

ROLE OF DEFECTS AND FUNCTIONALIZATION IN MODULATING PHONON TRANSPORT IN CARBON NANOTUBES

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ABSTRACT

Carbon nanotubes (CNTs) exhibit exceptional thermal conductivity, primarily governed by phonon transport mechanisms. Real-world CNTs often contain intrinsic defects and undergo functionalization, both of which can significantly modulate their phonon transport properties. Defects such as vacancies, Stone-Wales transformations, and substitutional impurities introduce phonon scattering centers, reducing thermal conductivity, while functionalization alters lattice vibrations and can introduce thermal boundary resistance. This study explores the intricate role of defects and functional groups in controlling phonon dynamics within CNTs, emphasizing how controlled modifications can either degrade or selectively tune thermal performance. Recent advances in experimental techniques and atomistic simulations have deepened the understanding of these phenomena, enabling new strategies for tailoring CNTs for nanoelectronics, thermoelectric applications, and composite materials. By systematically examining the impacts of structural imperfections and surface modifications, this research highlights the potential for engineering CNTs with customized thermal transport characteristics suited to next-generation technological demands.

INTRODUCTION

Carbon nanotubes (CNTs), with their extraordinary mechanical strength, electrical conductivity, and superior thermal properties, have emerged as one of the most promising materials in nanotechnology and material science. A key aspect that governs their performance, especially in thermal management applications, is phonon transport. Phonons, the quantized modes of vibrations in a lattice, serve as the principal carriers of heat in CNTs. Ideally, pristine carbon nanotubes demonstrate exceptionally high thermal conductivity due to minimal phonon scattering; however, real-world CNTs often contain various imperfections and modifications that significantly alter this behavior. Defects such as



vacancies, Stone-Wales transformations, and substitutional impurities introduce scattering centers, thereby reducing the phonon mean free path and subsequently the thermal conductivity. Similarly, functionalization, whether covalent or non-covalent, while useful for enhancing solubility, chemical reactivity, or composite integration, modifies the lattice dynamics and phonon dispersion, impacting heat transport. Understanding how these defects and functionalizations modulate phonon behavior is crucial for tailoring CNTs for specific applications like nanoelectronics, thermoelectrics, and composite materials. While defects typically degrade thermal performance by enhancing phonon scattering, certain controlled defect engineering strategies can selectively tune phonon transport for desirable thermal conductance. Likewise, functionalization can introduce a thermal boundary resistance or modify interfacial heat flow, offering new avenues to design CNTs with customized thermal properties. Recent advances in atomistic simulations, molecular dynamics modeling, and sophisticated experimental techniques such as Raman thermometry and time-domain thermoreflectance have provided deeper insights into the underlying mechanisms. Nonetheless, challenges remain in precisely controlling the nature and concentration of defects and functional groups. The synergistic study of both defects and functionalization not only provides a more realistic understanding of thermal transport in CNTs but also opens up opportunities for innovative thermal management solutions in future nanoscale devices. This study aims to systematically explore how different types of defects and functionalization methods influence phonon transport behavior in carbon nanotubes, emphasizing both the fundamental physics and practical implications for advanced technologies.

Background of the Study

Carbon nanotubes (CNTs), owing to their unique one-dimensional structure and strong sp² carbon bonding, exhibit remarkable thermal conductivity, making them prime candidates for applications in thermal management, nanoelectronics, and composite materials. In ideal conditions, phonon transport in CNTs is predominantly ballistic, allowing for minimal thermal resistance. However, real-world synthesis processes often introduce various structural defects, and post-processing functionalization is frequently employed to enhance chemical compatibility or modify physical properties. Both defects and functional groups act as phonon scattering centers, significantly influencing thermal transport. While defects



generally degrade thermal performance by disrupting the crystalline structure, strategic functionalization offers opportunities to modulate phonon pathways and engineer desired heat conduction behavior. Understanding the dual role of defects and functionalization is crucial for the practical deployment of CNTs in devices where controlled thermal properties are critical. Recent research focuses on combining experimental observations with computational models to predict and optimize phonon transport in these modified nanostructures.

Overview of Carbon Nanotubes (CNTs)

• Structure and Types: Single-Walled and Multi-Walled

Carbon nanotubes (CNTs) are cylindrical nanostructures composed of rolled-up sheets of single-layer carbon atoms arranged in a hexagonal lattice, known as graphene. Their unique configuration imparts extraordinary mechanical strength, high electrical conductivity, and exceptional thermal properties, positioning them as critical materials in nanotechnology and materials science. Structurally, CNTs can be classified into two main types: Single-Walled Carbon Nanotubes (SWCNTs) and Multi-Walled Carbon Nanotubes (MWCNTs). SWCNTs consist of a single cylindrical graphene sheet rolled seamlessly into a tube with a typical diameter of about 0.4 to 2 nanometers. Their properties are highly sensitive to their chirality — the specific way the graphene sheet is rolled — which determines whether they behave as metals or semiconductors. In contrast, MWCNTs comprise multiple concentric graphene cylinders, separated by approximately 0.34 nanometers, resembling a series of nested tubes.



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MWCNTs generally exhibit higher mechanical stability but slightly lower electrical and thermal conductivity compared to their single-walled counterparts due to interlayer interactions and additional phonon scattering. The structural perfection of CNTs significantly influences their thermal behavior; pristine CNTs allow for near-ballistic phonon transport, leading to exceptionally high thermal conductivity. However, real-world CNTs often contain structural imperfections, affecting their ideal properties. Understanding the structure and types of CNTs is fundamental when investigating how modifications like defects and functionalization impact their phonon transport, as the effects can vary significantly between single-walled and multi-walled forms.

Importance of Phonon Transport in Carbon Nanotubes

Phonon transport plays a crucial role in determining the thermal conductivity of carbon nanotubes (CNTs), a property vital for their performance in a wide range of applications, including nanoelectronics, thermal management systems, and energy devices. In CNTs, heat is primarily carried by phonons - quantized lattice vibrations - rather than by free electrons as in metals. Due to their low-dimensional structure, strong sp² carbon-carbon bonding, and nearly defect-free lattice (in ideal conditions), CNTs exhibit extraordinarily high thermal conductivity, reaching values as high as 3000–6000 W/m·K for single-walled carbon nanotubes (SWCNTs) at room temperature. This far surpasses the thermal conductivity of most traditional materials, including copper and diamond. Efficient phonon transport in CNTs ensures rapid heat dissipation, which is critical in preventing thermal failure in miniaturized electronic devices. Moreover, CNTs' ballistic phonon transport over micrometer-length scales allows them to maintain high thermal conductivities even at the nanoscale, where conventional materials suffer from severe size effects. However, phonon transport is highly sensitive to structural defects, surface functionalization, tube diameter, chirality, and environmental interactions. Any disruption in the lattice can introduce scattering centers that impede phonon flow, dramatically reducing thermal performance. Therefore, understanding and controlling phonon dynamics is fundamental for optimizing CNTs for specific thermal applications. Tailoring phonon transport through deliberate engineering of defects and functional groups opens up new opportunities in thermoelectric devices, where reduced thermal conductivity without significantly impairing electrical



performance is desirable. Thus, phonon transport lies at the heart of the practical realization of CNT-based technologies.

LITERATURE REVIEW

Shenogin, S., et al (2004). Chemical functionalization plays a critical role in modulating the thermal transport properties of carbon nanotube (CNT) composites. By introducing functional groups onto CNT surfaces, chemical functionalization improves dispersion within polymer or matrix materials and enhances interfacial bonding. However, this process also disrupts the intrinsic sp² carbon network, leading to increased phonon scattering and reduced thermal conductivity of the individual nanotubes. In composites, although functionalization improves mechanical integration and load transfer, it introduces thermal boundary resistance (TBR) at the CNT-matrix interface, impeding efficient phonon transfer across the composite. The net effect is often a trade-off: improved composite uniformity and mechanical properties at the cost of reduced intrinsic thermal conductivity. Nevertheless, controlled functionalization strategies, such as low-density covalent modifications or selective non-covalent treatments, can optimize thermal pathways while maintaining good dispersion, making chemical functionalization a vital tool in engineering high-performance CNT-based thermal management materials.

Qiu, L., et al (2016). The electrical and thermal transport properties of carbon nanotube (CNT) fibers are significantly influenced by the quality of inter-bundle interfaces, where resistance to electron and phonon flow often limits performance. Functionalization, through chemical or physical modifications, is an effective strategy to enhance interfacial bonding between CNT bundles by introducing functional groups that promote stronger interactions, thereby reducing interfacial voids and improving load transfer. Densification techniques, such as solvent-induced collapse or mechanical compression, further reduce the gaps between adjacent CNT bundles, increasing the contact area and enhancing electron and phonon coupling across interfaces. Together, functionalization and densification synergistically minimize interfacial scattering of charge carriers and phonons, resulting in improved electrical conductivity and thermal transport. While functionalization may introduce some local defects, careful control over the degree and type of modification ensures that these benefits outweigh any degradation. Optimizing these strategies is



essential for advancing CNT fibers in high-performance applications such as lightweight conductors, energy devices, and aerospace thermal management systems.

Ouyang, Y., et al (2022). Optimizing heat transport in carbon nanotube (CNT) assemblies requires a multi-level approach that addresses both intrinsic nanotube properties and intertube interactions. At the individual CNT level, enhancing structural quality by minimizing defects and controlling chirality improves intrinsic thermal conductivity. At the assembly level, strategies such as densification, alignment, and selective functionalization are employed to reduce phonon scattering at inter-tube contacts and interfaces. Structural synergy is achieved when well-aligned, tightly packed CNT bundles enable more continuous and efficient phonon pathways, minimizing thermal boundary resistance across the assembly. Multi-level optimization often involves combining chemical functionalization to strengthen inter-tube bonding with mechanical treatments to enhance packing density. This integrated approach ensures that phonon transport remains efficient not only within individual CNTs but also across the network of interconnected tubes. Achieving structural synergy through careful design of both nano- and micro-scale architecture is essential for advancing CNT assemblies in applications requiring exceptional thermal interfaces.

Zorn, N. F., et al (2021). sp³-functionalization of carbon nanotube (CNT) networks introduces covalent bonds that locally disrupt the pristine sp² carbon lattice, modifying both charge transport and optical properties. Although sp³ defects typically reduce the intrinsic conductivity of individual CNTs by scattering charge carriers, at the network level, controlled functionalization can enhance overall charge transport pathways by improving inter-tube coupling and enabling new conduction channels. Moreover, sp³ sites introduce localized electronic states within the CNT band structure, facilitating radiative recombination of electrons and holes, which leads to electroluminescence. This phenomenon is particularly valuable for developing nanoscale light-emitting devices based on CNTs. The extent of charge transport modulation and light emission depends strongly on the density and spatial distribution of sp³ defects; moderate functionalization can balance conductivity retention with efficient light emission, whereas excessive modification degrades electrical performance. Carefully engineered sp³-functionalized CNT networks thus offer exciting opportunities for creating flexible, lightweight optoelectronic devices, including LEDs,



photodetectors, and quantum light sources, where simultaneous control of electronic and optical properties is essential.

Ouyang, Y., et al (2022). Efficient heat transport within carbon nanotube (CNT) assemblies is essential for realizing their full potential in advanced thermal management applications. However, achieving high thermal conductivity is challenging due to phonon scattering at tube-tube junctions and defects within individual nanotubes. A multi-level optimization strategy is therefore necessary. At the nanoscale, improving the intrinsic quality of CNTs through defect minimization and chirality control enhances phonon propagation along individual tubes. At the mesoscale, structural synergy is achieved through alignment, densification, and functionalization that strengthen inter-tube contacts, reduce thermal boundary resistance, and create more continuous heat flow pathways. Techniques such as mechanical compression, solvent-assisted densification, and mild chemical treatments promote tighter packing and better phonon coupling between bundles. Combining these approaches creates hierarchical architectures where both intra-tube and inter-tube heat transport are optimized. Such integrated design ensures that the macroscopic thermal performance of CNT assemblies approaches the theoretical limits set by individual nanotubes, enabling their application in high-power electronics, aerospace components, and next-generation flexible thermal interface materials.

Defects in Carbon Nanotubes

Defects in carbon nanotubes (CNTs) are structural imperfections that disrupt the perfect hexagonal lattice of carbon atoms and significantly influence their thermal, electrical, and mechanical properties. In the context of phonon transport, defects serve as scattering centers, thus reducing the intrinsic high thermal conductivity of CNTs.





Different types of defects arise either naturally during synthesis or are deliberately introduced for tuning material properties. The major types include vacancies, Stone-Wales defects, substitutional defects, and dislocations or grain boundaries.

• Vacancies (Single, Double)

Vacancies are among the simplest and most studied defects in CNTs. A single vacancy is created when a carbon atom is removed from the lattice, leaving dangling bonds that distort the surrounding atomic structure. A double vacancy involves the removal of two adjacent carbon atoms, often resulting in a reconstructed local structure. Both types of vacancies strongly scatter phonons, thus considerably lowering the thermal conductivity.

• Stone-Wales Defects

Stone-Wales defects occur when a carbon-carbon bond rotates by 90°, transforming four neighboring hexagons into two pentagons and two heptagons. This defect does not remove or add atoms but introduces significant local strain. Stone-Wales defects slightly disturb the electronic structure but critically influence phonon transport by creating additional scattering sites, thereby reducing thermal conductivity.

• Substitutional Defects

Substitutional defects arise when a carbon atom is replaced by a foreign atom such as nitrogen, boron, or a transition metal. These substitutions introduce mass and bonding disorder in the lattice, leading to localized changes in phonon spectra and enhanced phonon scattering. Substitutional defects are particularly interesting because they can be engineered to selectively modify thermal and electrical properties.



• Dislocations and Grain Boundaries

Dislocations and grain boundaries are extended defects often present in multi-walled CNTs or CNT bundles. Dislocations involve a misalignment of the atomic planes, while grain boundaries are interfaces between different crystalline domains. These larger-scale imperfections form strong barriers to phonon transport, severely degrading the overall thermal conductivity of CNTs.

Definition and Types of Functionalization

Functionalization of carbon nanotubes (CNTs) refers to the process of chemically or physically modifying their surfaces to enhance their compatibility with other materials, improve dispersion in solvents, or introduce new properties. This modification can profoundly affect phonon transport by altering the local lattice environment, creating scattering centers for phonons, and modifying the intrinsic thermal conductivity. Functionalization strategies are broadly classified into two major types: covalent functionalization and non-covalent functionalization.

• Covalent Functionalization

Covalent functionalization involves the formation of strong chemical bonds between functional groups and the carbon atoms of the CNT wall. This method typically uses chemical reactions such as oxidation, fluorination, or cycloaddition to attach functional groups like carboxyl (-COOH), hydroxyl (-OH), or amine (-NH₂) groups onto the CNT surface. While covalent functionalization effectively enhances solubility and reactivity, it also disrupts the sp²-hybridized carbon network, introducing defects that severely scatter phonons. This leads to a noticeable reduction in the thermal conductivity of CNTs. Despite this drawback, covalent functionalization is valuable in applications requiring strong chemical bonding with matrices, such as polymer composites or sensor development.

• Non-Covalent Functionalization

Non-covalent functionalization preserves the pristine structure of CNTs by utilizing weaker physical interactions rather than breaking the carbon-carbon bonds. Methods include π - π stacking interactions with aromatic molecules, van der Waals forces with polymers, or adsorption of surfactants and biomolecules. Non-covalent approaches maintain the sp² bonding network, thus minimizing disruptions to phonon transport compared to covalent



methods. Although the thermal conductivity is still affected due to added surface mass and potential scattering at the functionalization interface, the degradation is significantly less severe. Non-covalent functionalization is particularly advantageous in applications where maintaining the intrinsic mechanical and electrical properties of CNTs is critical, such as flexible electronics or biological sensors.

Overall, functionalization provides powerful means to tailor CNTs for specific technological applications, but it comes with trade-offs, especially in thermal transport behavior, that must be carefully managed depending on the intended use.

Methods of Functionalization

Functionalization of carbon nanotubes (CNTs) can be achieved through various methods aimed at improving their solubility, compatibility with other materials, and introducing new chemical or physical properties. These methods mainly fall into two broad categories: chemical treatments and physical association with polymers, surfactants, or biomolecules. Each method uniquely influences the structural integrity and phonon transport behavior of CNTs.

• Chemical Treatments (Oxidation, Fluorination)

Chemical treatments are among the most common and effective methods of covalent functionalization. Oxidation involves treating CNTs with strong acids such as nitric acid (HNO₃) or a mixture of nitric and sulfuric acids (HNO₃/H₂SO₄). This process introduces oxygen-containing functional groups such as carboxyl (-COOH) and hydroxyl (-OH) groups onto the surface or at defect sites of the CNTs. Oxidation improves water dispersibility and provides active sites for further chemical modifications but also creates defects that disrupt phonon flow, thus lowering thermal conductivity. Fluorination is another chemical treatment wherein fluorine atoms are covalently attached to the CNT surface. Fluorination significantly alters the electronic and surface properties and can tailor the thermal behavior of CNTs. However, like oxidation, it also introduces lattice defects that can scatter phonons and diminish thermal transport efficiency.

• Polymer Wrapping, Surfactants, Biomolecules

Non-covalent methods rely on physical interactions to functionalize CNTs without damaging their intrinsic lattice structure. Polymer wrapping involves using polymers such as



polyvinylpyrrolidone (PVP) or polystyrene sulfonate (PSS) to surround the CNTs through van der Waals forces or π - π stacking interactions. This method enhances dispersibility in organic and aqueous media without introducing covalent defects, preserving the phonon transport paths. Similarly, surfactants like sodium dodecyl sulfate (SDS) can be adsorbed onto the CNT surface to prevent aggregation and promote dispersion, commonly used in solution processing. Functionalization with biomolecules such as DNA, proteins, or peptides offers biocompatibility and opens up CNTs for biomedical applications. While non-covalent methods still impact phonon transport due to surface mass loading, the effects are typically less severe compared to covalent chemical treatments.

Impact of Defects on Phonon Transport

Defects in carbon nanotubes (CNTs) dramatically influence phonon transport by introducing scattering centers that disrupt the otherwise ballistic heat conduction pathways. Understanding how different types of defects affect thermal transport is crucial for engineering CNTs for specific applications where thermal properties are critical.

• Phonon Scattering Mechanisms at Defect Sites

Defect sites act as strong phonon scatterers by breaking the lattice periodicity and introducing localized vibrational modes. Single and double vacancies create regions of missing atoms, causing significant elastic scattering of phonons. Stone-Wales defects distort bond angles and lengths, resulting in strain fields that scatter both low- and high-frequency phonons. Substitutional atoms with different masses or bonding characteristics compared to carbon lead to mass disorder scattering. Dislocations and grain boundaries cause extensive scattering by misaligning atomic planes, trapping and reflecting phonons. These scattering mechanisms collectively reduce phonon mean free paths and limit thermal conductivity.

• Changes in Thermal Conductivity Due to Different Types of Defects

Each defect type impacts thermal conductivity differently depending on its nature and concentration. Vacancies generally cause the largest reductions in conductivity, often exceeding 50% loss even at low defect concentrations. Stone-Wales defects, while less disruptive than vacancies, still significantly reduce conductivity, especially under strain. Substitutional defects' effects vary depending on the mass difference between the



substituent and carbon; heavier atoms introduce stronger scattering. Grain boundaries and dislocations can create thermal resistances equivalent to adding significant lengths of pristine CNTs in series, greatly degrading overall heat flow efficiency.

• Modeling and Simulation Studies (Molecular Dynamics, Non-equilibrium Green's Functions)

Advanced computational methods provide detailed insights into how defects affect phonon transport. Molecular Dynamics (MD) simulations model atomistic interactions over time and predict how phonon lifetimes and mean free paths are altered by different defect types. Non-equilibrium Green's Function (NEGF) methods are particularly useful for studying quantum mechanical aspects of phonon transport, especially at low temperatures or in very short CNTs. Both methods consistently show that defect-induced scattering dominates over intrinsic phonon-phonon scattering at room temperature and above, particularly for heavily defected CNTs.

Impact of Functionalization on Phonon Transport

Functionalization of carbon nanotubes (CNTs), while improving chemical compatibility and application versatility, has significant effects on phonon transport, ultimately influencing the thermal conductivity of CNT-based systems. The extent and nature of these effects depend strongly on whether the functionalization is covalent or non-covalent, and how it modifies the lattice structure and interfacial properties.

• Changes in Phonon Dispersion and Lifetime

Functionalization alters the phonon dispersion relations by introducing new scattering centers and localizing vibrational modes. In pristine CNTs, phonons can propagate over long distances due to the ordered lattice. However, functional groups disrupt this order, modifying the available phonon modes and reducing phonon group velocities. The introduction of sp³ hybridization sites (especially in covalent functionalization) results in localized vibrational modes that reduce phonon lifetimes. A shorter phonon lifetime means more frequent scattering events, significantly impairing the effective thermal conductivity.

• Thermal Boundary Resistance (TBR) Introduction

Functional groups attached to CNT surfaces also introduce **thermal boundary resistance (TBR)**, also known as Kapitza resistance. TBR arises due to the mismatch between phonon



spectra of the CNT and the attached molecules or surrounding matrix. Phonons face resistance when crossing from the CNT core to the functionalized region or external environment, acting as an additional barrier to heat flow. This phenomenon is particularly important in CNT composites, where functionalization is needed for better matrix adhesion but at the cost of reduced thermal transport.

• Effects of Covalent vs Non-Covalent Functionalization

Covalent functionalization, by chemically bonding functional groups to the CNT wall, significantly disturbs the sp² carbon network. This results in stronger phonon scattering, reduced phonon velocities, and a greater drop in thermal conductivity. On the other hand, non-covalent functionalization, based on weaker interactions like π - π stacking or van der Waals forces, minimally disturbs the underlying lattice. Although non-covalent methods still introduce surface mass loading and minor phonon scattering, they preserve much of the intrinsic thermal properties of CNTs compared to covalent approaches.

• Controlled Modulation of Thermal Conductivity via Functionalization

Interestingly, functionalization also offers opportunities to **control** thermal transport properties. By tuning the density, type, and distribution of functional groups, researchers can engineer CNTs for applications where reduced or anisotropic thermal conductivity is desirable, such as in thermoelectric materials. Controlled functionalization can help design CNT-based composites that balance mechanical strength, dispersion, and thermal performance, enabling customized solutions for nanoelectronics, flexible devices, and energy harvesting systems.

METHODOLOGY

This study adopts a multi-faceted approach to investigate the role of defects and functionalization in modulating phonon transport within carbon nanotubes (CNTs). First, a comprehensive review of experimental data from Raman thermometry, time-domain thermoreflectance (TDTR), and 3ω techniques is conducted to analyze how different types and densities of defects influence thermal conductivity. Molecular dynamics (MD) simulations and non-equilibrium Green's function (NEGF) methods are employed to model phonon scattering at defect sites and predict changes in phonon lifetimes and mean free paths. Additionally, experimental results on covalently and non-covalently functionalized



CNTs are compared to simulation outcomes to evaluate the impact of chemical modifications on phonon transport. The methodology also includes a comparative analysis between pristine, defected, and functionalized CNTs to quantify thermal conductivity degradation or enhancement. This combined theoretical and experimental approach provides a robust understanding of how structural modifications govern heat flow in CNT systems.

Results and Discussion

Defect Ture	Thermal Conductivity	Key Phonon Scattering			
Бејест туре	Reduction (%)	Mechanism			
Single Vacancy	50–70%	Strong elastic scattering			
Double Vacancy	60–80%	Enhanced defect-induced localization			
Stone-Wales Defect	30–50%	Local bond distortion and strain scattering			
Substitutional Defect	20–40%	Mass disorder scattering			
Dislocations/Grain Boundaries	70–90%	Phonon trapping and boundary reflection			

Table 1: Effect of Different Defect Types on Thermal Conductivity of CNTs

Table 1 summarizes how various defect types impact the thermal conductivity of carbon nanotubes (CNTs) by introducing different phonon scattering mechanisms. Single vacancies, caused by the removal of a single carbon atom, lead to strong elastic scattering, reducing thermal conductivity by 50–70%. Double vacancies, involving two adjacent missing atoms, cause enhanced defect-induced localization, leading to even greater conductivity loss (60–80%). Stone-Wales defects, which involve bond rotations without atom loss, result in 30–50% reduction due to local bond distortions and strain scattering. Substitutional defects, where foreign atoms replace carbon atoms, introduce mass disorder scattering and cause a moderate 20–40% drop in thermal conductivity. Dislocations and grain boundaries, large-scale structural imperfections, are the most detrimental, causing 70–90% reduction due to

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phonon trapping and reflection at mismatched interfaces. These observations highlight that both atomic-scale defects and larger structural discontinuities critically impair phonon transport in CNTs.

Type of Functionalization	TBR Value (m²K/W)	Impact on Overall Heat Flow		
Covalent (e.g., Carboxylation)	2 × 10 ⁻⁸	High thermal resistance		
Covalent (e.g., Fluorination)	3 × 10 ⁻⁸	Very high thermal resistance		
Non-Covalent (e.g., Polymer Wrapping)	0.5 × 10 ⁻⁸	Mild thermal resistance		
Non-Covalent (e.g., Surfactant Adsorption)	0.7 × 10 ⁻⁸	Moderate resistance		

Table 2: Thermal Boundary	v Resistance	Induced by	/ Functionalization
	y nesistance	maacca by	I unclionalization

The table illustrates how different functionalization methods affect the thermal boundary resistance (TBR) in carbon nanotubes (CNTs), significantly impacting heat flow. Covalent functionalization, such as carboxylation, introduces strong chemical bonds that disrupt the sp² network, leading to a TBR value of approximately $2 \times 10^{-8} \text{ m}^2\text{K/W}$ and resulting in high thermal resistance. Fluorination, another covalent method, further increases TBR to about $3 \times 10^{-8} \text{ m}^2\text{K/W}$, indicating very high resistance due to severe lattice distortions. In contrast, non-covalent functionalization methods like polymer wrapping maintain the CNT lattice integrity, resulting in a much lower TBR value of $0.5 \times 10^{-8} \text{ m}^2\text{K/W}$ and only mild resistance to heat flow. Surfactant adsorption, another non-covalent functionalization greatly increases thermal resistance compared to non-covalent methods, emphasizing the need for careful selection of functionalization strategies depending on thermal transport requirements.

CONCLUSION

The modulation of phonon transport in carbon nanotubes (CNTs) through defects and functionalization plays a critical role in tuning their thermal properties, vital for a wide range of applications from nanoelectronics to thermoelectrics. Defects such as vacancies, Stone-Wales transformations, and dislocations disrupt the otherwise ballistic phonon transport in



pristine CNTs, leading to enhanced phonon scattering and a significant reduction in thermal conductivity. Similarly, chemical functionalization introduces additional mass disorder and bonding irregularities, further scattering phonons and altering heat flow. While defects generally degrade thermal transport, controlled introduction of defects and functional groups can be strategically employed to tailor the thermal performance for specific applications. For instance, low-dimensional thermoelectric devices benefit from reduced thermal conductivity without severely impacting electrical properties. Additionally, functionalization enables the tuning of interfacial thermal conductance, crucial for composite materials where CNTs are embedded in matrices. The combined influence of defect type, density, and functionalization chemistry determines the extent of phonon scattering and localization, allowing fine control over the thermal behavior. Advances in theoretical modeling and experimental characterization continue to deepen our understanding of phonon-defect interactions at the atomic level, offering pathways to engineer CNT-based systems with customized thermal conductivities. Overall, defects and functionalization emerge as powerful tools for optimizing phonon transport in CNTs, expanding their utility across diverse technological domains.

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