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Progress of Hybrid Nanocomposite Materials for Thermoelectric Applications

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In the present scenario, the energy crisis and environmental burden have become two major problems due to the mismanagement of thermal power. The tremendous amount of waste heat from various energy sectors can be utilized by thermoelectric generators as a green energy resource. Thermoelectric generators (TEGs) generally exhibits enormous potential for converting waste heat to electricity without involving any mechanical vibrations and noises. The expensive manufacturing techniques, low reliability, and availability of conventional thermoelectric materials have immensely attracted researcher’s interest in scavenging advanced new thermoelectric materials (TEMs). Recently, the promising thermoelectric properties of organic and inorganic nanomaterial-based hybrid nanocomposites have gained popularity among researchers. The engraving of conducting organic and inorganic thermoelectric nanoparticles onto graphene/CNTs matrices combines the advantage of both inorganic and organic materials. The present review comprehensively emphasizes on new hybrid nanocomposite-based TEMs used specifically for wearable TEGs. To encounter the performance requirement of these TEGs, we provided material synthesis methods, fabrication techniques and possible mechanisms in detail. For comparison purpose, few traditional TEMs have been also reported with the addition of current performance requirement of these TEGs, we provided material synthesis methods, fabrication techniques and possible mechanisms in detail. For comparison purpose, few traditional TEMs have been also reported with the addition of current performance requirement of these TEGs, we provided material synthesis methods, fabrication techniques and possible mechanisms in detail. For comparison purpose, few traditional TEMs have been also reported with the addition of current performance requirement of these TEGs, we provided material synthesis methods, fabrication techniques and possible mechanisms in detail. 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In the last two decades, academic researchers have paid great attention to exploring the high-performance thermoelectric materials which are rare, expensive, brittle, and toxic in nature. Therefore, the achieved efficiencies of these materials are still lagging behind maximum possible Carnot efficiency. Besides, the thermoelectric generator requires dozens or even hundreds of thermoelectric modules assembly to achieve higher performance. Therefore, a large gap exists between the efficacy of TE materials and their modules for advanced applications. Hence, to make efficient use of TE materials in practical applications for energy conversion, we may have to consider a) stability of TE materials under large temperature gradient, b) change in mechanical properties under thermal cycling, and c) large interfacial contact resistances such as thermal and electrical.

Recently, due to technological challenges, researchers started developing advanced materials with enhanced thermoelectric properties, e.g., binary hybrid nanocomposites of organic-conducting polymer and ternary hybrid nanocomposites comprising of organic-inorganic nanoparticles-conducting polymer to augment the thermoelectric performance. In general, organic materials such as graphene (GR), carbon nanotubes (CNT), multi-walled carbon nanotubes (MWCNTs), and reduced graphene oxide (RGO) possess higher thermal conductivities and poor thermoelectric conversion efficiency in comparison to their inorganic counterpart. However, carbon-based organic materials are abundant, non-toxic and shows...
superior mechanical properties such as low mass density (~1 g/cm³), which is almost seven times lesser than that of bulk inorganic Bi₂Te₃ (7.86 g/cm³). Therefore, single-phase thermoelectric material difficulties can be overcome by blending organic-inorganic nano-material to attain superior tensile strength and controllable Seebeck coefficient in nanocomposite materials. In addition, conducting polymers such as Poly(aniline) (PANI), Poly(phenylene) (PP), Polythiophene (PT), Polyacetylene (PA), Poly(3,4-ethylenedioxythiophene) (PEDOT), Polystyrene sulfonate (PSS), and Poly(3-hexylthiophene) (P3HT) acquire modest electrical conductivity and lower thermal conductivity. The maximum reported TE properties of conducting polymer PEDOT:PSS near room temperature is power factor of 469 μW/mK² with a ZT value of 0.42. In this regard, impregnating conducting polymers into carbon-based materials can increase the Seebeck coefficient and overall power factor by lowering the thermal conductivity of carbon material. However, embedding nanoparticles of inorganic materials alone onto a conducting polymer matrix may adversely affect the overall electrical conductivity of the composite due to poor interconnectivity between the particles as compared to their inorganic counterpart. Furthermore, the sensitive nature of charge transport properties of conducting polymer to oxygen and inorganic nanostructure to di-oxygen (formation of an oxide layer) have shown to potentially damage the electrical conductivity of the conducting polymer, which limits the use of this material for TE application. Additionally, solution processability of conducting polymer at low temperature has a great advantage in large-scale production of hybrid nanocomposites. Therefore, fascinating printing methods such as aerosol jet printing, screen printing, drop-casting, inkjet printing, spin coating, slot-die coating, spray coating, and dispenser printing are possible to fabricate fully flexible TE devices. For example, Polyacetylene exhibits highest thermoelectric properties with the highest power factor of 10⁴ W/mK² due to its excellent electrical conductivity as compared to other conducting polymers, but ageing and environmental instabilities excluded polyacetylene from the TE list. Contrary to Polyacetylene, other conducting polymers such as PEDOT:PSS and PANI are also the prospective candidates for TE applications. PANI exhibit large electrical conductivity of 10⁴ S/m. These are used widely because of easy processing and environmental stability. However, the reduced electrical conductivity and lower power factor of the order of 10³ to 10⁴ W/mK² limited the use of conducting polymers as single-phase material in TE application. Furthermore, hybrid nanocomposites furnish lightweight, flexible, low cost, easily processable and scalable TE materials. Therefore, the attractive features of organic-inorganic conducting polymer composites such as superior mechanical strength, good thermoelectric properties and solution processability are favorable for highly efficient wearable thermoelectric generators.

Generally, there are three types of thermoelectric generators (TEGs) 1) bulk TEGs are useful for high power application such as in automobiles, power plants, aerospace, and various factories, and 2) thin-film TEGs that may be handy for low power applications such as electronic and biomedical devices. Thin-film TEGs requires a thickness of fewer than 50 micrometres, and they are smaller in size than bulk TEGs. 3) smart and intelligent textile TEGs which work based on their functionality in astronaut suits, biomedical devices, military and other intelligent devices where a portable power source is preferred. Despite various efforts made for inserting TE materials into textiles for harvesting energy from body heat, the power level of these arrangements is quite low for practical wearable applications. In addition, on various deformation resistances such as stretching, bending, twisting, folding and pressing the wearable TE devices should maintain steady performance. Although, approaches for bulk TEGs in comparison to thin-film, printed and textile based TEGs demonstrate significantly higher power conversion due to maintenance of appropriate temperature difference across the TE junction.

To obtain higher performance from wearable TE devices, it must be optimized by TE material selection, preparation method, device fabrication, choice of filler materials, geometry of legs, heat spreaders, type of metal electrodes and substrate, and matching of thermal load. The major requirement for an embedded TEG in wearable textiles includes greater ZT (>1), higher thermopower and lower thermal conductivity at room temperature. The low thermal conductivity of material will maintain higher temperature gradient across the hot and cold surfaces and higher Seebeck coefficient will provide sufficient voltage for the smooth operation of subsequent DC-DC boost converter.

Another challenge for thermoelectrics is low ZT of n-type materials which can be improved by increasing large number of valleys near the conduction band edge. These factors can be addressed by developing a new synthesis method. The generated power output per unit area does not depend on the number of thermoelectric legs and the cross-sectional area of legs. It only deals with the ratio of the insulated cross-sectional areas and the length of the thermoelectric leg. Therefore, finding a very low thermally conducting filler material can minimize the lateral heat losses through spaces and can improve power output. Fill factor is the ratio of space occupied...
by TE material to total surface area occupied by the module.\textsuperscript{56} The geometry of leg greatly influences the TEG performance. By increasing the leg length in an aspect ratio, changing the leg shape, and reducing fill factor can elevate $\Delta T$.\textsuperscript{57} Heat spreaders possessing high thermal conductivity can be placed on both sides of wearable TEGs to thrive overall power output. These are preferred instead of fin based heat sink because of their flexibility and light weight.\textsuperscript{41} Selecting a metal interconnect with high electrical conductivity and matching thermal expansion coefficient with TE leg, for wearable TEGs is an important parameter.\textsuperscript{48} The device performance can be improved by minimizing interfacial contact resistance between the legs and interconnects. Wearable TEGs require a flexible substrate which should be compatible with human body and possess low thermal resistance for improved performance e.g. Polydimethylsiloxane (PDMS) and Kapton.\textsuperscript{58} The another necessary factor for improving device performance is TEG thermal resistances, which must be equal and comparable to the parasitic thermal resistances. The TEG thermal resistances can be enhanced by two ways, lowering the fill factor or reducing thermal conductivity of leg material.\textsuperscript{44}

Despite, the TE device compact size, easy operation, longer lifetime, and low maintenance cost\textsuperscript{3}, they are still lagging behind in competition with other conventional energy generation technologies. Since, in the current market thermoelectric device efficiency is limited to 5-6 %.\textsuperscript{59,60} Therefore, this type of energy transformative technologies requires four vital conditions for bringing them into practice i.e. (1) simple processes and scalable materials to match the energy usage in terms of economic and physical magnitude (2) the capability of economical maintenance during manufacturing and recycling, (3) compatibility and integrality with the existing manufacturing infrastructure, and (4) improved performance for a specific niche application. With the development and advancement in nanotechnology, such energy devices can become practically more viable. Thus, the above four conditions establish a strong foundation for future research in flexible and rigid nanostructured thermoelectric generators.\textsuperscript{61} Presently, the thermoelectric technology market is growing and demanding because these are capable of converting any waste heat and solar radiation to generate more power. To extract the maximum power from TEGs and boost their efficiency, relevant investigations in many subareas are being carried out by researchers to optimize the TE device.\textsuperscript{2,59}

This review covers comprehensively about the progress of hybrid nanocomposites towards variety of applications including flexible/wearable devices. The introduction section covers the general background of thermoelectrics, their working principle, advancement, and requirement of TE materials. To bridge the knowledge gap between advanced and conventional TE materials, few traditional TE materials are also discussed. The next section highlights the well-developed hybrid nanocomposites in detail by focusing on their manufacturing technique, materials used, device fabrication, device performance, and working mechanism. In addition, traditional to hybrid TE materials uses in primary industrial applications have been addressed briefly. The application section covers both rigid and flexible/wearable thermoelectric use in various sectors. The final section covers conclusion by providing various solutions to improve TE efficiency.

2. Conventional TE Materials

Recently, various conventional TE materials and their devices have been reported by researchers. Different materials were utilized during the fabrication of TEGs for significantly improving their performance. The different characteristics of these materials compose them for appropriate use in device manufacturing techniques. In this regard, this section describes various traditional thermoelectric materials and their selection criteria based on the properties and working temperature range for use in thermoelectric application.\textsuperscript{62}

2.1. BiTe Alloys

Bismuth Tellurides and its alloys are widely established and efficient materials in the field of thermoelectric generators since the 1950s. The p-type Bi$_2$Sb$_2$Te$_3$ and n-type Bi$_x$Te$_{1-x}$Sb$_2$Se$_y$ is already being used in commercial TE cooling at RT and power generation modules at a temperature range not exceeding 500 K.\textsuperscript{63} Group- IV telluride’s generally works in the range of 600-800 K.\textsuperscript{64} In 1952 Ioffe reported an interesting behaviour of semiconductors according to their position in the periodic table. He discovered that the elements having large atomic weight shows lower thermal conductivity.\textsuperscript{65} Using this fact, Bi$_2$Te$_3$ and its alloys were selected as potential thermoelectric materials, because of their heavyweight, narrow bandgap, and large charge mobility, which imparts high phonon scattering due to smaller phonon group velocity and lower thermal conductivity compared to other heavyweight semiconductors.\textsuperscript{66} However, baseline alloys of bulk material show the highest ZT value of 1, which is inefficient. Therefore, to improve the ZT value, various nanocomposites of these alloys have been reported. Moreover, embedding of nanoparticles in the bulk matrix to prepare nanocomposites which are known as ‘nano-inclusion’ can bring down the lattice thermal conductivity of the nanocomposite without damaging the thermoelectric performance of materials.\textsuperscript{67} Based on this phenomenon, Fan et al.\textsuperscript{67} synthesized nanocomposites of p-type Bi$_{0.5}$Sb$_{0.5}$Te$_3$ in which 40 % of nanostructured particles were less than 200 nm in size and 60 % were in micron-size using spark plasma-sintering method to obtain a ZT value 1.8 at 43°C. Other p-type materials showed a ZT of 1.56 for Bi$_{0.5}$Sb$_{0.5}$Te$_3$ at 27 °C, 1.50 for Bi$_{0.5}$Sb$_{0.5}$Te$_3$ at 117 °C and 1.50 for (0.3 vol.% Al$_2$O$_3$) / Bi$_{0.5}$Sb$_{0.5}$Te$_3$ at 50 °C, respectively.\textsuperscript{68-70} Yan et al.\textsuperscript{71} reported n-type Bi$_2$Te$_3$Se$_{0.3}$ nanocomposite (NC) using ball milling and hot pressing to obtain high ZT value 1.04 at 125 °C. The obtained mean particle size of nanocomposite was 1-2 μm. The nanocomposites synthesized by spark plasma-sintering (SPS) method were better than high-energy ball milling (HEBM), because SPS shows coherent grain boundaries,
whereas HEBM method shows random grain boundaries.\(^5\) Cao et al.\(^7\) employed a hydrothermal method to prepare p-type (BiSb)\(_2\)Te\(_3\), where ZT of 1.47 at 167 °C was obtained. Some researchers had reported flexible wearable TEGs using BiTe alloys nanocomposites ink or paste using different methods and substrates. Cao et al.\(^7\) fabricated a screen-printed flexible thick film thermoelectric generator on a polycrystalline substrate from Bismuth and Antimony Tellurium with lowered material resistivity. The fabricated prototype resulted in an output voltage and power of 36.4 mV and 40.3 nW at \(\Delta T\) of 20 °C. Francioso et al.\(^5\) reported a wearable micro TEG generating an output voltage and power of 430 mV and 32 nW, respectively, using 100 thin-film pairs of p-type Antimony Tellurides and n-type Bismuth Tellurides at a \(\Delta T\) of 40 °C. Kim et al.\(^7\) reported a wearable type TEG on a polymer-based fabric by a dispenser printing method. The TE device consists of 12 pairs of Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3\) and Bi\(_2\)Se\(_0.3\)Te\(_2\) as over an area of 6×25 mm\(^2\), connected by a conductive thread, produced 224 nW power at a \(\Delta T\) of 15 K. Madan et al.\(^7\) reported n-type Bismuth Tellurides powders by mixing Bi and Te in a molar ratio of 36:64 and 2 wt % Selenium as a filler by mechanical blending. Epoxy resins were added to the material in 20:80 ratios as a binder. The obtained ZT was 0.17 at 300 K. A TEG (5 mm×400 μm×120 μm) was fabricated containing 20 single legs of n-type material on a polycrystalline substrate using evaporated gold contact as electrode, and generated an output power, voltage, and current of 1.6 μW, 40 mV and 40 μA at a \(\Delta T\) of 20 °C, respectively. The insulating effect of epoxy resins resulted in poor thermal conductivity and electrical conductivity that affected the overall ZT value. Nishino et al.\(^7\) fabricated two types of flexible TEGs using a 54 thermocouple (TCs)/cm\(^2\) of Bi\(_2\)Te\(_3\) based and Nickel alloy based in a 25 cm\(^2\) polycrystalline substrate. The Bi\(_2\)Te\(_3\) based TEG consists of Bi\(_{10}\)Sb\(_0.7\)Te\(_3\) as p-type and Bi\(_2\)Te\(_3\) as n-type material. Whereas, Nickel-based alloy consists of Ni\(_{0.6}\)Cr\(_{0.1}\) alloy as p-type and Ni\(_{0.6}\)Cu\(_{0.4}\) alloy as n-type material. The produced power output by Bi\(_2\)Te\(_3\) based and Nickel alloy based TEG was 100 μW and 75 μW at a \(\Delta T\) of 10 K, respectively. Shin et al.\(^7\) reported a flexible TEG on a fiberglass fabric using inks of p-type Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3\) and n-type Bi\(_2\)Te\(_2\)Se\(_0.3\). Organic solvents and methylcellulose as a binder were used in a very small concentration of 0.45–0.60 wt % for ink formation. The obtained ZT for p-type and n-type were 0.65 and 0.81 at RT, respectively. Suarez et al.\(^2\) reported a transformed rigid TEG to an EGaIn-based flexible TEG. Bulk thermoelectric legs of Bi\(_2\)Te\(_3\) and Sb\(_2\)Te\(_3\) were used as TE leg and connected by liquid gallium-indium on PDMS substrate. The obtained ZT value, voltage and power outputs were of 0.35, 11 mV and 29 μW (7.25 μW/cm\(^2\)) at a \(\Delta T\) of 1.6 K. Kim et al.\(^2\) reported a wearable flexible TEG by screen-printing technology to print thick films on a glass fabric using Bismuth and Antimony Tellurides paste. The power density exhibited by TEG was 3.8 mW/cm\(^2\) and 28 mW/gm at a temperature difference of 50 K. The device allows a minimum bending radius of 20 mm, and no major change was noticed in performance after 120 cycles of repeated bending. Since different ZT values were obtained from different synthesis method, one has to compensate with process simplicity, cost effectiveness and scalability of materials.\(^79\) The above reported data for thermoelectric properties of Bi/Te/Sb materials is presented in Table 1.

### 2.2 PbTe and PbSe Alloys

PbTe and its alloys are also heavy materials, similar to BiTe alloys.\(^60,81\) The p-type PbTe\(_{1-x}\)Se\(_x\) and n-type Pb\(_{1-x}\)Sn\(_x\)Te are types of PbTe alloys that usually show ZT of nearly 1 at 300 °C.\(^62,83\) whereas its bulk alloys show a ZT value nearly 0.7 at 467 °C.\(^60,81\) Most recently, the effort has been executed to obtain PbTe alloys ZT value in the range of 1.20 – 2.20 along with band engineering to optimize the performance of TEG by reducing thermal conductivity.\(^63,79,84\) The melt growth method was used by Hsu et al.\(^85\) to synthesize n-type Ag\(_{1-}\)Bi\(_{0.5}\)Sb\(_{20}\)Te\(_{80}\) for obtaining a higher ZT=2.2 at 527°C. The thermal conductivity of nanocomposite was reduced by placing the precipitates of Ag nanoparticles into the crystal matrix. In addition, similar results were obtained for n-type Pb\(_{0.95}\)Sn\(_{0.05}\)Te\(_{0.90}\)Sn\(_{0.10}\) and Pb\(_{0.90}\)Bi\(_{0.10}\)Sb\(_{0.10}\) as well as p-type Ag\(_{0.95}\)Bi\(_{0.05}\)Te\(_{0.90}\). Nao\(_{95}\)Pb\(_{0.5}\)Sb\(_{0.5}\)Te\(_{2}\) and 2% Sodium doped PbTe-PbS were doped. A ZT value of 2.2 at 642 °C was obtained for p-type Na doped PbTe-S\(_{2}\)Te in which endotaxial SrTe nanocrystals having a grain size of 2-10 nm embedded into Sodium loaded PbTe matrix. Further, Lead Selenides can be investigated as a substitute to Lead Tellurides, because tellurium is rarely found on earth’s crust (< 0.001 ppm), while selenium abundance is equal to 0.5 ppm. In addition, PbSe (n-type) doped with aluminium showed a ZT of 1.3 and PbSe (p-type) doped with sodium showed a ZT of 1.2 at 577 °C. However, ZT values of PbSe alloys were found to be less than that of PbTe alloys.\(^92,93\)

Later, Wang et al. reported that adding a small quantity of Sr into PbSe resulted in enhancement of ZT, where ultimate achieved ZT was 1.5 at 657 °C.\(^94\)

### 2.3 Skutterudites

The general molecular formula for Skutterudites is MX\(_3\) where M represents Co, Rh or Ir, and X represents P, As or Sb. Skutterudites as thermoelectric materials have the potential to sustain high temperature so that they can be used at high temp operating industries for power generation application. Complex crystal structures of these materials are responsible for the low value of thermal conductivity.\(^95\) Due to the existence of larger voids within the crystal lattice, the intrinsic sites can be doped with foreign ions that form the filled Skutterudites (T,\(_{Mx}\)X\(_{2}\)) and increases the scattering of low-frequency phonon. This phenomenon is known as “ rattling effect”\(^95\) which is responsible for improved thermoelectric properties. CoS\(_{2}\) based skutterudites elements exist in great abundance in the earth so that materials are becoming more interesting for researches. The versatility of these materials towards acceptance of various alkalis, alkaline earth metals, lanthanides, actinides and group IV elements as void filling towards acceptance of various alkalis, alkaline earth metals, lanthanides, actinides and group IV elements as void filling materials.

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Table 1.

| Material                  | p-Type ZT | n-Type ZT |
|---------------------------|-----------|-----------|
| Bi\(_2\)Te\(_3\)          | 2.2       | 1.5       |
| Ag\(_{1-}\)Bi\(_{0.5}\)Sb\(_{20}\)Te\(_{80}\) | 2.2       | 1.5       |
| Pb\(_{0.95}\)Sn\(_{0.05}\)Te\(_{0.90}\)Sn\(_{0.10}\) | 2.2       | 1.5       |
| Pb\(_{0.90}\)Bi\(_{0.10}\)Sb\(_{0.10}\) | 2.2       | 1.5       |

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Table 1: Thermoelectric properties of Bi/Sb/Te based thermoelectric materials.

| Author and Year | Methods | Materials (p-type/ n-type) | Substrate | Pairs used | σ (S/cm) | S (μV/K) | ZT | ΔT (K) | Voltage (V) | Power factor | Power/ O/t |
|-----------------|---------|---------------------------|-----------|------------|----------|----------|----|--------|-------------|-------------|-----------|
| Fan et al., 2010 | Melt spinning | Bi<sub>1.5</sub>Sb<sub>0.5</sub>Te<sub>2</sub> (p) | -         | -         | 76000 S/m | 225      | 1.80 at 43°C | 3.7 * 10<sup>8</sup> W/m K<sup>2</sup> | -        |
| Xie et al., 2009 | Melt spinning, Spark Plasma sintering (SPS) | Bi<sub>1.5</sub>Sb<sub>0.5</sub>Te<sub>2</sub> (p) | -         | -         | 69000 S/m | 228      | 1.56 at 27°C | 35 W/cm K<sup>2</sup> | -        |
| Xie et al., 2010 | Melt spinning, SPS | Bi<sub>1.5</sub>Sb<sub>0.5</sub>Te<sub>2</sub> (p) | -         | -         | 667 S/cm | 226      | 1.50 at 117°C | -        |
| Kim et al., 2013 | Mechanochemical, SPS | (0.3 vol.% Al<sub>2</sub>O<sub>3</sub>/ Bi<sub>2</sub>Sb<sub>0.5</sub>Te<sub>2</sub> (p) | -         | -         | 64103 S/m | 227      | 1.50 at 50°C | 34 W/cm K<sup>2</sup> | -        |
| Yan et al., 2010 | High energy ball-milling and hot pressing | Bi<sub>1</sub>Te<sub>2</sub>Se<sub>2</sub> (n) | -         | -         | 5.56 * 10<sup>-4</sup> S/m | 202 | 1.04 at 125°C | 23 * 10<sup>4</sup> W/m K<sup>2</sup> | -        |
| Z. Cao et al., 2014 | Screen printing/CIP | SbTe / BiTe | Kapton | 8 | - | 100 | 80000 S/m | ~170 | 1.47 at 167°C | - | |
| Y. Cao et al., 2008 | Hydrothermal/ hot pressing | Sb<sub>2</sub>Te<sub>3</sub> / Bi<sub>2</sub>Te<sub>3</sub> | -         | -         | ~80000 S/m | ~170 | 1.47 at 167°C | - | -    |
| Francisco et al., 2011 | RF magnetron co-sputtering technique | Sb<sub>2</sub>Te<sub>3</sub> / Bi<sub>2</sub>Te<sub>3</sub> | PDMS/ Kapton | 100 | - | 108 for each TC | - | 40 K | 430 mV | 32 mW |
| Kim et al., 2014 | Dispenser printing | Bi<sub>0.9</sub>Sb<sub>0.1</sub>Te / Bi<sub>2</sub>Sb<sub>0.5</sub>Te<sub>2</sub> (ink) | Polymer fabric | 12 | - | 0.72 nV/K | 15 | 14.2 mV | 224 mW |
| Madan et al., 2012 | Dispenser printing | MA n-type 2% Se Bi<sub>2</sub>Te<sub>3</sub>, epoxy resin | Polyimide | 20 | single leg | - | 200 μV/K | 0.17 | 20 K | 40 mV | 1.6 μW (25 μW/cm<sup>2</sup>) |
| Nishino et al., 2017 | Sputtering | Bi<sub>2</sub>Sb<sub>2</sub>Te<sub>2</sub> / Bi<sub>2</sub>Te<sub>3</sub> | Polyimide | 54 | TC's/cm<sup>2</sup> in 25 cm<sup>2</sup> | - | - | 129(n) | - | 10 K | 11 mV/K | 100 μW/K cm<sup>2</sup> (0.1 μW/cm<sup>2</sup>) |
| Shin et al., 2017 | Spark erosion/screen printing | Bi<sub>0.9</sub>Sb<sub>0.1</sub>Te<sub>2</sub>, methyl cellulose / Bi<sub>2</sub>Te<sub>3</sub>, methyl cellulose | Fiber glass fabric | - | - | 639(p), 763(n) | 209(p), 165(n) at 300 K | 0.65(p), 0.81(n) | - | - | - |
| Suarez et al., 2017 | Bulk TE legs cut from solid ingots | Bi<sub>0.9</sub>Sb<sub>0.1</sub>Te<sub>2</sub> / Bi<sub>2</sub>Te<sub>3</sub> (ink) | PDMS | 64 legs | 900 | 210 | 0.80 | 1.6 K | 11 mV | 29 μW/ K (7.25 μW/cm<sup>2</sup>) |
| Kim et al., 2014 | Screen printing | Sb<sub>2</sub>Te<sub>3</sub> / Bi<sub>2</sub>Te<sub>3</sub> | Glass fabric | 8 | - | 1500(p), 670(n) | 98(p), 141(n) | - | 50 K | 90 mV | 28 mW/ cm (3.8 W/cm<sup>2</sup>) |
the system. This was proved by Zhao et al.\textsuperscript{100} when they synthesized n-type $\text{Ba}_{0.14}\text{In}_{0.23}\text{Co}_{0.57}\text{Sb}_{1.14}$ showing ZT value of 1.34 at 577 °C. Shi et al.\textsuperscript{101} reported n-type $\text{Ba}_{0.08}\text{La}_{0.05}\text{Yb}_{0.04}\text{CoSb}_{12}$ with resulting ZT value of 1.70 at 577 °C using high-energy ball milling and nanostructured spark plasma-sintering method. Rogl et al.\textsuperscript{102} reported p-type $\text{Sr}_{0.13}\text{Ba}_{0.18}\text{DD}_{0.39}\text{Fe}_{0.25}\text{CoSb}_{12}$ with a ZT of 1.30 at 527 °C. P-type skutterudites ZT value cannot be improved beyond a limit in comparison to n-type skutterudites because more filling in p-type material tends to force them strongly into n-type materials.\textsuperscript{64}

2.4. Half-Heuslers

Half-Heuslers compounds show a composition of $X_2YZ$, where $X$ and $Y$ represent transition metals position and $Z$ represents the p-block element. Half-Heuslers (HH) compounds are other promising TE materials having a face-centred cubic crystal structure with excellent thermal stability at higher temperatures. Additionally, these are intermetallic compounds with higher thermopower and relatively higher thermal conductivity as compared to other TE materials.\textsuperscript{95,103} However, the development of bulk HH compounds for thermoelectric application has faced challenges due to their high thermal conductivity. Therefore, improvement in crystal structure was imparted by nano-dimensions showed better thermoelectric properties than bulk HH compounds because nanostructures reduce lattice thermal conductivity of compounds. This effect can be linked to the work of Joshi et al.\textsuperscript{104} where n-type $\text{Hf}_{0.25}\text{Zr}_{0.25}\text{Ti}_{0.5}\text{NiSn}_{0.95}\text{Sb}_{0.05}$ compound was synthesized using ball milling and hot pressing resulted in ZT of 1 at 500 °C. Further, Yan et al.\textsuperscript{105} prepared a p-type $\text{Hf}_{0.5}\text{Ti}_{0.1}\text{CoSb}_{0.8}\text{Sn}_{0.2}$ compound by applying Arc Melting method followed by high-energy ball milling and hot pressing that resulted in ZT of 1 at 800 °C.

2.5. SiGe Alloys

SiGe alloys are another promising candidate for high-temperature application. These alloys serve the highest ZT value at a temperature of greater than 900 °C and possess low-temperature deterioration up to 1000 °C. Bulk $\text{Si}_9\text{Ge}_{0.2}$ shows ZT value nearly equal to 1 and 0.6 for n-type and p-type, respectively.\textsuperscript{9} Wang et al.\textsuperscript{106} reported high-energy ball mill and hot pressing for nanostructured SiGe alloys to attain a peak ZT value up to 1.3 for n-type at 900 °C and 1 for p-type at 900-950 °C, whereas its bulk counterpart shows a ZT of 1 at 900 °C and 0.6 at 900-950 °C.\textsuperscript{107} Since SiGe are the most expensive thermoelectric materials they could be widely employed for power generation in space application where solar cells are not so common.\textsuperscript{108} Furthermore, to improve thermoelectric material performance nanostructured inclusion in intrinsic of material is necessary. The nanostructured defect reduces the thermal conductivity by imparting more phonon scattering at the junctions. The anharmonic large vibration of guest ions within the oversized atomic cages is known as rattling motion.\textsuperscript{109} Due to the rattling effect in some nanocomposites, nanoparticles might precipitate within crystal matrices leading to the scattering of acoustic phonons, which helps in reducing lattice thermal conductivity without altering the power factor value. The rattling effect has been also observed in thermoelectric materials that exhibit complex crystal structure. Besides, the power factor can enlarge by enforcing resonant electronic state in valance band. If nanocomposite materials development becomes easy and scalable, it could be used in industrial applications as an economic and efficient conversion technology.\textsuperscript{64,79}

3. Hybrid Nanocomposites based TE Materials

Recently, researches have been focused on improving the efficacy of TE materials by doping them with suitable p-type or n-type dopants, and synthesizing hybrid combination of organic and inorganic materials. Historically, after the discovery of $\text{Bi}_2\text{Te}_3$ alloys as a TE material in the 1960s, various efforts have been made by researchers to marginally revamp the TE efficiency of semimetals, which was a challenging task. As discussed above, the conventional thermoelectric semiconducting materials are expensive, difficult in processing, and suffering from low reliability, which hinders their widespread use in TEGs for commercial applications. The simple leg type structure of thermoelectric module without any moving part has a great advantage over conventional energy generation sources (e.g. compressors, turbiners and engines). TEGs generally attribute high energy densities based on per unit volume and weight, which is perfect for mobile distribution systems. Hybrid Nanocomposites and doped organic/inorganic materials are very fascinating as they possess lower thermal conductivity, higher Seebeck coefficient, and higher electrical conductivity, simple processing and manufacturing, and lightweight compared to conventional thermoelectric materials.\textsuperscript{110} Herein, we have compiled various hybrid nanocomposites reported for their application in wearable TEGs.

3.1. Doped CNTs/Graphene based TE Materials

CNTs and graphene are universally known for their unique physical and chemical properties. A roadmap has been aimed at graphene to make it a potential candidate for flexible TE devices. As compared to conventional inorganic Bismuth telluride, graphene presents good electrical properties at RT, but poor Seebeck coefficient due to high thermal conductivity. To overcome this issue, some researchers initiated doping the graphene by various dopants to reduce the thermal conductivity by imparting defects on CNTs/graphene webs. Particularly, most of the researches were mainly focused on p-type organic TE materials as compared to their n-type counterpart. In this regard, the n-type TE materials can be achieved by doping CNT webs with appropriate n-type dopants to increase the carrier concentration. Thus far, a charge transfer doping process\textsuperscript{111,112} was developed to prepare electron rich n-type CNT material with outstanding TE efficiency. The method was different than the conventional doping methods (substitution) as it does not impart any
defects in the sp² hybridization of the CNT. Most of the reported n-type CNT based TE materials were developed by direct doping method. For example: Yu et al. reported a combined doping method to prepare n-type CNT by polyethyleneimine (PEI) and sodium borohydride to achieve a Seebeck coefficient of 80 mV/K. Similarly, Nonoguchi et al. efficiently modulated the n-type single walled CNTs electron concentration by doping with phosphine containing aromatics. However, all these reports on direct doping method, could not achieve the optimal TE performance because the presence of ambient oxygen adversely effects the n-type doping by occupying n-dopants sites of the CNT. In contrast, An et al. reported a-nCNT webs doped with n-type and p-type molecular dopants in conjunction with annealing to prepare organic semiconductor. The n-type TE material was prepared (Figure 4) by treating annealed CNT (desorption of oxygen from p-CNT) webs with Benzyl viologen (BV), resulted in the highest PF of 3103 μW/mK². The obtained n-type TE value was superior than the non-annealed BV doped pristine CNT web (p-type) having a power factor of 1901 μW/mK². Therefore, their achieved thermoelectric properties for n-type CNT webs were as electrical conductivity of 2228 S/cm, thermopower of -116 μV/K, thermal conductivity of 5 W/mK and ZT of 0.19 at 300 K. Similarly, they prepared a p-type TE by doping the p-CNT web with F₄TCNQ with a concentration of 10 mM that helped in controlling the large electrical affinity. The maximum power factor obtained for p-type TE was 2252 μW/mK², with electrical conductivity of 3000 S/cm, Seebeck coefficient of 50 μV/K, the thermal conductivity of 6 W/mK and ZT of 0.11. The authors claimed that the synthesized materials showed enhanced power factor compared to previously reported organic TE materials, and results were identical to the conventional inorganic semiconducting (Bi₂Te₃) materials at room temperature. Additionally, to fabricate a TE module from p-type and n-type materials, they used a dispensing method. The free-standing CNT webs were adhered on Polyethylene terephthalate (PET) flexible substrate by Ag paste to make Y-shape (cross) electrical contacts between n and p legs. The dimensions of the n-type or p-type effective leg were as the width of 1.5 mm, length of 12 mm, and thickness of 20 μm for a single TE module. The 10 couples of p–n junctions were attached electrically in series and thermally in parallel and sandwiched in the middle of two ceramics plates to deliver homogeneous heat to the TEG. The highest power output of the thermoelectric module was 123 μW at ΔT = 20 K and the corresponding power density with a planar module structure was 1180 μW/cm². The mechanical flexibility of the TE web was checked by subjecting it to the 25 repeatable folding cycles at 180° and 25 at -180° (total 50 cycles), in which only a small deflection 1.65 % was observed in internal resistances. Kim et al. fabricated both p- and n-type flexible, lightweight fabric like material based on CNT. They prepared p-type CNT films by adding SDSB on CNT solution followed by vacuum filtration on the PTFE membrane. Similarly, n-type films were prepared by the same procedure except the dopants used were PEI and DETA in a specific ratio. According to the authors, another desired feature for improving CNTs practical TE efficiency is by creating many junctions in their films and designing proper junctions between CNTs and the surface of CNTs through controlled debundling process. Also, by doping CNT surfaces with chemical reagents, a small energy barrier can be created across the CNT-molecule-CNT junctions for optimizing electronic transport to enhance overall power factor. Here, the obtained thermoelectric properties were high enough to produce a voltage of 465 mV at ΔT= 49 K and output power of 1.8 μW. They successfully operated a glucose sensor with the help of this TEG as shown in Figure 5.

Further, to suppress the effect of contact resistances due to presence of metal connectors on CNT based TEGs. A purely carbon-based flexible and lightweight thermoelectric generator was framed by Choi et al. using carbon nanotube yarn (CNTY) without any additional metal connector. The CNTY was doped with n-type polyethyleneimine and p-type FeCl₃ alternately to obtain p–n TE. The highly conductive CNTY space in the doped zone was utilized as an electrical connection to reduce the contact resistance in the TE module. The CNT was synthesized by a floating catalyst method, where ferrocene was used as catalyst precursor, thiophene as a promoter, and methane as a carbon source at 1200 °C. The CNTY were fabricated by continuously withdrawing aerogels of yarns from the bottom of the reactor wounded on a roller and passing the roller through a water bath, containing hundreds of threads. The as-produced CNTY showed high electrical conductivity of...
nearly 3147 S/cm due to highly aligned structure of CNT yarn which resulted in increased longitudinal carrier mobility. Therefore, the flexible TEG containing 60 pairs of p-type and n-type doped CNTY emerged maximal power density of 10.85 μW/g and 697 μW/g, and output voltage density of 0.15 V/g and 1.2 V/g at ΔT of 5 K and 40 K, respectively. Additionally, a red LED powered by fabricated flexible TEG containing 240 PN pair at ΔT of 50 K as demonstrated in Figure 6. Although good TE performances were validated by doped CNT webs, still few researches were investigated on other carbon-based matrices such as single-walled and double-walled CNTs and graphene. Presently, the two major difficulties in fabricating thin film devices are traditional deposition technique and maintaining 3-D structural design for mechanical flexibility. To overcome these issues, Ito et al. presented a wearable flexible device based on Single-walled carbon nanotubes composite threads. In this study author introduced a new enhanced direct-injection pyrolytic (eDIP) method for synthesizing single-wall CNT, doped with p-type and n-type dopants. In the process they reported a fabric based thermoelectric generator (TEG) via assembling carbon nanotubes composite threads. The device even can be used for low-temperature energy harvesting. The CNT threads (p-type) were prepared by dispersing CNTs in the aqueous solution of Sodium dodecyl sulfate (SDS), then by adding 0.01 wt % polyethylene glycols (PEG) using a homogenizer. Further, methanol was added as a coagulant and wet thread pulled out of vessel for air drying. The n-type CNT thread was prepared by doping partially CNT/PEG thread with 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF6) consisting 10 wt % of dimethyl sulfoxide (DMSO) as a doping agent, and after immersion for 24 hour in doping agent, the thread was wiped off with a cotton ball. Here, the obtained Seebeck coefficient for p-n CNT thread was 101.5 μV/K. The generated output voltage and power were 2.3 mV at ΔT of 5 K and 1.6 mW/m² for fifty single threads, respectively. Even after 160 cycle of bending-stretching test on sample, with nearly zero inner radius of curvature, no change was observed in resistance.

On the other hand, to address lack of exceptional performance of n-type TE material, Cho et al. explored a highly ordered 3-D conjugated network of n-type organic TE nanocomposite by depositing alternate layers of Polyethyleneimine (PEI) stabilized double walled-nanotubes (DWNT) and polyvinylpyrrolidone (PVP) stabilized graphene by utilizing layer-by-layer (LbL) deposition method. They prepared DWNT and graphene solution by adding 0.03 wt % of DWNT and 0.2 wt % of graphene in deionized (DI) water comprising 1 wt % PEI and 0.1 wt % of PVP, respectively. Later, both solutions were homogenized by tip sonicator followed by bath sonication. The solutions were centrifuged, and supernatants were collected for preparing thin films of n-type nanocomposite. Through a robotic system, thin n-type TE films were prepared by alternatively dipping the PET substrate into Graphene-PVP and DWNT-PEI solutions followed by DI water rinse. The graphene and DWNT present in nanocomposite built an interconnected network between the upper and lower layer of the films. These bridges helped in transporting electron more efficiently, hence enhancing the Seebeck coefficient due to increased carrier mobility. In addition, randomly oriented graphene nanoplatelets which were aligned parallel to the substrate had obstructed penetration of oxygen into the film and accomplished the environmental stability of the film. Thus, the n-type film demonstrated electrical conductivity of ~ 300 S/cm, Seebeck coefficient -80 μV/K at 80 BL and power factor of 190 μW/mK² at room temperature. Figure 7 shows the process of LBL technique and formation of CNT thread with the functioning of wearable TEG by the heat of human fingertip. After scanning all the above-reported data of carbon-based TE materials, we concluded that the main reason behind obtaining better TE properties from CNT web was the quasi 1-D nanostructure of CNTs and suitable doping. The quasi 1-D nanostructure and doping affect the band gap between conduction and valence band in CNTs. The CNT yarns based TE devices showed excellent power output, higher flexibility, and less bending cyclic resistance because of high aligning of structured yarns, resulted in promoted longitudinal carrier mobility. Although the use of 2-D planar nanostructure of graphene is suitable for harsh environmental conditions, one has to compensate with TE performance. The data compilation of doped organic/inorganic dopants in carbon-based TE materials has been shown in Table 2.

3.2. Binary Nanocomposites based TE Materials

Apart from single organic-based TE, a new class of materials such as binary nanocomposites based TEGs has also been investigated by researchers. Mostly reported combinations of binary-based nanocomposites are of organic material (graphene/CNTs)/conducting polymer (PEDOT:PSS/PANI/PS) and conducting polymer/inorganic nanoparticle.
Table 2: Data compilation of doped organic/inorganic dopants Carbon based TE materials.

| Author and Year | Methods                        | Materials                                           | Substrate | Pairs used | $\Sigma$ | S (µV/K) | ZT | $\Delta T$ (K) | Voltage (V) | PF (µW/m K$^2$) | P O/t |
|-----------------|--------------------------------|-----------------------------------------------------|-----------|------------|----------|-----------|----|----------------|-------------|----------------|-------|
| An et al., 2017 | Dispenser printing             | $F_{x}$TCNQ doped p-CNT web/ BV doped p-CNT web     | PET       | 200        | 3000(p)  | 50(p),  28(n) | -116(n) | 0.11(p), 0.19(n) | 20 K        | 2252 (p), 3103 (n) | 123 µW |
| Kim S. et al., 2014 | Vacuum filtered               | CNTs doped with SDBS/ CNTs doped with PEI and DETA | PTFE membrane | 72        | 5200 S/m | -86      | -    | 32             | 150 mV     | 38              | 1.8 µW |
| Choi et al., 2017 | Yarn spinning method          | $FeCl_3$ doped CNTY/ Polyethylenimine doped CNTY  | PDMS      | 240        | 74769(p) | 57(p),  -56(n) | -      | 40 K       | 1.2 V/g    | 2387 (p), 2456(n) | 697 µW |
| Cho et al., 2016 | LBL deposition                | PEI stabilized DWNTs and PVP stabilized graphene   | PET       | -          | 300(n)   | -80      | -    | RT            | -           | -               | 190 |
| Ito et al., 2017 | eDIPS method                  | SDS and PEG doped CNT/[BMIM][PF$_6$] and DMSO doped CNT | -         | 50 single | -        | 101.5    | -    | 5 K           | 2.3 mV     | -               | 0.5 nW |

Graphene/CNT and inorganic materials based combinations were not investigated vastly, possibly because of the high electrical and thermal conductivity of both materials, which can result in reduced performance of the TEGs. Here, we emphasized mainly on organic/conducting polymer and conducting polymer/inorganic nanoparticles based TE nanocomposites prepared by novel methods.

3.2.1 Conducting Polymer/CNTs/Graphene based Binary TE Materials

Towards the advancement of nanocomposite formation, graphene and CNTs are the best candidates as a filler material in polymer matrices. However, the major obstacle in the progress of CNT/polymer composite is regulating the dispersion of CNTs within polymer matrix. Interestingly, dispersing carbon nanotubes (CNTs) into polyvinyl acetate (PVAc) latex can enhance the electrical conductivity by keeping Seebeck coefficient and thermal conductivity values relatively constant due to formation of electrically connected but thermally disconnected bridges between the CNT junctions. A small energy barriers for the transportation of electrons across the junctions can be significantly tuned by altering stabilizers. These stabilizers impart dispersion and exfoliation in CNTs due to Vander Waals force which form natural bundles between them. Theoretically, various strategies such as electronic states of CNTs, inter-particle distance, potential barriers, electrostatic charges of CNTs and matrices, have been established by researchers to improve the electron transport across the junctions. Here, the several stabilizers which are required for dispersing CNTs into polymer matrices are summarized in Table 2.
include surfactants, inorganic nanoparticles, polymers, and biomolecules. Most of the stabilizing agents act as electrical insulators to inhibit electrical transport across the CNTs junctions. For example: single walled carbon nanotubes (SWCNTs) dispersion and stabilization in water have been achieved by introducing an intrinsic conducting polymer PEDOT:PSS. Here, the conducting polymer stimulated the electrical conductivity by hampering settling and aggregation of SWCNTs. Further, electrically conductivity of conducting polymer PEDOT:PSS can be enhanced by doping it with DMSO solvent. Using the above facts, Grunlan et al. described a modification in CNTs junction by filling DMSO doped poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) on the surface of CNTs which resulted in enhanced TE properties. When PEDOT:PSS particles were embellished on the carbon nanotubes surface, electrical bridges were formed between CNTs that greatly reduced the thermal transport through carriers. Further, this procedure yielded high electrical conductivity (~4000 S/m) without altering the thermopower of thermoelectric material (TEM). Additionally, the influence of various parameters such as types of CNTs with varying concentration, stabilizers, and different drying temperatures were noted for thermoelectric properties. However, for a CNT concentration of 2-15 wt % with CNT to PEDOT: PSS ratios of 1:1-1:4, observed thermal conductivities were similar to typical polymeric materials (0.2-0.4 W/mK). Highest ZT value of 0.02, Seebeck coefficient of ~25 μV/K, the thermal conductivity of ~0.4 W/mK, and power factor of ~25 μW/mK² were accomplished with 35 wt % SWCNT and 35 wt % PEDOT: PSS in a copolymer latex composed nanocomposite matrix. Later, it was dried at RT subsequently at a temperature of 80°C. Similarly, Meng et al. produced Carbon nanotubes (CNTs) and polyaniline (PANI) based nanocomposites as TE materials. Since nanocomposites possess low dimensional network structure, they demonstrate better TE properties than their parental components. In this regard, the CNT/PANI nanocomposites were firstly synthesized by filtering a typical polymer composite (0.2-0.4 W/mK). The highest thermal conductivity of ~350 W/mK and electrical conductivity of ~2 × 10⁵ S/m at 300 K. The obtained values were as high as four times of CNT sheets and 10 times of PANI. Yao et al. prepared a nanocomposite of Single-Walled Carbon Nanotube (SWNT) and ordered polyaniline by in-situ polymerization of aniline on SWNT template. Since SWNT shows more superior electrical properties than Multi-walled Carbon Nanotubes (MWCNT) due to little structural defects. Therefore, thermoelectric module performance can be increased by increasing both the Seebeck coefficient and electrical conductivity, which is only possible by increasing carrier mobility within the material. However, in most of the conducting polymers, carrier transport was governed by the inter-chain and intra-chain hoping process. Arrangement and conformation of conducting polymers chains affect the carrier mobility. Therefore, it is necessary to develop an ordered chain arrangement which reduces the barriers for inter-chain and intra-chain hopping process and increases carrier mobility, and ultimately TE performance. Here, the author used a Template-directed synthesis method for preparing ordered 1D structures in which reactants are located within the templates. Results obtained by TEM, SEM, XRD, and Raman analysis shows that PANI within the composite is in more ordered form as compared to pure PANI, which arise by substantial π-π interaction between the PANI molecules and SWNT. The increased Seebeck coefficient at 41.4 wt % SWNT content was 40 μV/K, and electrical conductivity was 1.24×10⁴ S/m. The maximum power factor obtained at this composition was 2×10⁻⁵ W/mK², and ZT value reaches 0.004 at RT that was 2 times larger than the pure Polyaniline value.

Yu et al. reported another lightweight flexible Carbon Nanotube/PEDOT:PSS or Polyvinyl acetate based organic composite with high thermoelectric power factors. The group demonstrated that, without incorporating high concentrated binders such as polyvinyl acetate (PVAc) in a composite, CNT concentration could be increased up to 75 wt %. These hybrid composites were prepared by mixing SWNT onto PEDOT: PSS matrix and /or PVAc emulsion using a homogenizer. Herein, PEDOT: PSS acted as a stabilizer that stabilizes the dispersion of nanotubes in water. Different ratios of nanotubes to stabilizers in weight percentage were taken to demonstrate the effect of corresponding concentration on thermoelectric properties. The higher electrical conductivity and modest Seebeck coefficient recorded (in-plane direction) were 105 S/m and 41 μV/K respectively, at RT. Therefore, an optimal nanotube concentration of 60 wt % with the highest power factor obtained was 160 μW/mK², which is higher than the typical polymer composites. The highest thermal conductivity measured in out of the plane was 0.2-0.4 W/mK at RT. Additionally, a possible schematic of junction formation between CNT and PEDOT: PSS has been presented by authors as shown in Figure 8 (a) with a photograph of free-standing flexible film Figure 8 (b). In this regard, the method could be beneficial to manufacture lightweight, low cost, and less dangerous organic composite for efficient thermoelectric generator. Generally, the reduced thermal conductivity in the composites is a consequence of high surface area and strong Vander Waals attractive forces between the CNTs and polymer molecules due to formation of nanotubes aggregates. The high specific surface area and high thermal conductivity of
single walled CNTs enables more interfaces between crystalline polymers/amorphous nanoparticles to reduce thermal conductivity by increasing phonon scattering. Aghelinejad et al.\(^1\) reported a lightweight, flexible, low-cost TE polymer nanocomposite foams by using the multilayered network of graphene nanoplatelets (GnPs) and multi-walled carbon nanotubes (MWCNTs) in macroporous foam templates of polyvinylidene fluoride (PVDF). PVDF macroporous foam templates were synthesized by salt-leaching method followed by drying of disc-shaped molds in an oven. The Layer-by-Layer (LBL) processing method was adopted to deposit the layers of GnPs and MWCNTs on open cellular structures of foam templates that furnished a platform to mold segregated 3D networks of 1-D and 2-D carbon nanoparticles. Herein, the aqueous solution of GnPs was formulated by using sodium dodecyl sulfate (SDS) as a surfactant to strengthen stable dispersion of GnP in a solvent for a mass ratio equals to 1. Furthermore, various solutions of MWCNT-GnP mixture were formulated with 0.1 wt % to 1 wt % as filler content in the hybrid nanocomposite. This hybrid nanocomposite (Figure 8(c)) provides enhanced electrical conductivity of the system due to the synergetic effect of GnPs and MWCNTs 3-D network, and reduced thermal conductivity due to the highly porous structure of the polymer foam substrate. The calculated figure of merit ZT was 10\(^-3\) by using 1.5 vol % of GnP loading in macroporous PVDF foam substrate. The highest Seebeck coefficient obtained for PVDF-GnP nanocomposite was 37 µV/K. According to the author, this is the highest reported ZT value of nanocomposite using non-conducting polymer and MWCNT/GnP as nanofiller. In this context, Suemori et al.\(^2\) described a flexible and lightweight TEG composed of carbon nanotube (single-walled Carbon Nanotubes) and polyethylene composites on a substrate (polyethylene naphthalate film) by utilizing a printing method. Herein, the used composite material which contains nearly 35 vol % of voids, reduces the CNT-polystyrene composite density and resulted in the lightweight of TEG (weight/unit area: 15.1 mg/cm\(^2\)). This TEG only consists of p-type lightweight material because the n-type lightweight material shows a lower performance. Each thermoelectric leg of CNT-polystyrene composite (CNT 75 wt %) is sandwiched between top and bottom electrodes. A solution of composite was made by dispersing CNTs and dissolving polystyrene in 1,2-dichlorobenzene. Then, the polystyrene-CNT composite was deposited onto the substrate by a printing plate containing holes, which acted as similar to template. After drying of pattern, the template was removed, and gold electrode was deposited by vacuum deposition method on top of it. The cross electrical connection was provided from top of each individual leg to the bottom of next individual leg, and in this way connected serially. The TEG contains 1985 legs of p-type composite (Figure 9) and generated an output voltage, current, and power density of 254 V/m, 0.86 mA, and 55 mW/m\(^2\), respectively at ΔT of 70°C. The Seebeck coefficient (S) and electrical conductivity of the CNT-polystyrene composite were 57 µV/K and 2.1 S/cm, respectively.

Figure 8: (a) Schematic of a junction formation between CNT and PEDOT/PSS for increasing phonon scattering, (b) Image of a free standing flexible film prepared from the composite. Reprinted with permission from Ref. 134 (C. Yu, K. Choi, L. Yin, J.C. Grunlan, ACS Nano. 7 (2013) 9506–9506). Copyright (2013) ACS Publications. (c) A schematic of hybrid 3-D network for transferring electron and phonon by combining 1D and 2D conducting nanoparticles effects. Reprinted with permission from Ref. 144 (M. Aghelinejad, S.N. Leung, Materials (Basel). 11 (2018) 1–13), copyright Authors 2018, Open access MDPI.

Figure 9: (a) Schematic of fabrication steps, (b) Photograph of a CNT-polystyrene composite film (thickness: 75 µm) fabricated on a film substrate, (c) Photograph of the fabricated TEG, (d) Graph of generated power output, and (e) Open circuit voltage and short-circuit current with temperature difference. Reproduced from Ref. 144 (K. Suemori, S. Hoshino, T. Kamata, Appl. Phys. Lett. 103 (2013)) with the permission of AIP Publishing.
Therefore, the calculated PF was 0.15 μW/m²K. Since 40 % area of the TEG which includes space occupied by substrate and electrodes had not contributed to thermoelectric conversion of heat to power output, the overall efficiency of the device was consequently lower. By optimizing the ratio between the area of CNT-PS composite to the whole area of the TEG, the performance of such TEGs can be improved around 50 %.

Similarly, Hewitt et al. fabricated a flexible TEG containing 72 individual layers of CNT and PVDF. Here, CNTs and PVDF layers were used as conducting and insulating layers, respectively. The CNTs and PVDF individual films were placed alternatively and then the stack was pressed together to form a felt fabric at the polymer melting point. For a 72 layer of (PEDOT:PSS) thin films could improve its thermoelectric coefficient was 550 μV/K at ΔT of 50 K which is quite low, respectively. Additionally, the obtained Seebeck coefficient was 550 μV/K at ΔT of 95 K. Kim et al. reported that addition of 2 wt % graphene on conducting polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) thin films could improve its thermoelectric properties by 10 times. However, for achieving the same result, 30-40 wt % of CNT was required. Further, when graphene incorporated into conducting polymer matrix the interfacial area associated with the molecules increased by a factor of 2-10, as compared to CNT molecules for the equivalent weight percentage. The nanocomposite thin films prepared by combining graphene and 2 wt % PEDOT: PSS solution in isoproopyl alcohol/deionized water followed by sonication to form a homogeneous solution. The stronger π-π interaction between graphene and conducting polymer stimulate dispersion and increased carrier concentration by reducing the π-π conjugated defects of PEDOT: PSS backbone as represented by a mechanism shown in Figure 10. Thereafter, spin coating technique was used to fabricate thin film on Si/SiO₂ substrate, followed by heating of thin films in an oven for solvent removal. The obtained power factor, Seebeck coefficient, electrical conductivity, thermal conductivity, and ZT value of nanocomposite thin film were 11.09 μW/mK², 58.77 μV/K, 32.13 S/cm, 0.14 W/mK and 0.021, respectively. Therefore, a higher ZT value was an outcome of high electron mobility of graphene and porous structure of thin film which reduces the thermal conductivity.

Similarly, Luo et al. reported a CNT and block copolymer poly(ether-b- amidic12) (PEBA) blended TE films that were utilized for fabricating a flexible TEG. Firstly, PEBA was doped with LiClO₄ to prepare PEBA-Li⁺ solution. Then, separately n-type CNT solution was prepared by doping it with DETA followed by vacuum filtration and vacuum drying at 45 °C for 24 hours. Next, the 20 wt % p-type CNT and DETA doped n-type CNT powders were re-dispersed in formic acid and added to the PEBA-Li⁺ solution, then mixed by stirring at 45 °C for 24 hours. The mixed PEBA/CNT p-type and n-type bilayer heterogeneous films were cast on a glass substrate and later peeled off from the substrate after long-time drying to obtain heterogeneous structure. The obtained Seebeck coefficient and electrical conductivity for p and n-type TE films were 36.88 μV/K, -33.25 μV/K and 456 S/m, 492 S/m, respectively. Additionally, a flexible TEG was fabricated by connecting p-type and n-type TE films in series on a polyimide substrate. The TE device with 3 pairs of p-n showed an output voltage of 120 mV at a temp difference of 60 K. Thus, from all the above-reported data, we observed that the distinct bonding and different vibrational spectra between CNTs and PEDOT: PSS/PANI molecules yielded factorial enhancement in power factor as compared to...
their parental groups. Additionally, different polymeric molecules can be used as filler for increasing the power factor by obstructing the direct thermal transport of carriers.

### 3.2.2. Conducting Polymer/Inorganic Semiconductor based Binary TE Materials

The ability to print various nanocomposite based TEM on flexible substrate for wearable applications envisaged development of different printing methods. A fully in-situ aerosol jet printed organic/inorganic nanocomposite based flexible TEG were reported by Ou and group. In this work, they synthesized Bi$_2$Te$_3$/Sb$_2$Te$_3$ nanoflakes by solvothermal method. The low-temperature solution-based process conceded good size and shape control at the nanoscale, which could help in synergistically tuning the TE parameters. Bi$_2$Te$_3$/Sb$_2$Te$_3$ inorganic ink and PEDOT: PSS organic inks were separately prepared in pneumatic atomizer (PA) and ultrasonic atomizer (UA), respectively. Then, in-situ mixing was employed in an aerosol-jet printer and deposited on a malleable polyimide substrate as shown in Figure 11. Based on loading fraction of inorganic component in the mixture, various thermoelectric properties and morphology of the printed structure have been examined. The maximum power factor produced with a minimal loading fraction of 85 wt % Sb$_2$Te$_3$ nanoflakes was ~30 μW/mK$^2$. The best TE properties obtained at this composition was $S \sim 33.8 \mu$V/K, $\sigma \sim 247.3$ S/cm, with superior mechanical properties. Upon repeated flexing on a curvature up to 300/m, the printed nanocomposite TEG was consistently stable and healthy. The aerosol jet printing technique has several benefits over other printing methods. AJP is a scalable, large area deposition, commercially viable for electronic materials and custom formulations technique.

The Continuous demand for wearable mobile electronics in the market evoked the requirement of flexible TEG module. Thus, We et al. presented a screen-printed flexible thermoelectric power generator depends on the hybrid composite of inorganic/organic conducting polymer TE film. The inorganic material paste consists of various weight composition such as 75 % metal powder Bi, Sb, and Te, 0.2 % of binder, 2.4% of glass powder, and 22.4% of solvent. Both pastes were homogeneously blended in ball mill equipment for 24 hours. The pastes were screen printed through a 150-mesh screen onto a flexible polyimide film substrate. Afterwards, samples were dried for solvent removal, followed by a two-step annealing method. The first step includes removal of the organic binder in vacuum condition, and the second step conducted at a higher temperature under N$_2$ ambient conditions to get the best TE properties. After annealing, (PEDOT:PSS) coating has been done that penetrate through micropores of the screen printed Bismuth and Antimony Tellurides TE thick films, induce flexibility in the TE module without affecting its output performance. Ag paste was used to make electrical contacts. Also, the area ratio of p to n legs was optimized for maximizing the output power density of the TEG module. TE legs acquire different thermal and electrical properties which affect the figure of merit of the TE module. The relation of the figure of merit was given as: $ZT = \frac{L_p \rho_p}{L_n \rho_n}$, where $S_p$ and $S_n$ are Seebeck coefficient of p-type and n-type TE material, and $R$ and $K$ represent resistance and thermal conductance of TE module respectively. The electrical resistance (R) and thermal conductance (K) can be defined as:-

\[
R = \frac{L_p \rho_p}{A_p} + \frac{L_n \rho_n}{A_n}
\]

\[
K = \frac{\kappa_p}{A_p} + \frac{\kappa_n}{A_n}
\]

Figure 11: (a) Schematic of aerosol jet printing method for preparing nanocomposites of PEDOT:PSS and Bi$_2$Se$_3$Sb$_2$Te$_3$, Image of flexible bent to different degrees: (b) flat, (c) lower degree, and (d) higher degree, (e) Flexibility test based on ratio of flat to flexed resistance vs curvature and ratio of flat to flexed Seebeck coefficient vs loading of semiconducting materials. Reprinted with permission from Ref. 23 (C. Ou, A.L. Sangle, A. Datta, Q. Jing, T. Busolo, T. Chalklen, V. Narayan, S. Kar-Narayan, ACS Appl. Mater. Interfaces. 10 (2018) 19580–19587). Copyright (2018), ACS Publications.
Where, L, ρ, A, and k represents length, electrical resistivity, area of TE leg, and thermal conductivity, respectively. The maximum value of ZT can be obtained when the product RK is minimized by differentiating the RK value concerning An/Ap and keeping that value equal to zero.

\[ RK = \frac{L_\rho n \Delta T}{A_p} \left( \frac{n_\rho A_p \Delta T}{L_n} + \frac{k_\rho A_p}{L_p} \right) \]

The obtained maximum Seebeck coefficient with an area ratio of 3 for a TEG module was 240.5±4.2 μV/K. The output voltage and power density produced by TEG for a p-n pair of 7 was 85.2 mV and 1.2 mW/cm² at ΔT of 50 K with a hot side temperature of 333 K, respectively. In addition, flexible TEG module with 15 p-n pairs was demonstrated using body heat and ambient temperature conditions showed 12.5 mV of the output voltage at a ΔT of 5 K. A Thermoelectric Nano Generator (TENG) is composed by simply mixing Te nanowires and P3HT polymer. Te nanowires were synthesized by reducing TeO₂ with hydrazine hydrate at room temp under constant stirring. When Te nanowires were grown on the surface of Te nanocrystallites by depositing Te atom, the solution appeared in a colour change from colourless to blue at the end of the reaction. For device fabrication, composite of Te nanowires and poly(3-hexylthiophene) (P3HT) polymer were prepared in benzene chloride solution. The composite solution was dropped on a flexible Kapton substrate and silver paste was used as the electrode. The fabricated TENG was packaged by a thin layer of poly(dimethylsiloxane) (PDMS) to protect it from the ambient environment. The produced output voltage/current was (14 mV/254 nA) at a ΔT of 50K. A linear variation between temperature difference and the output voltage was observed during testing. The Yang group stated that when two TENGs connected in series, the output voltage of 38 mV and current density of 320 nA in parallel connection at ΔT of 55 K were achieved. The calculated Seebeck coefficient was 285 μV/K. By utilizing the temperature of the human body as a heat source, these thermoelectric nano generators (TENGs) could be used as a wearable energy harvester. Additionally, these were used as a self-powered temperature sensor which displayed a response time of 17 sec and reset time of 9 sec. At ambient conditions, the detection sensitivity of the sensor had reached up to 0.15 K.²⁴²

Wang et al.²⁴³ reported PEDOT: PSS based aerogel films and PEDOT:PSS/TeNW based composite aerogel film for flexible thermoelectric power generator because of high flexibility and ultralow thermal conductivity. With different organic solvents, the PEDOT: PSS aerogel films were cast by vacuum freeze-drying followed by pressing. Similarly, PEDOT:PSS/TeNW (PPT) films were prepared by the same method, including the hydrothermal method which was used for TeNW. Finally, vapour annealing of PPT composite aerogel films was done with DMSO solvent under a Teflon-lined stainless steel autoclave. The PEDOT: PSS/30 wt % Te-NWs aerogel composite film treated with DMSO vapour for 20 min, resulted in a PF of 11.3 μW/MK, ZT of 2.0×10⁻², the electrical conductivity of ~ 100 S/cm, and Seebeck coefficient of ~ 32.1 μV/K. The device was fabricated by connecting PEDOT-PSS based aerogel films as p-type and carbon nanotube fibres (CNFs) as an n-type leg in series by silver paste. The maximum output voltage, output current, and output power obtained were 31.2 mV, ~0.17 mA and 1.28 μW at ΔT of 60 K, respectively. The optimized composite aerogel films had provided an efficient TE generator with high-performance values. Wang and coworkers²⁴⁴ fabricated a highly flexible solution printable n-type hybrid TE based on fullerene/TiS₂ organic/inorganic material. The TiS₂ powder exfoliated to 2D nanosheets and intercalated with N-methyl-2-pyrrolidone (NMP) by grinding it in mortar-pestle. Then, the powder was sonicated in Isopropyl alcohol (IPA) followed by centrifugation to remove the bulk particles. Thereafter, C₆₀ (fullerene) solution prepared in toluene was added slowly to the TiS₂ supernatant in various amounts. The mixing of both solutions provided a path to deposit C₆₀ particles onto the surface of nanosheets. Then, the final solution was passed through vacuum filtration with the help of membranes to obtain hybrid flexible films, followed by vacuum drying and annealing. This solution was used as n-type ink for TEG fabrication. Additionally, the p-type ink was developed by dispersing and sonicating 50 wt % SWNTs in PEDOT:PSS. Further, by using both inks, a flexible TEG was printed on a plastic substrate. The n-type C₆₀/TiS₂ showed a ZT value of ~0.3 at 400 K. For 1 wt % concentration of C₆₀, the obtained thermoelectric properties for n-type hybrid were as- Seebeck coefficient of -101 μV/K, electrical conductivity of ~390 S/cm, and power factor of ~ 400 μW/mK² at 300 K. The obtained flexible TEG data was as, output voltage of ~ 4.8 mV, maximum power output of 335 nW, and power density of 1.68 W/m² at a temp difference of 20 K. Hence, these hybrid nanocomposites are better than the previously reported nanocomposite because of the higher thermopower of inorganic particles and low thermal conductivity of the conducting polymer. The novel aerosol jet printing technique can provide versatile, economic, and easily scalable method for printing flexible nanocomposite based TEGs. In addition to this, other factors such as optimization of TE legs and TE area show great impact on TEGs performance. Reported data of binary hybrid nanocomposite based TE materials demonstrated in Table 3.

### 3.3. Ternary Hybrid Nanocomposites based TE Materials

Even after covering the entire binary hybrid nanocomposites, the high electrical conductivity of nanocomposites still remained a great challenging task. To overcome this difficulty, the ternary hybrid nanocomposite based TE materials were combined to obtain the benefit of all the three components in the nanocomposite. A prospective strategy to enhance the Seebeck coefficient and electrical conductivity of the hybrid nanocomposite could be developed by integrating higher S inorganic NPs and higher σ conducting elements together.²⁴⁵ However, the power factor of these hybrids could not exceed the values of those individual constitutes. Besides, the limitations have been alleviated by providing large energy carriers filtering at hybrid heterojunctions.²⁴⁶,²⁴⁷
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Table 3: Reported data for binary hybrid nanocomposites based TE materials.

| Author and Year | Methods | Materials (p-type / n-type) | Substrate | Pairs used | T | S (µV/K) | ZT | ΔT (K) | Voltage (V) | PF (µW/mK²) | PO/t |
|-----------------|---------|---------------------------|-----------|------------|---|---------|---|--------|--------------|-------------|------|
| Kim D. et al., 2018 | - | SWCNT-PEDOT:PSS (p) | - | - | 4000 S/m | 26 | 0.02 | - | - | 25 | - |
| Meng C. et al., 2018 | Vacuum filtering | CNT-PANI (p) | - | - | 6147 S/m | 28.6 | - | - | - | 5.0433 | - |
| Zhao et al., 2018 | Template-directed synthesis | SWNT-PANI (p) | - | - | 12400 | 40 | 0.004 | RT | - | 0.00002 | - |
| Fu et al., 2013 | - | SWNT-PEDOT:PSS-PVAc (p) | - | - | 105 S/m | 41 | - | - | 160 | - |
| Tao et al., 2018 | IN-situ aerosol jet printing | Sb₂Te₃-PEDOT-PSS (p) | - | - | 247.3 S/cm | 33.8 | - | - | 30 | - |
| Ashlinejad et al., 2014 | LBL deposition | GnPss-MWCNTs-PVDF (p) | - | - | - | 37 | 0.001 | - | - | - |
| Hemori et al., 2019 | Printing process | SWCNT-polystyrene (p) | PEN | 1985 | 2.1 S/cm | 57 | - | 70 K | 254 V/m² | 0.15 | 55 mW/°C |
| Witt et al., 2012 | Layer deposition | CNT-PVDF/ CNT-PVDF Films | 72 layers | ~ 420(p), 800(n) | S/m | 10.05(p), -5.049n | - | 50 | 26 mV | - | 137 W/°C |
| Kim G. et al., 2015 | Spin coating | Graphene-PEDOT-PSS | Silica substrate | - | 32.13 S/cm | 58.77 | 0.021 | - | - | 11.09 | - |
| Yang H. et al., 2015 | - | DWCNTs-PANI-CSA | - | - | 610 S/cm | 61 | - | RT | - | 220 | - |
| Luo et al., 2018 | Solution casting | LiClO₃, doped PEBA - 20 wt % CNT/ LiClO₃, doped PEBA/ DETA doped CNT | Polyimide substrate | 3 | 456(p), 492(n) | S/m | 36.88(p)- 33.25(n) | - | 60 | 120 mV | - |
| Wei J. et al., 2014 | Screen printing | Sb₂Te₃-PEDOT-PSS/ Bi₂Te₃-PEDOT-PSS | Polymide film | 7 | - | 240.5 ± 4.2 | - | 50 K | 85.2 mV | - | 1.2 mW/cm² |
| Suemori et al., 2017 | - | TeNW-P3HT (p) | Kapton and PDMS films | 2 TEGN | - | 285 | - | 55 K | 38 mV | - |
| Wang X. et al., 2018 | Vacuum freeze drying method | PEDOT-PSS-TeNW/ CNTs fiber | - | 100 | 32.1 | 0.02 | 60 | 31.2 mV | 11.3 | 1.28 W/°C |
| Yang L. et al., 2018 | Printing | SWNT-PEDOT-PSS/ CTe₃ | Flexible plastic substrate | 2 | 390 S/cm | -101 | 0.3 | 20 | 4.8 | 400 | 335 nW/°C |

Generally, ternary nanocomposites are composed of an organic-based matrix on which surface inorganic nanoparticle and conducting polymers were grown by either physical mixing or in-situ polymerization. Therefore, Ou et al. used ternary nanocomposite ink as thermoelectric material in different viscosities and ratios to fabricate flexible TEG with various substrates using a modified aerosol-jet printing method. Highly dispersible antimony tellurides nanoflakes and multi-walled carbon nanotubes (MWCNTs) incorporated into poly(3,4-ethylenedioxythiophene) polystyrene sulphonate (PEDOT: PSS) structures to enlarge the TE properties of conducting polymer on flexible polyimide substrates. PEDOT: PSS ink and MWCNT ink were formulated by dispersing within DI water and loaded into ultrasonic atomizer and pneumatic atomizer, respectively. To prepare a stable dispersion of MWCNT in DI water, 0.1 wt% of sodium dodecyl sulphate (SDS), and 0.5 wt% of polyvinylpyrrolidone (PVP) as surfactants were used. Sb₂Te₃ nanoflakes were prepared by solvothermal synthesis method and added to atomizer to enhance the TE performance. Later, two different atomized aerosols were in-situ mixed to form stable ink for printing. Higher Seebeck coefficient of Sb₂Te₃ nanoflakes and larger electrical conductivity of MWCNT lowers the thermal conductivity of nanocomposite by phonon scattering, and significantly enhanced the performance parameter by providing good inter-particle connectivity between the components of nanocomposites. Further, the
electrical conductivity of nanocomposite device was improved by treating it with different polar solvents i.e. de-doping of PSS. Minimal loading fraction of 85 wt % in Sb$_2$Te$_3$-MWCNTs-PVP-PEDOT: PSS nanocomposite treated with DMSO showed power factor of ~ 41 μW/mK$^2$, Seebeck coefficient of 29 μV/K, and electrical conductivity of 496 S/cm. After subjecting the printed TE nanocomposite generator with 60 hours of continuous flexibility testing cycles, the device showed stable performance and greater mechanical strength. Jung et al. developed a flexible hybrid thermoelectric generator (TEG) based on Bi/Te powder, carbon nanotubes (CNTs) and polydimethyl siloxane (PDMS). When bismuth telluride powder (Bi/Te) was incorporated into CNTs, it converted to p-type and n-type TE material. Here CNTs were used to raise the thermal conductivity of TE materials. These TE materials were then blended with PDMS solution and stirred in an overhead stirrer. To obtain a homogeneous distribution of components within the solution, it was ultra-sonicated for 3 hours with a frequency of 40 kHz. To strengthen the composite, a hardener was required, in which principal material to hardener ratio taken as 10:1. The composite was then stirred, ultra-sonicated, and degassed under vacuum conditions. Here, PDMS also used as the substrate to attain flexible TEG. Moreover, to reduce contact resistances amid thermoelectric material and electrodes, it was selectively etched from the top and bottom of PDMS surfaces. The recorded Seebeck coefficients for p-type and n-type TE materials were 143 and -174 μV/K, respectively. The generated output voltage and power was 920 mV and 570 mW/cm$^2$ at ΔT of 60°C. Even during bending reliability test on a small curvature radius of 5 mm and 20 mm over continuous repetition, the TEG maintained its reliability and stability as shown in Figure 12. Choi et al. reported a highly flexible, mechanically, and chemically durable power conversion device using a ternary hybrid nanocomposite of graphene/polymer/inorganic nanocrystal on a paper substrate with higher performance. Te nanowires (TeNW) were used as inorganic nanocrystals and PEDOT:PSS as a conducting polymer. The hybrid nanocomposite showed two hetero-junctions of rGO/PEDOT:PSS and PEDOT:PSS/TeNW which stimulated the double carrier filtering of low energy carriers by scattering, and ultimately increased the electrical conductivity without sacrificing a considerable loss in thermopower of the nanocomposite. PEDOT:PSS coated TeNW (DTe) was synthesized by surfactant facilitated chemical reduction method. This method utilized a prepared clear mixture of L-ascorbic acid and dimethyl sulfoxide in DI water, followed by addition of PEDOT:PSS solution, and Na$_2$TeO$_3$ under continuous stirring till white suspension. To obtain a precipitate the suspension was heated to 90°C followed by natural cooling to 25°C. Finally, the product was recovered by centrifugation followed by several washings with DI water, and ethanol, and freeze-drying for 2 days. The homogenous suspension of GO-DTe was prepared by re-dispersing the GO-DTe powder in DI water, followed by sonication. The films were prepared by passing the GO-DTe suspension through anodic membrane filters by applying vacuum filtration. Then, the films were delicately exfoliated from the membrane and dried by air and vacuum. The GO$_x$DTe$_{0.9}$ hybrid papers were fabricated by treating GO-DTe films with HI vapour-phase for chemical graphitization of the GO phase within the as shown in Figure 13. The reported TE properties were as: ZT~ 0.21, power factor 143 μW/mK$^2$ at 300 K, electrical conductivity 3496 S/m, thermopower 202 μV/K, and produced output voltage 58 mV at ΔT of 50 K.
Polyethyleneimine (PEI)-doped single-walled carbon nanotubes (SWCNTs) were used as n-type material, and hybrid nanocomposite paper as p-type material to fabricate a flexible power generator. Thus, for a pair of 5 legs, the generated maximal power density was 650 nW/cm² at ΔT of 50 K. Even, after 1000 bending cycles, the performance of the device remained unaltered. Erden et al. reported a ternary hybrid nanocomposite of TiO₂/CNT/PANI where Seebeck coefficient of binary CNT/PANI composite can be increased by integrating the TiO₂ nanoparticles into it. Ternary nanocomposites provide two interfaces as TiO₂/a-CNT and TiO₂/PANI for the scattering of low energy carriers, which helped in lowering the thermal conductivity and increasing the thermopower of the composite. The binary a-CNT/PANI composites were formulated by in-situ polymerization of aniline in 1M HCl at 0°C with stirring, followed by washing and drying. The prepared samples were de-doped in ammonium solution for 24 hours followed by washing and drying overnight. Again, re-doping was done with CSA in m-cresol, and TiO₂ (Anatase) was added to re-doped samples in varying concentration and different temperature to check the effect on thermoelectric properties. Finally, to prepare hybrid nanocomposite films on a glass substrate, drop-casting method was used, and films were air-dried at 40°C. To further improve the performance of thermoelectric nanocomposite films, they were water treated and processed with various temperatures. To achieve a better TE performance, the ratio of TiO₂ nanoparticle to CNT/PANI in composite was optimized. Therefore, for an optimized ratio of 30% TiO₂ with 70% (a-CNT 70%//PANI 30%), the gained power factor, electrical conductivity, and thermopower at a temp of 40°C were 114.5 μW/mK², 2183 S/cm, and 22.9 μV/K, respectively. Lu et al. reported ternary nanocomposite films of Te/PEDOT:PSS/Cu₇Te₄ for flexible TE power generator. Here, the nanocomposite films were prepared by physically mixing the PEDOT: PSS coated Te nanorods (PC-Te) solution and PEDOT: PSS coated Cu₇Te₄ nanorods (PC-Cu₇Te₄) solution using a drop-casting method on a glass substrate. The PC-Te nanorod solution was synthesized by dissolving ascorbic acid into DI water and addition of PEDOT:PSS into solution. The PC-Cu₇Te₄ nanorods solution was synthesized by adding CuCl in DI water and then pouring into PC-Te solution with vigorous stirring as shown in Figure 14. Two heterojunctions of Te/PEDOT:PSS and PEDOT:PSS/Cu₇Te₄ increases phonon scattering by refining the double carriers, which reduces thermal conductivity and increases the power factor of nanocomposite film. The nanocomposite films consisting 95 wt% Cu₇Te₄ were treated with 50% PEDOT:PSS solution and finally processed in 70% DI water.
conductivity, and power factor of 163.5 µW/mK could be the degradation of nanorod to nanorod junctions, density were 31.2 mV, 94.7 nW, and 39.5 µW/cm² pastes, the produced output voltage, output power, and power factor and power density from these ternary nanocomposite showed enhanced thermoelectric properties. The PANI/SWNT nanocomposites were synthesized using in-situ polymerization of aniline with ammonium persulfate as an oxidant in the presence of a solution of poly(styrenesulfonic acid) (PSSA) containing SWNTs followed by sonication and vacuum drying. The PANI/SWNT/Te nanocomposite solution was synthesized by dispersing hydroxyl citric acid (C₆H₈O₇), Na₂TeO₃, and PANI/SWNT in different ratios in DI water forming a milky-white bluish solution by stirring at 90 °C for 15 hours. Stable films were fabricated form an optimal concentration of 10 wt % Te/PANI/SWNT solution. Since PANI coating was formed around SWNTs and Te nanorods which created two heterojunction, these two energy filtering junctions of PANI/SWNTs and PANI/Te helped in scattering low energy carriers; resulted in higher Seebeck coefficient of 54 µV/K and higher electrical conductivity of 345 S/cm. The obtained power factor and power density from these ternary nanocomposite were 66 K. This fabric TEG can be used in winter wears where a large temp difference can be maintained between the body skin and ambient air. This device can be easily scalable because of its simple structure and cost-effectiveness.

Wang et al. [160] reported a novel in-situ method for synthesizing ternary PANI/SWNT/Te nanocomposites soluble in water, showed enhanced thermoelectric properties. The PANI/SWNT nanocomposites were synthesized using in-situ polymerization of aniline with ammonium persulfate as an oxidant in the presence of a solution of poly(styrenesulfonic acid) (PSSA) containing SWNTs followed by sonication and vacuum drying. The PANI/SWNT/Te nanocomposite solution was synthesized by dispersing hydroxyl citric acid (C₆H₈O₇), Na₂TeO₃, and PANI/SWNT in different ratios in DI water forming a milky-white bluish solution by stirring at 90 °C for 15 hours. Stable films were fabricated form an optimal concentration of 10 wt % Te/PANI/SWNT solution. Since PANI coating was formed around SWNTs and Te nanorods which created two heterojunction, these two energy filtering junctions of PANI/SWNTs and PANI/Te helped in scattering low energy carriers; resulted in higher Seebeck coefficient of 54 µV/K and higher electrical conductivity of 345 S/cm. The obtained power factor and power density from these ternary nanocomposite were 66 K. This fabric TEG can be used in winter wears where a large temp difference can be maintained between the body skin and ambient air. This device can be easily scalable because of its simple structure and cost-effectiveness.

% PC-Te nanorods showed Seebeck coefficient, electrical conductivity, and power factor of 163.5 µV/K, 42 S/cm, and 112.3 µW/mK at 380 K, respectively, which was 5 times higher than a single component. The detailed study of nanocomposite showed single-crystalline nature of Te nanorods, whereas polycrystalline nature of Cu₇Te₄. When 8 single legs of TE films were connected in series on polyimide substrate by silver paste, the produced output voltage, output power, and power density were 31.2 mV, 94.7 nW, and 39.5 µW/cm² at temp difference of 39 K, respectively. However, in bending reliability test after 350 bending cycles, the film resistance increased by a factor of 55 % and became almost constant when subjected to more bending cycles. Additionally, after 500 bending cycles, the S decreased by about 21%. The reason for the decrease was the degradation of nanorod to nanorod junctions, which affected the performance of TE. However, the composite showed good mechanical stability in the harsh mechanical environment.

Q. Wu and group[160] reported a unique design of wearable TEG, in which thermoelectric materials coated yarns were used as legs, and 3-D fabric as substrate, as shown in Figure 15. The p-type thermoelectric yarn fabricated by coating it with nonionic waterborne polyurethane (NWPU)/PEDOT:PSS/multi-walled carbon nanotube (MWCNT) composite containing 20 wt % MWCNTs and 1:4 ratio of MWCNTs to PEDOT: PSS. Similarly, for n-type yarn NWPU/ nitrogen-doped multi-walled carbon nanotube (N-MWCNT) composite consisting of 30 wt % of N-MWCNTs was used as a coating agent. The commercial polyester yarns were directly coated with composites using a dip-coating method for 5 times. After coating of yarn, it was dried in an oven. These composites were synthesized by dispersing MWCNTs/(N-MWCNT) in PEDOT:PSS solutions containing 5 wt % DMSO/water, respectively, followed by addition of NWPU and sonication. The p and n-type yarns were stitched onto the spacer fabric substrate alternatively and serially connected by silver paste. The 3-D fabric generator produced an output voltage of ~ 800 µV and output power of ~ 2.6 nW at ΔT of 66 K. This fabric TEG can be used in winter wears where a large temp difference can be maintained between the body skin and ambient air. This device can be easily scalable because of its simple structure and cost-effectiveness.

Figure 14: (a) A schematic of fabrication steps of PC-Cu₇Te₄/PC-Te composite film and (b) Photograph of a fabricated TE device by using as-prepared film. Reprinted with permission from Ref. 160 (Y. Lu, Y. Qiu, Q. Jiang, K. Cai, Y. Du, H. Song, M. Gao, C. Huang, J. He, D. Hu, Appl. Mater. Interfaces. 10 (2018) 42310-42319). Copyright (2018) ACS Publications.

Figure 15: (a) A systematically structured design of TEG based on 3D fabric, (b) Yarn legs embroidered into the spacer fabric matrix, (c) Flexibility of fabricated prototype fabric TEG, (d) Image showing conversion of body heat into output power using prototype TEG. Reprinted with permission from Ref. 160 (Q. Wu, J. Hu, , Smart Mater. Struct. 26 (2017) 045037). Copyright (2017) IOP Science Publications.
films were 101 μW/mK² and 62.4 μW/cm², respectively. Wang et al. announced a ternary nanocomposite of Polypyrrole/Graphene/Polyaniline (PPy/GNs/PANI) by solution method and in-situ polymerization process. The homogenous dispersion of graphene into polymer matrix increases the carrier mobility and augments the nano-interfaces of the composite to scatter low energy carriers. The major ordered structure of composite was an outcome of potent π-π interaction between PPy, GNS, and PANI. However, after cold pressing, the enhanced TE properties of PPy/GNs, PANI/GNs, and PPy/GNs/PANI composites were recorded at different temperatures. Therefore, the resultant superior electrical conductivity, Seebeck coefficient, and higher power factor were due to the synergetic effect of both the processes. Further, for an optimal concentration of 32 wt % graphene, the ternary composite of PPy/GNs/PANI exhibited higher PF up to 52.5 μW/mK², electrical conductivity reaches 50000 S/m, and Seebeck coefficient up to 32.4 μV/K. Cho et al. reported uniformly ordered polyelectrolyte carbon nanocomposites (PCNs) of PANI, graphene, and double-walled carbon nanotubes (DWNT), by the sequential layer deposition technique. As mentioned, the superior electrical conductivity associated with graphene and the strong π-π interaction between PANI and DWNT emerged in increased carrier mobility and enhanced thermoelectric properties. Thus, to obtain thermoelectric films, bilayers (BLs) of PANI/graphene, PANI/DWNT and quad layers (QLs) of PANI/graphene/PANI/DWNT had been assembled on a Si-wafer by utilizing layer by layer (LBL) deposition technique. For LBL deposition technique, the precursors such as cationic PANI having a pH value of 2.5, negatively-charged sodium dodecylbenzenesulfonate (SDBS) stabilized DWNT, and poly(4-styrenesulfonic acid) (PSS) stabilized graphene were used. During deposition of samples, linear growth with number of cycles was observed for PANI/graphene, PANI/DWNT BL films, and PANI/graphene/PANI/DWNT QL films with a mean thickness of 4.8 nm, 6.3 nm per BL, and 11.8 nm per QL, respectively. The determined concentration ratio of QL-PCN was 37.7 wt % for PANI, 21.4 wt % for graphene, and 40.9 wt % for DWNT. At a threshold limit of 40 cycles, the QL films of PANI/graphene/PANI/DWNT showed maximum electrical conductivity of 1080 S/cm, Seebeck coefficient of 130 μV/K, and minimum sheet resistance of 19.8 Ω/sq, respectively. The layer by layer (LBL) deposited films of PCN demonstrated a power factor of 1825 μW/mK² which was better than the lead telluride and more than half of the value of bulk Bi₂Te₃. The deposited QL films contain many nano interfaces which were enough to scatter low energy phonons to reduce thermal conductivity.

Meng et al. used a vacuum-assisted filtering method to develop single-walled carbon nanotube (SWCNT)/PEDOT: PSS coated Te nanorod (PC-Te) composite films. To prepare PC-Te nanorods, ascorbic acid was dissolved into distilled water with the addition of PEDOT: PSS and Na₂TeO₃. The suspension was stirred for 20 hours at a temperature of 90 °C. The precipitate was centrifuged and washed with distilled water till the light blue colour of the supernatant obtained. Then, SWCNT/PC-Te nanocomposite solution was prepared by mixing aqueous solutions of both materials in different mass ratios followed by ultra-sonication. The composite films were obtained using vacuum filtration through a porous nylon membrane filter and drying in a vacuum oven. Later, to boost the thermoelectric properties of nanocomposite films, these were treated with H₂SO₄ and heated and washed with deionized water and ethyl alcohol. Composite films containing 70 wt % SWCNT resulted in highest thermoelectric properties i.e. Seebeck coefficient of ~48 μV/K, the electrical conductivity of 361.6 S/cm, and power factor of 79.9 μW/mK². A flexible TEG prototype was fabricated by electrically connecting six strips of composite film in series through the silver paste. The obtained power output and voltage were 53.6 mW and 5.6 mV at ΔT of 44 K, respectively, with a power density of 21.4 μW/cm².

A ternary hybrid nanocomposite of RGO/Cds/PANI using two steps in-situ method were developed by More and coworkers. In the first step, by varying concentration of RGO, CdS quantum dots were grown on RGO sheets to form RGO-Cds nanocomposite where 2-mercaptoacetic acid was used as capping agent. The authors reported in-situ polymerization of aniline in presence of ammonium persulfate as an oxidizing agent to prepare polyaniline (PANI). Here, PANI served as connecting bridge between RGO/Cds nanocomposite to increase the carrier mobility. With 0.4 wt % RGO loading, the highest obtained Seebeck coefficient, electrical conductivity, thermal conductivity, and power factor were 18 μV/K, 2.9×10⁴ S/m, 0.14 W/mK, and 92 μW/mK² (ZT = 1.97), respectively. Additionally, the authors have described the possible charge transfer mechanism in ternary hybrid nanocomposite that was responsible for high TE properties as shown in Figure 16. Kshirsagar et al. reported an I/III/V-VI binary metal selenide-MWCNTs-PANI based nanocomposite for the thermoelectric application that provided good thermoelectric properties at room temperature. Here, the ex-situ synthesis method was used to prepare all the ternary hybrid nanocomposites. Nanoparticles of CuSe, Ag₃Se, In₃Se₃, Sb₂Se₃ and PANI were synthesized separately by already reported known methods. Then, the synthesized nanoparticles, PANI, and commercial MWCNTs were mixed properly with the help of mortar-pestle to form homogeneous powder. Therefore, the obtained Ag₃Se-MWCNT-PANI (ASCP) nanocomposite showed p-type behavior with a ZT value of 0.012 at room temperature and other thermoelectric properties i.e. electrical conductivity of 2962 S/m, Seebeck coefficient of 65 μV/K, and power factor of 12.5 μW/mK². Whereas, hybrid nanocomposites of CuSe, In₃Se₃, Sb₂Se₃ NPs with MWCNTs and PANI showed n-type behavior. Here, CSCP, ISCP and SSCP showed electrical conductivity of 4057, 3048, 4975 S/m, Seebeck coefficient of -28.1, -24, -10 μV/K, and power factor of 3.6, 1.75, 0.49 μW/mK², respectively. Consequently, all the reviewed ternary hybrid nanocomposites have provided a new opportunity to synergistically alter the thermoelectric parameters to harvest energy efficiently. Literature report of ternary hybrid nanocomposite TE materials is shown in Table 4.
4. Applications of Thermoelectric Energy

Over the past years, it has been estimated that all the primary energy sectors such as nuclear power plant, hydrothermal power plant, thermal power plant, geothermal power plant, and solar system utilizes only one-third part (34%) of energy effectively and rest two-third (66%) of heat losses to the environment as unusable energy including automobiles, residential heating systems and various industrial processes as shown in Figure 17.167,168 This waste heat can be utilized by thermoelectric to produce power, which increases the overall efficiency of a plant for power generation. Additionally, this will bring down the warming level of the troposphere by utilizing the lost heat which transfers to the atmosphere. Thermoelectric devices became popular in 1933 when the US government office of Naval Research and Defense Advanced Research Projects Agency asked the researcher to find a solution for improving the ZT value.169 Thermoelectric materials have been used in deep-space research since 1961. These materials were used in the Apollo mission for providing long term energy supply for the first time. In the current scenario, radioisotope based thermoelectric generators (RTGs) are becoming the main power source (350 W) in deep-space mission beyond Mars where solar cells are not sufficient to supply power.170,171

Near two decade ago in 1997, the Cassini satellite was launched to Saturn with three RETGs, where Pu 238 was used as the thermal energy resource and SiGe as the TE material. In 1920 the Russians cited first thermoelectric powered radio systems. In 1954 Chrysler automobile showed the scope of thermoelectric climate control systems technology in luxury cars in which various thermoelectric based climate control seats can be used as seat cooler and seat warmer. In addition, nowadays the thermoelectric coolers are becoming attractive for refrigeration purposes. Currently, researchers are focusing on the fabrication of wearable thermoelectric generators for wristwatches, bio-thermoelectric pace-makers, ECG, etc. that can be powered by the temp difference between the body and its surrounding.2 In this regard, textile materials are widely being used as flexible substrate in TE devices because they possess excellent wearability and air-permeability. The continuous demand of wearable and flexible devices leading researchers to textile based TE materials. Textile based flexible TEGs can be used for hotter regions where generally surrounding temperature is higher than the average temperature of human body. These textiles based TEGs can provide microclimate cool environment to daily working personnel under high temperature conditions such as coal miners, metal workers, refectory workers to prevent them from heat-strokes.172 Interestingly, TE materials can also be utilized as a readily available self-powered temperature sensor where driving force for temperature sensing can be acquired by working environment.

Even though, the thermoelectric power generators are already being utilized by remote “self-powered” systems for wireless data communications in the microwatt power range and for automotive system and deep space mission in the intermediate range of hundreds of watts. However, scientists are still trying to convert industrial waste heat to several kilowatts of power for environmental protection.173 Hence, TEGs are the clean energy source studied in current research efforts. The recent advancement in nanotechnology has achieved a lot of increment in the efficacy of TE materials for generating power, heating and cooling applications. However, due to the limited efficiency of about 5-6 %, these materials are still developing and not yet suitable for competing with other electrical energy generation technologies in the commercial market.60,174 Some of the applications of rigid and wearable TE generators based on their working temperature range are given below:

4.1. Automobile Industry

The automobile industry is the largest industry where thermoelectric generators can be potentially used. Only 25% of the energy stored in gasoline has been used in moving the vehicle, and the rest of the energy has been lost to the environment through the vehicle exhaust system, and radiator. The waste heat produced from the vehicle exhaust system falls normally in a wide temperature range from 100°C - 800 °C which depends on driving conditions. Thus, to develop TEGs for a vehicle heat engine, appropriate aspects should be included such as (1) varying thermal stresses caused by various driving conditions such as brake, acceleration, stop and different road conditions such as steep and rough, (2) wide temp range sustaining TE materials, (3) moving state of TEG, and (4) exhaust temperature dependence on the consumption of different types of fuel.175
Table 4: Literature report of ternary hybrid nanocomposites based TE materials.

| Author and Year | Methods                  | Materials (p-type / n-type) | Substrate | Pairs used | σ (μV/K) | S (μV/K) | ZT | ΔT (K) | Voltage (V) | PF (μW/mK²) | P O/t          |
|-----------------|--------------------------|-----------------------------|-----------|------------|----------|-----------|----|--------|-------------|-------------|---------------|
| Ou et al., 2018  | Aerosol-jet printing     | Sb₂Te₃-MWCNTs-PEDOT:PSS (p) | Polyimide | -          | 496      | 29        |    |        | -           | -           | 41            |
| Jung et al., 2016 | Deposition              | Bi powder-CNTs-PDMS/Te powder-CNTs-PDMS | PDMS      | 50         | 6.51(p), 6.13(n) | 143(p), - | 174(n) mV/K | - | 60     | 920 mV      | 0.13(p), 0.18(n) | 570 mW/cm² |
| Choi et al., 2016 | Vacuum filtration       | rGO-TeNW-PEDOT:PSS/PEI doped SWCNTs | Paper     | 5          | 3496     | S/m       | 202 | 0.21   | 50          | 58          | 143           |
| Erden et al., 2018 | Drip casting            | TiO₂-CNT-PANI (p)           | Glass for film | -          | 2183     | 22.9      |    |        | -           | -           | 114.3         |
| Lu et al., 2018   | Drop casting             | Te-PEDOT:PSS-Cu₃Te₄ (p)     | Polyimide | 8 single legs | 42       | 163.5     |    |        | -           | 39          | 112.3         |
| Wu et al., 2017   | Yarn coating             | NWPU-PEDOT:PSS-MWCNT/ NWPU-n-MWCNT | 3-D fabric | 10         | -        | -         | 66  | 800 μV | -           | -           | 2.6 nW        |
| Wang L. et al., 2016 | -                      | PANI-SWNT-Te (p)           | -          | -          | 345      | 54        |    |        | -           | -           | 101           |
| Wang Y. et al., 2017 | -                      | PPy-GNs-PANI (p)           | -          | -          | 5000     | 32.4      |    |        | -           | -           | 52.5          |
| Ro et al., 2015   | LBL deposition           | PANI-GR-DWNTs (p)          | -          | -          | 1080     | 130       |    |        | -           | -           | 1825          |
| Xing et al., 2019 | -                       | SWCNT-PEDOT:PSS coated Te nanorods (p) | -          | 6 single legs | 361.6    | 48        | -  | 44     | 5.6 mV      | 79.9         | 53.6 μW/cm²   |
| More et al., 2017  | In-situ method          | RGO-CdS-PANI (p)           | -          | -          | 2.9 × 10⁴ S/m | 18    | 1.97   | -        | -           | 92            |
| Kshirsagar et al., 2019 | In-situ method         | Ag₄Se-MWCNT-PANI/Cu₄Se-MWCNT-PANI | -          | -          | 2962 (p), 4057 (n) S/m | 65 (p)/ 28.1 (n) mV/K | 0.012 (p) @RT | - | -      | -           | -           | -             |
The main attraction of using this technology in the automobile is the minimization of fuel consumption and protection of the environment. First time in 1914, TEGs were used in vehicles with reciprocating heat engine to recover some of the waste heat, patented by Creveling JL (US).\textsuperscript{177} The hot exhaust gases from the engine were used as heat source whereas the circulated cooling water functioned as a heat sink. Applications of thermoelectric generators in automobiles were deeply investigated over 90 years to recover waste heat from engines.\textsuperscript{178,179} Some of the companies had developed TEGs that can produce 0.5-1 kW of electrical energy from the waste of a vehicle heat engine with an overall efficiency of 5-10 %.\textsuperscript{180,181} The BMW Group presented a typical photograph of a car with a typical arrangement of the rigid thermoelectric generator in Figure 18.\textsuperscript{182}

Additionally, to provide comfort zone to passengers Amerigon Incorporation has represented a schematic of car seats integrated with TE devices for climate control.\textsuperscript{183} We know that thermoelectric refrigerators are less efficient than mechanical refrigerators in automobile, but it still can maintain part, noise and working fluid which results in leakage problem. These devices could also provide a long working life by careful the efficiency down to very low cooling power of the order of milli-watts. These could be operated easily without any moving device process design and construction. Currently, TE devices perform the main role in Heating Ventilation and Air Conditioning (HVAC) system of vehicle to provide simultaneous heating and cooling by simply reversing the current. During heating mode, the TE HVAC system shows COP of 2-3 without following any energy consumption procedures, whereas traditional HVAC system requires additional pump to extract the thermal energy into working fluid and transfer it through heat exchanger to other components with lower COP. These TE devices in compact form could be inserted into the seats, floor, back of the front seat, dashboard and overhead of the driver. These installed devices will be used only to cool or heat the particular person, not the whole cabin. The current air conditioner available in the vehicle needs 3500-4000 W of power to cool the cabin, whereas thermoelectric cooler (TEC) needs less than 700 W to cool the driver seat. It can also be activated remotely at a distance of 50 m or more. This technology has been used by several car manufacturing companies.
companies like Ford, GM, Jaguar, Range Rover, Toyota, Hyundai, and Nissan. Recently, flexible TE devices based on polymers can be used on car radiator and exhaust pipe in which temperature can reach up to 500 °C and 100 °C respectively. However, polymers stability is a challenging task for high temperature operations. Therefore, textile based TE as a flexible device can be installed at pipe or radiator regardless of their irregular surface and size. Thus, large amount of waste heat can be utilized using textile based TEGs. Moreover, use of thermoelectric materials for heating/cooling in vehicles can improve fuel economy, reduction of toxic, and greenhouse gas emission, lower volume, reduced cost, and greater availability for other applications. The advantages associated with TEGs can achieve significant enhancement in the development of more efficient thermoelectric materials, devices and commercially executable fabrication techniques.

Figure 18: Integration of thermoelectrics into vehicles for improved fuel efficiency. The image is a BMW 530i concept car with a thermoelectric generator (yellow; and inset) and radiator (red/blue). Reprinted by permission from (Springer Nature), (Nat. Mater.) Ref. 162 [An inconvenient truth about thermoelectrics, C.B. Vining, 8 (2009) 83–85], copyright 2009.

4.2. Aerospace Industry

The aerospace industry is one of the biggest and most expensive industries where a continuous supply of electrical power is required for excellent performance. Deployment of satellites in earth’s orbit for exploring the marine life, geography of the earth, terrestrial surveillance systems, and communication systems need long-life sources of electricity. In addition, the long space missions need a better source of power which can run up to several years without damaging in harsh conditions. Thus, the thermoelectric generators could be a suitable solution for all these applications, due to their good adaptability for various types of heat sources, no movable parts, and no position dependency. TEGs can provide larger steady-state operation time equals to 10^4 hours, and accurate temperature control within the system. NASA (National Aeronautics and Space Administration) the USA has used high-performance radioisotope generators (RTGs) for the first time in 1961 to provide electrical supply to spacecraft. Also, TEGs can be used in greater number for various types of space missions. RTGs are being used in deep space missions for years, but the changing scenario of small light-weight, and compact spacecraft demand, need the development of new advanced power sources. Nowadays, thin-film technology-based TEGs are getting popular because of their high performance. These thin films can be fabricated by combining with semiconductor technology, which is suitable for developing ultra-lightweight thin films TE compact devices to generate maximum voltage with excellent performance. The supremacy of using TEGs in space mission can be seen in various examples such as the Voyager spacecraft with Voyager 1 fleeting into the Helio sheath around 8.3 billion miles from Earth on May 24th, 2006. The successful application also goes to TAGS-85 which has been used in numerous space and terrestrial applications. Other TEGs applications include long-lasting power to the Viking Landers 1 and 2 and devices which are used in inaccessible or hostile areas such as meteorological data collection and transmission system in off-coast areas and seismic detectors in Alaska. Additionally, during extravehicular activities in space missions, astronauts wear hermetical space suits where temperature of outer space varies between -233–212 °C. Traditionally, thermal control in a space suit is maintained by liquid cooling and ventilation, which shows bad air permeability of the garments due to installation of ventilation unit over the garment. Therefore, combination of textile based thermoelectric generators and coolers can modify current space suit issues such as thermal and moisture comfort of the astronauts. When the outer space temperature is greater than the body temperature, TEGs will supply the electrical power for supporting the operation of TE coolers. Aircraft industries which include both commercial and military aircraft can use thermoelectric devices to capture waste heat produced from the engine and supply the generated electric power to the whole aircraft system without affecting the engine performance. This will cut down fuel consumption and ultimately reduces the cost of passengers and cargo airlines.

4.3. Electronic Devices

Considering the shorter service life of portable batteries, the scientific community is keen to develop low-cost solutions of portable power generators for autonomous energy and wearable biometric monitoring sensors, which can extract energy from different waste heat resources and convert it to useful electricity. Hence, the technological transformation of such advanced microsystems onto a flexible substrate can lead to low cost, unobtrusive, and wearable omnipresent integrated devices for monitoring health and biometric parameter. Many electronic devices such as power amplifiers and microprocessors are operated at high temperature which affects the performance, reliability, and lifetime of the device. To overcome these issues, thermoelectric coolers (TEC) can be utilized as cooling media to eliminate the generated excess heat during the process. Conventional cooling devices are not feasible here due to the requirement of large cooling area. TEC can couple with the surface of electronic devices to provide effective local cooling.
TECs do not make any noise because of no involvement of any moving parts. Min et al. showed an electronic component of infrared arrays integrated with thermoelectric micro coolers to lower the thermal noise and current leakage produced from the electronic device. Bale et al. showed a cooling of CdZnTe detector between temperatures of -30 to -40°C, which is used in X-ray astronomy. The cooling of the detector can minimize the current leakage and permit the usage of a pulsed reset preamplifier and long pulse shaping times which significantly enhance the energy solution. For this small application, only 3W of electrical power was used. Thermoelectric coolers/generators can also be used in conjunction with solar photovoltaic (PV) to cool or generate electrical power form them, respectively. To obtain maximum performance from solar PV and to reduce the cost of the panel, thermoelectric coolers should be used to cool the solar PV rather than recovering heat through thermoelectric generator. In addition, several attempts were made to attach the Peltier modules in residential doors and windows to generate the warmer air inside the house in colder regions, although the heat supply was not enough to keep the residential space warm. Presently, e-textiles based on conducting polymer PEDOT:PSS are getting popular among wearable TEGs. The fabricated 3-D textile as out of plane TE device generated a power output of 1.2 µW at ΔT of 65 K, which can be used in biomedical devices.

4.4. Biomedical Industry

In the medical industry, refrigeration of medicine, blood serum, vaccination, and other biological products are necessary to prevent degradation. The properties of these products will only stabilize in a certain temperature range for excellent results. Here, thermoelectric coolers can be used as a microprocessor-based controlled portable type medical cooling kit for protecting medical products during storage condition and freightage, which requires 12 V and 4 A DC for a smooth operation. In remote areas of developing countries, the on door medical services can be provided with sufficient medicines by these TE refrigerators. In addition, doctors can deal with emergency issues by getting the right vaccines on time. TE refrigerators can also work in the food industry where food products need a certain temp during transportation and storage to preserve their shelf life. Flexible or wearable type of thermoelectric generators (TEGs) can be used in medical devices to provide real-time monitoring of patient health. These wearable devices can be easily wrapped and bent onto the curved skin surface to utilize a large amount of body heat as a source. By using a large surface area of TEG, contact between the TEG and skin surface can be enhanced to produce more power. This increased surface area of TEG can extinguish the necessity of a boost converter. Several small lightweight TEG based medical sensors with wireless communication can be attached to a patient’s body to form a wireless body area network (WBAN) that can provide remote health care service.

These devices can perform health monitoring activities like EEG, ECG, blood pressure, respiration rate, heart rate, pulse oximetry, body temperature, and sleep period (actigraphy) at different locations of wearer’s body. The data collected by medical sensors can be transmitted through various short-range wireless communication protocols such as ANT, Bluetooth, Zigbee, and collected on a personal server as the cell phone. Then, health service providers can collect this data from the internet to provide real-time health monitoring. Therefore, integration of short-range wireless communication technology with TEG-based medical sensors can provide efficient and ultra-low power consumption devices. Dementyev et al., reported a Bluetooth Low Energy (BLE) wireless technique that requires only 35 µW at 3.3 V supply in 120 sec transmission intervals. Recently, Rose et al. developed a band type wearable sensor for sensing the heat stress and hydration through the electrolytes present in wearer’s sweat by using battery-free passive radio frequency identification (RFID) and paper microfluidics technology. Further, technological advancement in integrated circuits, wireless communications, and medical sensors have enabled miniaturization, light weight, ultra-low powering, and wearable health monitoring of devices.

5. Conclusion and Future Scope

It is understood that the traditional inorganic TE materials deliver high output but possesses poor processability, higher cost, and severe toxicity. In comparison, the organic-based TE materials such as conducting polymers can be advantageous in terms of low-cost, environmentally friendly, and low intrinsic thermal conductivity. However, the reported TE performance of organic TE materials is relatively low, and thus, researchers combined them with other semiconducting materials and developed better performing hybrid nanocomposites. These hybrid nanocomposites showed drastic improvements in Seebeck coefficient, power factor, and ZT values owing to the resultant “band engineering” and energy filtering effect. The formation of extra heterojunctions within the hybrid TE materials leads to scattering of low energy charge carriers in favoured directions to give energy filtering effect. The alignment of energy levels of these component materials may result in a selective transfer of charges delivering either p- or n-type behaviour for the entire hybrid nanocomposites. The use of ternary systems allows researchers to overcome the disadvantages of single components to achieve better TE performance. However, for practical applications, development of outstanding TE performing materials is a persisting challenge as better control of charge carrier in these composites remains elusive. The use of common conducting polymers limits the high-temperature TE applications of these hybrid nanocomposites, as the thermal stability of the conducting polymers is limited. Additionally, the cost of graphene CNTs and other semiconductor nanoparticles still remains relatively high, creating another issue in their technological transfer. Thus, effective synthetic methods are needed to develop hybrid nanocomposites with controlled
structures and refined heterojunctions for better TE efficiency. In terms of thermoelectric devices, the performance can be enhanced by various ways as follows:

1. Improving the properties of thermoelectric material by computational screening. Here, nanoscale range materials, doping of inorganic/organic materials, and formation of hybrid composites are very promising routes to improve TE conversion efficiency.

2. Thermal matching of materials, the effect of heat transfer law, the temperature dependency of the material properties, and the greater temperature difference between the two sides of the TE device are possible routes for improvement.

3. Geometrical design including amongst other legs length, the thickness of the generator, and the size of hot and cold side substrate have a strong impact on the TEGs efficiency. Contact quality and resistance likewise become important parameters for improvement.

4. Fixing a working temperature range for TE materials by enforcing potential heat dissipater on the cold side.

5. Design optimization of device structure through computer simulations, including the arrangement of TE elements and device to amend the improved packaging technology for the TEGs.

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