



# Preparation and thermoelectric properties of two types of nanostructured tellurium with multi-walled carbon nanotubes

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## ABSTRACT

Two types of MWCNT/Te nanostructure composites with two different types of Te particles (powder and nanorods) and various MWCNT contents were synthesized and their thermoelectric properties were analyzed. Te powder was prepared by ball-milling Te beads and Te nanorods were synthesized by PVP-assisted solution-phase mixing. The highest power factor was achieved with 2 wt% of MWCNTs in both types of MWCNT/Te composites, attributed to the extremely high electrical conductivity of the MWCNTs. Above 2 wt%, the low Seebeck coefficient of the MWCNTs caused a decrease in the power factor. Additionally, the introduction of the MWCNTs into the Te matrix reduced the thermal conductivity of the composite by generating numerous boundaries. The maximum thermoelectric figure of merit ( $ZT$ ) (0.0037 at room temperature) is achieved with 2 wt% of MWCNTs in the MWCNT/Te nanorod composites; this value is larger than the  $ZT$  values of pure Te and the MWCNT/Te powder composite.

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## 1. Introduction

Green and renewable energy sources have attracted much attention because of concerns of environmental pollution and limited carbon-based fossil fuels. Thermoelectric (TE) materials, which can generate electricity by harnessing the waste heat and may be used as solid-state cooling devices, have recently attracted significant interest because of their great potential to offer improved energy efficiency for energy harvesting [1–3]. The performance of TE materials is evaluated based on the figure of merit,  $ZT = S^2\sigma T/\kappa$ , where  $S$  is the Seebeck coefficient,  $\sigma$  is the electrical conductivity,  $\kappa$  is the thermal conductivity, and  $T$  is the absolute temperature. So far, considerable efforts have been dedicated to enhancing the figure of merit values in other existing classes of TE materials including half-Heulelers [4], lead telluride [5], and germanium telluride [6]. In general, a high power factor ( $PF = S^2\sigma$ ) and low thermal conductivity are the requisite factors for achieving a high  $ZT$ . A high power factor is generally achieved by enhancing the Seebeck coefficient or the electrical conductivity of the material. The  $S$  value of a material is generally considered to be inversely proportional to the carrier concentration  $\eta$ , represented by the following relatively simple model of electron transport,

$$S = \frac{8 \cdot \pi^2 \cdot k_B^2}{3 \cdot e \cdot h^2} \cdot m^* \cdot T \cdot \left( \frac{\pi}{3 \cdot \eta} \right)^{\frac{2}{3}}$$

Here,  $k_B$  is the Boltzmann constant,  $h$  is the Planck constant, and  $m^*$  ( $m^* = 0.58m_e$  [7–9], where  $m_e$  is the electron rest mass). From this viewpoint, it can be seen that the Seebeck coefficient increases as the carrier concentration decreases.

Low thermal conductivity can be achieved by nanostructuring thermoelectric materials. Nanostructured materials have a large number of phonon scattering sites that scatter phonons more efficiently than their bulk counterparts, which significantly decreases the thermal conductivity [10–12]. There are two methods of fabricating nanostructures, namely, bottom-up and top-down techniques. The top-down methods being with a bulk solid that is subjected to structural decomposition by techniques such as ball milling to produce a nanostructure. In contrast, the bottom-up methods utilize the growth of atoms to generate a nanostructure. Atoms create building blocks that are subsequently assembled into nanostructures. Xu et al. [13] achieved a significant decrease in the thermal conductivity with a nanostructured BiSbTe alloy via hot deformation of ingots using a top-down method. Yang et al. [14] prepared Bi<sub>2</sub>Te<sub>3</sub> nanoflakes via a bottom-up method and demonstrated their remarkably lowered thermal conductivity. In addition to low thermal conductivity, a large power factor is another significant factor that is required to achieve high thermoelectric

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performance.

Using materials with a high Seebeck coefficient is one of the simplest strategies to achieve a high power factor. Recent studies have mainly focused on high-efficiency inorganic thermoelectric materials because of their high Seebeck coefficients owing to their crystalline structure [15–17]. Recently, tellurium and its alloys have found widespread use in thermoelectric devices, owing to their high Seebeck coefficients. Te has an outstanding Seebeck coefficient of  $\sim 400 \mu\text{V/K}$  at room temperature, which is higher than that of Te alloys such as  $\text{Bi}_2\text{Te}_3$  ( $\sim 170 \mu\text{V/K}$  [18]),  $\text{Sb}_2\text{Te}_3$  ( $\sim 125 \mu\text{V/K}$  [19]) and  $\text{Ag}_2\text{Te}$  ( $\sim 90 \mu\text{V/K}$  [20]). However, Te is not perfectly suitable for high efficiency thermoelectric devices owing to certain drawbacks [21]. Among the demerits, the low electrical conductivity ( $\sim 10 \text{ S/m}$  at room temperature) is a serious limitation precluding the achievement of a high power factor.

Because of this drawback, many studies have focused on enhancing the thermoelectric properties of Te [22–25]. Hybridization with other materials is the simplest approach for enhancing the thermoelectric properties of a given material. Carbon nanotubes (CNTs) have various merits as suitable candidates for the preparation of thermoelectric composites, because they are mechanically robust [26], chemically stable [27], and highly electrically conductive [28]. Moreover, owing to their nanostructure as well as holey and low-dimensional features, CNTs show outstanding thermoelectric performance. Therefore, there have been numerous studies for improving the thermoelectric power factor of inorganic materials by introducing carbon-based fillers such as graphene and CNTs. For example, single-walled carbon nanotubes (SWCNTs) were added to  $\text{Ag}_2\text{Te}$  matrix to improve its thermoelectric power factor by enhancing the electrical conductivity [20]. Ren et al. [29] embedded multi-walled carbon nanotubes (MWCNTs) into  $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$  powder, thereby achieving an enhanced  $ZT$  by reducing the thermal conductivity. The incorporation of graphene sheets into a  $\text{Bi}_2\text{Te}_3$  nanowire matrix caused the enhancement of  $S$ , and resulted in improved thermoelectric properties [30]. Suh et al. [31] introduced expanded graphene into a  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  system and achieved a 1.45-fold increase in the  $ZT$  due to the enhancement of the electrical conductivity and decrease of the thermal conductivity.

In this study, a strategy for improving the thermoelectric properties of two different Te matrices, viz., powder and nanorod samples, via the incorporation of MWCNTs, is evaluated. Te samples with two different nanostructures were prepared by different methods. Te powder was produced by ball milling Te beads, in a top-down method, whereas Te nanorods were fabricated from a Te precursor solution via a polyvinylpyrrolidone (PVP)-assisted solution-phase process. Before the fabrication of the composite, carboxyl groups were generated on the surface of the MWCNTs by acid-treatment, to enhance their reactivity. The two MWCNT/Te composites were prepared with various MWCNT contents by a subsequent sintering process and wet chemical synthesis route. It was anticipated that random dispersion of the MWCNTs in the Te matrices should produce a synergistic effect that could improve the thermoelectric properties of the prepared MWCNT/Te composites. The effect of the MWCNT content on the thermoelectric properties (such as  $\sigma$ ,  $S$ ,  $\kappa$ , power factor, and  $ZT$ ) of the MWCNT/Te composites is also investigated.

## 2. Experimental

### 2.1. Materials

The following chemicals were purchased from Daejung Chemicals & Metals Co. (Seoul, Korea): tellurium (Te) beads, ethylene glycol (EG,  $\text{C}_2\text{H}_6\text{O}_2$ , 99.5%), tellurium(IV) oxide ( $\text{TeO}_2$ , 99%), sodium

hydroxide (NaOH, 98%), hydrazine monohydrate ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ , 80%), ethanol ( $\text{C}_2\text{H}_5\text{OH}$ , 94%), hydrochloric acid (HCl, 35–37%), nitric acid ( $\text{HNO}_3$ , 60%), and sulfuric acid ( $\text{H}_2\text{SO}_4$ , 95%). Polyvinylpyrrolidone (PVP) [molecular weight ( $M_W$ ) =  $\sim 40,000$ ] was purchased from Sigma Aldrich (St. Louis, USA). The multi-walled carbon nanotubes (MWCNTs) used in this study were supplied by Hanwha Nanotech (Seoul, Korea). All materials were used without further purification. Te powder was prepared from the Te beads by a conventional ball milling process using zirconia balls under an inert atmosphere to avoid oxidizing the surface of the particles. The ball-milled powder was then rinsed with a dilute HCl solution to remove the oxidation layer on the surface.

### 2.2. Preparation of surface-treated MWCNTs

The received MWCNTs (1.0 g) were added to 400 mL of a  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  (3:1 by volume) mixture. This mixture was then heated and stirred at  $80^\circ\text{C}$  for 6 h. The purpose of this acid treatment is to ensure that carboxylic groups were attached to the surfaces of the MWCNTs. The treated CNTs were centrifuged several times and filtered with deionized (DI) water until the pH of the MWCNTs reached  $\sim 7$ . The functionalized MWCNTs were then dried in a vacuum oven at  $60^\circ\text{C}$  for 24 h.

### 2.3. Synthesis of Te nanorods

A 0.98 g sample of  $\text{TeO}_2$  ( $M_W = 159.6$ ), 1.2 g of NaOH ( $M_W = 40$ ), and 0.4 g of PVP were dissolved in 40 mL of EG in a round-bottom flask. This solution was heated to  $120^\circ\text{C}$  with magnetic stirring. At this stage, the mixture turned white, indicating the formation of  $\text{TeO}_2$  colloids. After the temperature reached  $120^\circ\text{C}$ , 2.45 mL of  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  was injected into the solution, causing the solution to turn dark gray. The reaction was allowed to continue for 90 min and a dark blue solution containing the Te nanorods was obtained. The obtained mixture was poured into DI water containing 10 vol%  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ . After the reaction, the resulting solution was centrifuged with the volumetric addition of water twice, and the supernatant was decanted. Finally, the product was dried in a vacuum oven at  $60^\circ\text{C}$  for 24 h.

### 2.4. Fabrication of MWCNT/Te composites

The hybrid composite was prepared by solvent mixing and filtration. Te powder (0.2 g) was dispersed in 100 mL of ethanol containing 1, 2, 3, 5, and 10 wt% of MWCNTs. The mixture was ultrasonicated for 1 h. The dispersion was subsequently reduced by the addition of a sufficient amount of  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ . The mixture was heated at  $80^\circ\text{C}$  for 1 h with stirring. The resulting product was filtered with DI water and dried at  $60^\circ\text{C}$  for 24 h. The final product was ground into a fine powder, loaded into a Fe mold, and pressed at  $200^\circ\text{C}$  under a pressure of 50 MPa for 10 min. The same procedure was employed to prepare the composites with the Te nanorods.

### 2.5. Characterization

The morphology and structural properties of the as-prepared products were analyzed by field-emission scanning electron microscopy (FE-SEM, SIGMA). X-ray diffraction (XRD; New D8 Advance, Bruker AXS) was used to characterize the crystalline structure of the synthesized materials. The analysis was performed at 40 mA and 40 kV at a scan rate of  $1^\circ/\text{sin}$  the  $2\theta$  range of  $5\text{--}70^\circ$ , using  $\text{Cu-K}\alpha$  radiation ( $\lambda = 0.154056 \text{ nm}$ ). The states of the elements in the synthesized materials were analyzed based on the binding energy peaks using X-ray photoelectron spectroscopy

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