그래핀에 의해 유도된 스파크 플라즈마 소결 텔루늄화 구리의 열전성능 향상

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Thermoelectric Enhancement of Spark-Plasma-Sintered Cu₂Te Induced by Graphene Sheets

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초록: 텔루늄화 구리(Cu₂Te)는 이론적으로 우수한 열전 성능을 가질 수 있는 잠재력있는 고체상 열전 물질이다. 그러나, 지금까지의 다양한 연구들 에서는 아직 우수한 열전성능을 달성하지 못하여 왔고, 성능 개선의 여지가 있는 물질이다. 우리는 이 연구에서 텔루늄화 구리에 그래핀을 도입함으로써 효과적으로 열전성능을 향상시킬 수 있는 유망한 연구 전략을 제시한다. 열전 특성치들의 조합을 통해 그래핀 도입은 기존 텔루늄화 구리에 비해 열전성능 향상을 가능하게 한다는 것을 보여준다. 실험적으로 최고 열전성능지수 *ZT* 값은 1000 K의 온도에서 ~1.14를 달성하였고, 이는 기존 텔루늄화 구리에 비해 270% 향상된 수치이다. 이 연구전략은 구리 칼코겐화물 기반 고성능 열전 연구에까지 확장 연구가 가능하다.

Abstract: Copper telluride (Cu₂Te) is theoretically a potential solid-state thermoelectric material with excellent thermoelectric performance. However, it has not achieved excellent thermoelectric performance in various copper chalcogenide-based research to data, and it is a materials with the potential to improve the performance. We suggest a promising strategy to effectively improve the thermoelectric performance of Cu₂Te by introducing graphene sheets. A combination of thermoelectric properties reveals that graphene incorporation facilitates enhancing thermoelectric performance. The maximum thermoelectric *ZT* value of about 1.14 is achieved at 1000 K, 270% higher than for pristine Cu₂Te. This strategy can provide insight that can extend copper chalcogenide-based high-performance thermoelectrics.

Keywords: thermoelectrics, copper telluride, graphene, solid-state material.

Introduction

Exploring energy technology for clean resources is vital for overcoming the universal energy crisis. Thermoelectric energy harvesting technology that can gain electrical energies infinitely from waste heat resources is essential. A dimensionless figure of merit, $ZT = \sigma S^2 T k^{-1}$, where the variables σ, S, κ, and T are the electrical conductivity, Seebeck coefficient, absolute temperature, and thermal conductivity, respectively, is used to calculate the thermoelectric performance for conversion efficiency.[1-5]

The betterment of σS^2 or reduction of k is intensely required based on the ZT equation to accomplish the excellent conversion efficiency.

Copper-based liquid-like chalcogenides (Cu₂S, Cu₂Se, and Cu₂Te) have recently attracted interest in chalcogenide-based thermoelectric research with ZT values.[6] Moreover, Cu₂Te has the theoretically highest ZT value among Cu-chalcogenides because of efficient electrical transports from the less ionic chemical bond of Cu-Te and low lattice thermal transports originating from the heavier Te element.[6] However, the thermoelectric ZT of experimental Cu₂Te is only about 0.5 at 1000 K due to its complex multiphase transitions during the elevated temperature[7-9] and high carrier concentrations originating from severe Cu deficiency.[10] Many strategies have been recently

proposed to overcome these intrinsic issues, such as excess Cu components to lower Cu deficiency,[6] cold press and annealing methods,[6] and alloying with transition metals.[6,11,12] However, exploring the strategy to effectively enhance the thermoelectric performance of Cu_2Te is still necessary to realize practical thermoelectric applications.

In this study, we employ graphene sheets to pristine Cu_2Te to carefully manipulate the thermoelectric transport properties in Cu_2Te. The carbonaceous materials have been widely studied in the role of change in thermoelectric transport of other copper chalcogenides, Cu_2S, and Cu_2Se.[13-15] Therefore, we expect that the introduced graphene can change thermoelectric properties in pristine Cu_2Te. The fully distributed graphene particles in Cu_2Te substantially improve the power factor ($S^2 \cdot \sigma$) and reduce the thermal conductivity, which finally achieves significantly enhanced ZT.

Experimental

Fabrication of Composite Materials. High purity Cu (Sigma Aldrich, 99.999%, St. Louis, MO, USA) and Te (Sigma Aldrich, 99.999%, St. Louis, MO, USA) were weighed and loaded in boron nitride crucibles sealed in a fused silica tube under a vacuum. The loaded tubes were slowly heated to 1,403 K over 7 h and were kept at this temperature for 8 h, then rapidly quenched to room temperature in water. Next, the sealed tubes were heated to 833 K for 5 days and were subsequently cooled to room temperature by turning off the furnace power. The Cu_2Te ingot was ground into powder and mixed with 0.4 wt% of graphene oxide (Sigma Aldrich, St. Louis, MO, USA). This mixture was heated at 773 K for 1 h to reduce the graphene oxide under an N_2 atmosphere. The resulting composite powder was loaded in a graphite die with a diameter of 10 mm and consolidated *via* spark plasma sintering (SPS) at 833 K under 55 MPa for 10 min. The pristine Cu_2Te powder was also sintered in the same conditions for comparison.

Characterization. Next, X-ray diffraction (XRD; New D8-Advance/ Bruker-AXS, Billerica, MA, USA) at 40 mA and 40 kV using a Cu-Kα radiation (0.154056 nm) source and a scan rate of 1° s⁻¹ in the 2θ range of 5 to 70° was employed to characterize the material crystal structure. Field-emission transmission electron microscopy (FE-TEM; JEM-F200, ZEISS, Oberkochen, Germany) was used to determine the morphology and microstructure of the materials. Elemental maps of the samples were analyzed using energy-dispersive X-ray spec-

troscopy (EDS; JEOL Dual SDD Type, Messachusetts, USA). The electrical conductivity and Seebeck coefficient were investigated using an Ulvac Riko ZEM-3 (Messachusetts, USA) instrument under a helium atmosphere. The thermal conductivity of the sample was calculated from the relation: $\kappa = \alpha \cdot \rho_d \cdot C_P$, where α, C_P, and ρ_d are the thermal diffusivity, specific heat, and bulk density of the material, respectively. The xenon flash method was conducted using a NETZSCH, LFA 457 (Sedanstraße, Germany) Nanoflash instrument to evaluate α, whereas the C_P was indirectly derived using a reference sample (Pyroceram 9606).

Results and Discussion

The pristine composite of Cu_2Te and Cu_2Te with graphene sheets (Cu_2Te-graphene) was prepared using vacuum melting combined with the SPS process. The Cu_2Te ingot was prepared, and a small number of graphene sheets was added to improve the thermoelectric performance of the Cu_2Te. First, an XRD analysis was performed to examine the crystallinity of the pristine Cu_2Te and Cu_2Te-graphene composite. The XRD pattern of pristine Cu_2Te in Figure 1 exhibited complicated multiphase crystal orthorhombic, hexagonal, and monoclinic structures, in keeping with the previously reported data.[6,10] Because the prominent characteristic peak of graphene at 2θ= ~25° exhibited a relatively weak intensity compared to strong Cu_2Te peaks, the XRD pattern of the Cu_2Te-graphene composite was almost the same without considerable changes from the graphene sheets.
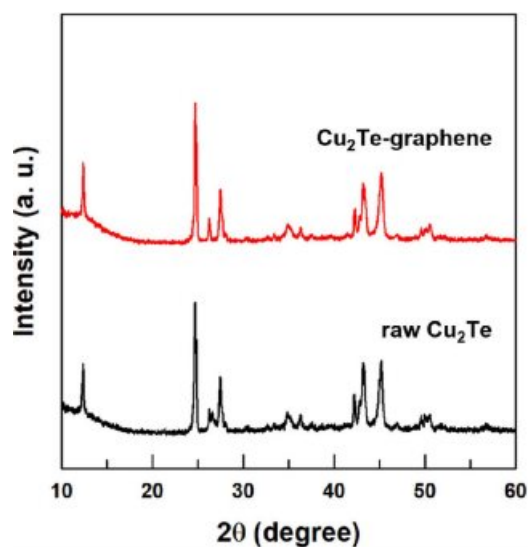

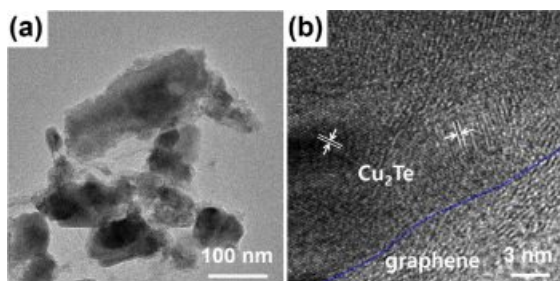**Figure 1.** XRD results of raw Cu_2Te and Cu_2Te-graphene composite.

Figure 2. FE-TEM images of Cu$_2$Te-graphene composite sample: (a) low-resolution; (b) high-resolution.
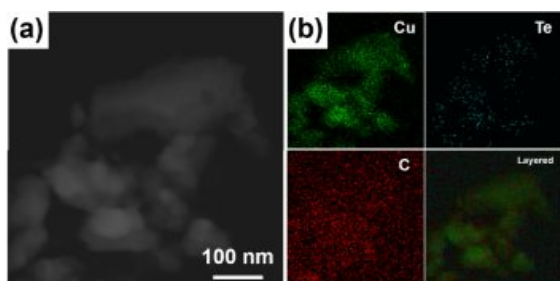

Figure 3. (a) STEM image; (b) corresponding STEM-EDS images of Cu$_2$Te-graphene sample.

After incorporating graphene sheets into Cu$_2$Te, the FE-TEM with scanning transmission electron microscopy (STEM) mode and EDS analyses were conducted to investigate the microstructure and composition of the Cu$_2$Te-graphene sample. Figures 2(a) and 2(b) illustrate low- and high-resolution FE-TEM images of the Cu$_2$Te-graphene composite, revealing the random distribution of Cu$_2$Te nanoparticles on the graphene surface. The coexistence of distinct lattice domains of the crystalline Cu$_2$Te and graphene orientation was observed in the high-resolution FE-TEM image (Figure 2(b)). In addition, Figures 3(a) and 3(b) depict STEM and STEM-EDS images for the Cu$_2$Te-graphene composite. These atomic and layered EDS images demonstrated the even distribution of the atomic compositions for Cu, Te, and C atoms on the composite sample.

The electrical conductivity (σ), Seebeck coefficient (S), power factor ($S^2 \cdot \sigma$), thermal conductivity (κ), and figure of merit (ZT) values of the Cu$_2$Te-graphene composite sample were investigated and compared to that of pristine Cu$_2$Te to demonstrate the effect of adding graphene on the thermoelectric transport properties. In the entire temperature range, several discontinuities of the transport properties attribute to the intrinsic phase transitions of Cu$_2$Te.[6,10]

Figure 4 reveals the electrical conductivities of pristine Cu$_2$Te and the Cu$_2$Te-graphene composite, which decrease
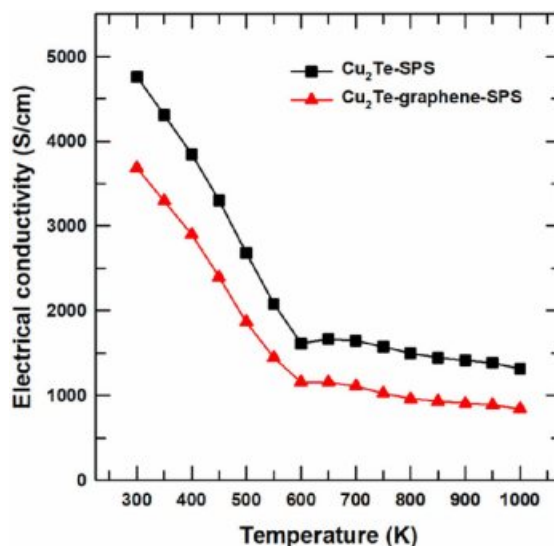

Figure 4. Electrical conductivity of the Cu$_2$Te and Cu$_2$Te-graphene composite as a function of the measuring temperature.
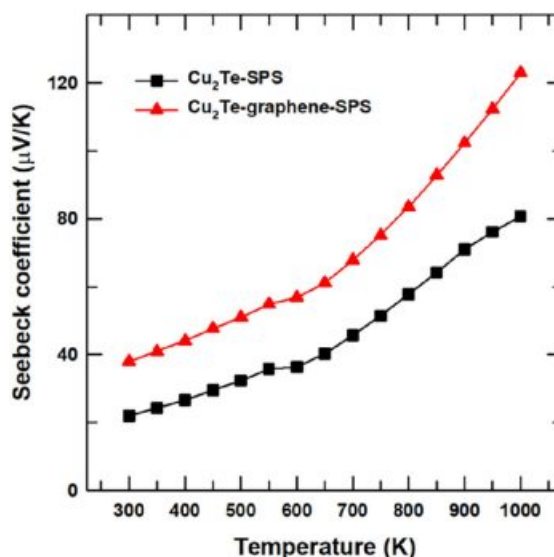

Figure 5. Seebeck coefficient of the Cu$_2$Te and Cu$_2$Te-graphene composite as a function of the measuring temperature.

with increased measuring temperature, similar to degenerate-semiconductor behavior. First, they decreased significantly until about 600 K and then gradually decreased with increasing temperature. After adding graphene in Cu$_2$Te, the electrical conductivity at 300 K decreased from 4763 S cm^{-1} for the pristine Cu$_2$Te to 3684 S cm^{-1} for Cu$_2$Te-graphene composite. This result was attributed to the relatively low electrical conductivity of graphene.

Figure 5 illustrates the positive Seebeck coefficient values of pristine Cu$_2$Te and Cu$_2$Te-xG, which demonstrate the signif-
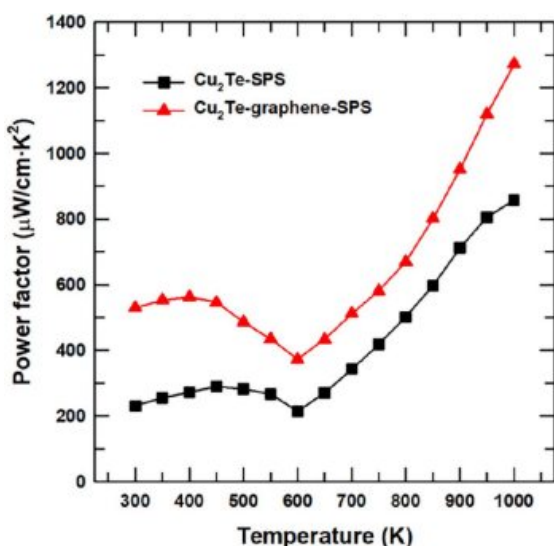
Figure 6. Temperature dependent power factor values of the Cu₂Te and Cu₂Te-graphene composite.
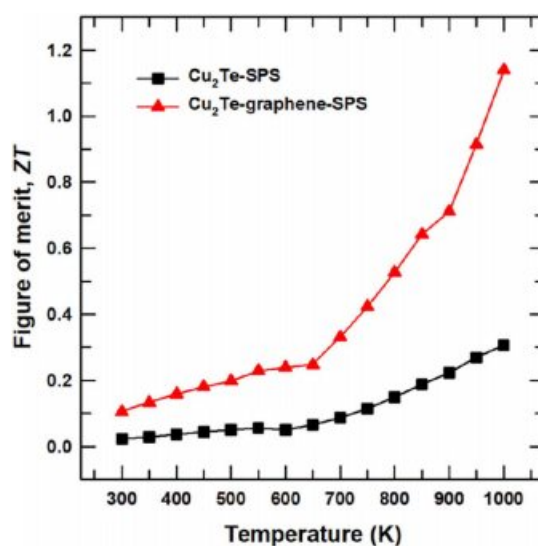

Figure 8. ZT values of the Cu₂Te and Cu₂Te-graphene composite as a function of the measuring temperature.
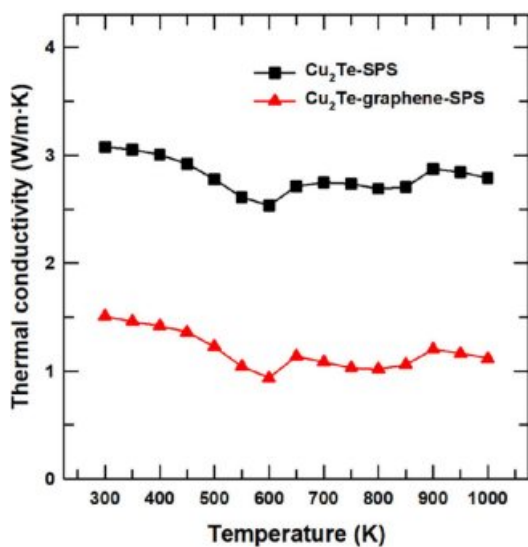

Figure 7. Thermal conductivity of the Cu₂Te and Cu₂Te-graphene composite as a function of the measuring temperature.

icant charge carriers of holes. The Seebeck coefficient was increased after adding graphene from 22 μV K^{-1} for pristine Cu₂Te to 37 μV K^{-1} for the Cu₂Te-graphene composite. The combination of electrical conductivity and the Seebeck coefficient values of the Cu₂Te-graphene composite produced enhanced power factor values (Figure 6), providing the maximum value of 1272 μW cm^{-1} K^{-2} at 1000 K, much higher than that of the pristine Cu₂Te.

Figure 7 displays the thermal conductivity of pristine Cu₂Te and Cu₂Te-graphene composite, describing complicated features with several discontinuities in the entire temperature

range due to the inherent multiphase transitions of Cu₂Te.[6,10] The thermal conductivity of the Cu₂Te-graphene composite was reduced significantly after incorporating graphene sheets, attributed to the graphene sheets effectively suppressing charge carriers and the lattice thermal transport in Cu₂Te.

Figure 8 depicts the calculated ZT values of the pristine Cu₂Te and Cu₂Te-graphene composite. Despite the relatively low ZT values at a low-temperature range, the combination of thermoelectric transport properties of the Cu₂Te-graphene composite resulted in the highest ZT value of about 1.14 at 1000 K. The outstanding ZT was 270% greater than that of the pristine Cu₂Te. These results demonstrate that the introduced graphene manipulates the inherent thermoelectric transport in Cu₂Te, leading to the substantial enhancement of thermoelectric performance.

Conclusions

The Cu₂Te-graphene composite was fabricated through vacuum melting combined with the SPS process, and the graphene particles were randomly distributed in the composite structure. The thermoelectric properties of the Cu₂Te-graphene composite were precisely examined and compared to those of the pristine Cu₂Te to elucidate the effect of adding graphene on the thermoelectrical properties of Cu₂Te. The Seebeck coefficient value significantly increased as graphene was added to Cu₂Te whereas the electrical conductivity decreased, producing an improved power factor value in the Cu₂Te-graphene com-

posite. Consequently, the effective reduction of thermal conductivity and improved Seebeck coefficient of the Cu_2Te-graphene composite resulted in a remarkable *ZT* value of about 1.14 at 1000 K. This value was 270% greater than that of the pristine Cu_2Te. This study highlights that incorporating graphene could manipulate the thermoelectric transport in Cu_2Te, facilitating excellent thermoelectric performance in Cu_2Te and realizing high-performance thermoelectrics.

Conflict of Interest: The authors declare that there is no conflict of interest.

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