



In-situ synthesis of flexible hybrid composite films for improved thermoelectric performance

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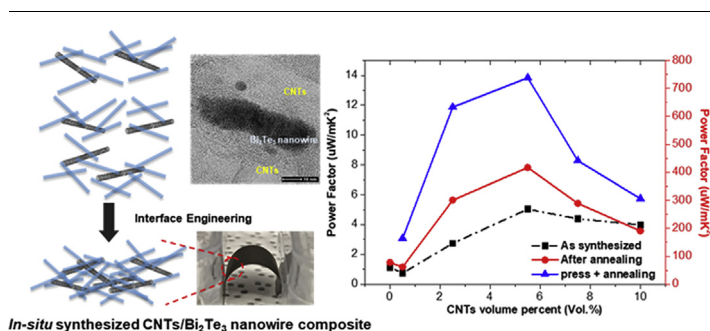
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HIGHLIGHTS

- CNTs/ Bi₂Te₃ nanowires composite was fabricated using a simple *in-situ* synthesis.
- The electric transport enhanced by mechanical pressing and post-annealing.
- Electron energy filtering occurred at newly created interfaces by densification.
- Annealing process led to making high crystalline phase and stoichiometry of Bi₂Te₃.
- The composite has a high thermoelectric power factor with superior flexibility.

GRAPHICAL ABSTRACT



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ABSTRACT

Thermoelectric (TE) materials and devices, which enable direct conversion of thermal energy into electricity and vice versa, are a favorable technology for waste heat recovery and flexible energy generators and coolers. Here, we report the enhanced thermoelectric properties of flexible hybrid films composed of carbon nanotubes (CNTs) with good electrical and mechanical properties and inorganic nanowires with high Seebeck coefficient synthesized through an *in-situ* facile solution method. A two-step interface engineering process is applied to the flexible composite aiming to enhance thermoelectric properties: (1) Bi₂Te₃ nanowires are grown from the surface of uniformly dispersed CNTs by *in-situ* synthesis, and (2) a mechanical pressing and a post heat-treatment were employed to form tight interface bonding and adjust the nanowires close to stoichiometric composition. Impressively, the CNTs/Bi₂Te₃ nanowires composite films exhibited a peak TE power factor of approximately 0.74 mW m⁻¹K⁻² at room temperature along with admirable flexibility. The Seebeck coefficient and electrical conductivity were improved by a factor of 30 and 2.2, respectively, through mechanical pressing and post-annealing. This increase is attributed to the phase homogenization of inorganic nanowires to its stoichiometric phase and electron filtering effects due to enhanced interfaces both qualitatively and quantitatively. The flexibility and retention of the conductivity were evaluated via two different methods. This composite with high TE performance will be utilized to create flexible thermoelectric devices for energy harvesting. In addition, the findings from this study can be applied to other flexible thermoelectric materials systems to enhance thermoelectric properties.

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1. Introduction

Thermoelectric (TE) conversion, which enables direct generation between electricity and heat, is a simple and environmentally friendly energy-conversion technology for waste heat recovery and solid-state heating/cooling applications [1]. However, most TE devices are currently fabricated by costly and inefficient inorganic material processing methods, which has retarded their development for practical use. To employ cost-effective manufacturing technologies, such as printing techniques, flexible TE materials with a high TE figure of merit (i.e., ZT value) are required [2–4]. These properties are also important for the realization of wearable self-powered mobile electronics [3–5]. Utilizing TE materials for wearable electronics requires high mechanical and electrical stability while undergoing repeated tensile and compressive strains as well as bending cycles.

The enhancement of TE properties for energy conversion at room temperature have been observed in materials based on bismuth telluride (Bi_2Te_3) by taking advantages of its narrow energy bandgap and layered crystal structure [6,7]. Bi_2Te_3 has a layered rhombohedral structure characterized by Bi in octahedral coordination with Te, and a van der Waals gap separating five-atomic-layers of the type Te–Bi–Te–Bi–Te [8]. In the Bi_2Te_3 phase diagram, a wide solid solubility region exists on both sides of the intrinsic stoichiometric composition. [9–11]. The deviations from stoichiometry in this region are adapted by native point defects, which are electrically and thermally active [12]. Even small variation in stoichiometry due to native point defects have a strong effect on the charge carrier type and mobility and consequently on the thermoelectric properties [12–15]. To clarify further, the majority carrier type of Bi_2Te_3 (n-type or p-type) is dependent on how much excess Bi or Te exists in the material. For this reason, Bi_2Te_3 crystals tend to have anti-structure defects in which excess Bi atoms are found on Te sites [16]. As a result, the TE properties of Bi_2Te_3 are shown to be strongly dependent on their stoichiometry [9,17].

Since the effect of the low-dimensional materials were proposed [18], nanostructured TE materials have been studied extensively [19–22]. Low-dimensional materials show a significantly lower thermal conductivity without sacrificing the electrical conductivity due to the ability to tailor electron and phonon transport [18,23].

The strategy in this study was to create a new TE composite material composed of a Bi_2Te_3 -nanowire matrix with a homogeneous dispersion of carbon nanotubes (CNTs) through *in-situ* synthesis to enhance thermoelectric properties. Most prior studies into synthesis-based thermoelectric materials have developed the composite by *ex-situ* synthesis, meaning the dispersion of pre-made materials are introduced directly into a matrix to form the composite [24–26]. Compared to *ex-situ* synthesis, *in-situ* synthesis is a simple and effective one-step fabrication process. This method is beneficial for a uniform distribution of the CNTs, a cleaner interface, and stronger interfacial bonding between CNTs and other materials within the composites [27,28].

CNTs have extraordinary electrical, mechanical, and geometrical properties [29,30]. Moreover, the interconnected network of CNTs can provide a mechanical skeleton increasing mechanical strength and toughness while also benefiting from the CNTs very high electrical conductivity, even when using a minimum concentration of CNTs in a composite material. Thus, CNTs are expected to be suitable for implementation into a nanostructured matrix of TE materials [31]. Studies have shown that nano-sized dispersoids can be successfully embedded into a TE bulk matrix, resulting in an increase of the ZT value in TE systems [32–35]. Phonon scattering at newly formed dispersoid and matrix boundaries are believed to reduce the thermal conductivity in composite materials [36,37] while the Seebeck coefficient is enhanced due to electron energy filtering effect caused by electron scattering [33,36,37]. The electron energy filtering effect is caused by the scattering of electrons due to band bending at the interfaces between nano-sized dispersoids inclusions and the TE host material which produces a potential barrier. As a result, it could preferentially scatter the lower

energy electrons, as demonstrated in other host matrix-nanoinclusion composite systems [32,38–41]. In addition, post-synthesis annealing has been used to increase the ZT values further, which is known to have favorable effects on the ZT values of bismuth-telluride bulk compounds [42,43].

This paper discusses the interface engineering of a flexible n-type TE material composed of Bi_2Te_3 nanowires and CNTs, using a feasible *in-situ* synthesis process. The effects of mechanical pressing and annealing of this material on thermoelectric performance are examined. The maximum TE power factor of the composite films is enhanced up to $0.74 \text{ mW m}^{-1}\text{K}^{-2}$, an increase by a factor of 30 when compared to the as-synthesized composite. This is due to a combination of improved Seebeck coefficient and increased electrical conductivity. The introduction of CNTs into Bi_2Te_3 nanowires not only enables a dramatically enhanced TE power factor but also allows for increased flexibility. In this material system, single-walled carbon nanotubes (SWCNTs) provide carrier transport paths helping to increase electrical conductivity. The dispersion of SWCNTs forms new interfaces in the Bi_2Te_3 -nanowire matrix and introduces scattering barrier defects that cause low-energy electron scattering, resulting in an improved Seebeck coefficient [19]. Mechanical pressing and post-heat treatment are employed to form tight interface bonding as well as to adjust the Bi_2Te_3 composition close to the stoichiometric composition. In addition, the composite films exhibit admirable flexibility properties with negligible changes in electrical resistance after repeated bending cycles.

2. Material and methods

2.1. *In-situ* synthesis of a CNTs/ Bi_2Te_3 nanowire composite

The CNTs/ Bi_2Te_3 nanowire composite using single-wall structured CNTs (95% purity, Sigma-Aldrich) was fabricated by a two-step solution phase reaction by first growing Te nanowires followed by Bi diffusion into the Te nanowires to form the Bi_2Te_3 nanowires. The various proportions of CNTs (0.5–10 vol% (vol%) in 10 mL of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$, 99%, British Drug Houses) were dispersed homogeneously using tip sonication for 1 h. The CNT suspension was supplemented with 1.1 g of tellurium (IV) dioxide (TeO_2 , 99% Sigma-Aldrich) as a metal precursor, 2.3 g of polyvinylpyrrolidone (PVP, MW = ~40,000, Sigma-Aldrich) as a surfactant, and 2.1 g of potassium hydroxide (KOH, 93%, Sigma-Aldrich) for pH adjustment. 60 mL of ethylene glycol was added and stirred until the powders were dissolved.

The mixed solution was heated to 120°C , and then 2.3 mL of hydrazine monohydrate ($\text{N}_2\text{H}_2\cdot\text{H}_2\text{O}$, 98%, Tokyo Chemical Industry Co.) was injected into the solution for synthesizing the Te nanowires on the surfaces of the CNTs. For the Bi precursor solution, 2.3 g of bismuth (III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$, 98%, Sigma-Aldrich) and 0.45 g of PVP were dissolved into 15 mL of ethylene glycol separately. After 40 min of heating to create the Te nanowires, the as-prepared Bi precursor solution and 2.3 mL of hydrazine monohydrate (N_2H_4) were injected into the as-prepared CNT/Te nanowire solution to complete the synthesis of CNTs/ Bi_2Te_3 nanowires. After an additional 40 min of heating, the synthesized CNTs/ Bi_2Te_3 nanowire solution was obtained. The hydrazine - ethanol mixture (10 vol% hydrazine monohydrate) was added into the final solution and stirred overnight to remove surfactant (PVP) at room temperature [17,25]. The precipitates were collected by centrifugation at 9000 rpm and purified with ethanol ($\text{C}_2\text{H}_6\text{O}$) and 10 vol% hydrazine monohydrate.

The final product was re-dispersed into ethanol with 10 vol% hydrazine monohydrate to prevent oxidation. The mixture was vacuum-filtered through a polytetrafluoroethylene (PTFE) membrane with a pore size of $0.45 \mu\text{m}$ (Cole Parmer Inc.), and dried in a vacuum. The composite film was gently peeled off the membrane and, in succession, post-annealed at 300°C for 2 h in an ambient pressure tube furnace with flowing argon (Ar) gas. The film consisting of only Bi_2Te_3 nanowires (i.e., 100% Bi_2Te_3 + 0% CNTs) were fabricated using the same

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