ENHANCED ELECTRICAL CONDUCTIVITY IN GRAPHENE-BISMUTH TELLURIDE NANOCOMPOSITE FILM

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ABSTRACT: This study presents a novel method for synthesizing a bismuth telluride nanocomposite film with the inclusion of graphene nanoparticles. The process involves an electrodeposition technique, which has shown to improve the suspension and dispersion of N-Methyl-2-pyrrolidone (NMP) coated Graphene nanoparticles in the electrolyte solution. This leads to a more effective deposition of dispersed graphene nanoparticles in the nanocomposite film. The research successfully deposited up to 2.7 wt.% of graphene in the nanocomposite film, significantly reducing issues related to aggregated deposition. The inclusion of graphene nanoparticles in the bismuth telluride matrix has resulted in a substantial enhancement of the thermoelectric properties compared to the pristine bismuth telluride film. The most notable improvement is observed in the electrical conductivity of the nanocomposite film. The conductivity increased by over 200%, up to 1956.18 S/cm, when compared to the pure bismuth telluride film. This increase is attributed to the high electrical conductivity of the graphene nanoparticles. The findings of this research could have significant implications for the development of more efficient thermoelectric materials. Future work may focus on optimizing the graphene content and investigating the impact on other thermoelectric properties. This research represents a significant step forward in the field of thermoelectric materials, demonstrating the potential of graphene-bismuth telluride nanocomposites.

KEYWORDS: *Thermoelectric Film; Bismuth Telluride; Graphene; Electrodeposition; Nanocomposite*

1.0 INTRODUCTION

As the Internet of Things (IoT) continues to evolve and expand, the demand for efficient and sustainable power sources is becoming increasingly critical. These thermoelectric materials offer unique characteristics that make them particularly suitable for IoT applications. The efficiency of a thermoelectric material is quantified by a dimensionless parameter known as the figure of merit (ZT). A high ZT value indicates a material's superior ability to convert heat into electricity. This value is determined by three key factors: the Seebeck coefficient, electrical conductivity, and thermal conductivity. Specifically, a high ZT value requires a high Seebeck coefficient, high electrical conductivity, and low thermal conductivity.

Nanocomposites are essential for enhancing thermoelectric performance, particularly in terms of electrical conductivity. The inclusion of graphene demonstrates significant progress in enhancing thermoelectric performance, Wu et al. report the findings of their study on flexible thermoelectric devices that incorporate reduced graphene oxide (RGO)/Bi_2Te_3 hybrid films. The researchers highlight the notable enhancements in electrical conductivity achieved by optimising the planar orientation and network structure of the films. This configuration enables effective electron transportation, hence enhancing the power factor of the devices [1]. In addition, Pyun et al. examine the thermal contact conductance at the interface of graphene-Bi_2Te_3 heterostructures. The researchers discover that the enhanced thermal transport qualities at the interfaces lead to higher electrical conductivity by decreasing scattering and offering effective paths for electron migration [2]. Kulsi et al. conducted a study on the composites of Bi_2Te_3 with reduced graphene oxide (RGO). They discovered that greatly enhances the thermoelectric performance of these composites. Specifically, the Bi_2Te_3-RGO composite exhibits greater electrical conductivity and ZT value at room temperature [3].

Graphene greatly improves the performance of Bi_2Te_3 thermoelectric films principally by augmenting electrical conductivity, enhancing carrier mobility, and increasing carrier concentration. The remarkable electrical conductivity of graphene creates more routes for electron transportation within the Bi_2Te_3 structure, resulting in decreased resistance and enhanced electrical performance [4]. The high carrier mobility of the material allows charge carriers to flow more effectively, encountering fewer obstacles that can disperse them, hence increasing electrical conductivity. Moreover, graphene has the ability to function as a donor carrier, hence augmenting the quantity of charge carriers within the Bi_2Te_3 matrix [5]. The increased concentration of carriers immediately enhances the electrical conductivity and overall thermoelectric performance of the composite material. The combination of these effects makes graphene a potent addition to Bi2Te3 films, leading to a substantial improvement in thermoelectric efficiency.

2.0 METHODOLOGY

In this study, an electrolyte solution was prepared with 3.2 mM Bi^{3+} and 7.2 mM $HTeO_2+$ in HNO_3, and graphene nanoparticles were added at concentrations ranging from 0.3 to 1.3 g/ℓ. The solution was stirred and sonicated periodically to ensure optimal dispersion and suspension of the nanoparticles. A nanocomposite film was then synthesized on the working electrode at an applied potential of -0.09V using a potentiostatic electrodeposition system in a three-electrode cell. Prior to this, the graphene nanoparticles were coated with N-Methyl-2-pyrrolidone (NMP) and mixed and sonicated in diluted NMP for over two hours to ensure complete coverage of the nanoparticle surfaces by the polymer molecules. The material's surface morphology and elemental composition were analyzed using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX), respectively, and a 4-point probe measurement was conducted to assess its electrical conductivity.

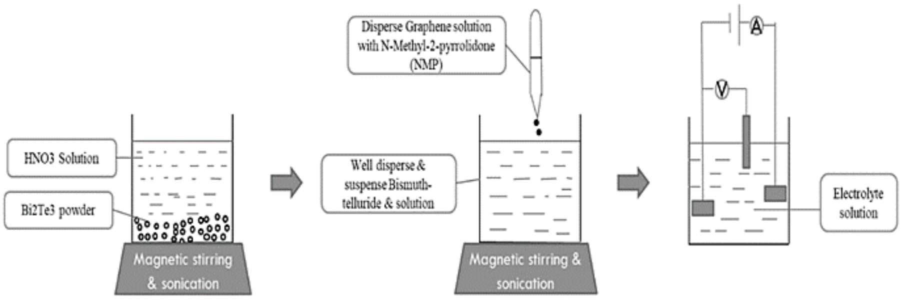


Figure 1: Overview of the electrodeposition process

3.0 RESULTS AND DISCUSSION

Figure 2 shows the improved graphene in bismuth-telluride and stable condition of graphene in the bismuth-telluride. NMP, being a polar aprotic solvent, can effectively interact with graphene sheets and suppress their aggregation. When graphene is combined with NMP and subjected to sonication, the NMP molecules attach to the graphene sheets, resulting in a steric barrier that inhibits the sheets from merging and forming aggregates. This leads to an enhanced dispersion of graphene in the electrolyte solution [6]. When the graphene nanoparticles achieved good dispersion and suspension, it increased the stability of the electrolyte and lessened the impact of the Van de Waals attraction force between the nanoparticles.

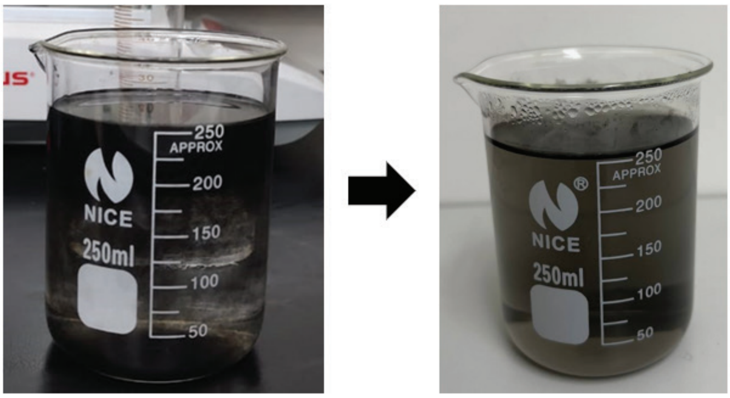
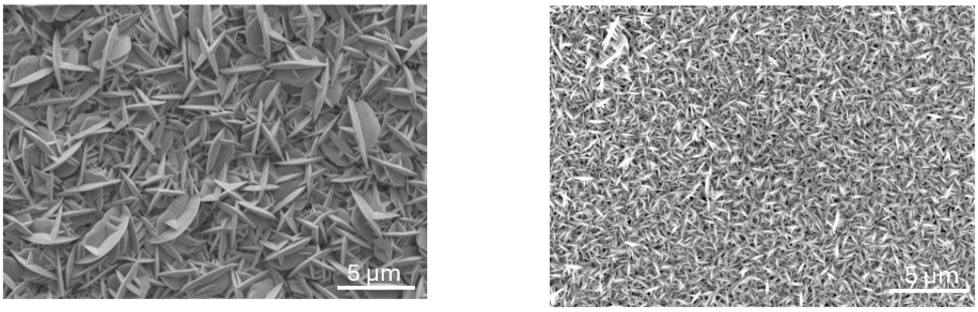


Figure 2: Improved graphene in electrolyte solution

The morphological analysis was conducted to study the microstructure of the pristine bismuth-telluride and graphene inclusion bismuth-telluride. The inclusion of graphene was affecting the microstructure of the pristine Bi_2Te_3. Figure 3 (a) displays an electrodeposited film growing normally, pristine Bi_2Te_3 microstructure is known as a plate-like structure or a needle-like structure. The micro-structure of the nanocomposite films with different amounts of graphene, as seen in the image, has the characteristic needle-like shape but is much smaller than the microstructure size, giving it the same appearance. The addition of graphene to Bi_2Te_3 resulted in a change in size that had an impact on the microstructure's size. The microstructure size of inclusion of graphene gradually becomes smaller when compere to each other. When the microstructure decreases the gap between it causes an increase in porosity. It evidently can compete with figures 3 (a) and (b). In figure 3 (a) the needle-like structure packs very closely and there is low porosity when compared to the smaller structure size in figure (b).



(a) Bi_2Te_3 (b) 2.7 wt. % graphene/Bi_2Te_3

Figure 3: Electrodeposited film surface images captured by SEM
(a) Bi_2Te_3; (b) 2.7 wt. % graphene/Bi_2Te_3.

According to Hosseini et al., porosity in the thermoelectric (TE) material will increase the *ZT* value by decreasing the thermal conductivity [7]"ISSN":"25740962","abstract":"The addition of porosity to thermoelectric (TE. However, the porosity will have a negative side effect on the TE power factor in the numerator of the figure of merit, *ZT* but the effect can be covered by a vast number of electron density in graphene. The lower porosity might not affect the overall thermoelectric performance since it did not significantly modify the electrical to thermal conductance ratio due to the increment of both properties.

Table 1 summarizes the composition of the elements in the deposited Graphene-Bi_2Te_3 nanocomposite films with the respective electrolyte used in the study. There are four electrolyte solutions that were distinguished by the amount of graphene that were blended. These included an electrolyte that did not include any graphene at all, which was used to produce the pristine Bi_2Te_3 film. Another three electrolytes comprised of the inclusion of graphene up to 1.3 gL^{-1} in the electrolyte solution. Using average values from an EDX measurement system, the amount of co-deposited graphene in the nanocomposite film was evaluated as C-wt.%. Up to 2.7% graphene has successfully been deposited in the nanocomposite film with fewer issues compared to the aggregated deposition. There is a pattern where the graphene content starts from sample two to four gradually increases. Which show that as graphene increases in electrolyte, the composition carbon rate in the deposited film also increases. The nanomaterial content in bismuth telluride, synthesis nanocomposites deposited films will be optimized, increased the electrical conductivity, and reduced the effect of Seeback coefficient reduction.

Table 1: Result of Energy Dispersive X-Ray

Electrolyte	**Graphene content in electrolyte (gL^{-1})**	**Electrodeposited film**	**Composition in the deposited film**		
			Graphene (wt%)	**Bi:Te (at%)**	**Atomic percentage error due to Bi_2Te_3 phase ratio (%)**
1	0.0	Bi_2Te_3	0.00	40:60	0
2	0.3	Graphene/ Bi_2Te_3	1.2	42:58	± 2
3	0.8	Graphene/ Bi_2Te_3	1.6	37:63	± 3
4	1.3	Graphene/ Bi_2Te_3	2.7	42:58	± 2

As shown in Figure 4, the inclusion of graphene into Bi_2Te_3 thermoelectric films greatly enhances their electrical conductivity, owing to the remarkable features exhibited by graphene. The highest electrical conductivity that has been achieved in this study was at 1956.18 S/cm from the 2.7wt% graphene-bismuth telluride deposited film. It was an increase of more than 200% compared to the pristine bismuth telluride at 618.65 S/cm.

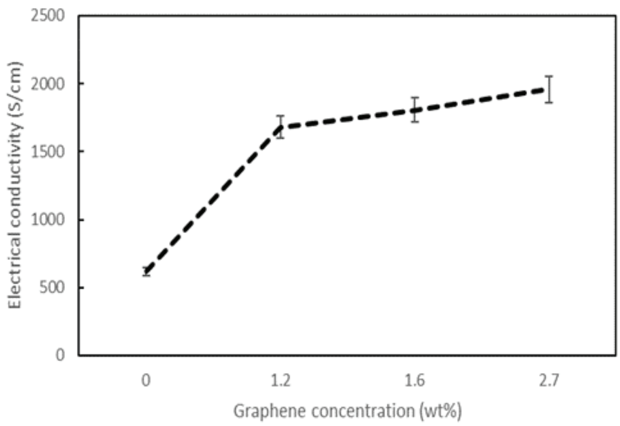


Figure 4: Result of electrical conductivity of deposited films

The high electrical conductivity of graphene creates additional pathways for electron transport in the Bi_2Te_3 matrix, resulting in reduced resistance and improved overall electrical performance. Moreover, the two-dimensional structure of graphene guarantees exceptional carrier mobility, enabling electrons to navigate the material with little dispersion, hence enhancing electrical conductivity. Moreover, graphene could function as a donor of carriers, thereby introducing additional charge carriers into the Bi_2Te_3 matrix and subsequently elevating the concentration of carriers. This, in turn, leads to an enhancement in electrical conductivity [2][8]. The combination of these features renders graphene a highly effective additive for enhancing the performance of Bi_2Te_3 thermoelectric films.

4.0 CONCLUSION

This study presents a novel technique for fabricating bismuth telluride nanocomposite films inclusion graphene nanoparticles. The utilization of the electrodeposition approach has demonstrated its effectiveness in improving the dispersion of graphene nanoparticles in the electrolyte solution, resulting in a more efficient deposition process. The research effectively resolved problems associated with aggregated deposition by introducing graphene at a concentration of up to 2.7 wt.% in the nanocomposite film. The addition of graphene nanoparticles to the film led to a substantial improvement in its thermoelectric properties, particularly a more than 200% rise in electrical conductivity, which can be attributed to the excellent conductivity of the graphene nanoparticles. These discoveries present new opportunities for the advancement of thermoelectric materials with enhanced efficiency. Further investigation could concentrate on enhancing the graphene concentration and investigating its influence on additional thermoelectric characteristics, representing a notable progression in the realm of thermoelectric materials by showcasing the potential of graphene-bismuth telluride nanocomposites.

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REFERENCES

[1] B. Wu, Y. Guo, C. Hou, Q. Zhang, Y. Li, and H. Wang, "High-Performance Flexible Thermoelectric Devices Based on All-Inorganic Hybrid Films for Harvesting Low-Grade Heat," *Adv. Funct. Mater.*, vol. 29, no. 25, 2019, doi: 10.1002/adfm.201900304.

[2] K. R. Pyun *et al.*, "Interfacial Thermal Contact Conductance inside the Graphene–Bi2Te3 Heterostructure," *Adv. Mater. Interfaces*, vol. 6, no. 11, pp. 1–10, 2019, doi: 10.1002/admi.201900275.

[3] C. Kulsi, M. Mitra, K. Kargupta, and D. Banerjee, "Thermoelectric properties of nanostructured bismuth telluride (Bi2Te3) with annealing time and its composite with reduced graphene oxide (RGO)," *J. Mater. Sci. Mater. Electron.*, vol. 30, no. 2, pp. 1850–1860, 2019, doi: 10.1007/s10854-018-0457-3.

[4] R. R. K. Kumar, Sunil; Singh, Simrjit; Dhawan, Punit Kumar; Yadav, "Effect of graphene nanofillers on the enhanced thermoelectric properties of Bi2Te3 nanosheets: elucidating the role of interface in de-coupling the electrical and thermal characteristics," *Nanotechnology*, vol. 29, 2018.

[5] M. A. Alias *et al.*, "Electrodeposited Bismuth Telluride Nanocomposite Thermoelectric Film with Improved Graphene Deposition," *J. Adv. Res. Appl. Mech.*, vol. 111, no. 1, pp. 161–172, 2023, doi: 10.37934/aram.111.1.161172.

[6] W. Zhao *et al.*, "Surfactant-free stabilization of aqueous graphene dispersions using starch as a dispersing agent," *ACS Omega*, vol. 6, no. 18, pp. 12050–12062, 2021, doi: 10.1021/acsomega.1c00699.

[7] S. A. Hosseini, G. Romano, and P. A. Greaney, "Mitigating the Effect of Nanoscale Porosity on Thermoelectric Power Factor of Si," *ACS Appl. Energy Mater.*, vol. 4, no. 2, pp. 1915–1923, 2021, doi: 10.1021/acsaem.0c02640.

[8] B. Wu, Y. Guo, C. Hou, Q. Zhang, Y. Li, and H. Wang, "High-Performance Flexible Thermoelectric Devices Based on All-Inorganic Hybrid Films for Harvesting Low-Grade Heat," *Adv. Funct. Mater.*, vol. 29, no. 25, pp. 1–11, 2019, doi: 10.1002/adfm.201900304.