

# Overview of the Optimization of Thermoelectric Materials by Nanoscale Adjustment

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## Abstract:

At present, with the continuous development of human science, the world is committed to finding new energy sources and energy conversion technologies, thermoelectric materials have received widespread attention for their superior environmental performance. In the field of thermoelectric materials, the thermoelectric figure of merit  $Z$  of the material is an important index to judge the thermoelectric performance. This article mainly introduces how to improve the thermoelectric figure of merit of thermoelectric materials by adjusting the nanometer scale, and the specific methods are mainly doped nanoparticles and nanomaterials. For semiconductors, methods such as nanoparticle doping to reduce thermal conductivity and increase the thermoelectric figure of merit are effective. For high molecular polymers, they have low thermal conductivity. Therefore, the research on polymers is devoted to the composite of polymers and high-conductivity materials, and the resulting composite materials have both excellent thermoelectric properties and mechanical properties. The research on semiconductors and polymers through the adjustment of nanoscale has found that whether it is semiconductor materials or polymer composite materials, nanotechnology provides more possibilities for the development of materials, and nanotechnology also shows great advantages and potential.

**Keywords:** nanostructures, nanotechnology, thermoelectric materials, reducing thermal conductivity

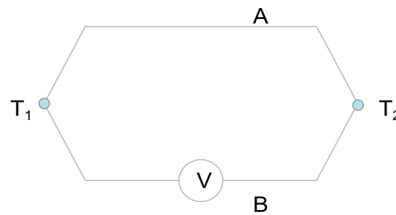
## Introduction

At present, the global chemical industry with petroleum, coal, and natural gas as the main fuels has different degrees of restrictions. Global environmental optimization measures have set strict standards for existing companies and put forward strict requirements, prompting them to vigorously seek to develop environmentally friendly and renewable new energy and energy conversion technologies. Thermoelectric materials have the advantages of small size, light weight, sturdiness, no noise, long life, and easy to control <sup>[1]</sup>. It is precisely because of these advantages that thermoelectric materials are currently the most potential important material in line with sustainable development strategies. The thermoelectric conversion technology is an environmentally friendly new energy conversion technology, which mainly uses the Seebeck effect, Peltier effect and Thomson effect of thermoelectric materials to realize the conversion between heat and electricity. As a new clean energy conversion technology, it has broad application prospects in solar power generation, industrial waste heat and waste heat recovery and utilization, and automobile exhaust waste heat recovery.

In 1821, the German physicist Seebeck observed that in a closed circuit composed of two different materials (conductors or semiconductors), a phenomenon in which thermal energy was converted into electrical energy occurred. This phenomenon is called the Seebeck effect <sup>[2]</sup>. The micro-physical essence of Seebeck effect is the carrier migration that occurs when there is a temperature difference. Since the two ends of the thermoelectric material form an electric potential difference  $U$ , the Seebeck electromotive force is also called thermoelectromotive force. The thermoelectromotive force is expressed as follows:

$$U=(T_1-T_2) \cdot |S_A-S_B| \quad (1)$$

The two conductor materials A and B have different Seebeck coefficients,  $S_A$  and  $S_B$ .



**Figure 1:** principle diagram of Seebeck effect

The important parameter to characterize the performance of thermoelectric materials is the thermoelectric figure of merit  $Z$ , which is usually expressed as the dimensionless figure of merit of the material by the product of  $Z$  and the absolute temperature  $T$ . The thermoelectric figure of merit is usually used when judging and selecting whether a new type of thermoelectric material has superior performance. The thermoelectric figure of merit  $Z$  is expressed as follows:

$$ZT=(S^2\sigma/\kappa)T \quad (2)$$

In formula (2),  $S$  is the Seebeck coefficient,  $\sigma$  is the electrical conductivity, and  $\kappa$  is the thermal conductivity.

From formula (2), it can be seen that the thermoelectric figure of merit of a material is related to the Seebeck coefficient, electrical conductivity, and thermal conductivity. Therefore, these three parameters are important parameters for the study of thermoelectric figure of merit. Studying the changing laws and control methods of these physical quantities has a key guiding effect on the improvement of thermoelectric performance.

Traditional thermoelectric materials are mainly used for thermoelectric power generation and thermoelectric cooling. Thermoelectric power generation refers to the use of the Seebeck effect to convert thermal energy into electrical energy. The first application of thermoelectric materials in power generation occurred in the former Soviet Union. With the development of space exploration, the advantages of thermoelectric materials have also been revealed. Thermoelectric materials can be used in areas hard to reach for resource exploration, and they can supply the electricity without human care. Thermoelectric power generation materials are particularly suitable for this application. In 1962, the United States used thermoelectric materials in space and installed thermoelectric materials on artificial satellites to ensure that the satellites can continue to work without human intervention. For remote deep space probes, thermoelectric generators (RTG) have been used in satellites and spacecraft. For example, the Voyager spacecraft launched by the United States in 1977 installed 1,200 thermoelectric generators [3].

With the development of the times, traditional thermoelectric materials can no longer meet the existing production, and there is an urgent need to improve the performance of thermoelectric materials to meet the existing technical needs. From the research status at home and abroad, the main methods to improve the thermoelectric properties of materials are doping and reducing the lattice thermal conductivity. Doping can enhance the scattering ability of phonons, thereby reducing the thermal conductivity of the material. In recent years, the research on thermoelectric materials has reached the nanometer scale, and the ideas of nanometer and low-dimensionality have been successfully applied in thermoelectric materials. Nanostructures can effectively enhance phonon scattering, which has become one of the most widely used and effective methods to reduce the thermal conductivity of materials so far. Currently, thermoelectric materials are mainly doped and nano-sized to reduce their thermal conductivity and ultimately improve their thermoelectric performance.

## 1. Nano-scale adjustment to optimize semiconductor materials

Semiconductor thermoelectric materials are the most widely used, with the earliest discovery and the longest development time. Among them, the telluride represented by  $\text{Bi}_2\text{Te}_3$  is the most typical. Telluride materials have lower thermal conductivity, so the thermoelectric materials improved based on  $\text{Bi}_2\text{Te}_3$  are most widely used. However, the performance of traditional thermoelectric materials can no longer meet the various needs of the present, so it is necessary to improve the traditional thermoelectric materials, such as using doping or low-dimensional processes. The current research on thermoelectric materials has gone deep into the nanoscale. The optimization of thermoelectric materials by the adjustment of nanoscale is also the most advanced technology in the world. Researchers have achieved a maximum ZT value of more than 2.0 in inorganic thermoelectric materials with a new nanophase structure<sup>[4-5]</sup>.

### 1.1 Doping

The most common use of doping to change the thermoelectric properties is the introduction of a new interface, which enhances phonon scattering and reduces the thermal conductivity of the material. In 2019, Li Yihuai and others prepared Bi-doped nano-PbS thermoelectric materials and concluded that at 723 K, when the molar ratio of doped Bi is 10%, the lowest thermal conductivity is  $0.75 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ . Doping Bi effectively reduces the thermal conductivity of PbS by 33%.<sup>[6]</sup> In 2019, Pei Jun successfully prepared a series of  $\text{Fe}_x(\text{Bi}_{0.15}\text{Sb}_{0.85})_{2-x}\text{Te}_3$  samples through mechanical alloying combined with spark plasma sintering. When  $x=0.05$ , the maximum ZT value of 1.2 was obtained at 303K. At the same time, he also studied the effect of Al doping combined with Sn self-compensation on SnTe thermoelectric materials. Due to the enhancement of carrier scattering, the room temperature power factor of SnTe was effectively improved. The sample with  $x=0.05$  obtains the maximum ZT value of 0.65 when the temperature is around 823K. When the temperature range is 323~723K, the maximum conversion efficiency of the sample with  $x=0.05$  can reach 5.26%, which is about 2.45 times higher than that of the SnTe sample before the non-doping<sup>[7]</sup>. There is also the Sn-GST deposited film researched by Yuan Pengyue when the Sn doping power is 50W and the temperature is 723K, the maximum power factor is  $1.88 \text{ m}\cdot\text{W}\cdot\text{K}^{-2}\cdot\text{m}^{-1}$ . It exceeds the thermoelectric properties of GST bulk and pure GST thin films reported in the literature<sup>[8]</sup>. A large number of studies have shown that doping has a significant optimization effect on thermoelectric materials.

### 1.2 Nanoscale adjustment

Nanoscale adjustment methods are mainly to reduce the lattice thermal conductivity of materials by introducing various interfaces and increasing the density of grain boundaries. The specific method is to dope nanoparticles to enhance phonon scattering; or make bulk materials into low-dimensional materials, such as two-dimensional films or even nanowires or nanotubes; or directly precipitate nanoparticles inside the material to enhance phonon scattering. These methods can effectively reduce the lattice thermal conductivity.

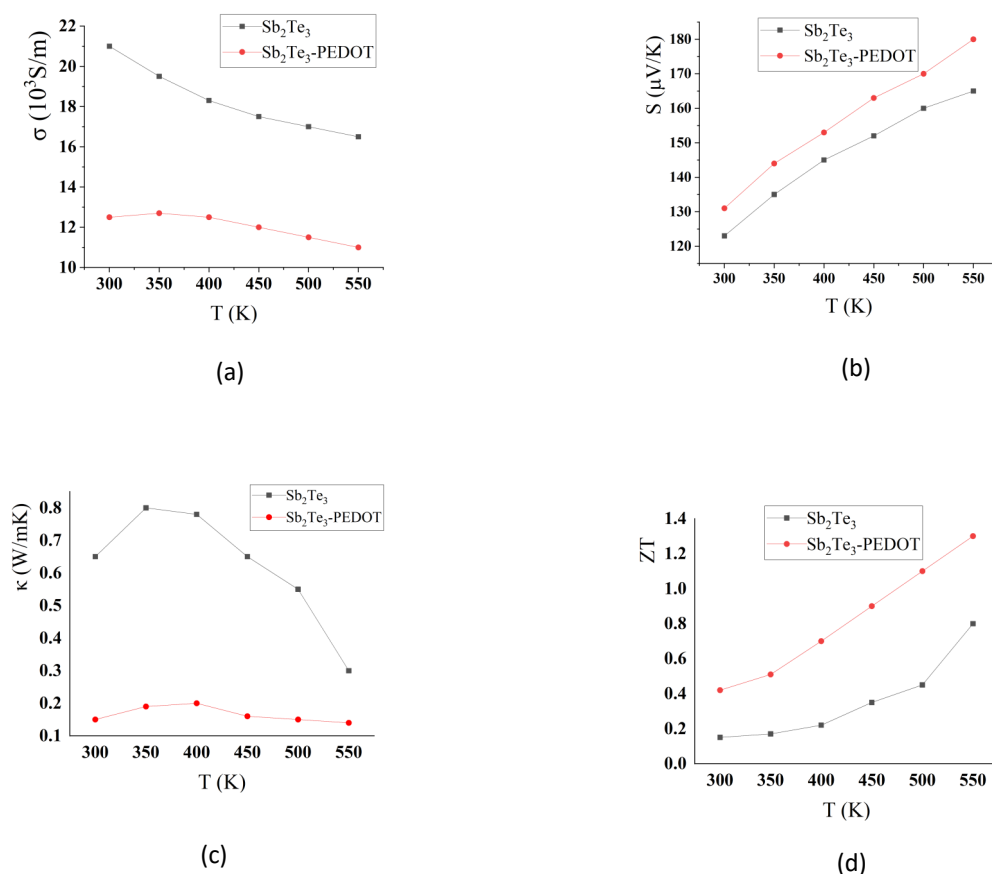
#### 1.2.1 Low dimensionality

Low-dimensional materials refer to materials with dimensions less than three, such as two-dimensional films, one-dimensional nanowires, and even zero-dimensional nanoparticles. With the development of technology, various industries have put forward more requirements on the size of thermoelectric materials. For example, computer chips are getting smaller and smaller, so the corresponding thermoelectric elements are also required to have smaller sizes. Therefore, the phenomenon of low-dimensional thinning of thermoelectric materials more and more, the demand for micron-scale and nanoscale thermoelectric film materials is increasing. Take BiCuSeO as an example. At present, the thermoelectric properties of BiCuSeO-based three-dimensional bulk materials are mainly studied in the world, and there are very few studies on the two-dimensional thin films of this material. Compared with three-dimensional bulk materials, two-dimensional thin films are easier to realize the integration of thermoelectric devices and have irreplaceable advantages in the field of micro-zone thermoelectric power generation.

In 2018, Guo Shuang used PLD technology to prepare BiCuSeO thin films on three single crystal substrates. The film exhibits metal conductivity in the temperature range of 20~350 K, and the room temperature resistivity is only  $12.5 \text{ m}\Omega\cdot\text{cm}$ , which is much lower than the resistivity of the corresponding polycrystalline bulk materials. The calculated room temperature power factor is about  $3.3 \mu\text{W}\cdot\text{cm}^{-1}\cdot\text{K}^{-2}$ , which is higher than the factor of the corresponding polycrystalline bulk material<sup>[9]</sup>. Guo Shuang's research shows the advantages of two-dimensional oriented films, while one-dimensional nanowires have better thermoelectric properties. The outstanding progress made in one-dimensional nanowire is found in Si nanowires. The PD YANG team found that as the size of the nanowires decreases, the thermal conductivity decreases drastically. The final measurement of such Si nanowires obtained a ZT value of 0.6 at 300 K, which is 60 times the figure of merit for bulk silicon thermoelectric.

The AI BOUKAI team conducted a detailed study on the thermoelectric properties of Si nanowires with smaller diameters. By optimizing the doped 20nm wide Si nanowires, the excellent thermoelectric performance of  $ZT=1$  can be achieved at 200 K, which is 100 times higher than that of bulk silicon. When the diameter is reduced to 10nm, the thermal conductivity has more than doubled. The above results indicate that one-dimensional nanowire materials can indeed effectively reduce the lattice thermal conductivity and improve the thermoelectric performance<sup>[10-11]</sup>. Zhao Xinbing<sup>[12]</sup> added 15% of the powder containing  $\text{Bi}_2\text{Te}_3$  nanotubes to the traditional  $\text{Bi}_2\text{Te}_3$  based thermoelectric material, which can improve the performance of the material by about 20%. SCOVILLET and SLACKT<sup>[13]</sup> tried to dope  $\text{B}_4\text{C}$  and BN nanoparticles with a diameter of 40nm in SiGe thermoelectric materials, respectively, and the thermal conductivity of the composite material was reduced by 40%. Low-dimensionality is an important way to achieve breakthroughs in the performance of thermoelectric materials.

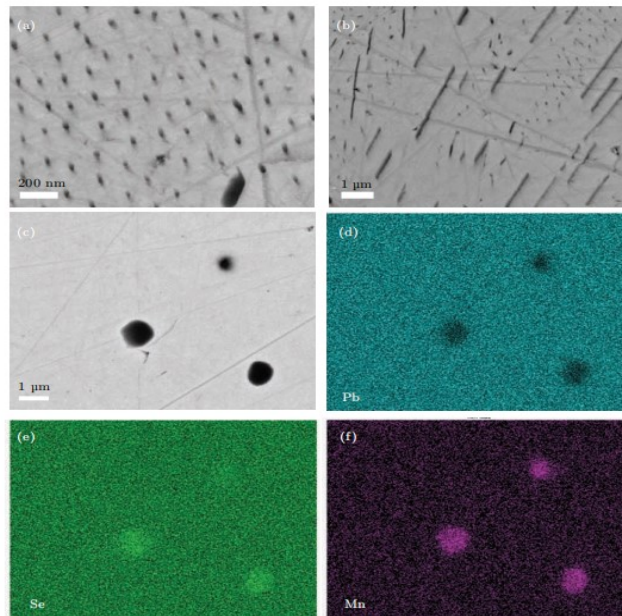
However, low-dimensionality is not limited to semiconductors. As early as 2016, Zheng Wenwen added PEDOT, an organic conductive polymer thermoelectric material, to the  $\text{Sb}_2\text{Te}_3$  block. As shown in Figure 2, by studying the comparison of the thermoelectric parameters of the pure phase and the  $\text{Sb}_2\text{Te}_3$ -PEDOT composite, it can be seen that the thermal conductivity of the composite is significantly reduced, the Seebeck coefficient of the  $\text{Sb}_2\text{Te}_3$ -PEDOT composite is significantly improved, while the conductivity is not significantly deteriorated. When the temperature is 523K, the  $ZT$  value of the  $\text{Sb}_2\text{Te}_3$ -PEDOT composite reaches 1.18, which is 60% higher than the pure phase. Later, on this basis, he researched a composite of  $\text{Sb}_2\text{Te}_3$ /PEDOT/ $\text{Sb}_2\text{Te}_3$  sandwich structure, the  $ZT$  value increased to 1.3, which is twice that of the pure phase<sup>[14]</sup>.



**Figure 2 :**  $\text{Sb}_2\text{Te}_3$ /PEDOT composite (a) electrical conductivity, (b) Seebeck coefficient, (c) thermal conductivity, (d)  $ZT$  value versus temperature curve<sup>[14]</sup>

### 1.2.2 Nano precipitates

The nano-precipitated phase is a method of controlling the phase separation to realize the formation of a large number of nano-precipitates inside the particle. In 2016, Zhang Yu and Wu Lihua from the School of Materials Science and Engineering of Shanghai University prepared a series of  $\text{Pb}_{0.98-x}\text{Mn}_x\text{Na}_{0.02}\text{Se}$  nanocomposites through a vacuum melting-quenching-rapid hot pressing sintering process. In the sample with Mn content  $x=0.02$ , the PbSe-MnSe nanocomposite thermoelectric material with  $ZT=0.65$  is finally obtained. During the research process, spherical and thin-layered nano-precipitates appeared in the PbSe matrix at the same time as shown in Figure 3. The diameters of these spherical and thin-layered nano-precipitates were about 50nm-100nm. These discontinuous particle precipitates effectively scatter phonons, reduce lattice thermal conductivity, and optimize the thermoelectric properties of the material<sup>[15]</sup>.

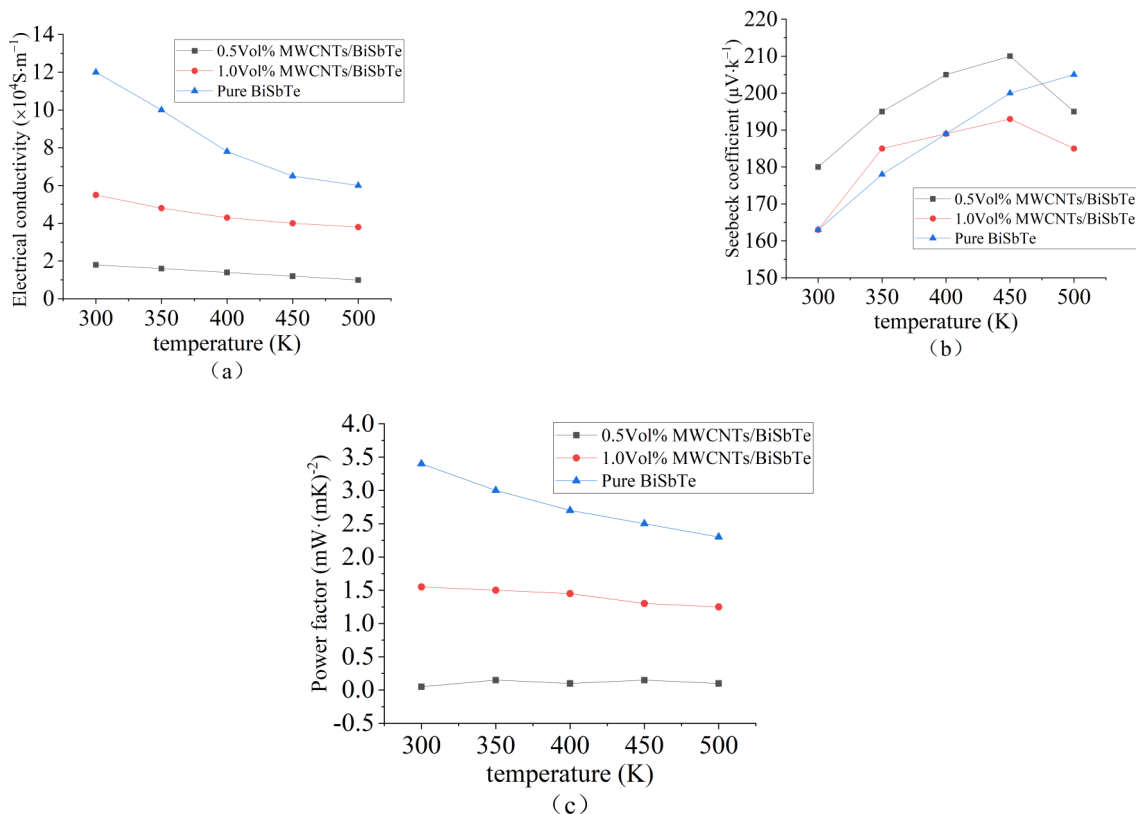


**Figure 3:** (Web Journal color) the backscattered electron image and element scanning result of  $Pb_{0.98-x}Mn_xNa_{0.02}Se(x=0.02)$  sample<sup>[15]</sup>

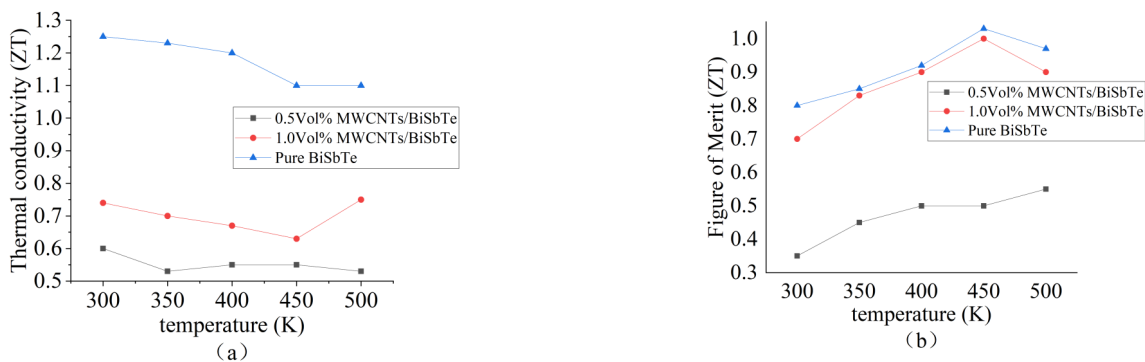
### 1.2.3 Second phase nanoparticles

The introduction of nanoparticles of other phases can optimize thermoelectric performance. Common nanoparticles include carbon nanotubes and other nanoparticles. In 2018, Kaleem Ahmad of King Saud University and Wan Chunlei and Zong Peng'an of Tsinghua University studied the preparation of BiSbTe/multi-walled carbon nanotubes (MWCNTs) composites by ball milling and their thermoelectric properties (300~500K). Commercially available BiSbTe blocks were used as the matrix material, ball milling and pressure-assisted induction heating sintering were used for densification to obtain BiSbTe/0.5, 1.0 vol% MWCNTs composite materials with different composite ratios. Figure 4 and Figure 5 show that the addition of MWCNT enhances phonon scattering and greatly reduces thermal conductivity. However, due to the enhancement of carrier scattering and lower density, the electrical conductivity is also reduced, which is not beneficial to the optimization of thermoelectric material performance. Therefore, it is necessary to optimize the processing parameters to increase the electrical conductivity. The thermoelectric figure of merit of the BiSbTe/1.0 vol% MWCNT composite is close to that of the BiSbTe matrix, and the thermoelectric figure of merit of the composite can be improved by adjusting the processing parameters<sup>[16]</sup>. Zhang et al. successfully reduced the grain size of the material from 2~3 microns to 200~300nm by mixing Si nanoparticles in a PbTe material co-doped with Tl and Na. The corresponding room temperature lattice thermal conductivity can be reduced from  $2 \text{ Wm}^{-1}\text{K}^{-1}$  to  $1.2\sim 1.3 \text{ Wm}^{-1}\text{K}^{-1}$ <sup>[17]</sup>. The addition of second-phase nanoparticles has played an important role in the optimization of thermoelectric material performance.

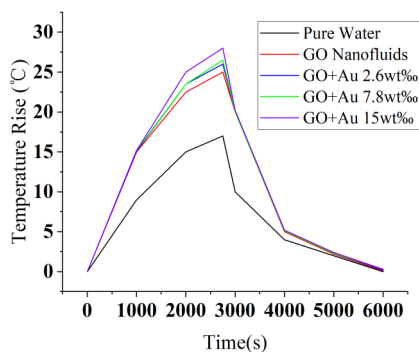
Many thermoelectric materials use sunlight as a heat source. When using solar energy as a heat source, heat collection must be considered. Due to the inevitable heat dissipation loss of heat collection materials, the traditional solar energy conversion efficiency is only about 30%, while the solar steam technology can use steam as the heat source and save 80% of solar energy. It converts solar energy into steam and then use it as heat source<sup>[18-19]</sup>. In 2017, Fu Yang used simple graphene oxide nanofluid and gold sol to mix gold nanoparticles into graphene oxide nanofluid to obtain gold/graphene oxide nanofluid. It is concluded that the photothermal conversion performance of GO nanofluids can be enhanced by adding Au nanoparticles<sup>[20]</sup>, which can also be seen from the experimental data in Figure 6. Fu Yang's research is of great significance to the development of thermoelectric materials using solar energy as a heat source.



**Figure 4:** Electrical conductivity (a), Seebeck coefficient (b), and power factor (c) of pure BiSbTe, 0.5 and 1.0 vol% MWCNTs/BiSbTe composites<sup>[16]</sup>



**Figure 5 :** Thermal conductivity (a) and figure of merit (b) of pure BiSbTe, 0.5 and 1.0 vol% MWCNTs/BiSbTe composites<sup>[16]</sup>



**Figure 6:** The temperature variation curve of different nanofluids with time

## 2. Nano-level adjustment to optimize polymer conductive materials

Traditional thermoelectric materials are inorganic semiconductor materials, such as bismuth telluride ( $\text{Bi}_2\text{Te}_3$ ), lead telluride ( $\text{PbTe}$ ), etc. However, these elements are scarce in the earth's crust, expensive, and some elements are toxic. These have seriously hindered its further industrial application. Therefore, people gradually shift their attention to organic polymer thermoelectric materials. Compared with inorganic thermoelectric materials, organic thermoelectric materials are not only richer in resources and have lower cost, but also have better electrical properties, mechanical properties, processability and environmental stability than semiconductor materials. The most important point is that the thermal conductivity of the matrix of organic thermoelectric materials is very low. It exhibits an order of magnitude lower thermal conductivity ( $0.05\sim 0.6\text{Wm}^{-1}\text{K}^{-1}$ ) than inorganic thermoelectric materials at room temperature<sup>[21]</sup>. Therefore, the optimization of organic thermoelectric materials is more realized by adjusting the conductivity and Seebeck coefficient.

At present, the nanocomposite method has been recognized as one of the best ways to improve the properties of materials. A good composite can combine the advantages of two or more materials, thereby effectively improving the thermoelectric properties of the material. For example, the use of carbon nanotubes (CNTs), graphene and other high-conductivity carbon nanoparticles combined with traditional insulating polymer matrix. This method can effectively combine the high electrical conductivity of carbon nanoparticles with the low thermal conductivity of the polymer matrix and excellent mechanical properties, thereby preparing composite materials with high thermoelectric properties and mechanical properties.

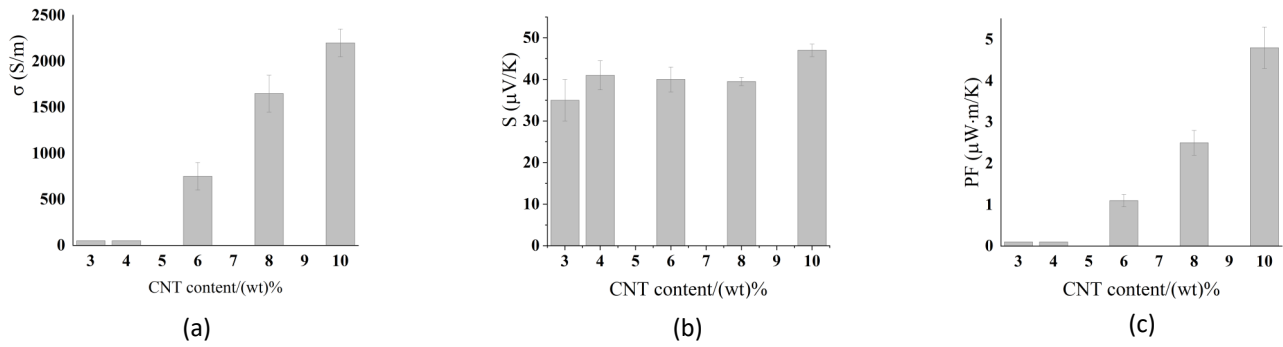
### 2.1 Carbon nanomaterials/polymer thermoelectric composite materials

The introduction of carbon nanomaterials into polymers to prepare composite materials can effectively improve the thermoelectric properties of the materials. CNTs have a very stable one-dimensional nanostructure with extremely high long-range electrical conductivity, and the macrostructure of the three-dimensional random network of CNTs has a very low thermal conductivity. When it is introduced into the polymer matrix, the thermoelectric properties of the material will be greatly improved.

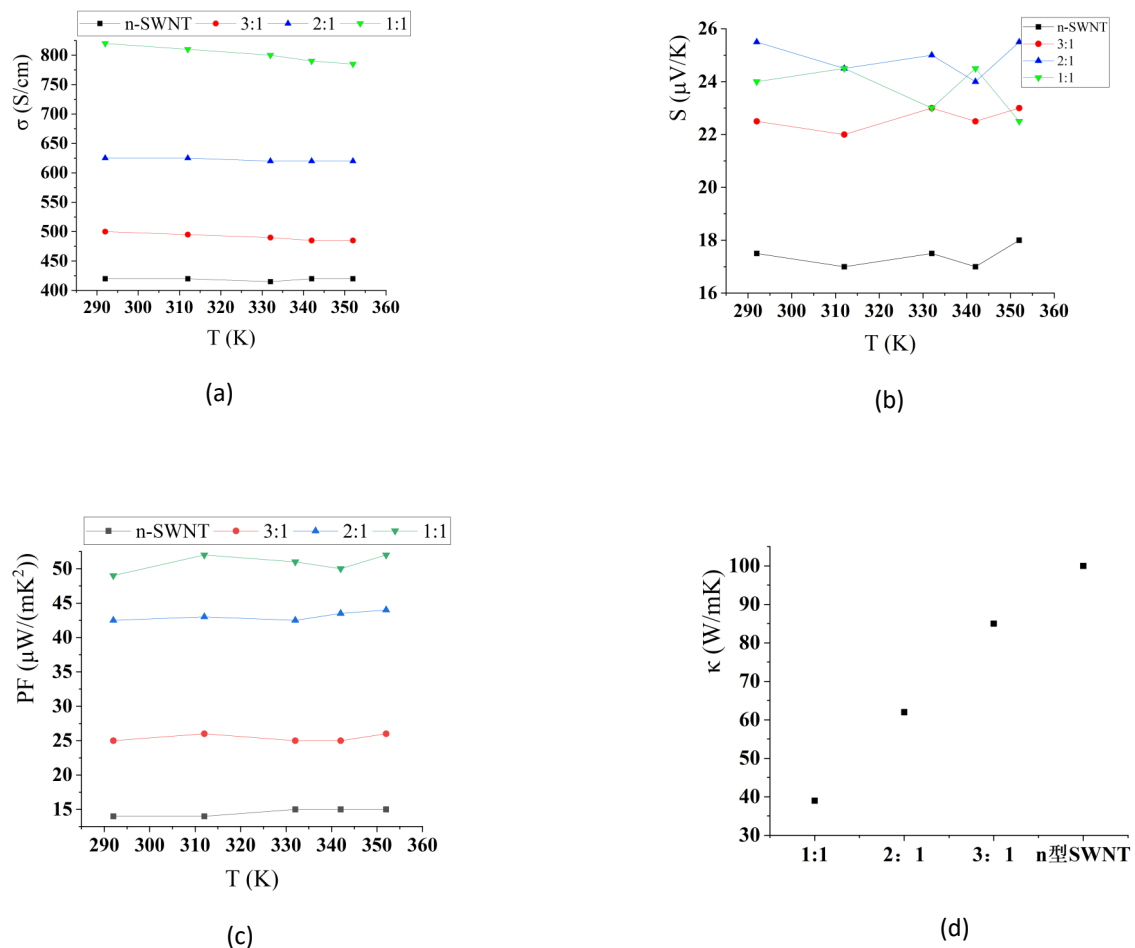
Kim et al.<sup>[22]</sup> found that adding carbon nanotubes to PEDOT:PSS can greatly increase the conductivity of PEDOT:PSS and has little effect on the Seebeck coefficient. The maximum thermoelectric figure of merit at room temperature is estimated to be 0.02. In 2020, Chen Jiliang of Handan Zhiyuan Middle School and Zhang Yichuan of the School of Materials Science and Engineering of Shenzhen University prepared a flexible PC/CNT composite with high thermoelectric properties, Figure 7 is a graph showing the dependence of the conductivity ( $\sigma$ ), seebeck coefficient ( $S$ ) and thermoelectric power factor ( $\text{PF} = S^2\sigma$ ) of the PC/CNT film on the content of CNTs. The conductivity of the PC/CNT composite material increases sharply with the increase of CNTs content, while the seebeck coefficient remains almost constant, making the power factor of the material increase rapidly with the increase of CNTs content, and the maximum power factor reaches  $4.6\mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ <sup>[23]</sup>. In 2019, Wu Ruili prepared the composite film SWCNT/EB-PANI of carbon nanotubes and polyaniline by vacuum filtration. The power factors at room temperature were  $328\mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$  and  $402\mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ . Compared with the composite film SWCNT/CSA-PANI composed with CSA-doped PANI and SWCNT under the same method, the increase is 71.2% and 81.2%. The SWCNT/CSA-PANI prepared by the vacuum filtration method is 40% and 90.6% higher than the composite prepared by the solution casting method. The power factor of the polymer of carbon nanotubes and polyaniline reaches the maximum when the SWCNT content is 60wt%,  $56\mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$  at room temperature, which is 28 times higher than that of pure PANI<sup>[24]</sup>.

It can be seen that the combination of carbon nanomaterials and polymers can improve the thermoelectric properties of the material, that is, doping other particles in the composite material can improve the thermoelectric properties of the composite material. This is a new method for preparing composite materials. This discovery in thermoelectric properties shows great potential for polymer development.

In 2017, Li Peng used polyethyleneimine (PEI) and diethylene triamine (DETA) to dope single-walled carbon nanotubes to prepare n-type carbon nanotube films, and at the same time made graphite oxide and carbon nanotubes in different proportions (3:1/2:1/1:1). The RGO/PANI/O-SWNT composite was prepared as a p-type thermoelectric film, which solved the problem of insufficient flexibility of nitrided RGO. Figure 8 obtained from the experiment shows that, relative to the RGO/PANI composite film, the increase in the proportion of O-SWNT increases the electrical conductivity and Seebeck coefficient of the composite, and the thermal conductivity is significantly reduced. Moreover, the power factor of the RGO/PANI/O-SWNT complex can reach up to  $50\mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ , which is 25 times higher than that of RGO/PANI. A thermoelectric device composed of 100 thermoelectric units can meet the normal operation of medical equipment hearing aids, which lays a solid foundation for the application of organic thermoelectric materials<sup>[25]</sup>.



**Figure 7:** The relationship between the electrical conductivity (a), Seebeck coefficient (b) and power factor (c) of PC/CNT film and the content of CNTs<sup>[23]</sup>



**Figure 8:** Conductivity (a), Seebeck coefficient (b), power factor (c), and thermal conductivity (d) of RGO/PANI/O-SWNT composite materials<sup>[25]</sup>



## 2.2 Graphene materials/polymer thermoelectric composite materials

Graphene has very good mechanical properties and thermoelectric properties, It also has high electrical conductivity. Graphene that has been specifically modified and cut has a high Seebeck coefficient. Therefore, the composite material of graphene material and polymer has both high Seebeck coefficient and electrical conductivity, as well as low thermal conductivity, which is a very promising thermoelectric material. Dohyuk et al.<sup>[26]</sup> used reduced graphene to increase the conductivity of PEDOT:PSS by 41%. Li et al.<sup>[27]</sup> explored the effect of reduced graphene oxide (rGO) on the thermoelectric properties of PEDOT:PSS thin films. The power factor of the composite membrane is  $32.6\mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ , which is 1.5 times that of the PEDOT:PSS membrane prepared by the same method. Xu et al.<sup>[28]</sup> prepared a PEDOT/reduced graphene oxide nanomaterial in a coated form by in-situ polymerization directly on the template. The power factor of this nanomaterial at room temperature is about  $5.2\mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ , which is 13.3 times that of pure PEDOT.

Xu et al.<sup>[29]</sup> also studied PEDOT/reduced graphene oxide composites synthesized by different preparation methods, namely (A) spin-coated and polymerized in liquid, (B) spin-coated and polymerized in vapor, (C) original After bit polymerization, it is immersed in ethylene glycol for post-treatment. The thermoelectric performance of the composite prepared by method (C) is the best, with a power factor of  $14.1\mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ , which is 10.8 times that of pure PEDOT. In 2015, Zhao<sup>[30]</sup> and others prepared graphene/multi-walled carbon nanotube (MWCNT) aerogels. In this aerogel, the Seebeck coefficient and conductivity can be enhanced at the same time. At the same time, due to its porous permeability The structure reduces the thermal conductivity of the composite system. In 2017, Fu Yang added gold nanoparticles to graphene oxide to improve the light-to-heat conversion performance of solar energy and increase the absorption capacity of the heat source part of the thermoelectric material, thereby indirectly enhancing the thermoelectric performance. In 2019, Guo Chunxi et al. studied the preparation of polyaniline/graphene paper thermoelectric materials and their performance by freezing grinding, and obtained polyaniline (PANI)/graphene paper (rGO) thermoelectric composite materials. When the composite content is 2.5wt% , The maximum value of ZT reached  $5.32\times 10^{-4}$ , an increase of 4.83 times<sup>[31]</sup>.

In 2019, Li Jia explored the preparation and performance of graphene, bismuth telluride, and PEDOT:PSS nanocomposite thermoelectric materials. The maximum power factor of the rGO/Bi<sub>2</sub>Te<sub>3</sub>/PEDOT:PSS composite bulk material containing 3-MPA with a pore-forming agent (NaCl) content of 10 wt% during pore formation is  $851\mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ <sup>[32]</sup>. In 2016, Zhang Ruixin introduced PEDOT-modified graphene microchips PEDOT-GN@PANS into polyaniline with high crystallinity. Subsequent addition of doping acid can significantly improve the thermoelectric properties of the composite material. Among them, the ZT value of the composite material is the largest when hydrochloric acid-sulfosalicylic acid is used as the doping acid. When the temperature is around 180°, the ZT value of the composite material can reach  $2.38\times 10^{-3}$ , which is 3.7 times the original PEDOT-GN@PANS composite material<sup>[33]</sup>. The composite film of graphene and polymer has high conductivity, high Seebeck coefficient and low thermal conductivity. Graphene, since its discovery of in 2004, has been attracting attention and has great development potential.

## 3. Conclusion

Based on nano-level adjustments, this article studies semiconductors and polymers separately, achieving the goal of reducing thermal conductivity through doping and using nano-level semiconductor materials, and ultimately improving thermoelectric performance. However, because of the extremely low thermal conductivity of the polymer itself, it is only necessary to start with the conductivity and the Seebeck coefficient to improve the thermoelectric merit of the polymer. Therefore, the polymer and the high-conductivity material are nano-composited to achieve the performance of the polymer optimization. No matter it is semiconductor materials or polymer composite materials, despite their difference, nanotechnology provides more possibilities for the development of materials, showing great advantages and potential. Whether it is for application or performance optimization, the development of thermoelectric materials will inevitably rely on nanotechnology to make greater breakthroughs.

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