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Tailoring thermoelectric properties of copper selenide through engineering nano/micro-sized particles

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Copper selenide has emerged as a promising thermoelectric material due to its unique structural properties and tunable electronic band structure. However, its practical application is hindered by its relatively high thermal conductivity. In this study, we report on the turning of thermal conductivity and thermoelectric energy conversion by preparing a hybrid composite material including nano- and micro-sized Cu_2Se. By employing a hydrothermal synthesis method with cetyltrimethylammonium bromide (CTAB) as a surfactant, we successfully synthesized nano-sized Cu_2Se particles with uniform size distribution. The incorporation of these nano-sized particles with micro-sized Cu_2Se resulted in a significant reduction in thermal conductivity, leading to adjustment of the thermoelectric performances. Our findings provide a promising strategy for designing high-performance thermoelectric materials for waste heat recovery and energy conversion applications in the medium temperature range.

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Keywords: Thermoelectric, Copper selenide, Nanostructure, Hydrothermal synthesis, Energy conversion

1. Introduction

With the increasing global demand for sustainable energy technologies, thermoelectric materials have emerged as an attractive solution for waste heat recovery, enabling the direct conversion of heat into electricity without moving parts or greenhouse gas emissions.[1-3] Among the various thermoelectric materials studied, copper selenide has drawn considerable attention in the field of thermoelectric conversion in the medium temperature range (450 K – 650 K) due to its remarkable properties, including low thermal conductivity, good electrical conductivity, and easy composition control.[4-6] These properties are largely attributed to its unique superionic crystal structure, where highly mobile Cu ions within a rigid Se sublattice significantly suppress lattice thermal conductivity while maintaining good electrical performance.[4] However, despite its promising thermoelectric performance, the practical application of copper selenide faces challenges related to optimizing its thermal and electrical properties simultaneously. One of the key strategies to address these challenges involves manipulating the microstructure of copper selenide to enhance its phonon scattering mechanisms.[7] Furthermore, reducing the particle size to the nanoscale can create additional grain boundaries that effectively scatter phonons, thereby lowering lattice thermal conductivity.[8-10] Additionally, hybridizing nano-sized particles with micro-sized particles enables better control over the overall structure of materials, ensuring consistent thermoelectric performance.[11]

In this study, we focus on the controlled synthesis of Cu_2Se nano-sized particles and their integration with micro-sized particles to form a hybrid composite material toward the application to thermoelectric energy conversion. To limit the crystal growth of copper selenide to the nano-size, a synthetic environment with two surfactants (ethylenediaminetetraacetic acid (EDTA) and cetyltrimethylammonium bromide (CTAB)) were created, where these surfactants can be coated on the surface of copper selenide to control the growth. EDTA has been widely used for chelating and capping agent in the synthesis of nanostructured materials. [12] CTAB, a typical cationic surfactant,

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has been used to kinetically control the growth rates of different crystallographic facets of nanostructures by preferentially adsorbing on these facets. [13] Nano-sized Cu_2Se from using surfactants effectively reduced thermal conductivity compared to micro-sized one. In addition, by controlling the ratio of micro- and nano-sized Cu_2Se composites, the thermal conductivity and thermoelectric properties could be controlled. This approach is expected to enable the development of tailor-made thermoelectric materials suited to desired thermoelectric figure of merit (ZT) values for medium-temperature applications.

2. Experimental section

2.1. Sample preparation

To synthesize nano-sized Cu2Se smaller than that of the previous study, CTAB or EDTA was introduced to control the size and shape of the nanoparticles. In a 120 ml beaker, 40 ml of distilled water, 1.364 g of copper(II) chloride dihydrate, 0.444 g of selenium dioxide, and 6.667 ml of hydrazine monohydrate were added. CTAB or EDTA was added by adjusting the content, and the mixture was stirred at room temperature for more than 3 hours. The stirred solution was transferred to a PTFE liner, placed in an autoclave, and synthesized at 180 °C for 24 hours (Figure 1(a)). To prepare a film-shaped sample (Figure 1(b)), the solution after synthesis was filtered using a vacuum filter with distilled water and washed with ethanol to remove unnecessary solvents. The filtered copper selenide was dried in a vacuum oven at 60 °C for 12 hours to remove moisture. For the sample preparation in the form of sintered pellets (Figure 1(c)), the synthesized solution was centrifuged 2-3 times at 8000 rpm for 20 minutes to separate the solute. The separated copper selenide was dried in a vacuum oven at 60 °C for 12 hours to remove moisture, producing powder-shaped samples. Micro-sized Cu_2Se samples were prepared following the method reported elsewhere. [14] To prepare a composite powder with a different ratio of nano- and micro-sized samples, ball mixing was performed at 300 rpm for 2 hours. The mixed composites were ground and sieved to produce fine powder, which was then placed in a mold and compressed at 400 °C and 50 MPa for sintering. The amount of powder required for the sintering process was 5 g.

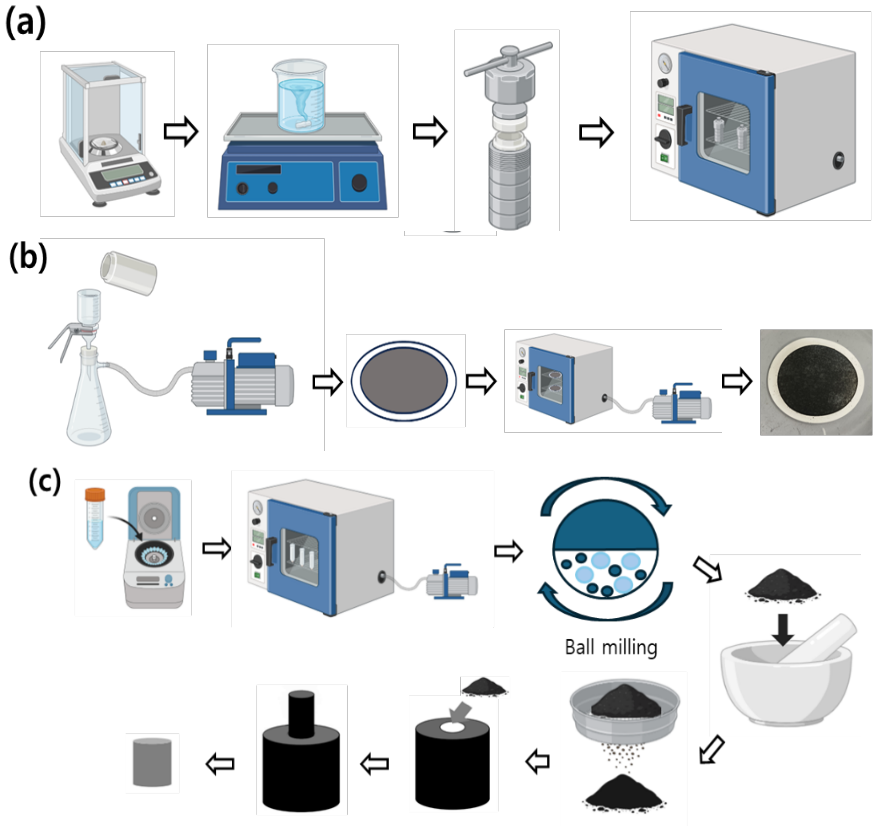

Fig. 1. Schematic illustration showing (a) hydrothermal synthesis process, (b) film-type sample preparation process, and (c) sintered pellet preparation process.

2.2. Characterization

The thermoelectric properties of the film-shaped sample were measured using Keithley 2636B, 2182A, and 2700. The thermoelectric properties of the sintered pellet were measured using a thermal constant measurement system (TC-9000H) and a thermoelectric property measurement system (ZEM-III). The surface properties were observed using an environmental scanning electron microscope (SEM). X-ray diffraction pattern (XRD) was measured to analyze the crystal structure of copper selenide (the measurement range was 2θ = 10˚ ~ 90˚).

3. Result and discussion

Cu_2Se can be synthesized through the reduction process of Cu and Se ions. Since Se is generally reduced more easily than Cu, copper selenides with different stoichiometries (from $CuSe_2$ to Cu_2Se) can be produced by controlling the reduction of Cu cations. [14] For thermoelectric applications, Cu_2Se is the most promising among the copper selenide family due to its high Seebeck coefficient.

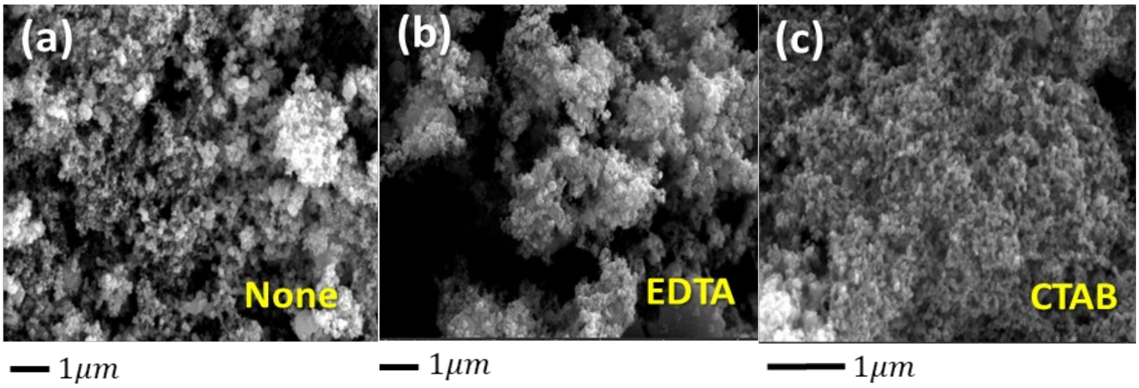

Fig. 2. SEM images of synthesized copper selenide samples prepared (a) without surfactant (none), (b) under EDTA condition, and (c) under CTAB condition.

To obtain Cu_2Se nanoparticles with suppressed crystalline growth, we adjusted the hydrothermal synthesis conditions and introduced two surfactants: EDTA as a chelating agent, capping agent, and structure-directing template, and CTAB as a cationic surfactant. [12, 13] Figure 2 show the SEM images obtained to observe the structural changes according to the presence or absence of surfactants during the Cu_2Se synthesis process. Overall, it was confirmed that copper selenide was formed in a form where the crystal size was simply limited to the nanoscale, rather than growing in a specific direction. Samples synthesized without surfactant and samples containing EDTA showed non-uniform structures and appeared to agglomerate slightly (Figure 2(a) and 2(b)). On the other hand, Cu_2Se prepared under CTAB condition was found to have a particle size of approximately 60 nm in diameter, and the structures appeared to be formed more uniformly compared to other samples (Figure 2c). This indicates that the adsorption property of CTAB kinetically controlled the growth in the formation of microscale crystals.

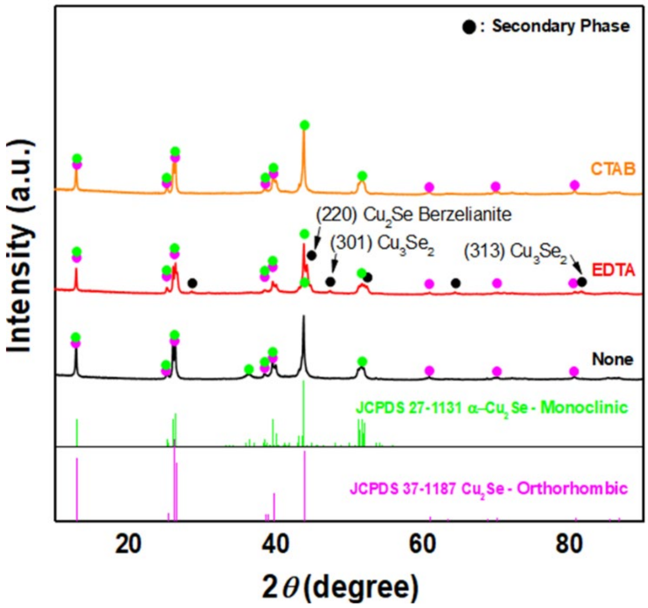

Fig. 3. XRD patterns of synthesized copper selenide samples prepared without surfactant (none), under EDTA condition, and under CTAB condition.

Figure 3 presents the XRD spectra results of copper selenide according to the synthesis conditions. All samples exhibited strong intensity peaks at $2\theta = 12.96°$, $26.46°$, and $43.94°$, and additional small peaks were observed, corresponding to the signals of monoclinic Cu_2Se and orthorhombic Cu_2Se (JCPDS 27-1131 and JCPDS 37-1187). [15, 16] It should be noted that the XRD pattern of copper selenide under EDTA condition included a secondary peak (see black colored circle in Figure 3). This indicates the presence of the Cu_3Se_2 phase or Cu_2Se Berzelianite. This may be due to the chelating effects of EDTA with Cu^{2+}, which can change the forms of the aqueous ions, producing a solution with less free metal ions. [17] In other words, since EDTA captures Cu ions, insufficient reduction may occur, resulting in a secondary phase with a 1.5:1 ratio.

Figure 4 presents the measured Seebeck coefficient (α), electrical conductivity (σ), and power factor (PF) of copper selenide samples synthesized under different conditions. The α plot in Figure 4(a) revealed that the copper selenide prepared under CTAB condition has the highest value, while the sample under EDTA condition has the lowest value. On the other hand, σ showed the opposite trend: the σ of the EDTA sample exhibited a higher value than that of the CTAB sample. Based on the XRD results, it can be concluded that the CTAB sample, which formed pure Cu_2Se without a secondary phase, has a high α value. Conversely, it is generally known that the electrical conductivity increases as the Cu composition ratio in Cu-Se compounds decreases (for example, the σ of $CuSe_2$ is higher than CuSe and Cu_2Se) because the metallic Cu can provide free electrons that annihilate holes in Cu^+ vacancies. [18] Therefore, the copper selenide from the EDTA condition, which contains a secondary phase such as Cu_3Se_2, is considered to have a higher σ value. As a result, the copper selenide prepared under CTAB condition exhibited the best PF performance. This is attributed to the formation of a uniform Cu_2Se structure without a secondary phase.

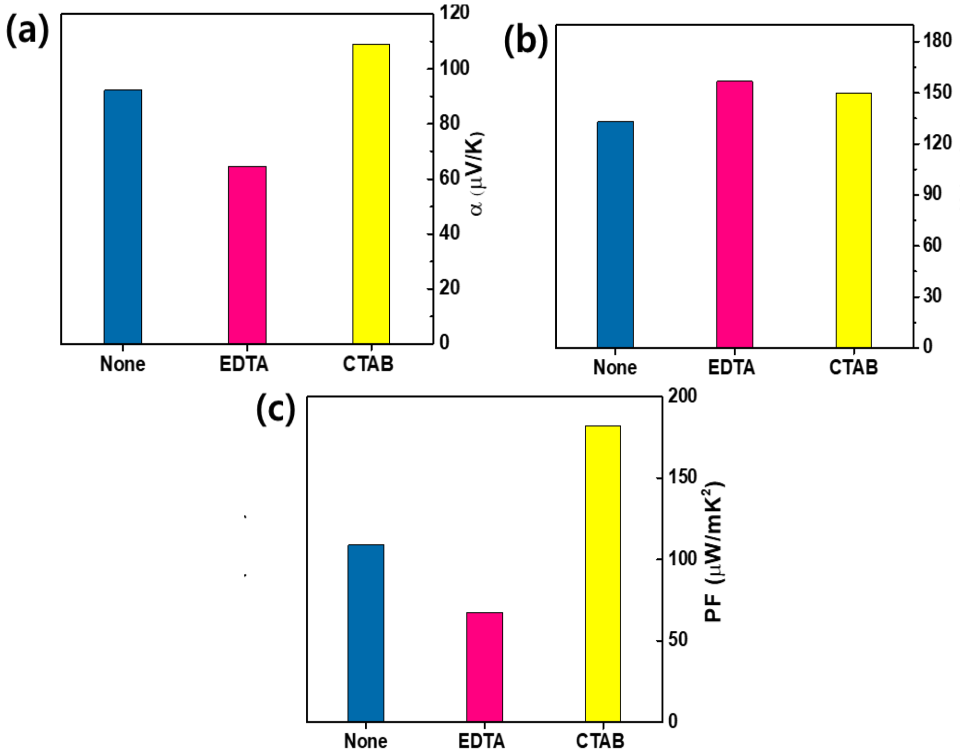

Fig. 4. Thermoelectric performances of synthesized copper selenide samples prepared without surfactant (none), under EDTA condition, and under CTAB condition: (a) Seebeck coefficient (α), (b) electrical conductivity (σ), and (c) Power factor (PF).

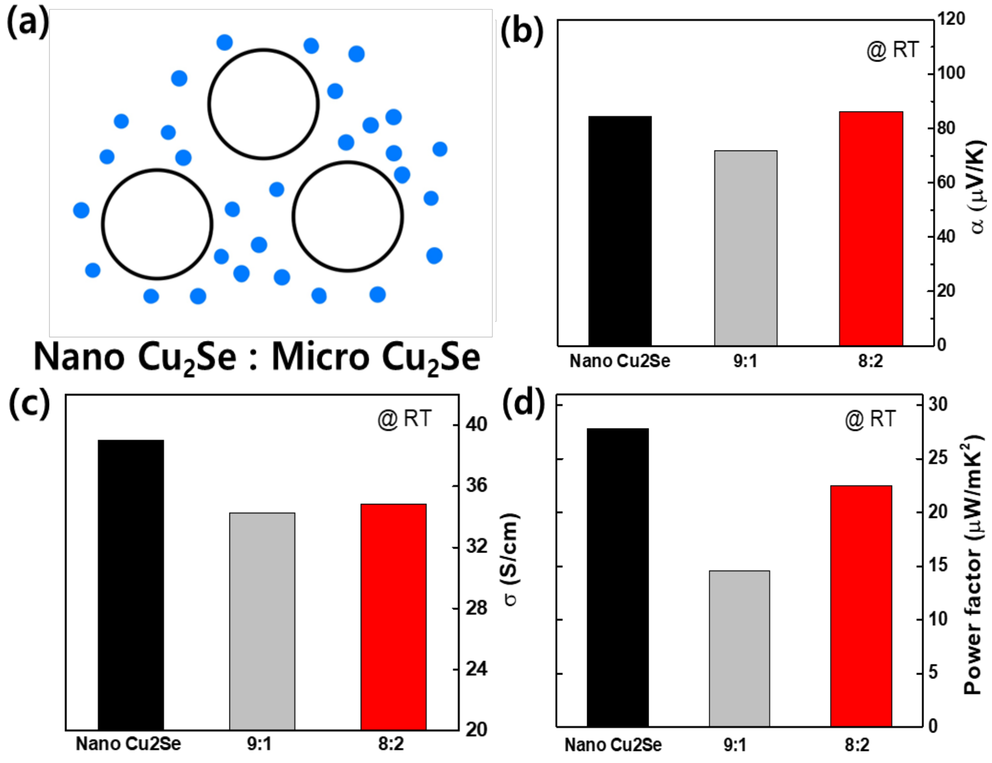

Fig. 5. (a) Schematic illustration showing mixture of nano- and micro-sized Cu_2Se. Thermoelectric performances of nano-sized Cu_2Se and mixture of nano- and micro-sized Cu_2Se with the ratio of 9:1 and 8:2: (b) Seebeck coefficient (α), (c) electrical conductivity (σ), and (d) Power factor (PF).

The use of CTAB as a surfactant enabled us to limit the crystal growth and obtain nano-sized Cu_2Se particles. Subsequently, the changes in thermoelectric properties through the mixing of these nano-sized Cu_2Se with micro-sized Cu_2Se was analyzed. Figure 5(a) provides a schematic representation of the nano and microstructures within the Cu_2Se composites. Nano-sized Cu_2Se particles have a more dense and uniform distribution than micro-sized particles, and thus, their mixing may provide a synergistic effect to control α and σ. Hereafter, nano-sized Cu_2Se refers to the Cu_2Se prepared under the CTAB condition. Figure 5(b)-5(d) presents the thermoelectric performance analysis results for different mixing ratios of nano-sized and micro-sized Cu_2Se. Thermoelectric performance was measured at room temperature using film-type samples. In the plots, 'nano' represents the performance of pure nano-sized Cu_2Se, and 9:1, 8:2 represent the ratio of nano-sized Cu_2Se to micro-sized Cu_2Se. The 8:2 ratio mixture exhibits the highest α value, surpassing that of pure nano-structured Cu_2Se. This implies a synergistic effect between the nano and microstructures in enhancing α properties. Perhaps, creating many interfaces between particles enables the effective filtering of general electrons rather than hot electrons. Although the σ decreased due to the trade-off relationship, which resulted in a decrease in PF, it was confirmed that the Seebeck coefficient and electrical conductivity can be adjusted by mixing the same material with different sizes.

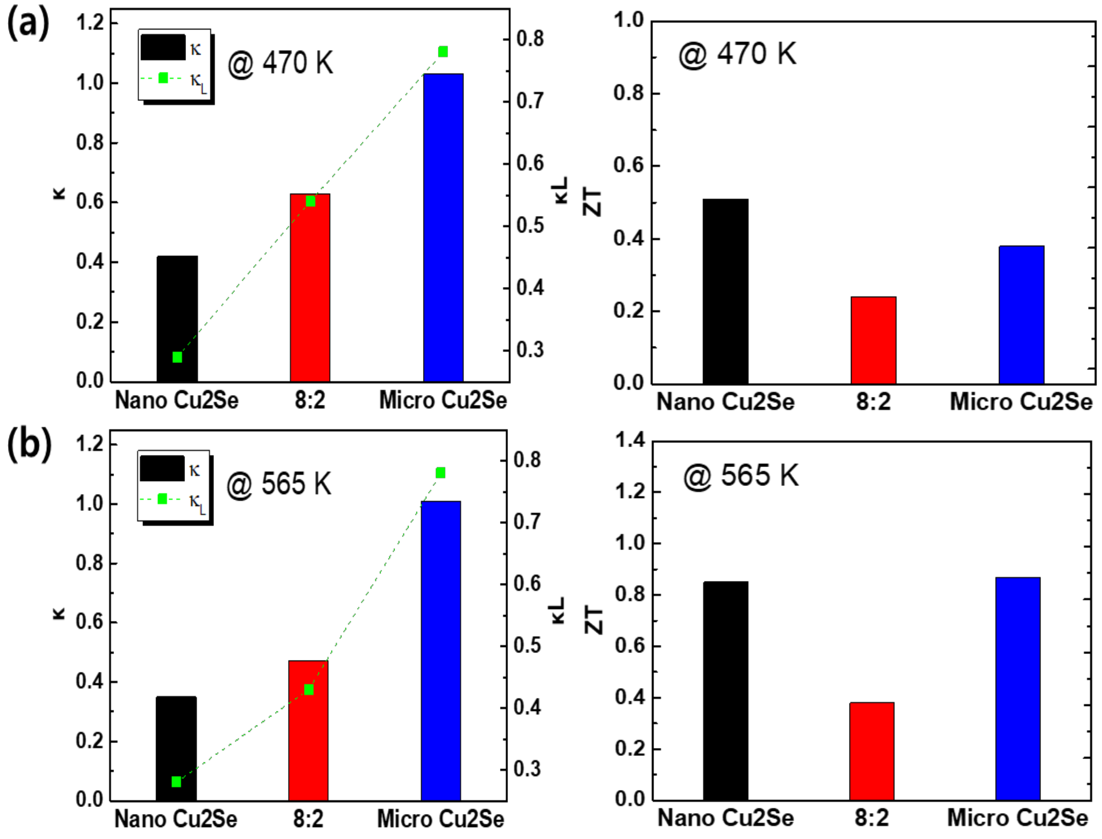

Fig. 6. Comparison of thermal conductivity (κ) and figure of merit ZT value of nano-sized Cu_2Se, micro-sized Cu_2Se, and mixture of nano- and micro-sized Cu_2Se with the ratio of 8:2 at given temperature: 470 K (a) and 565 K (b).

Figure 6 shows the thermal conductivity and ZT values of nano-sized Cu_2Se, micro-sized Cu_2Se, and the 8:2 mixed sample. Thermoelectric performance measurements were conducted at intermediate temperatures of (a) 470 K and (b) 565 K, which are within the temperature range where the transition from the α-Cu_2Se phase with a monoclinic crystal structure to a cubic β-Cu_2Se structure occurs (350 K ~ 400 K),[14] as this is a temperature range where copper selenide can be applied to heating elements. The thermal conductivity of nano-sized Cu_2Se was significantly lower than that of micro-sized Cu_2Se, which can be attributed to the decrease in lattice thermal conductivity (κL). As expected, due to the increased number of scattering positions between the nano-sized Cu_2Se particles with a large specific surface area, the thermal conductivity decreased due to the phonon scattering effect. The thermal conductivity of the 8:2 mixed sample was between that of the nano-sized and micro-sized samples. This indicates that the thermal conductivity can be adjusted as desired by controlling the mixing ratio. The figure of merit ZT values were calculated from the measured thermal conductivity. Although the 8:2 sample showed a slight increase in the Seebeck coefficient, the figure of merit ZT value was lower than that of both micro-sized and nano-sized Cu_2Se. For the nano-sized Cu_2Se synthesized in this work, a maximum ZT value of 0.85 was obtained at 565 K. Overall, the proper control of surfactant in the hydrothermal synthesis of copper selenide family can control the electrical conductivity, thermal conductivity, and Seebeck coefficient by limiting the crystal particle size, and can facilitate the application of auxiliary power supplies or coolers of chips by modulating the thermoelectric performance with a simple approach.

4. Conclusions

In this study, nano-sized Cu_2Se particles were successfully synthesized using a hydrothermal method with CTAB as a surfactant. CTAB surfactants acted as a structure-directing agent, which effectively suppressed crystal growth and produce uniformly sized Cu_2Se nanoparticles compared to the sample using EDTA surfactant. The synthesized nano-sized Cu_2Se exhibited meaningful thermoelectric properties, particularly a lower thermal conductivity compared to micro-sized Cu_2Se. Furthermore, we investigated the effects of mixing nano-sized and micro-sized Cu_2Se on the thermoelectric performance. Mixing nano-sized and micro-sized Cu_2Se could adjust thermal conductivity as desired, but the overall ZT value was lower than that of both pure nano-sized and micro-sized Cu_2Se. Our results demonstrate that nano/micro Cu_2Se composite has potential as a promising thermoelectric material by optimizing the synthetic process and exploring various compositions, which can further improve the thermoelectric performance of Cu_2Se-based materials and contribute to the development of efficient thermoelectric devices.

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