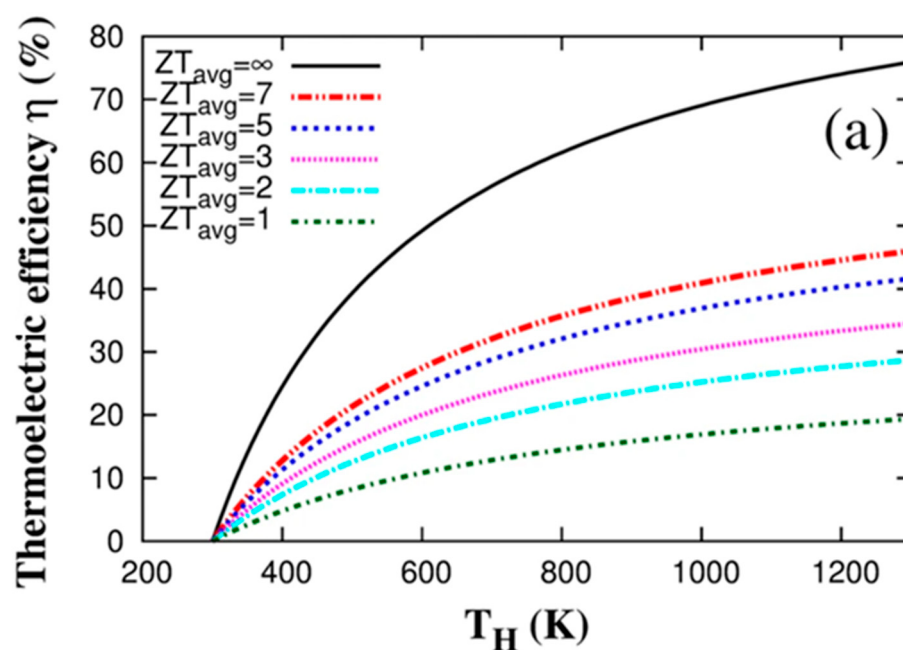


Figure 2. Cont.

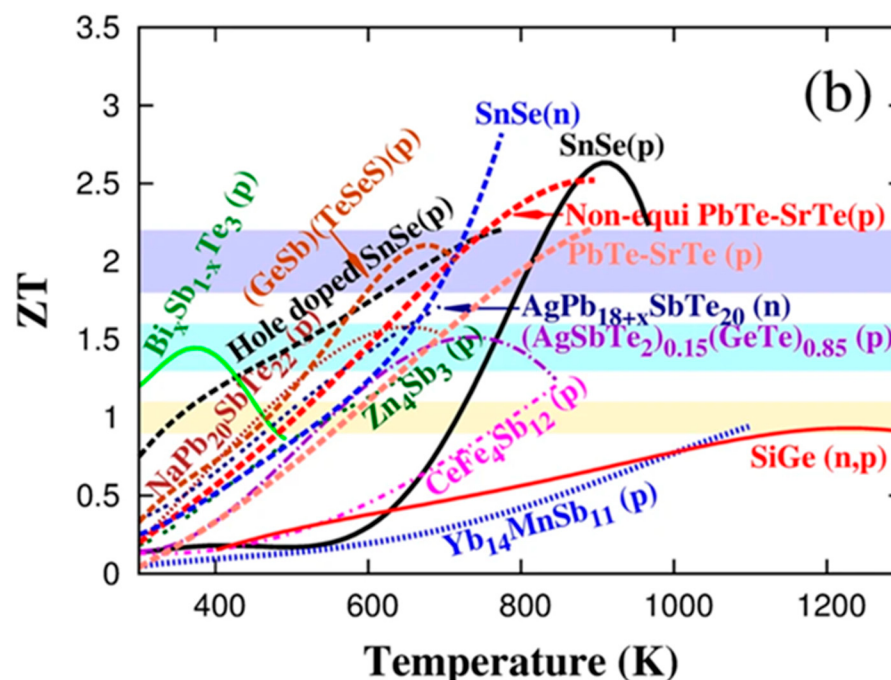


Figure 2. (a): Thermoelectric efficiency as a function of the hot temperature with a fixed low temperature $T_C = 300$ K and fixed ZT_{avg} values. It is worth mentioning that the efficiency range of 20–30% is a threshold band to replace fossil fuel for that level of energy gain. (b) ZT performance for several representative materials as a function of temperature. The color bars at approximately 1, 1.5, and 2 represent the first-, second-, and third-generation thermoelectric achievements. (Figure reprinted from Ref. [63].

4. Comparative Analysis of Thermoelectric Performance in Representative Nanostructured Materials

Thermoelectric performance is governed by the dimensionless figure of merit $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is electrical conductivity, and κ is total thermal conductivity. Advancements in nano-engineering have enabled significant enhancements in ZT by simultaneously reducing thermal conductivity and optimizing electronic transport properties. Table 2 summarizes recent data on high-performance nanostructured thermoelectric materials, focusing on their ZT values, Seebeck coefficients, and thermal conductivities. This comparison highlights the role of nano-structural design in elevating thermoelectric efficiency.

Table 2. Key thermoelectric parameters (ZT, Seebeck coefficient, and thermal conductivity) of various material systems.

Material System	ZT Value	Seebeck Coefficient ($\mu\text{V/K}$)	Thermal Conductivity ($\text{W/m}\cdot\text{K}$)	Remarks
PbTe-based materials	~1.9	~200	~2	Mid-temperature performance; nanostructuring and band convergence [64,65]
GeTe	~2.0	~220	~1.5	Used in thermoelectric modules; phase tuning and doping [66]
$\text{Mg}_3(\text{Sb,Bi})_2$	~2.0	~250	~1.2	High ZT via electron filtering and alloy scattering [66]
SnSe (single crystal)	>2.0	~500	~0.4	Record-low κ due to anharmonic bonding [67]

Table 2. Cont.

Material System	ZT Value	Seebeck Coefficient ($\mu\text{V/K}$)	Thermal Conductivity ($\text{W/m}\cdot\text{K}$)	Remarks
SiGe-based nanocomposites	~ 1.3	~ 150	~ 2	Interface and alloy scattering reduce thermal transport [58]
$\text{CuCrO}_2\text{:Mg}$ thin films	~ 0.02	~ 60	> 5	Demonstrates limitations in oxide thin films [68]
PbTe–PbSe–PbS quaternary	~ 2.3	~ 250	~ 1.5	Band convergence with nanoscale inclusions [65]
Oxide-based thermoelectrics	$0.1\text{--}0.4$	~ 100	$5\text{--}10$	Electrically resistive but thermally stable [69]
UNCD nanomaterials	~ 10 (theoretical)	~ 1000	~ 0.1	Theoretical high ZT via extreme boundary scattering [70]

5. Microstructural Analysis of Nanostructured BCFZY ($\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$)

Lowering the operating temperature of solid oxide fuel cells (SOFCs) is essential for advancing their commercial viability. In this context, enhancing electrode performance at reduced temperatures can be effectively achieved through nanoscale microstructural engineering. This study presents alternative microstructural strategies to improve the electrochemical efficiency of the $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BCFZY) cathode. A cost-effective and scalable spray-pyrolysis deposition technique is employed to fabricate various electrode architectures in a single processing step. The resulting microstructures and electrochemical properties are systematically compared with those of electrodes produced from ceramic powders using conventional screen-printing methods. Comprehensive structural, morphological, and electrochemical characterizations are conducted. Notably, nanostructured cathodes exhibit significantly reduced area-specific resistance (ASR), achieving values as low as $0.067\ \Omega\cdot\text{cm}^2$ at $600\ ^\circ\text{C}$, in contrast to $0.520\ \Omega\cdot\text{cm}^2$ for screen-printed counterparts. Furthermore, an anode-supported SOFC incorporating the nanostructured BCFZY cathode delivers a peak power density of $1\ \text{W}\cdot\text{cm}^{-2}$ at $600\ ^\circ\text{C}$, underscoring the potential of nanoscale microstructural design to enable high-performance SOFC operation at intermediate temperatures [71].

Figure 3 presents scanning electron microscopy (SEM) images of three distinct BCFZY cathode architectures fabricated using freeze-drying and spray-pyrolysis deposition methods on different CGO ($\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$) substrates. Panels (a) and (b) show the cathode prepared by freeze-drying (FD) followed by spray pyrolysis onto a dense CGO substrate, resulting in a porous microstructure with loosely packed grains and an average particle size of approximately $340\ \text{nm}$, as shown in the inset. In contrast, panels (c) and (d) depict a cathode formed by direct spray pyrolysis (SP) on a polished CGO surface, yielding a highly porous nanostructure with well-connected grains and a significantly smaller average particle size of around $65\ \text{nm}$. Panels (e) and (f) demonstrate a more integrated architecture, where spray pyrolysis is applied onto a porous CGO backbone (SP-CGO), enabling BCFZY nanoparticles to infiltrate deeply and uniformly into the porous scaffold. This configuration shows similar nanoscale grain size ($\sim 67\ \text{nm}$) while ensuring strong adhesion and enhanced triple-phase boundary connectivity due to the intimate contact with the CGO framework. Overall, the figure highlights how substrate morphology and deposition technique critically influence the resulting microstructure, with nanostructured electrodes offering superior electrochemical characteristics through reduced particle size and improved interfacial integration.

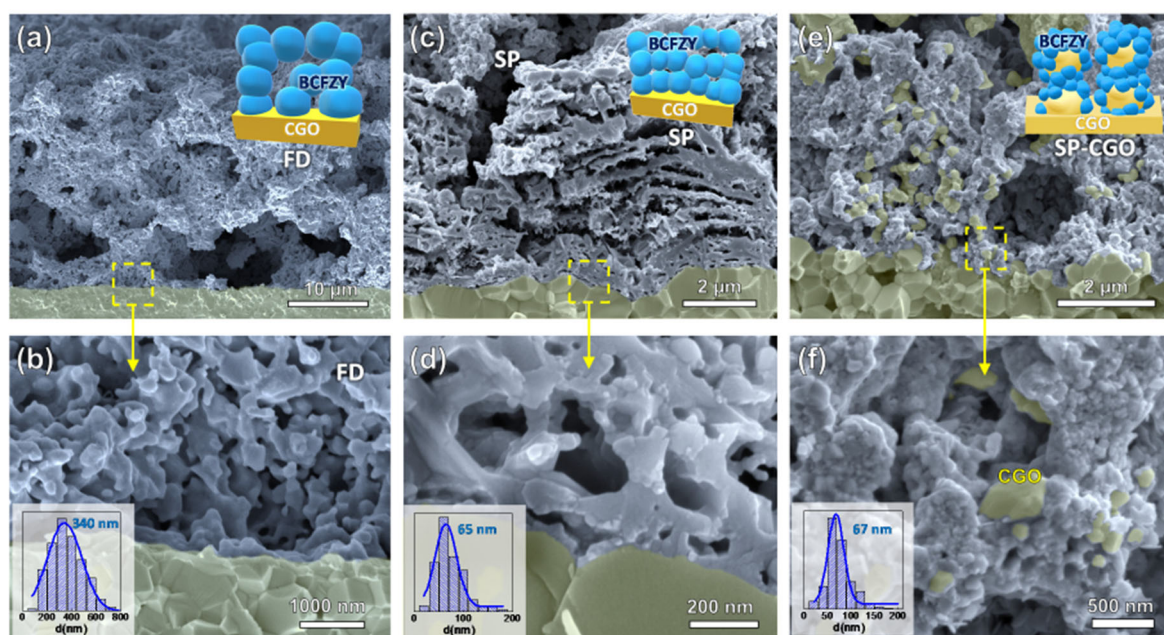


Figure 3. Scanning electron microscopy (SEM) of the different electrode architectures obtained by (a,b) freeze-drying and spray-pyrolysis deposition onto (c,d) polished CGO and (e,f) porous CGO backbone. The grain size distributions are included in the insets (Reprinted from Ref. [71]).

6. Recent Advances in Key Nanostructured Materials

Turning waste heat into electricity through thermoelectric processes is a big step toward sustainable energy recovery. Thanks to recent advances in nanostructured semiconductors, this process has become much more efficient. Scientists have been able to improve key properties like the Seebeck coefficient, electrical conductivity, and thermal transport. Together, these improvements boost the thermoelectric figure of merit (ZT)—a number that shows how well a material can convert heat into electricity [15,72]. Bismuth telluride (Bi_2Te_3) is one of the most popular thermoelectric materials, especially near room temperature. When mixed with antimony, it forms $(\text{Bi,Sb})_2\text{Te}_3$, which performs even better. Using electrodeposition techniques, researchers can now create nanowires and thin films of this material with precise control. These nanostructures move electrical charges more easily and scatter less heat, leading to better energy conversion and the ability to scale up for real devices [73,74]. In III–V semiconductors like InAsSb nanowires, engineers have added special patterns called twinning superlattices. These patterns drastically cut down heat flow while keeping electrical performance strong. As a result, ZT has improved nearly tenfold, showing how powerful lattice engineering can be in nano-sized materials [15]. PbTe–GeTe alloys are another exciting option. These materials naturally form tiny separate phases, thanks to spinodal decomposition. This helps scatter heat more effectively and lowers thermal conductivity. Even after repeated heating and cooling, they remain stable—making them perfect for high-temperature waste heat recovery [19]. Although bulk silicon is not great for thermoelectrics, nanostructured silicon is a different story. It is cheap, safe, and readily available. New designs—like vertical nanowire forests and paper-like nanotube sheets—have boosted its power factor while cutting heat flow. These silicon-based nanostructures now perform similarly to traditional telluride-based materials, showing real promise for future applications [59,72,75]. The current status of thermoelectric modules (TEMs) reflects a field advancing rapidly due to growing interest in energy efficiency and sustainability. TEMs are solid-state devices that utilize the Seebeck and Peltier effects to convert temperature differences directly into electrical energy or provide localized cooling. They are already employed in diverse applications, including industrial waste heat recovery, automotive

energy harvesting, cooling in consumer electronics, and powering space missions [76–78]. Recent research also highlights their integration in hybrid systems with photovoltaics to boost overall system efficiency by utilizing solar heat [79,80]. Material development has been a critical driver of improved performance, with advances such as nanostructured and quantum well materials achieving figures of merit (ZT) above 3, translating to conversion efficiencies exceeding 20% [81]. Simultaneously, efforts to enhance thermal management and geometric designs have led to better module performance and reliability [82,83]. Despite these advances, widespread commercial adoption is constrained by persistent challenges, including low overall efficiency, high material and manufacturing costs, and stability under high temperatures [84]. Solutions include the development of robust materials like $\text{Mg}_3(\text{Bi,Sb})_2$ for operation up to 750 K ([77]), and environmentally friendly materials like flexible, transparent CuI-based films for wearable and IoT applications [85,86]. Emerging trends also focus on integrating TEMs into self-powered IoT devices and using advanced modeling tools for better design optimization [87]. As research continues, thermoelectric modules are poised to play a crucial role in future energy systems through improved materials, innovative applications, and scalable, sustainable technologies.

7. Scalability and Fabrication of Nanostructured Semiconductors

The design and production of nanostructured thermoelectric materials require a multi-stage process (as shown in Figure 4) involving material selection, synthesis route determination, nanostructuring, and property optimization. This integrated approach aims to enhance the figure of merit (ZT) by optimizing both electrical transport and thermal resistance.



Figure 4. Selection and fabrication pathways for nanostructured thermoelectric materials.

The development of high-performance nanostructured thermoelectric materials begins with careful material selection. Base compounds must exhibit inherent thermoelectric potential and match the desired operational temperature range, which typically ranges from 100 to 1300 K. Commonly used materials include bismuth telluride (Bi_2Te_3) for near-room-temperature applications, lead telluride (PbTe) and tin selenide (SnSe) for mid-temperature ranges, and SiGe alloys for high-temperature conditions [88,89]. Selection also hinges on

electronic band structure favorability and low intrinsic thermal conductivity to optimize ZT values [90,91]. Following material selection, the synthesis method defines the fabrication route. Bulk synthesis techniques include melt spinning, which enables rapid solidification and microstructural refinement; spark plasma sintering (SPS), which densifies materials with minimal grain growth; and extrusion, which allows directional texturing of thermoelectric pellets [88]. In contrast, solution-phase synthesis offers greater control at the nanoscale and cost efficiency. Notably, the modified polyol process facilitates metal precursor reduction at low temperatures, enabling size-controlled nanoparticle production [90]. Similarly, electrodeposition supports thin-film deposition and template-based nanostructure growth, offering scalability and precise control [92]. Template-based synthesis further diversifies the possibilities. Emulsion-based techniques use surfactant systems to form uniform nanostructures, while template-filling methods, such as anodic alumina membrane deposition, yield well-defined nanowires and porous structures [93]. To improve thermoelectric efficiency, materials undergo nanostructuring using advanced engineering techniques. Nanocomposites are formed by embedding nanoparticles or secondary phases into a host matrix, enhancing phonon scattering while maintaining carrier mobility—especially effective in PbTe systems and Heusler phases [94,95]. Low-dimensional materials, such as nanowires and nanotubes, exploit quantum confinement effects to increase power factors [96], while thin films serve in device-level integration, allowing for precise control of heat and electron flow [97]. Additionally, hybrid nanostructures—including organic/inorganic composites—strike a balance between thermal insulation and electronic conductivity by leveraging interfacial phenomena and enhancing compatibility [89,98]. Finally, comprehensive characterization and optimization ensure material viability and performance tuning. Structural and compositional analyses are conducted using X-ray diffraction (XRD) for crystallographic information, scanning and transmission electron microscopy (SEM/TEM) for microstructural imaging, and energy-dispersive X-ray spectroscopy (EDS) for elemental profiling [90]. Optimization involves adjusting synthesis parameters—such as temperature, processing time, and precursor ratios—as well as controlling the dimensions of nanostructures to simultaneously maximize phonon scattering and carrier mobility [91]. Scaling up the fabrication of nanostructured semiconductors is not easy. It involves balancing precision, material compatibility, and cost. Even though nanoscience has made big advances, scalability remains a major hurdle. Many of the best fabrication methods are still expensive and slow. This makes it hard to move from lab research to real-world production [99,100]. Some of the most accurate techniques, like physical and chemical nanolithography, can create very fine patterns. But they struggle when it comes to making multilayer nanostructures that need precise alignment and pattern transfer [101]. Methods like electron-beam lithography (EBL) give excellent resolution. However, they are too time-consuming and costly for large-scale manufacturing [102,103]. To tackle these issues, researchers have explored different strategies. Top-down methods—including photolithography, focused ion beams, and EBL—are still widely used. These approaches are vital for making nanodevices like transistors and diodes, where precision and uniformity are critical [104,105]. On the other hand, bottom-up methods offer promising alternatives. Techniques like molecular beam epitaxy and self-assembled masked growth can build nanostructures directly on various surfaces. These methods are more scalable, flexible, and cost-efficient, especially for hybrid devices where perfect crystal alignment is not always necessary [103,104]. Among the many new tools being explored, nanoimprint lithography (NIL) is gaining popularity. It can quickly and accurately create features smaller than 100 nm, making it a strong option for semiconductor patterning [105]. Another promising method is displacement Talbot lithography (DTL). It helps create regular nanopatterns fast and reliably, which improves the performance of optoelectronic materials. At the same time,

micro/nano additive manufacturing (AM) is making progress. It offers design freedom and can handle multiple materials at once. However, it still faces problems with scaling up and maintaining structural consistency [100]. Innovative techniques are also changing how semiconductors are made. For example, nanostenciling enables the local growth of nanostructures in a single step. It avoids complex processes and does not require resist layers [105]. A combination of adhesion lithography and hydrothermal growth has been used to make nano-in-nano Schottky diodes on a large scale. These show great performance for future electronics [103]. Microtomy, paired with vapor–liquid–solid growth, allows for large-area transfer of nanocrystal arrays. It gives precise control and works well on different surfaces, supporting integration with many types of devices [106]. These new fabrication methods have a wide range of uses. In optoelectronics, nano-engineering of III-nitride semiconductors with DTL has improved light extraction, making it useful for LEDs and lasers at industrial scales [107]. In energy devices, metal-oxide semiconductor nanostructures built through scalable methods help improve piezoelectric nanogenerators and photodetectors, leading to better energy conversion [108]. A breakthrough is also being seen in bioelectronics. DNA-directed self-assembly offers atomic-level precision and works well with semiconductor processes. This makes it ideal for biosensors and molecular circuits [109]. Altogether, the use of NIL, DTL, nanostenciling, microtomy, and similar techniques helps make high-performance energy, optoelectronic, and bioelectronic devices more practical. These methods mark a major shift in how semiconductors can be produced on a large scale [100,103,105–107,109].

8. Challenges of Nanostructured Semiconductors

Nanostructured semiconductors have gained considerable attention due to their exceptional physical, chemical, and electronic properties, which enable applications in photovoltaics, photocatalysis, sensing, and nanoelectronics. However, despite their immense potential, several challenges hinder their large-scale implementation and long-term reliability. One of the major hurdles lies in manufacturing and fabrication. The agglomeration of nanopowders remains a persistent issue, as nanoparticles tend to cluster due to high surface energies, leading to poor flowability and non-uniform dispersion. Achieving high solids loading in suspensions without significantly increasing viscosity is difficult, limiting the ability to form dense nanostructured films. Techniques such as microwave processing have shown promise in transforming unfired nanopowder compacts into dense, sintered forms while maintaining nanoscale features. Traditional top–down fabrication techniques, including photolithography and etching, struggle to pattern nanoscale features on irregular or non-planar surfaces, thereby restricting the structural complexity of nanomaterials. To overcome this, alternative methods like nanoimprint lithography and nanostenciling have been explored to enhance precision and reproducibility in nanoscale structuring [105]. Another fabrication-related challenge involves cost reduction: producing nanostructured semiconductors with low-cost yet high-efficiency processes remains difficult. Researchers are investigating black silicon and transparent conductive oxides to lower manufacturing costs in photovoltaic devices while retaining high performance [110,111]. In terms of material properties and stability, efficient charge separation and transport are crucial for functional performance, especially in photocatalytic and optoelectronic applications. However, achieving balanced charge mobility while minimizing recombination losses at the nanoscale remains difficult. Ensuring photoelectrochemical stability under illumination and thermal stress is another challenge, as nanostructured semiconductors often degrade faster than their bulk counterparts due to surface defects and oxidation [112]. Additionally, controlling defects and grain boundaries with atomic precision is essential, since even minimal structural irregularities can significantly alter conductivity and carrier lifetimes.

This requires advanced synthesis techniques capable of producing near-perfect crystalline nanostructures. Integrating these materials into functional devices introduces additional complexities. For example, in gas sensing, achieving reliable and repeatable responses demands precise control over nanostructure morphology and surface chemistry. Beyond device performance, the environmental impact of nanostructured semiconductor production must also be carefully evaluated. While such materials can contribute to clean technologies, their synthesis and disposal may introduce ecological concerns, particularly regarding heavy metal quantum dots such as CdSe [7]. On the technological and theoretical front, effective doping strategies at the nanoscale remain a key challenge. Quantum confinement alters electronic band structures, complicating conventional doping approaches used for bulk semiconductors. Developing controlled doping for materials such as GaN, ZnO, and TiO₂ is critical for optimizing electrical conductivity and carrier concentration [113]. Furthermore, advancements in characterization techniques are required to better understand nanoscale properties. Electron beam-based microscopy and cathodoluminescence have proven useful for probing semiconductor nanowires, yet further improvements are needed to bridge the gap between material characterization and device-scale engineering [114]. Recent progress offers potential solutions to these long-standing issues. Methods like microwave sintering can retain nanostructural integrity during consolidation, while atomic layer deposition (ALD) has emerged as a precise tool for depositing ultrathin, conformal films with atomic-level control, useful for high-k dielectrics in integrated circuits. The development of freestanding photoelectrochemical nanodevices presents a pathway toward stable and efficient light-driven systems [112].

9. Future Scope of Nanostructured Semiconductors in Energy Harvesting

The future of nanostructured semiconductors in energy harvesting is poised for remarkable advancement, owing to their exceptional optical, electrical, and mechanical properties that enable efficient energy conversion and storage. These materials have emerged as essential components for sustainable and renewable energy technologies, particularly in solar energy conversion, hydrogen production, and thermoelectric applications.

In solar energy conversion, nanostructured semiconductors have already demonstrated outstanding potential through applications in dye-sensitized solar cells (DSSCs) and hybrid nanocomposite photovoltaics. Titanium dioxide (TiO₂) and related nanostructures have been effectively employed in DSSCs due to their high photoactivity, stability, and cost-efficiency [5,115,116]. Moreover, semiconductor nanowires (NWs) and quantum dots (QDs) have significantly enhanced photovoltaic efficiency by increasing light absorption and optimizing charge carrier separation [117,118]. These innovations are not limited to traditional solar cells but extend to photocatalytic systems that convert solar energy into chemical energy, such as in solar-driven hydrogen production and environmental remediation [112,119].

Hydrogen production and storage represent another crucial frontier for nanostructured semiconductors. In photoelectrochemical (PEC) water-splitting systems, nanostructured materials facilitate efficient photon absorption and charge separation, enabling sustainable hydrogen generation [117,119]. Simultaneously, their potential in solid-state hydrogen storage systems is being extensively investigated to enhance storage capacity, reversibility, and safety, key factors for the global hydrogen economy [119]. In the domain of energy storage, nanostructured semiconductors play a transformative role in developing next-generation batteries and supercapacitors. Silicon nanowires, graphene, and other nanoscale architectures have shown superior electrochemical performance, providing higher energy densities, improved cycling stability, and faster charge–discharge rates [26,120]. These materials optimize both the thermodynamic and kinetic aspects of energy storage reactions, making

them indispensable for high-performance lithium-ion and post-lithium-ion batteries [26]. Likewise, nanostructured materials integrated into fuel cells, especially those utilizing carbon nanotubes and other conductive nanostructures, promise greater energy conversion efficiency and longer operational lifetimes [121]. Thermoelectric and piezoelectric energy harvesting systems also stand to benefit substantially from advances in nanostructured semiconductor technology. Nanowires and other nanoscale semiconductor materials are capable of converting waste heat into electrical energy with enhanced efficiency due to their tunable thermal and electronic conductivities [117,122,123]. Similarly, piezoelectric nanogenerators (PENGs), based on materials such as zinc sulfide (ZnS) and polyvinylidene fluoride (PVDF), can harvest mechanical energy from vibrations, body movements, or ambient mechanical stress. Recent developments in multicomponent nanostructured materials have achieved higher piezoelectric conversion efficiencies, expanding potential applications in self-powered Internet of Things (IoT) devices [124–126]. Emerging technologies such as quantum dots coupled with nanocavities are opening new research avenues in quantum electrodynamics, nanoscale lasers, and optical energy manipulation, potentially creating novel pathways for energy harvesting at the quantum level [127–129]. Furthermore, flexible and wearable nanostructured semiconductors are gaining momentum for powering portable electronics, medical sensors, and smart textiles. These devices leverage flexibility, transparency, and stretchability to create efficient, lightweight, and portable energy harvesting systems [30].

A strategic roadmap for advancing nanostructured thermoelectric technology spans three key phases over a ten-year timeline. Phase 1 (Years 1–3) begins with foundational research focused on identifying and synthesizing promising thermoelectric materials such as Bi_2Te_3 , PbTe , SnSe , and SiGe , tailored to specific temperature ranges. Detailed characterization follows, including measurement of Seebeck coefficients, electrical and thermal conductivities, and microstructural analysis using tools like XRD, SEM, and TEM. Lab-scale prototypes are fabricated to evaluate initial device performance. In Phase 2 (Years 4–6), the focus shifts toward scaling and optimization. Scalable fabrication methods such as melt spinning, spark plasma sintering, roll-to-roll processing, and spray coating are developed and refined. Pilot-scale production is initiated, and performance testing is conducted under real-world conditions. Market analysis and feasibility studies help identify target applications, such as waste heat recovery or portable power devices. Phase 3 (Years 7–10) involves full commercialization. Final products are developed based on pilot feedback, regulatory compliance is pursued, and commercial products are launched. Expansion into diverse applications and global markets follows, positioning the technology for widespread adoption. This phased roadmap ensures a systematic transition from laboratory innovation to practical, scalable, and economically viable thermoelectric solutions.

10. Conclusions

Nanostructured semiconductors have emerged as transformative materials in thermoelectric energy conversion, particularly for the efficient transformation of waste heat into usable electricity. Their superior performance is rooted in nanoscale phenomena such as quantum confinement, interface engineering, and enhanced phonon scattering. These mechanisms decouple electrical and thermal transport properties, enabling the simultaneous optimization of the Seebeck coefficient, electrical conductivity, and reduced lattice thermal conductivity—critical factors in maximizing the thermoelectric figure of merit (ZT). Significant breakthroughs have been achieved in improving ZT values. A standout example is the development of PbTe -based thermoelectrics embedded with Ge nanoprecipitates, which achieved a ZT of 1.9 at 805 K, representing a major advancement for mid- to high-temperature applications. Likewise, nanostructured bulk silicon, historically

considered a poor thermoelectric material, showed a 3.5-fold improvement in ZT due to enhanced phonon boundary scattering. III–V semiconductor nanowires, engineered with periodic twin planes, achieved a tenfold reduction in thermal conductivity without degrading electrical properties, highlighting the importance of crystalline structure manipulation. Low-dimensional systems such as quantum dots, single-walled carbon nanotubes (SWCNTs), and 2D materials like MoS₂ and WS₂ exhibit remarkable improvements in carrier mobility and tunable band gaps. These properties are vital for achieving Seebeck coefficients in the range of 200–500 $\mu\text{V/K}$, as demonstrated in PbTe and SnSe systems. Bi₂Sb_xTe₃ nanolayers and PbSe-based composites have maintained consistently high ZT values over wide temperature ranges, making them attractive for both wearable electronics and industrial-scale waste heat recovery systems.

Advances extend beyond materials to include device-level improvements. For instance, integrating periodic dielectric gratings in GaAs solar cells has reduced optical losses and improved photovoltaic efficiency, indicating that the synergy between photonic and thermoelectric nanostructures can be exploited for multifunctional energy harvesting platforms. Figure 2 in this study emphasizes the need for ZT values exceeding 2.0–3.0 to achieve conversion efficiencies of 20–30%, a threshold necessary for viable replacement of fossil fuels in power generation. This goal has been approached in third-generation thermoelectric materials like SnSe and PbTe–PbSe–PbS quaternary alloys, the latter reaching ZT values of approximately 2.3. These hybrid systems benefit from both band convergence and nanoinclusion engineering, which effectively suppress thermal conductivity while preserving high power factors. Despite these impressive results, several critical challenges remain. Chief among them are issues of scalability, environmental sustainability, and long-term material stability. Current fabrication methods such as electron-beam lithography and molecular beam epitaxy are precise but cost-prohibitive for large-scale deployment. Promising alternatives like spray pyrolysis, displacement Talbot lithography, and nanoimprint lithography offer lower-cost, scalable solutions. Additional techniques, including isotope doping and hierarchical nanostructuring, provide further avenues to reduce thermal conductivity without impairing electrical performance.

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