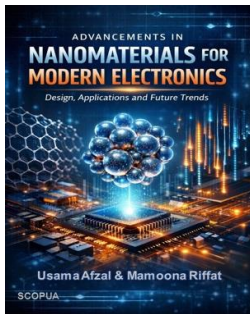


# CHAPTER 4

## ENERGY STORAGE AND HARVESTING TECHNOLOGIES USING NANOMATERIALS

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## Abstract

The global transition toward sustainable energy systems has intensified interest in nanomaterials for efficient energy storage and harvesting. This chapter reviews recent progress in nanostructured materials that enhance electrochemical, thermal, and photonic energy conversion processes. In batteries and supercapacitors, nanoscale design through graphene, silicon nanowires, and transition metal oxides enables high energy and power densities, rapid charge–discharge kinetics, and long-term stability. Similarly, nanomaterials revolutionise thermoelectric, piezoelectric, and triboelectric systems by improving charge transport, phonon scattering, and mechanical flexibility, while perovskite and quantum dot solar cells exploit quantum confinement and tunable bandgaps for superior photovoltaic performance. Hybrid energy platforms that integrate multiple nanomaterial-based mechanisms, such as battery–supercapacitor or solar–thermoelectric systems, demonstrate multifunctionality, flexibility, and self-powering capabilities vital for wearable and autonomous devices. The chapter also highlights scalable fabrication approaches, eco-friendly synthesis, and the emerging use of biodegradable and self-healing nanocomposites. Together, these advances position nanomaterials as the cornerstone of next-generation energy technologies, offering pathways toward high-performance, sustainable, and adaptive power solutions aligned with the global clean energy agenda.

**Keywords:** *Energy harvesting; Energy storage; Hybrid energy systems; Lithium–ion batteries; Lithium–sulfur batteries; Nanomaterials; Perovskite solar cells; Piezoelectric nanogenerators; Quantum dot solar cells; Solid–state batteries; Supercapacitors; Sustainable energy; Thermoelectric materials; Triboelectric nanogenerators; Wearable electronics.*

The global transition toward sustainable energy systems has intensified the demand for efficient energy storage and harvesting technologies [1],[2],[3],[4]. As the world moves away from fossil fuels and embraces cleaner energy alternatives, the need to develop advanced materials and systems that can store and convert energy efficiently, reliably, and economically has become increasingly critical. Energy storage systems, such as batteries and supercapacitors, play a vital role in



balancing energy supply and demand, supporting the integration of intermittent renewable sources like solar and wind into power grids, and enabling the advancement of electric vehicles and portable electronics. At the same time, energy harvesting technologies such as thermoelectric, photovoltaic, and hybrid energy systems are essential for capturing and converting ambient energy from various sources, including heat, light, and mechanical vibrations, into usable electrical energy. Nanomaterials have emerged as key enablers in this rapidly evolving landscape [5],[6],[7] as shown in Figure 4.1. Their unique properties, including high surface-area-to-volume ratio, tunable band structures, improved charge transport capabilities, and enhanced mechanical strength, make them ideal candidates for use in energy-related applications. The nanoscale dimension allows for better control over physical and chemical interactions at the material interface, which is crucial for enhancing the performance and efficiency of energy storage and harvesting devices. By tailoring the morphology, composition, and architecture of nanomaterials, researchers have achieved significant progress in overcoming the limitations of conventional bulk materials.

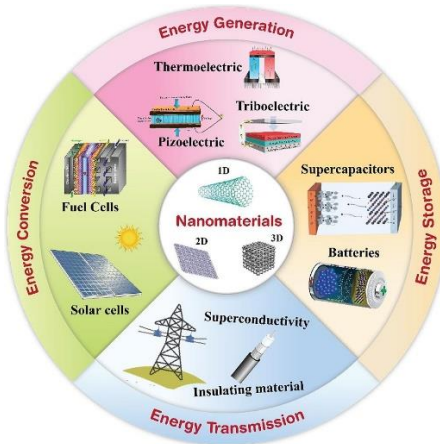


**Figure 4.1:** Overview of nanomaterials in energy systems, highlighting their roles in energy generation, storage, conversion, and transmission through diverse structures (1D, 2D and 3D) [8].



In the context of energy storage, nanomaterials have been instrumental in improving the energy and power densities of lithium-ion batteries (LIBs), lithium-sulfur batteries (LSBs), and next-generation solid-state batteries [9],[10],[11]. For instance, nanostructured electrodes offer shorter ion diffusion paths, larger surface areas for electrochemical reactions, and greater mechanical resilience against volume expansion during charge-discharge cycles. Similarly, supercapacitors benefit from nanostructured carbon materials, metal oxides, and conductive polymers that provide fast charge-discharge capabilities, long cycle life, and enhanced capacitance. On the energy harvesting front, nanomaterials have revolutionised thermoelectric generators by enhancing their thermoelectric figure of merit (ZT) through phonon scattering and electronic transport optimisation. In solar energy conversion, materials such as perovskites and quantum dots have demonstrated remarkable efficiency improvements due to their tunable optical properties and facile solution processability. The integration of nanomaterials into photovoltaic architectures has also led to improved light absorption, better charge carrier mobility, and increased device stability. Furthermore, hybrid energy systems that combine multiple storage and harvesting technologies have shown great promise in addressing the dynamic energy needs of modern applications. Nanomaterials play a central role in these systems by enabling multifunctional behaviour and compact integration, which are particularly important for self-powered wearable electronics, implantable medical devices, and remote sensing systems.

This chapter provides an in-depth overview of how nanomaterials are reshaping the field of energy storage and harvesting. It explores recent developments, technological advancements, and challenges in deploying nanomaterials in various systems, including batteries, supercapacitors, thermoelectric devices, and solar cells. Through a critical analysis of state-of-the-



art research and emerging trends, this chapter aims to highlight the potential of nanomaterials in driving sustainable energy solutions for the future.

#### **4.1. Nanomaterials for High-Efficiency Batteries**

The continuous pursuit of high-efficiency, lightweight, and durable energy storage systems has driven significant advancements in battery technologies. Among these, lithium-based batteries have dominated the market, particularly in consumer electronics, electric vehicles, and grid storage systems. A central challenge in battery technology is balancing high energy density with long cycle life, fast charge/discharge rates, and safety. The application of nanomaterials has emerged as a transformative approach in addressing these multifaceted challenges. Nanostructured materials possess unique characteristics such as high surface area-to-volume ratios, tunable electronic and ionic conductivity, and structural flexibility, making them ideal for use in modern battery systems [12],[13].

Nanomaterials enhance battery performance by reducing ion diffusion lengths, increasing active surface areas for electrochemical reactions, and providing robust structural integrity to accommodate the stresses of repeated cycling. Nanostructured electrodes, nanocomposite electrolytes, and engineered nanointerfaces are increasingly employed across various battery chemistries to achieve superior energy and power densities. This section delves into three key lithium-based battery types where nanomaterials have shown profound impact: lithium-ion batteries (LIBs), solid-state batteries, and lithium-sulfur batteries.

##### **4.1.1. Lithium-Ion Batteries (LIBs)**

Lithium-ion batteries have revolutionised portable electronics and are a cornerstone of the emerging electric mobility



industry. Their widespread adoption is attributed to their high energy density, long cycle life, and relatively mature manufacturing infrastructure. However, conventional LIBs still face limitations in terms of rate capability, safety, and capacity retention under extreme operating conditions. Nanomaterials offer promising solutions to these challenges [14].

- **Anode materials**, particularly graphite, have been modified with nanomaterials to enhance lithium intercalation and conductivity. Silicon, with its high theoretical capacity ( $\sim 4200$  mAh/g), is a prime candidate for next-generation anodes. However, silicon undergoes drastic volume expansion ( $>300\%$ ) during lithiation, which leads to mechanical degradation. Nanostructured silicon, such as silicon nanowires, hollow nanospheres, and core-shell structures, has shown improved mechanical resilience and capacity retention. These nanostructures effectively accommodate volume changes and minimise the formation of stress-induced cracks.
- **Carbon-based nanomaterials** such as graphene and carbon nanotubes (CNTs) are extensively used to create conductive matrices that buffer volume changes and maintain electrical contact throughout cycling. These nanostructures facilitate efficient electron transport and enhance the structural stability of the electrode. Additionally, nanostructured transition metal oxides (e.g.,  $\text{Fe}_3\text{O}_4$ ,  $\text{MnO}_2$ ,  $\text{Co}_3\text{O}_4$ ) and composite nanomaterials have demonstrated improved lithium storage capacities and rate performance. Their ability to undergo reversible redox reactions and sustain high capacity over prolonged cycles makes them promising candidates for future anode designs.
- **Cathode performance** also benefits from nanoscale engineering. Layered transition metal oxides (e.g.,  $\text{LiCoO}_2$ ,  $\text{LiNiMnCoO}_2$ ), spinels ( $\text{LiMn}_2\text{O}_4$ ), and olivines ( $\text{LiFePO}_4$ )



have been synthesised in nanostructured forms to increase surface area and shorten lithium diffusion pathways. Coating these materials with nanolayers of conductive agents or protective shells further enhances their electrochemical stability and suppresses phase transformations during cycling. For example,  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  coatings on  $\text{LiNiMnCoO}_2$  cathodes reduce the formation of detrimental surface films and improve cycling life.

Moreover, nanostructured cathodes provide faster lithium-ion kinetics due to their increased contact area with the electrolyte and reduced particle sizes. This enhances the rate performance and allows for high-power operation, which is essential for applications such as power tools and electric vehicles. In addition, doping strategies using nanoparticles such as Mg, Al, and Ti are employed to stabilise cathode structures and enhance capacity retention.

#### **4.1.2. Solid-State Batteries**

Solid-state batteries are considered the next leap in battery technology due to their potential for higher energy density, improved safety, and greater thermal stability. Unlike conventional LIBs that use flammable liquid electrolytes, solid-state batteries utilise solid electrolytes, which eliminate the risk of leakage and thermal runaway [15],[16]. Nanomaterials play a critical role in the development of solid electrolytes with enhanced ionic conductivity and mechanical properties. For instance, oxide-based electrolytes such as garnet-type  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) and sulfide-based electrolytes like  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  (LGPS) have shown significant promise [17]. Nanoscale engineering of these materials leads to improved densification during sintering, reduced grain boundary resistance, and better contact with electrode materials. These factors contribute to lower interfacial impedance and higher ionic mobility across the solid electrolyte.



Moreover, interface engineering using nanoscale coatings or interlayers enhances compatibility between the solid electrolyte and electrodes, mitigating issues such as dendrite formation and interfacial degradation. Composite solid electrolytes that integrate nanofillers like  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{SiO}_2$  within polymer matrices have demonstrated improved mechanical strength, flexibility, and ionic conductivity, enabling safer and more durable solid-state battery designs. These nanocomposite materials also offer better processability and allow for thin-film fabrication, which is advantageous for miniaturised applications. The development of nanostructured cathodes and anodes tailored for solid-state systems is also gaining momentum. Nanostructured lithium metal anodes, combined with protective nanolayers, can suppress dendritic growth and enhance cycling performance. For instance, lithium-metal foils coated with lithiophilic nanoparticles (e.g.,  $\text{ZnO}$ ,  $\text{Ag}$ ) promote uniform lithium deposition and reduce dendrite propagation [18]. On the cathode side, nanoscale coatings and dopants are employed to improve lithium-ion transport and interface stability. Strategies such as  $\text{LiNbO}_3$  and  $\text{Li}_3\text{PO}_4$  surface modifications have shown enhanced interfacial stability and reduced impedance.

Additionally, nanostructured interlayers and buffer layers are used to mitigate interfacial stress and accommodate volume changes during cycling. These layers help maintain physical integrity and electrical contact between electrodes and solid electrolytes. The integration of 3D nanostructured scaffolds has also been explored to improve mechanical robustness and facilitate ion transport, particularly in high-energy-density designs.

#### 4.1.3. Lithium-Sulfur Batteries

Lithium-sulfur (Li-S) batteries have attracted significant attention due to their high theoretical specific energy ( $\sim 2600$  Wh/kg), low cost, and environmental friendliness. However, their practical implementation is hindered by several challenges,



including the low electrical conductivity of sulfur, the dissolution of intermediate lithium polysulfides, and severe volume changes during cycling. Nanotechnology offers multiple strategies to overcome these limitations. One of the most successful approaches is the use of nanostructured carbon hosts to encapsulate sulfur and physically/chemically trap lithium polysulfides. Porous carbon matrices, such as mesoporous carbon, graphene frameworks, and carbon nanotube networks, provide conductive paths for electrons and confine active materials, mitigating polysulfide diffusion (shuttle effect). These carbon hosts also facilitate uniform sulfur distribution and improve rate capability [19],[20].

Furthermore, metal-organic frameworks (MOFs), hollow carbon spheres, and yolk-shell nanostructures have been employed to accommodate sulfur expansion and improve cycle stability. These hosts enable high sulfur loading and uniform sulfur distribution, thereby enhancing electrochemical performance. Polar metal oxide nanoparticles (e.g.,  $\text{TiO}_2$ ,  $\text{MnO}_2$ ) have also been integrated into cathode structures to chemically anchor polysulfides and suppress their migration. These polar interactions inhibit the shuttle effect and extend cycle life. On the electrolyte side, the incorporation of nanoscale additives and coatings improves ionic conductivity and inhibits undesirable side reactions. Solid and gel-based electrolytes with embedded nanofillers are also being explored to address the safety and polysulfide dissolution issues associated with liquid electrolytes. For instance, polyethylene oxide (PEO) or PVDF-based gel electrolytes combined with  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$  nanoparticles have demonstrated enhanced conductivity and mechanical stability [21]. For anode improvement, lithium-metal protection strategies using nanolayer coatings and artificial solid-electrolyte interphases (SEIs) are under investigation. These nanoscale barriers prevent dendritic growth and stabilise lithium deposition, extending battery life and enhancing safety. Materials such as graphene oxide, boron nitride, and polymer nanocomposites



have been used to form robust SEI layers that minimise side reactions and improve coulombic efficiency.

Emerging trends in Li-S battery research include the use of dual-functional interlayers, separator coatings, and advanced binders. Nanostructured interlayers placed between the cathode and separator can act as polysulfide reservoirs, capturing dissolved species and facilitating their reutilization. Similarly, functional coatings on separators (e.g., doped graphene, polymer composites) offer a physical and chemical barrier against polysulfide migration. Advanced binders incorporating nanofillers or conductive polymers (e.g., polyaniline, PEDOT: PSS) help maintain electrode integrity and enhance conductivity. These binders improve electrode flexibility and accommodate volume changes during cycling. Together, these strategies are enabling practical Li-S battery designs with high energy density, long cycle life, and enhanced safety.

#### **4.1.4. Emerging Nanomaterials for Next-Generation Batteries**

Beyond lithium-based systems, the next frontier in battery technology includes alternative chemistries such as sodium-ion, potassium-ion, magnesium-ion, and multivalent batteries. These systems offer advantages in cost, resource availability, and safety, especially for large-scale energy storage. Nanomaterials are central to the development of these alternative batteries by enhancing electrochemical kinetics, structural stability, and ion transport [22].

- **Sodium-Ion and Potassium-Ion Batteries:** Sodium-ion (Na-ion) and potassium-ion (K-ion) batteries have garnered attention due to the natural abundance and low cost of sodium and potassium [23]. However, their larger ionic radii compared to lithium present challenges in terms of electrode structural stability and diffusion kinetics. Nanostructured materials, such as carbon-based nanocomposites, metal oxides, and layered transition metal



sulfides, are being investigated to accommodate ion expansion and improve rate performance. Graphene, CNTs, and reduced graphene oxide (rGO) frameworks offer high conductivity and structural flexibility, which are essential for maintaining performance during large-volume changes. Additionally, nanostructured NASICON-type materials and Prussian blue analogs have shown promise as cathodes due to their open frameworks and stable cycling behaviour.

- **Magnesium and Multivalent Batteries:** Magnesium (Mg), zinc (Zn), and aluminium (Al) offer higher volumetric capacities and safety advantages due to dendrite-free deposition [24]. However, sluggish diffusion kinetics and limited electrolyte compatibility have hindered progress. Nanomaterials such as Mg-based metal oxides, transition metal chalcogenides, and polymer-gel nanocomposites are being explored to overcome these issues. For instance, nanostructured  $\text{MgTiO}_3$  and  $\text{V}_2\text{O}_5$  have shown enhanced Mg-ion diffusion and improved capacity retention. Similarly, hybrid nanocomposites with high surface area and tailored porosity facilitate ion transport and suppress parasitic reactions. The use of ionic liquids and solid electrolytes with embedded nanofillers is also advancing the development of stable, high-performance multivalent batteries.

## 4.2. Supercapacitors and Energy Density Enhancement with Nanomaterials

Supercapacitors, also known as electrochemical capacitors or ultracapacitors, are advanced energy storage devices that bridge the gap between traditional capacitors and batteries [25]. They possess unique attributes such as high-power density, long cycle life, and rapid charge-discharge cycles, making them ideal for



applications in electric vehicles, portable electronics, and renewable energy systems. However, despite these advantages, their relatively low energy density remains a critical limitation when compared to batteries. To overcome this barrier, significant research has focused on the integration of nanomaterials to enhance the electrochemical performance of supercapacitors. Nanomaterials offer an unprecedented ability to improve both specific capacitance and energy density due to their high surface area, unique physicochemical properties, and tunable morphology. The energy stored in a supercapacitor is fundamentally governed by the equation (4.1):

$$E = \frac{1}{2} \times C \times V^2 \quad (4.1)$$

Where  $E$  is the energy,  $C$  is the capacitance, and  $V$  is the operating voltage. Nanomaterials contribute to enhancing both the capacitance ( $C$ ) and, indirectly, the voltage window ( $V$ ) by enabling stable operation in broader electrochemical environments.

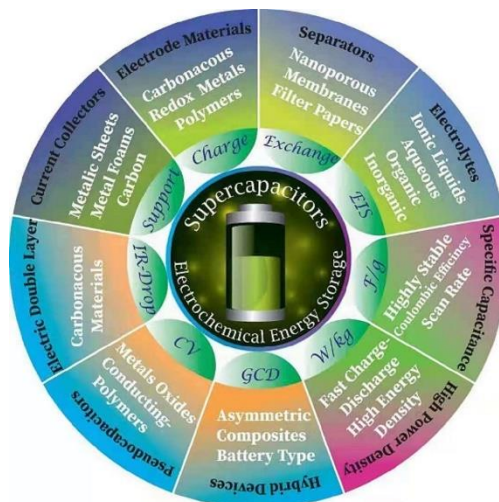


**Figure 4.1:** Overview of key components, mechanisms and performance parameters governing the operation of supercapacitors. [26].

There are two primary mechanisms of charge storage in supercapacitors: (1) Electrical double-layer capacitance (EDLC)



and (2) Pseudocapacitance. EDLCs depend on the physical separation of charges at the electrode-electrolyte interface, whereas pseudocapacitors involve fast and reversible redox reactions on or near the surface of the electrode material. Nanomaterials enhance both these mechanisms depending on their type and structure.

- **Carbon Nanomaterials:** Carbon-based nanomaterials are widely used for EDLC-type supercapacitors due to their high electrical conductivity, large surface area, and structural stability. Among them, carbon nanotubes (CNTs) and graphene are the most prominent [27]. CNTs offer a high aspect ratio, mesoporous structure, and excellent mechanical flexibility, making them ideal for high-rate performance. Graphene, a two-dimensional sheet of  $sp^2$ -bonded carbon atoms, provides an ultra-large theoretical surface area ( $\sim 2630 \text{ m}^2/\text{g}$ ) and exceptional electronic conductivity. These features enable the formation of a highly efficient electric double-layer, facilitating rapid charge transport and high power output. For instance, a supercapacitor composed of vertically aligned CNTs can provide both short ion diffusion paths and high electron mobility, leading to faster charging and improved power density. Similarly, reduced graphene oxide (rGO) based electrodes have been shown to deliver specific capacitances of up to  $200 \text{ F/g}$  with excellent cycle stability.
- **Pseudocapacitive Materials:** Beyond carbon materials, nanostructured pseudocapacitive materials play a crucial role in boosting energy density by providing redox-active sites for faradaic reactions [28],[29]. Transition metal oxides such as manganese dioxide ( $\text{MnO}_2$ ), ruthenium dioxide ( $\text{RuO}_2$ ), and nickel cobaltite ( $\text{NiCo}_2\text{O}_4$ ) are widely studied due to their high theoretical capacitance values. For example,  $\text{MnO}_2$  has a theoretical specific capacitance of approximately  $1370 \text{ F/g}$ . However, its intrinsic low



electrical conductivity poses a challenge. This limitation is often addressed by integrating  $\text{MnO}_2$  with conductive substrates like CNTs or graphene. A composite of  $\text{MnO}_2$  nanoparticles anchored on graphene sheets creates a synergistic effect:  $\text{MnO}_2$  provides redox activity while graphene ensures electron mobility. Such a hybrid design allows a high specific capacitance ( $>300 \text{ F/g}$ ) with improved cycle life and rate capability.  $\text{RuO}_2$ , another high-performance pseudocapacitive material, has gained attention for its high conductivity and fast redox kinetics. Although its cost and toxicity restrict its widespread application,  $\text{RuO}_2$ -based nanostructures, especially in hydrated or amorphous form, offer excellent electrochemical characteristics. In one study, mesoporous  $\text{RuO}_2$  thin films deposited on carbon paper electrodes demonstrated specific capacitances above  $700 \text{ F/g}$  and remarkable power density. This highlights the potential of nanostructured metal oxides in pushing the energy density boundaries of supercapacitors. Nickel cobaltite ( $\text{NiCo}_2\text{O}_4$ ) is a bimetallic oxide known for its rich redox activity, high theoretical capacity, and stability. Its unique spinel structure enables multiple redox reactions involving  $\text{Ni}^{2+}/\text{Ni}^{3+}$  and  $\text{Co}^{2+}/\text{Co}^{3+}$  couples. Synthesising  $\text{NiCo}_2\text{O}_4$  in nanowire or nanosheet morphology provides a high surface area and reduces ion diffusion length. When grown directly on conductive substrates like nickel foam, these nanostructures exhibit enhanced electrochemical accessibility and superior performance. For instance,  $\text{NiCo}_2\text{O}_4$  nanowire arrays have shown specific capacitances over  $1100 \text{ F/g}$  and outstanding cycling stability, positioning them as excellent candidates for high-energy supercapacitor applications.



- **MXenes**, a newer class of two-dimensional transition metal carbides and nitrides, have attracted substantial interest in recent years [30],[31]. These materials possess a metallic conductivity and tunable surface functionalities, making them suitable for high-performance supercapacitors. Their layered structure allows intercalation of electrolyte ions, while surface terminations (-OH, -F, -O) contribute to pseudocapacitive behaviour. For example,  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene exhibits a high volumetric capacitance ( $\sim 1500 \text{ F/cm}^3$ ) and excellent rate performance. When assembled into flexible or solid-state devices, MXene-based electrodes demonstrate high energy density and mechanical robustness, enabling their use in wearable and flexible electronics.
- **Conducting Polymers**: Conducting polymers such as polyaniline (PANI), polypyrrole (PPy), and polythiophene represent another class of pseudocapacitive materials [32]. These materials exhibit fast electron transfer rates and high capacitance due to their doping/dedoping behaviour during redox reactions. Nevertheless, their mechanical degradation during cycling remains a concern. To address this, nanostructured conducting polymers are synthesised as nanofibers, nanotubes, or composites with carbon materials to enhance their structural stability and conductivity. For example, PANI coated on CNTs or graphene forms a conductive network with improved mechanical integrity, enabling high specific capacitance and prolonged cycle life. A well-designed PANI/rGO composite electrode can deliver capacitances in the range of 600–800 F/g with over 90% capacitance retention after thousands of cycles.
- **Hybrid Supercapacitor**: Hybrid supercapacitor systems combine the advantages of EDLC and pseudocapacitance by integrating carbon-based materials with metal oxides or conducting polymers [33]. These hybrid designs leverage



the high conductivity and stability of carbon nanomaterials and the high redox activity of metal oxides or polymers. One exemplary configuration is a composite of graphene and  $\text{MnO}_2$ , where the carbon matrix provides a conductive backbone and structural support while the metal oxide contributes to enhanced capacitance through redox processes [34]. Such hybrid electrodes often exhibit improved overall electrochemical performance compared to their individual components. Another significant advancement is the development of asymmetric supercapacitors, where different electrode materials are used for the positive and negative electrodes to expand the voltage window and thus increase energy density. For example, a typical configuration might use  $\text{NiCo}_2\text{O}_4$  as the positive electrode and activated carbon as the negative electrode. This arrangement not only enhances the voltage range (up to 1.6–2.0 V) but also improves specific energy, bridging the gap between supercapacitors and batteries [35]. These systems are particularly useful in applications requiring both high energy and high-power delivery, such as regenerative braking systems in electric vehicles. In addition to material composition, nanostructuring techniques such as electrospinning, hydrothermal synthesis, atomic layer deposition, and chemical vapour deposition (CVD) play a pivotal role in fabricating high-performance supercapacitor electrodes. These methods allow precise control over particle size, morphology, porosity, and surface area, all of which significantly influence ion transport and charge storage behaviour. For instance, nanostructured hierarchical architectures such as core-shell structures or porous nanoflowers maximise the active surface area while maintaining efficient pathways for electron and ion transport. These architectures also help



accommodate volume changes during cycling, ensuring stable operation. Electrolytes also play a crucial role in determining the energy density of supercapacitors. Aqueous electrolytes like KOH or H<sub>2</sub>SO<sub>4</sub> offer high ionic conductivity but are limited by a narrow electrochemical window (~1.0 V). In contrast, organic or ionic liquid electrolytes enable a broader voltage range (2.5–3.5 V), thereby significantly enhancing energy density. Nanomaterials, due to their tunable surface chemistry, can be engineered to be compatible with these electrolytes, leading to improved electrochemical performance. For instance, surface-functionalized carbon nanomaterials can enhance wettability and compatibility with organic solvents, facilitating high-voltage operation.

Emerging trends also explore the development of solid-state and flexible supercapacitors, particularly for wearable and implantable electronics. In such applications, flexibility, safety, and mechanical robustness become key requirements. Nanomaterials are inherently suitable for such systems due to their mechanical properties and ability to form conformal coatings. For example, flexible electrodes composed of graphene foam decorated with MnO<sub>2</sub> nanosheets exhibit excellent bendability and high capacitance retention under mechanical deformation. Similarly, MXene-based inks can be printed onto flexible substrates, enabling the fabrication of lightweight, stretchable energy storage devices.

### **4.3. Nanomaterials in Energy Harvesting**

The continuous advancement in microelectronics, wearable technologies, and wireless sensor networks has intensified the demand for reliable, sustainable, and miniaturised energy sources. Conventional batteries, while widely used, pose challenges in terms of size, lifespan, environmental impact, and recharging



requirements. This has led to significant interest in energy harvesting technologies, which aim to capture and convert ambient energy from the environment into usable electrical energy. Among the enablers of efficient energy harvesting systems, nanomaterials stand out due to their unique electrical, mechanical, optical, and thermal properties. These materials, owing to their high surface-to-volume ratios and tunable physicochemical characteristics, significantly enhance the performance and efficiency of energy harvesters. This section explores how nanomaterials contribute to various energy harvesting mechanisms, including piezoelectric, triboelectric, thermoelectric, photovoltaic, electromagnetic, and hybrid systems, accompanied by specific examples and scientific insights.

#### 4.3.1. Piezoelectric Energy Harvesting with Nanomaterials

Piezoelectric energy harvesting relies on the ability of certain materials to generate an electrical voltage when subjected to mechanical stress [36]. Traditional piezoelectric materials such as lead zirconate titanate (PZT) offer high piezoelectric coefficients but lack flexibility and are environmentally hazardous. Nanomaterials, especially in one-dimensional forms like nanowires or nanorods, have provided innovative pathways to overcome these limitations.

- **Zinc oxide (ZnO) nanowires** have emerged as a seminal piezoelectric nanomaterial. Due to their high aspect ratio and ability to grow in vertically aligned arrays, ZnO nanowires generate substantial piezopotential under deformation. In a landmark study by Wang et al., ZnO nanowire arrays were grown on a flexible polymer substrate to construct a nanogenerator capable of powering nanoscale devices [37]. This setup demonstrated that even gentle human motion or ambient vibrations could be converted into electricity.



- **Polyvinylidene fluoride (PVDF)** and its copolymers, when embedded with piezoelectric nanoparticles like Barium Titanate ( $\text{BaTiO}_3$ ) or ZnO, form flexible nanocomposites with enhanced piezoelectric responses [38]. These composites are widely used in wearable applications, converting biomechanical energy from body movements into electrical signals.

Such nanogenerators are highly scalable and integrable into fabrics, shoe insoles, and biomedical implants, marking a shift toward self-powered wearable systems.

#### **4.3.2. Triboelectric Nanogenerators (TENGs) and Nanostructures**

Triboelectric nanogenerators harvest energy through contact electrification followed by electrostatic induction between two dissimilar materials. Nanomaterials enhance TENGs by increasing effective contact area, dielectric constants, and surface charge retention [39],[40].

Nanostructured polydimethylsiloxane (PDMS) surfaces embedded with carbon nanotubes (CNTs) or graphene oxide (GO) significantly enhance surface roughness, increasing the triboelectric effect. These surfaces create more friction and charge transfer during mechanical contact. Moreover, electrospinning or nanoparticle patterning on polymer surfaces introduces micro/nano textures that amplify the contact area and enhance charge separation. For example, a hybrid TENG developed using GO-coated PDMS and metallic nanodots generated enough power to drive low-energy sensors and LEDs from foot tapping and hand motion. Additionally, combining materials with distinct electron affinity, such as fluorinated ethylene propylene (FEP) and polyamide, further increases the triboelectric output.



These advances enable applications in motion tracking, environmental sensing, and powering wireless nodes, particularly where battery replacement is impractical.

#### **4.3.3. Thermoelectric Energy Harvesting Enhanced by Nanomaterials**

Thermoelectric energy harvesters convert temperature differences into electrical energy through the Seebeck effect, where a voltage is generated when a material experiences a heat gradient. The efficiency of thermoelectric materials is measured by the figure of merit (ZT), which depends on the Seebeck coefficient, electrical conductivity, and thermal conductivity. Achieving high ZT requires increasing electrical and Seebeck performance while reducing thermal losses [41],[42],[43]. Among available materials, bismuth telluride ( $\text{Bi}_2\text{Te}_3$ ) remains the most effective near room temperature. When synthesised as nanoplates or nanowires,  $\text{Bi}_2\text{Te}_3$  exhibits reduced thermal conductivity due to enhanced phonon scattering at grain boundaries, without significantly affecting electrical transport. Nanostructured  $\text{Bi}_2\text{Te}_3$  films have achieved ZT values exceeding 1.2 at 300 K, compared to  $\sim 0.9$  for bulk materials. Flexible thin films of  $\text{Bi}_2\text{Te}_3$  integrated into thermoelectric generators (TEGs) can maintain stable output during bending and produce open-circuit voltages around 80 mV under a  $50^\circ\text{C}$  temperature gradient. Similar improvements are observed in  $\text{Cu}_2\text{S}$  and  $\text{SnSe}$  nanostructures, where nanoscale control enhances Seebeck coefficients and power factors. Such advances demonstrate how nanoscale engineering enables efficient waste-heat recovery and wearable energy solutions, positioning thermoelectric nanomaterials as key enablers in self-powered and sustainable electronic systems.

Such devices are particularly promising for wearable electronics, where body heat can be harvested to power sensors, smart watches, and health monitors.



#### **4.3.4. Photovoltaic Energy Conversion with Nanomaterials**

Photovoltaic (PV) energy harvesting is based on the conversion of light into electricity. While traditional silicon solar cells dominate the market, they are limited by rigidity, cost, and complex fabrication. Nanomaterials provide alternatives by enabling flexible, lightweight, and potentially more efficient PV systems [44],[45].

Perovskite nanocrystals such as methylammonium lead halides ( $\text{MAPbI}_3$ ) offer tunable bandgaps, high absorption coefficients, and long carrier diffusion lengths. These nanomaterials have pushed power conversion efficiencies of perovskite solar cells beyond 25%. Nanostructured  $\text{TiO}_2$  and ZnO nanorods act as efficient electron transport layers that reduce recombination and improve charge separation in dye-sensitised and perovskite solar cells.

Quantum dots (QDs) like CdSe and PbS exhibit quantum confinement effects that enable absorption of a broader light spectrum. Graphene and reduced graphene oxide (rGO) are integrated as transparent conducting layers and electron transport materials to improve device stability and conductivity.

These innovations have led to the development of flexible and wearable solar panels, integrated into backpacks or clothing, providing sustainable power sources for mobile electronics and sensors.

#### **4.3.5. Electromagnetic and RF Energy Harvesting**

Harvesting ambient electromagnetic radiation, such as radiofrequency (RF) signals from Wi-Fi or cellular networks, is an emerging solution for low-power electronics. The basic components of an RF energy harvester include an antenna, rectifier circuit, and energy storage unit [46],[47].

Nanomaterials such as silver nanowires, graphene and metallic nanoparticles are used to fabricate transparent and flexible



antennas. These antennas maintain high conductivity while reducing material weight and cost. For instance, a graphene-based antenna integrated with a Schottky diode was able to harvest microwatts of power from a 2.4 GHz Wi-Fi signal. Additionally, ferromagnetic nanomaterials like cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) enhance the inductive components of RF circuits, improving energy capture and conversion. Emerging technologies such as spintronic devices, based on the electron spin in nanostructures, are being investigated for high-frequency energy harvesting.

This technology has applications in wireless sensor networks, passive RFID tags, and remote biomedical devices that require minimal power.

#### 4.3.6. Fabrication, Scalability and Environmental Considerations

Nanomaterials used in energy harvesting applications must be processed through fabrication techniques that support precise structural control, scalability, and economic feasibility. Modern fabrication techniques such as electrospinning, chemical vapour deposition (CVD), inkjet printing, and sol-gel processes have proven to be effective in producing nanostructured films, fibres, and composites with the desired morphology and functional performance. Each of these techniques offers distinct advantages in controlling the alignment, dispersion, and integration of nanomaterials for practical energy harvesting devices [48],[49],[50],[51].

- **Electrospinning** is a versatile and scalable technique for fabricating nanofibers, which can be employed to construct piezoelectric or triboelectric components. A common example involves the use of polyvinylidene fluoride (PVDF), a well-known piezoelectric polymer. When embedded with ZnO nanoparticles, the electrospun PVDF fibres enhance the piezoelectric response significantly due



to the synergistic interaction between the polymer matrix and inorganic filler. These hybrid fibres are lightweight, flexible, and can be integrated into wearable textiles, enabling the conversion of biomechanical energy into electrical signals for health monitoring or human-machine interfaces.

- ***Chemical vapor deposition (CVD)***, another widely used method, enables the growth of high-purity and uniform nanostructures such as CNTs, graphene sheets, and ZnO nanowires on various substrates. CVD-grown ZnO nanowires, for instance, can be aligned perpendicularly on flexible substrates to construct high-performance nanogenerators that are responsive to mechanical deformation. CVD techniques are especially critical in applications requiring precise control over nanomaterial geometry, crystallinity, and alignment, which directly influence the energy harvesting efficiency.
- ***Inkjet printing*** has emerged as a cost-effective and scalable fabrication technique for producing flexible energy devices. Functional inks made from nanocrystalline thermoelectric materials like Bi<sub>2</sub>Te<sub>3</sub> or 2D MXenes can be precisely deposited onto substrates to form patterned films. These printed thermoelectric layers can be incorporated into wearable power sources using roll-to-roll manufacturing, which is advantageous for large-scale production of flexible electronics. Inkjet printing also allows multi-material integration, enabling the simultaneous patterning of electrodes, active layers, and encapsulation on a single substrate.
- ***Sol-gel methods*** offer another low-cost and solution-processable route for fabricating metal oxide nanomaterials. By controlling the sol-gel chemistry, nanostructured ZnO, TiO<sub>2</sub>, or VO<sub>2</sub> films can be deposited onto flexible or rigid



substrates. These materials are key components in piezoelectric, photovoltaic, or thermochromic energy harvesters. Sol-gel-derived films can also be doped or hybridised with carbon-based materials to improve their functional performance.

In addition to performance and scalability, environmental considerations are becoming increasingly important in the design and fabrication of nanomaterial-based energy harvesting systems. The long-term goal of sustainable nanotechnology mandates the use of non-toxic, renewable, and biodegradable materials wherever possible. Researchers are actively exploring biocompatible alternatives to synthetic polymers and inorganic fillers. For example, cellulose nanocrystals derived from plant biomass exhibit impressive mechanical strength and are being developed as green fillers in piezoelectric or triboelectric nanogenerators. Other promising eco-friendly materials include silk fibroin and chitosan, both derived from natural sources. These biopolymers can form flexible, biodegradable films that serve as functional layers in wearable energy harvesters. Silk fibroin, when combined with carbon-based nanomaterials like graphene or CNTs, can yield conductive and durable films for sensors and energy storage components. Chitosan, with its inherent film-forming capability and ion-conductivity, is being utilised as a matrix in flexible supercapacitors and energy harvesting composites.

Environmental sustainability also involves minimising the carbon footprint and toxic by-products of synthesis routes. Green synthesis methods use plant extracts, bacteria, or water-based chemistry to produce nanomaterials under ambient conditions. These approaches avoid harsh chemicals and high-temperature processes, making them more suitable for large-scale and environmentally friendly production. For example, green synthesis of ZnO nanoparticles using aloe vera or tea extracts can produce bio-compatible nanostructures for piezoelectric devices without the



need for chemical surfactants or stabilisers. Furthermore, the integration of self-healing capabilities in nanocomposites extends the operational life and reliability of energy harvesting systems. Self-healing materials can autonomously repair micro-cracks or delamination caused by mechanical stress or environmental exposure, reducing the need for frequent replacement. Incorporating reversible covalent bonds, hydrogen bonding, or microencapsulated healing agents within the polymer matrix has shown promise in enhancing the durability of flexible nanogenerators.

In brief, the fabrication of nanomaterials for energy harvesting must balance performance, scalability, and environmental responsibility. Techniques like electrospinning, CVD, inkjet printing, and sol-gel processing enable precise and scalable manufacturing of nanostructured components. At the same time, a shift towards biodegradable materials, green synthesis methods, and self-healing nanocomposites is ensuring that these technologies evolve in harmony with ecological and sustainability goals. These efforts are crucial to realising the vision of future energy systems that are not only efficient and versatile but also safe and environmentally friendly.

#### **4.4. Nanomaterial-Based Solar Cells: Perovskite and Quantum Dot Solar Cells**

In the global shift toward sustainable and low-carbon energy systems, the innovation and diversification of photovoltaic (PV) technologies remain a high priority. Among the forefront of next-generation solar technologies are nanomaterial-based solar cells, which exploit the unique physicochemical properties of materials at the nanoscale to enhance light absorption, charge carrier mobility, and overall power conversion efficiency (PCE). In particular, perovskite solar cells (PSCs) and quantum dot solar cells (QDSCs) have garnered substantial attention due to their



extraordinary optoelectronic characteristics, scalability, and potential for low-cost fabrication. This section provides an in-depth exploration of the materials, operational mechanisms, current achievements, challenges, and future perspectives related to PSCs and QDSCs [52],[53].

#### 4.4.1. Perovskite Solar Cells (PSCs)

Perovskite materials refer to a class of compounds with a crystal structure analogous to the mineral  $\text{CaTiO}_3$ . The general formula of hybrid organic-inorganic perovskites used in photovoltaics is  $\text{ABX}_3$ , where ‘A’ typically represents an organic cation such as methylammonium ( $\text{MA}^+$ ), formamidinium ( $\text{FA}^+$ ), or cesium ( $\text{Cs}^+$ ); ‘B’ is a metal cation (commonly  $\text{Pb}^{2+}$  or  $\text{Sn}^{2+}$ ); and ‘X’ is a halide anion ( $\text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{I}^-$ ). This tunable composition allows for precise control over the material’s bandgap, optical absorption properties, and electronic structure, which are essential for efficient solar energy conversion. For example, methylammonium lead iodide ( $\text{CH}_3\text{NH}_3\text{PbI}_3$  or  $\text{MAPbI}_3$ ) exhibits a direct bandgap of  $\sim 1.55$  eV, suitable for single-junction solar cells. Additionally, these materials demonstrate high absorption coefficients (exceeding  $10^4 \text{ cm}^{-1}$ ), long charge carrier diffusion lengths ( $\sim 1 \text{ }\mu\text{m}$ ), and low exciton binding energies, enabling efficient charge separation and transport under solar illumination [54].

Perovskite solar cells are highly attractive for flexible, lightweight, and semi-transparent applications. For instance, flexible PSCs can be integrated into wearable devices, vehicle surfaces, and portable power generators. Japan has recently invested \$1.5 billion to develop and commercialise ultra-thin PSCs suitable for infrastructure integration, such as building facades and windows. Moreover, tandem configurations, where PSCs are stacked atop silicon or CIGS bottom cells, have demonstrated



synergetic effects and PCEs exceeding 30%, thus breaking the single-junction Shockley-Queisser limit.

Despite impressive efficiency gains, PSCs face significant challenges regarding operational stability, environmental safety, and scalability. A major concern is the inclusion of lead ( $\text{Pb}^{2+}$ ), which poses toxicity and environmental contamination risks if the devices degrade or are improperly disposed of. While tin ( $\text{Sn}^{2+}$ )-based perovskites (e.g.,  $\text{MASnI}_3$ ) have been proposed as alternatives, they suffer from rapid oxidation to  $\text{Sn}^{4+}$ , reducing stability and performance [55]. Additionally, perovskites are vulnerable to ambient moisture, oxygen, and ultraviolet light, causing degradation. Encapsulation strategies using polymeric barriers, atomic layer deposition (ALD), or hybrid encapsulants are under investigation to prolong device lifetimes under real-world conditions.

#### 4.4.2. Quantum Dot Solar Cells (QDSCs)

Quantum dots (QDs) are semiconductor nanocrystals with dimensions typically between 2–10 nm, exhibiting size-dependent optical and electronic properties due to quantum confinement. Unlike bulk semiconductors, QDs enable tunable bandgaps by simply adjusting particle size, composition, or surface ligands, allowing broad and controlled solar spectrum harvesting. Common QDs for photovoltaics include lead sulfide ( $\text{PbS}$ ), lead selenide ( $\text{PbSe}$ ), cadmium telluride ( $\text{CdTe}$ ), and indium phosphide ( $\text{InP}$ ). For instance,  $\text{PbS}$  QDs have been engineered to absorb near-infrared (NIR) light, complementing the visible absorption of traditional materials and extending the cell's spectral response beyond 1000 nm [56].

QDSCs operate via excitonic or carrier-transport mechanisms, depending on the quantum dot structure and interfaces. One notable advantage is multiple exciton generation



(MEG), where a single high-energy photon generates two or more electron-hole pairs, increasing theoretical efficiency beyond the Shockley–Queisser limit ( $\sim 33\%$ ). Although MEG has been demonstrated in PbSe QDs under high-photon energy conditions, its practical impact on full devices remains under optimisation. Efforts to enhance charge extraction and reduce recombination have led to the development of core-shell QDs (e.g., CdSe/ZnS) and passivation techniques using halide ligands or perovskite layers. For example, applying a triple-cation perovskite (Cs/MA/FA) passivation layer on PbS QDs improved both open-circuit voltage and stability, achieving PCEs over 12%. Currently, the highest certified efficiency for QDSCs exceeds 18%, showcasing their growing competitiveness with organic and perovskite solar cells.

A critical barrier to widespread adoption of QDSCs is the use of toxic elements such as cadmium (Cd) and lead (Pb). Regulatory constraints and environmental impact have prompted research into cadmium-free quantum dots such as InP/ZnS, CuInS<sub>2</sub>, and ZnSe-based systems. These QDs, while environmentally benign, typically offer lower PLQYs (photoluminescence quantum yields) and less efficient charge transport, necessitating ongoing development. Another persistent challenge is the chemical and photostability of QDs. Under illumination and air exposure, QDs can undergo photooxidation, altering their optical properties and reducing device lifetime. Surface ligand engineering, core-shell architectures, and encapsulation technologies (e.g., silica or polymer shells) are crucial to maintaining stability under operational conditions.

#### 4.5. Hybrid Energy Systems Integrating Nanomaterials

Hybrid energy systems that integrate nanomaterials represent a transformative direction in modern energy technology, combining multiple energy harvesting and/or storage mechanisms



into a unified framework. The primary motivation for these systems lies in their ability to overcome the limitations of individual technologies by leveraging the complementary strengths of each component. Nanomaterials play a central role in enhancing the performance of hybrid systems, owing to their unique properties such as high surface area-to-volume ratios, superior electrical conductivity, tunable bandgap characteristics, and remarkable mechanical stability [57].

One of the most widely studied configurations in this domain is the battery-supercapacitor hybrid system, which aims to merge the high energy density typically associated with batteries and the high-power density and fast charge–discharge capability of supercapacitors. In such systems, nanostructured materials with both faradaic (redox-based) and capacitive behaviours are employed to bridge the performance gap. A prime example includes  $\text{MnO}_2$ -decorated carbon nanotubes ( $\text{MnO}_2@\text{CNTs}$ ), where the manganese dioxide component contributes pseudocapacitance via redox reactions, while the carbon nanotube matrix provides a conductive network and enhances electrochemical stability. The synergistic effect results in significantly improved energy and power densities, as well as superior cycling life. Similarly, composite materials like graphene polyaniline integrate the conductive and high-surface-area features of graphene with the pseudocapacitive properties of polyaniline, making them ideal for fast-charging, flexible power sources in electronic devices and electric vehicles.

Another significant class of hybrid energy systems involves solar–thermoelectric hybrid configurations, wherein photovoltaic (PV) cells are combined with thermoelectric generators (TEGs) to enhance the overall energy conversion efficiency. Conventional solar cells convert only a portion of incident solar energy into electricity, while a substantial fraction is dissipated as heat. This waste heat can be effectively captured and converted into additional



electrical energy through thermoelectric mechanisms. In this context, nanomaterials such as bismuth telluride ( $\text{Bi}_2\text{Te}_3$ ) composites are employed to fabricate highly efficient TEGs. These materials benefit from nanoscale engineering that reduces thermal conductivity while enhancing the Seebeck coefficient, an essential factor in determining thermoelectric efficiency. For instance, a hybrid device consisting of a silicon-based solar cell coupled with a  $\text{Bi}_2\text{Te}_3$ -based nanostructured TEG can harvest both photonic and thermal energy, significantly improving total power output. These integrated platforms are particularly promising for applications in smart buildings, off-grid power systems, and wearable electronics, where space and efficiency are critical concerns.

A rapidly advancing area within hybrid energy systems is the development of self-powered nanogenerator-based systems, which utilise ambient energy sources such as mechanical movements, vibrations, or thermal fluctuations to autonomously power devices. These systems are vital for the next generation of IoT applications and wearable health monitoring devices. Three major types of nanogenerators are commonly integrated into self-powered systems: piezoelectric, triboelectric, and pyroelectric nanogenerators. PENGs rely on materials such as ZnO nanowires or polyvinylidene fluoride (PVDF) to generate electric charges under mechanical deformation. These are often used in flexible sensors that harvest energy from human motion. TENGs, which generate power through contact electrification and electrostatic induction, often use combinations of nanostructured polydimethylsiloxane (PDMS) with materials like *PTFE* to produce electricity from sliding or tapping motions. Pyroelectric nanogenerators, on the other hand, convert temporal temperature variations into electrical output using materials like  $\text{BaTiO}_3$  nanoparticles. These are particularly suitable for thermal sensing and energy harvesting from dynamic thermal environments.



A representative example of such a system is a wearable health-monitoring patch embedded with a ZnO-based piezoelectric nanogenerator. This device can continuously harvest biomechanical energy generated from movements such as walking, breathing, or even pulse rhythms, enabling self-sustained operation of physiological sensors without the need for external batteries. Furthermore, by integrating multiple types of nanogenerators within a single platform, hybrid self-powered systems can harvest energy from multiple ambient sources simultaneously, mechanical, thermal, and even acoustic, thus ensuring a consistent energy supply under varying environmental conditions.

#### 4.6. Summary of Chapter

The chapter presents a detailed exploration of how nanomaterials are revolutionising energy storage and harvesting technologies by enhancing performance, efficiency, and functionality across various systems. It begins with high-efficiency batteries, including lithium-ion, solid-state, and lithium-sulfur types, where nanostructures like graphene and silicon nanowires improve capacity, charge rates, and stability. It then examines the enhancement of supercapacitors using carbon-based materials, transition metal oxides, and conducting polymers to boost energy and power densities. The chapter further discusses nanomaterials in thermoelectric energy harvesting, such as  $\text{Bi}_2\text{Te}_3$  and  $\text{Cu}_2\text{S}$  composites for converting waste heat into usable electricity, and in photovoltaic systems, particularly perovskite and quantum dot solar cells, which offer high efficiencies, bandgap tunability, and flexible architectures. Finally, it addresses hybrid energy systems that integrate nanomaterials to combine multiple energy sources, such as battery-supercapacitor hybrids, solar, thermoelectric platforms and self-powered systems using piezoelectric and triboelectric nanogenerators. Overall, the chapter highlights the pivotal role of



nanomaterials in enabling next-generation, compact, and sustainable energy technologies for applications in wearable electronics, smart devices, and renewable energy infrastructure.

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