

IMPROVED CELLULOSE NANOFIBER-GRAPHENE/ Bi_2Te_3 NANOCOMPOSITES FILM SYNTHESIS BY ELECTROCHEMICAL DEPOSITION WITH CNF-PDDA COATING

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ABSTRACT: This paper presents a method to synthesize a new bismuth telluride nanocomposite film by including graphene and cellulose nanofiber through an electrodeposition process. A significant challenge in this process was the formation of cracks in the films due to excessive polymer content from poly (diallyldimethylammonium chloride) (PDDA) coating on CNF. This study found a significant improvement in the integrity of the film's structure when 1.5 ml of PDDA was used for coating the CNFs, the resulting films exhibited no cracks, maintaining their structural integrity and enhanced thermoelectric properties. An adequate PDDA solution is crucial for developing robust, high-performance thermoelectric materials for potential waste heat recovery and power generation applications. The inclusion of cellulose nanofibers increased the carbon content of the Bi_2Te_3 /graphene film. The carbon content increased from 1.6 wt.% in the baseline film to 3.7 wt.% and 5.57 wt.% for films with 1 g/L and 2 g/L CNF, respectively. This clearly demonstrates the substantial influence of CNFs on the composition and performance of the composite. The reduced volume of PDDA coated with CNF effectively reduced the issues with film brittleness.

KEYWORDS: Thermoelectric film; Electrodeposition; Nanocomposite; Cellulose Nanofiber (CNF); Graphene

1.0 INTRODUCTION

Thermoelectric generators (TEGs) are a very promising technology that directly turns waste heat into electricity and is one of the crucial initiatives in tackling the worldwide energy crisis and environmental issues. The overall performance of a thermoelectric (TE) material can be analyzed by figure of merit (ZT), and a high ZT value involves a combination of a high Seebeck coefficient, high electrical conductivity, and low thermal conductivity [1]. Nanocomposites are essential for enhancing thermoelectric performance, particularly in terms of electrical conductivity. Furthermore, utilizing the nanocomposite method can yield advantages regarding mechanical qualities. [2].(Ahmad & Almutairi, 2023) prove that including multi-wall carbon nanotubes (MWCNTs) enhanced the composites' electrical conductivity, Seebeck coefficient, and power factor [3]. This resulted in a considerable improvement in the thermoelectric figure of merit of the composites by 10% compared to the pure Bi_2Te_3 . Besides that, (Nour et al., 2023) emphasize that incorporating reduced graphene oxide (RGO) and carbon nitride ($\text{g-C}_3\text{N}_4$) into the bismuth telluride (Bi_2Te_3) matrix as nanocomposites has been proven to improve thermoelectric performance through several ways [4]. The ZT values of these nanocomposites exhibited a notable rise compared to the pure Bi_2Te_3 , suggesting a significant improvement in thermoelectric performance.

The inclusion of Cellulose nanofiber (CNF) and graphene could provide the same benefits as other carbon-based nanomaterial in thermoelectric nanocomposites by increasing electrical conductivity, decreasing thermal conductivity, and improving mechanical properties at

the same time [5]. The simultaneous use of Cellulose nanofiber (CNF) and graphene in thermoelectric nanocomposites can yield advantages similar to those of other carbon-based nanomaterials. This includes enhancing electrical conductivity, reducing thermal conductivity, and simultaneously enhancing mechanical characteristics. Adding Graphene nanoparticles to Bi_2Te_3 film enhances its electrical conductivity by enhancing charge carrier mobility. Furthermore, the presence of CNF improves the film's mechanical characteristics, particularly micro-hardness and young modulus. This study presents a novel advancement in the fabrication of a Bi_2Te_3 nanocomposite film by incorporating CNF/graphene nanoparticles using electrodeposition. There is a lack of comprehensive information regarding the synthesis technique, particularly with the previous deposition process used in electrolyte preparation to address the issue of crack formation in the film. This work also examines the impact of the polymer of CNF nanoparticles on the deposition process.

2.0 METHODOLOGY

The electrolyte solution prepared in this study consists of 3.2 mM Bi^{3+} and 7.2 mM HTeO_2^+ in HNO_3 . The electrolytes used for the deposition of nanocomposite films were prepared with a mixture of 0.75g/L graphene nanoparticles and CNF (2 g/ L). The mixing process underwent rigorous stirring conditions and was sonicated intermittently to ensure the optimum result of the graphene/CNF nanoparticles dispersion and suspension in the electrolyte solution. The synthesized nanocomposite film on the working electrode was established at -100mV of the applied potential in the three-electrode cell of the potentiostatic electrodeposition system. Before these processes, the CNF nanoparticles were coated with the Poly (diallyl dimethylammonium chloride) (PDDA). The nanoparticles were mixed and sonicated in the diluted PDDA to ensure the polymeric molecules fully covered the nanoparticle's surface. Then, the CNF nanoparticles in the PDDA solution went through the filtration process to filter the excessive PDDA solution. The surface morphology and element composition were analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX).

3.0 RESULTS AND DISCUSSION

The synthesis of cellulose nanofiber CNF/graphene-bismuth telluride (Bi_2Te_3) nanocomposite films faces a significant challenge in avoiding cracks during the deposition process, owing to the high polymer content of poly (diallyldimethylammonium chloride) (PDDA), which is used to coat the CNFs during the filtration process. Table 1 depicted the correlation between reducing the quantity of PDDA utilised to coat the CNF and the mitigation of cracking in the resultant film. When a significant quantity of PDDA (10ml) [6] was mixed with 2g of CNF, the films experienced fracturing irrespective of the amount of distilled water added. Therefore, a high PDDA concentration can result in cracks forming in the final film. The elevated concentration of PDDA is the probable explanation for creating a dense polymer layer that is prone to distortion and fracturing when the film is formed.

The films remained susceptible to cracking even when the quantity of PDDA was decreased to 5ml and 2.5 ml while maintaining the same amount of CNF and introducing 500ml of distilled water. This indicates that even small amounts of PDDA can disrupt the film's integrity. Nevertheless, when the dosage of PDDA was reduced to 1.5ml, accompanied by 2g of CNF and 500 ml of distilled water, the resulting film exhibited no cracks, as depicted in Figure 1. This demonstrates that maintaining an optimal ratio of PDDA to CNF is crucial to attaining a stable and devoid-of-cracks film structure. The study additionally discovered that reducing the dosage of CNF to 1g, while keeping PDDA at 1.5 ml and distilled water at 500 ml, led to the formation of a film without any cracks. This suggests that the proportion of PDDA to CNF is a more significant factor than the overall quantity of CNF in the prevention of cracking. The main factor responsible for this observation is the reduction in PDDA content

of the CNF, which enhances the quality of the polymer coating. This leads to a more consistent and durable film structure that is less likely to rupture during the deposition process [7,8]. An excessive amount of poly (diallyldimethylammonium chloride) (PDDA) may result in the creation of a thick and easily shaped layer that is likely to develop cracks. On the other hand, a lower amount of PDDA enables a more even distribution and integration of cellulose nanofibrils (CNF) in the film.

Table 1: Amount of PDDA content to prevent crack films.

NO	CNF (g/L)	PDDA (ml)	Film Condition
1	2	10	Crack
2	2	5	Crack
3	2	2.5	Crack
4	2	1.5	No Crack
5	1	1.5	No crack

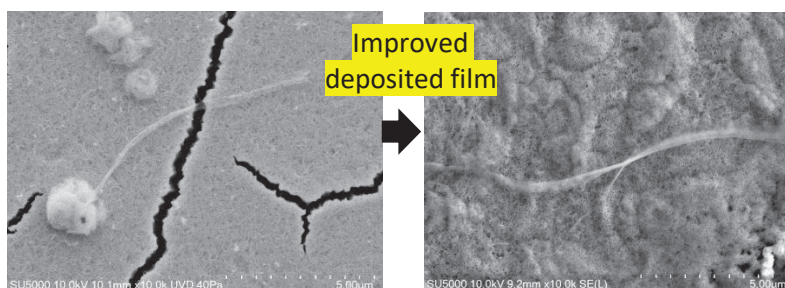


Figure 1 The improved film of CNF-Graphene/Bi₂Te₃

Table 2 shows the elemental composition found in graphene-CNF/Bi₂Te₃ nanocomposite films. The composition has been examined by Energy Dispersive X-ray Spectroscopy (EDX). The nanocomposite film has a maximum weight percentage of CNF-wt.% of 5.57%. The Bi/Te atomic ratio remained rather constant in the presence of various quantities of CNF nanoparticles, and the atomic percentage error, based on the stoichiometric ratio of the Bi₂Te₃ phase, was consistently below 3%. Based on the ideal ratio of Bi₂Te₃ (40:60), the atomic percentage error for the Bi-Te ratio was found to be quite acceptable, with such an error amounting to no more than three percent. It is recommended that the ratio fluctuation of Bi-Te should not exceed 5% error from the pristine one. This is done to prevent any potential ratio factor from affecting TE performance.

Table 2: The elemental composition found in graphene-CNF/Bi₂Te₃ nanocomposite films.

Electrolyte	Graphene Content in electrolyte (g/L)	Cellulose nanofiber (CNF) content in electrolyte (g/L)	Electrodeposited film	Composition in the deposited film		
				Carbon (wt%)	Bi: Te (at%)	Atomic percentage error due to Bi ₂ Te ₃ phase ratio (%)
I		0	Bi ₂ Te ₃ /Graphene	1.6	37:63	±3
II	0.75	1	Bi ₂ Te ₃ /Graphene (0.75 wt%) -CNF (3.80wt%)	3.8	42:58	±2
III		2	Bi ₂ Te ₃ /Graphene (0.75 wt%) -CNF (5.57wt%)	5.57	43:57	±3

4.0 CONCLUSION

This study utilized electrochemical deposition to synthesis nanocomposite films consisting of CNF-Graphene/Bi₂Te₃. The resulting films exhibited enhanced crack resistance. The deposited films contained up to 5.57 wt.% of CNF nanoparticles, effectively reducing issues with film brittleness. Ultimately, reducing the volume of PDDA to 1.5ml was essential to effectively prevent film cracking. The polymer content was optimized to achieve efficient dispersion and stabilization of CNF, while simultaneously reducing film cracking resulting from brittleness. The optimization process enhanced the mechanical strength and performance of the CNF/graphene – Bi₂Te₃ nanocomposite films.

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