

## PAPER

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# Synergetic enhancement of thermoelectric performances by localized carrier and phonon scattering in Cu<sub>2</sub>Se with incorporated fullerene nanoparticles†

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C<sub>60</sub>/Cu<sub>2</sub>Se thermoelectric nanocomposites were synthesized with various amounts of fullerene (C<sub>60</sub>; 0.03, 0.3, 0.5, 0.7 mol%) incorporated in Cu<sub>2</sub>Se. The thermoelectric figures of merits (*zT*) of the C<sub>60</sub>/Cu<sub>2</sub>Se nanocomposites were enhanced by 20–30% compared to that of pure Cu<sub>2</sub>Se, reaching a value of 1.4 at 773 K. The primary cause of *zT* enhancement is the synergetic effect of thermal conductivity reduction by phonon scattering and Seebeck coefficient increase by carrier localization that results from incorporation of C<sub>60</sub> nanoparticles. Theoretical calculations for Seebeck coefficient enhancement and lattice thermal conductivity reduction were performed. The Seebeck coefficients of C<sub>60</sub>/Cu<sub>2</sub>Se nanocomposites were around 43% higher than that of pure Cu<sub>2</sub>Se, whereas the reduction of lattice thermal conductivity with incorporation of C<sub>60</sub> was around 40–50%.

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## Introduction

Thermoelectric nanocomposites have powerful advantages with regard to overcoming the complex coupling of transport properties. A thermoelectric material can convert thermal energy to electrical energy and *vice versa*.<sup>1</sup> Thermoelectric conversion efficiency is a function of a dimensionless parameter known as the thermoelectric figure of merit,  $zT = (S^2\sigma/\kappa)T$ ,<sup>1</sup> where  $S$ ,  $\sigma$ ,  $\kappa$ , and  $T$  are the Seebeck coefficient, electrical conductivity, thermal conductivity, and temperature, respectively.<sup>1</sup> Conversion efficiency increases with  $zT$ .<sup>1</sup> However,  $zT$  increase is difficult due to the coupling of three interdependent parameters that determine  $zT$ . The thermal conductivity,  $\kappa$ , is composed of electron and phonon contributions; thus, the thermal conductivity is coupled to electrical conductivity,  $\sigma$ . The Seebeck coefficient,  $S$ , is reversely coupled to electrical conductivity.<sup>2</sup> The Seebeck coefficient can be derived from the Boltzmann transport equation. According to quantum statistical mechanics, the Seebeck coefficient can be determined with the following equation:<sup>2</sup>

$$S = \frac{1}{eT} \frac{\int_0^\infty E\tau(E)(E - E_F)D(E)\frac{\partial f}{\partial E}dE}{\int_0^\infty E\tau(E)D(E)\frac{\partial f}{\partial E}dE} \quad (1)$$

where  $E$ ,  $\tau$ ,  $D$ , and  $f$  are the electron energy, scattering time, density of states, and Fermi–Dirac distribution function, respectively. The denominator of eqn (1) is the electrical conductivity.<sup>2</sup> A nanocomposite with embedded nanoparticles can effectively scatter phonons reducing the lattice thermal conductivity.<sup>3–5</sup> Several studies<sup>6–14,39,40</sup> have reported that embedded nanoparticles in the form of precipitates can reduce lattice thermal conductivity and enhance the  $zT$ . Another useful effect of embedding nanoparticles is known as the energy filtering effect.<sup>15,16</sup> The numerator of eqn (1) can be rewritten as  $\int A(E)(E - E_F)dE$ , where  $A(E)$  is  $E\tau(E)D(E)\partial f/\partial E$ . Because the  $E - E_F$  term has point symmetry at the Fermi level,  $E_F$ , it is important to enhance the asymmetry of  $A(E)$  around the Fermi level to increase the Seebeck coefficient.<sup>16</sup> The derivative of Fermi–Dirac distribution ( $\partial f/\partial E$ ) has perfect symmetry around the Fermi level, thus it is important to enhance the energy dependence of  $\tau(E)$  and  $D(E)$ . The embedded nanoparticles have a different band structure from that of the matrix. Therefore, low energy conduction electrons could be scattered by a potential barrier or trapped by a potential well. In this study, the scattering time  $\tau(E)$  due to impurity scattering induced by the incorporated C<sub>60</sub> can be highly energy dependent,<sup>16</sup> a phenomenon known as the energy filtering effect. In our previous report,<sup>17</sup> embedded Au nanoparticles were shown to scatter electrons in a highly energy-dependent manner, resulting in the energy filtering effect and the Seebeck coefficient enhancement.

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Cu<sub>2</sub>Se is an excellent thermoelectric material due to its PLEC (Phonon Liquid Electron Crystal) characteristic.<sup>18</sup> The superionic conduction of Cu ions with liquid-like mobility can reduce the shear resistance of Cu<sub>2</sub>Se crystals, resulting in ultralow lattice thermal conductivity.<sup>18–22</sup> Recently, a graphene-incorporated Cu<sub>2</sub>Se nanocomposite was reported.<sup>23</sup> The study demonstrated that clustered graphene–Cu<sub>2</sub>Se mixtures could effectively reduce the lattice thermal conductivity.<sup>23</sup>

In this study, we found synergetic effects of embedding C<sub>60</sub> in Cu<sub>2</sub>Se to improve *zT*. The carrier localization (energy filtering effect) and phonon scattering caused by C<sub>60</sub> nanoparticles effectively enhanced the Seebeck coefficient and reduced the lattice thermal conductivity. Fullerenes behave as semiconductors with a band gap around 1.5–5 eV<sup>24,25</sup> which is suitable for the formation of a potential well in a matrix of the p-type semiconductor of Cu<sub>2</sub>Se with band gap around 1–2 eV. V. A. Kulbachinskii *et al.* have reported<sup>26</sup> that the electron acceptor behavior of C<sub>60</sub> molecules increases the hole concentration in a BST (Bi–Sb–Te) alloy system. Meanwhile, D. Zhao *et al.* have reported<sup>27</sup> the energy filtering effect of embedded C<sub>60</sub> in a Cu<sub>2</sub>–SnSe<sub>3</sub> system. In our study, we found that fullerenes act as potential wells to carriers and as scatterers to phonons. Theoretical calculations based on the Boltzmann transport equation for carrier localization clarifies that the source of Seebeck coefficient enhancement is formation of potential wells by embedded C<sub>60</sub>.<sup>2,15</sup> Phonon scattering by fullerene nanoparticles in the Cu<sub>2</sub>Se matrix is calculated using the model reported by W. Kim *et al.*<sup>3,4,28,29</sup>

## Results & discussion

The C<sub>60</sub>/Cu<sub>2</sub>Se nanocomposites were prepared with various amounts of C<sub>60</sub>; 0.03, 0.3, 0.5, 0.7 mol% incorporated in the Cu<sub>2</sub>Se matrix. Due to the lower density of C<sub>60</sub> compared to Cu<sub>2</sub>Se, C<sub>60</sub> molar percentages of 0.03, 0.3, 0.5, and 0.7% correspond to the higher volumetric percentages of

approximately 0.5, 5, 8, and 10%, respectively. These C<sub>60</sub> concentrations were used for phonon scattering calculations. From our previous report,<sup>12</sup> phonon scattering by embedded nanoparticles strongly depends on the interparticle distance between nanoparticles. To obtain optimal phonon scattering, the interparticle distances should be less than 15 nm.<sup>12</sup> Considering that the average size of C<sub>60</sub> is around 1 nm, a rough estimation as described in the ESI (Table S1†) suggests that volumetric percentages around 1–10 vol% yield interparticle distances on the few nanometer scale. Even though we assumed that our nanoparticles consisted of clustered C<sub>60</sub> in the fullerite form, the interparticle distances were estimated to be less than 15 nm (Table S1†). The microstructures of the fabricated samples are shown in Fig. 1. The resultant microstructures clearly differed for samples with varying C<sub>60</sub> contents. When comparing pure Cu<sub>2</sub>Se to the C<sub>60</sub>/Cu<sub>2</sub>Se nanocomposites, the most notable difference was average grain size. The grain size of pure Cu<sub>2</sub>Se is a few micrometers. However, the grain sizes of the C<sub>60</sub>/Cu<sub>2</sub>Se nanocomposites are less than 100 nm, which seemed to be due to the Zener pinning effect.<sup>30</sup> When small incoherent particles are dispersed in a material, a counter force is applied against grain growth by the dispersed particles, which is known as the Zener pinning pressure.<sup>31</sup> For this reason, the grain growth of a C<sub>60</sub>/Cu<sub>2</sub>Se nanocomposite is interrupted, resulting in a smaller grain size than in pure Cu<sub>2</sub>Se. D. Chen *et al.*<sup>32</sup> reported that the *R/d* ratio should be large to produce a strong Zener pinning pressure, where *R* is the particle size, and *d* is the interparticle distance. They reported that 0.4–0.8 nm sized particles

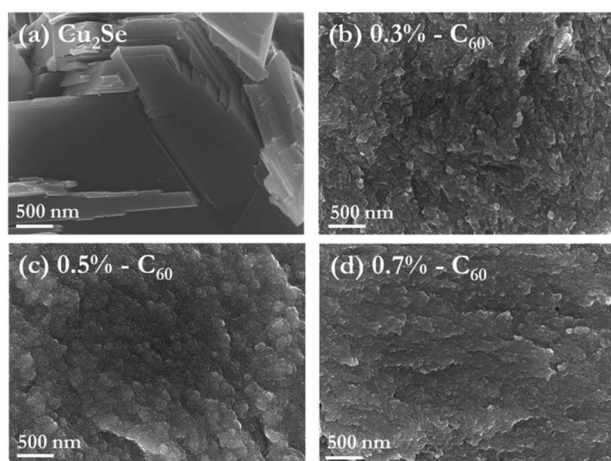


Fig. 1 SEM images of (a) pure Cu<sub>2</sub>Se and nanocomposites of Cu<sub>2</sub>Se embedded with (b) 0.3, (c) 0.5, and (d) 0.7 mol% C<sub>60</sub>. Images (a–d) are produced at mid-magnification (×50 000).<sup>38</sup>

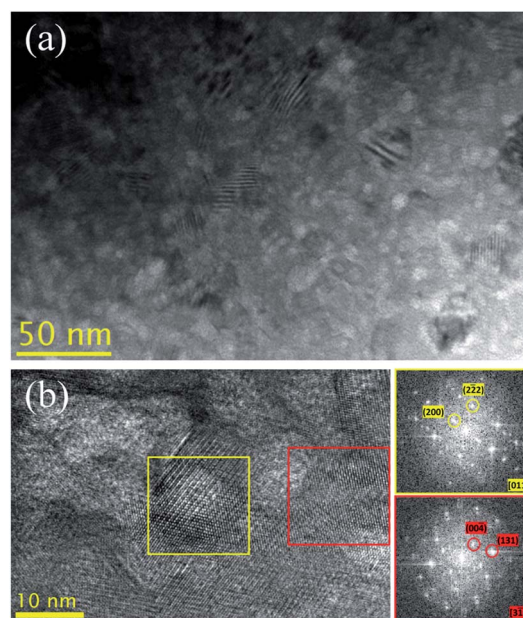


Fig. 2 (a) Low magnification and (b) high resolution TEM images of the 0.7 mol% C<sub>60</sub>/Cu<sub>2</sub>Se nanocomposite. The FFT pattern with a yellow border is obtained from a region of bright contrast (yellow box) and that with a red border is from a background region (red box).<sup>38</sup>



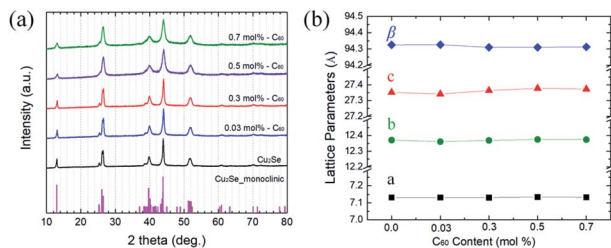


Fig. 3 (a) XRD data for pure Cu<sub>2</sub>Se and C<sub>60</sub>/Cu<sub>2</sub>Se nanocomposites. (b) Lattice parameters for *a* (black), *b* (green), *c* (red) in the monoclinic unit cell, and angle  $\beta$  (blue).<sup>38</sup>

with 4–13 nm interparticle distance are sufficient to create the pinning effect.<sup>32</sup>

The dispersed C<sub>60</sub> was analyzed in detail using transmission electron microscopy (TEM) as shown in Fig. 2. The low-magnification image shown in Fig. 2(a) shows that the 0.7 mol% C<sub>60</sub>/Cu<sub>2</sub>Se nanocomposite has a small grain size (below 50 nm) and a large number of bright contrast regions. The carbon atom is much lighter than Cu and Se, and C<sub>60</sub> produces bright contrast in TEM images. The high resolution TEM (HR-TEM) image shown in Fig. 2(b) clearly indicates that the bright contrast region has a lattice spacing different from that of the Cu<sub>2</sub>Se matrix. The fast Fourier transform (FFT) patterns showed that the bright contrast region contains lattice spacings of 7.42 and 4.46 Å, which correspond to the interplanar distance of the (200) and (222) planes, indexed based on FCC fullerite, respectively.<sup>33</sup> On the other hand, the FFT pattern

from the background shows lattice spacings of 6.84 and 3.52 Å, which correspond to the interplanar distance of the (004) and (131) planes of monoclinic  $\alpha$ -Cu<sub>2</sub>Se, respectively.<sup>34</sup> These results indicate that the C<sub>60</sub>s incorporated in the Cu<sub>2</sub>Se matrix are agglomerated in fullerite structures with sizes of 5–10 nm. The estimated interparticle distance is roughly 4–15 nm (Table S1<sup>†</sup>), which must be sufficient to produce the Zener pinning effect. XRD data and lattice parameters for each crystalline plane are plotted in Fig. 3. Peaks of all samples were indexed based on monoclinic  $\alpha$ -Cu<sub>2</sub>Se structures with space group *C2/c* (no. 15)<sup>20,21,34,35</sup> whose lattice parameter was consistent with those calculated by HR-TEM analysis in Fig. 2(b). The lattice parameters<sup>34</sup> *a* = 7.1379 Å, *b* = 12.3823 Å, *c* = 27.3904 Å, and  $\beta$  = 94.308° (Fig. 3(b)) were constant for the C<sub>60</sub>/Cu<sub>2</sub>Se nanocomposite with various C<sub>60</sub> contents, which suggests that the C<sub>60</sub>s are dispersed as a separate phase instead of reacting with the Cu<sub>2</sub>Se.

The electrical properties of the C<sub>60</sub>/Cu<sub>2</sub>Se nanocomposites are plotted in Fig. 4. The electrical transport properties showed metallic behavior, which is typical of heavily doped thermoelectric semiconductors. The slight variation of temperature dependence around 350–400 K is clear evidence for the phase transition of Cu<sub>2</sub>Se from monoclinic to cubic, consistent with previous reports.<sup>20,22,35</sup> The electrical conductivities of the C<sub>60</sub>/Cu<sub>2</sub>Se nanocomposites were less than that of pure Cu<sub>2</sub>Se for all temperatures. As shown in Table S2,<sup>†</sup> the carrier concentration and mobility of the C<sub>60</sub>/Cu<sub>2</sub>Se nanocomposites were less than those of pure Cu<sub>2</sub>Se, likely due to carrier localization by potential wells, as shown in Fig. 4(d).<sup>15</sup> C<sub>60</sub> and Cu<sub>2</sub>Se have

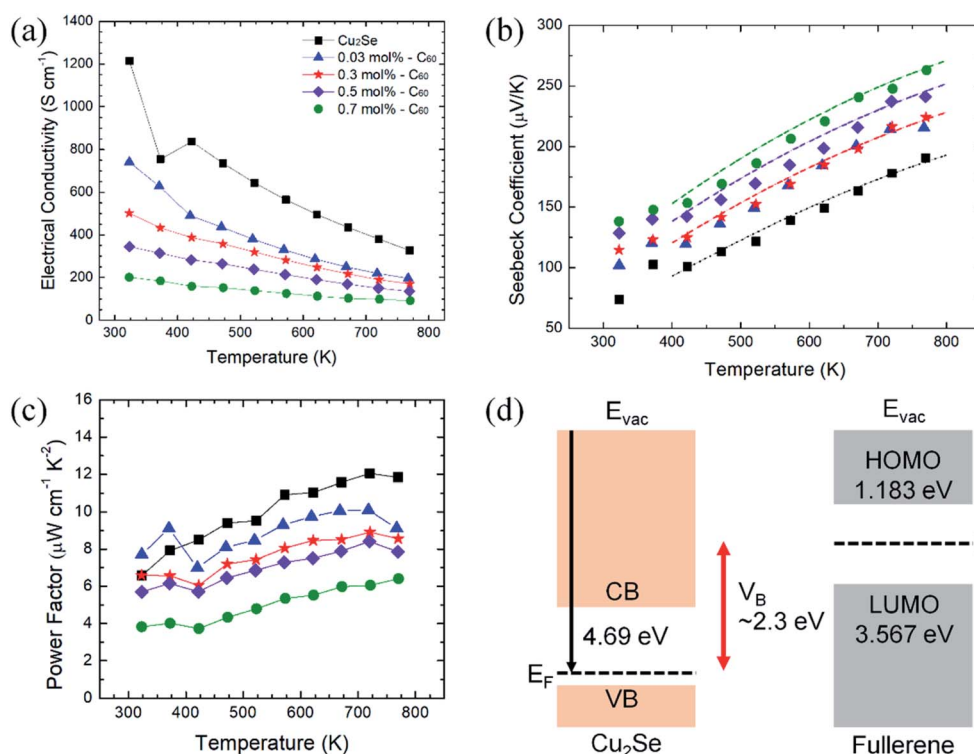


Fig. 4 Electrical properties of C<sub>60</sub>/Cu<sub>2</sub>Se nanocomposites. (a) Electrical conductivities, (b) experimental (markers) and calculated (dot-dash lines) Seebeck coefficients, (c) power factors, and (d) schematics of the band structures of Cu<sub>2</sub>Se, and C<sub>60</sub>.<sup>38</sup>



significantly different Fermi levels. The work function of Cu<sub>2</sub>Se is 4.69 eV,<sup>36</sup> whereas the HOMO and LUMO levels of C<sub>60</sub> are −1.183, and −3.567 eV, respectively.<sup>24</sup> Thus, the potential well depth is estimated to be around 2.3 eV, which could be the main reason for carrier localization. The Seebeck coefficient of C<sub>60</sub>/Cu<sub>2</sub>Se nanocomposites was significantly greater than that of pure Cu<sub>2</sub>Se (Fig. 4(b)), as expected due to carrier localization. The Seebeck coefficient was calculated using the following equation from the Boltzmann transport equation:<sup>2</sup>

$$S = \frac{k_B}{e} \left\{ \frac{\left(r + \frac{5}{2}\right) F_{r+\frac{5}{2}}(\eta)}{\left(r + \frac{3}{2}\right) F_{r+\frac{3}{2}}(\eta)} - \eta \right\} \quad (2)$$

where  $r$  is the scattering parameter,  $k_B$  is the Boltzmann constant,  $e$  is the electron charge,  $F$  is the Fermi-Dirac integral, and  $\eta$  is the reduced Fermi level.<sup>2</sup> The scattering parameter reflects the energy dependence of electron scattering time,  $\tau = \tau_0 E^r$ . In general, electron scattering is dominated by acoustic phonons in inorganic semiconductors.<sup>2,15,29</sup> The scattering parameter for acoustic phonon scattering is −0.5. To fit our experimental data from the C<sub>60</sub>/Cu<sub>2</sub>Se nanocomposites, the scattering parameters were determined to be −0.05, 0.25, and 0.5 for the 0.3, 0.5, and 0.7 mol% C<sub>60</sub>/Cu<sub>2</sub>Se nanocomposites, respectively. An increase of the scattering parameter indicates that the slope of the  $E\tau(E)D(E)$  term in eqn (1) is large, which results in enhancement of the Seebeck coefficient.<sup>16</sup> This result is clear evidence for carrier localization. The embedded C<sub>60</sub>s change the scattering mechanism of electrons. As shown in Fig. 4(b), the Seebeck coefficient of the 0.7 mol% C<sub>60</sub>/Cu<sub>2</sub>Se nanocomposite was enhanced by around 43% compared to that of pure Cu<sub>2</sub>Se. Because the electrical conductivity was reduced, the power factors of the C<sub>60</sub>/Cu<sub>2</sub>Se nanocomposites were not increased.

The thermal properties are plotted in Fig. 5. The thermal conductivities of the C<sub>60</sub>/Cu<sub>2</sub>Se nanocomposites were less than that of pure Cu<sub>2</sub>Se over the entire tested temperature range. Both electron thermal conductivities and lattice thermal conductivities were reduced for all C<sub>60</sub>/Cu<sub>2</sub>Se nanocomposites compared to those of pure Cu<sub>2</sub>Se. The reduction of electronic thermal conductivities is caused by reduction of electrical conductivities which are shown in Fig. 4(a). The lattice thermal conductivity reduction is due to phonon scattering by embedded C<sub>60</sub> nanoparticles, and can be calculated by a relaxation time approximation:<sup>4,28</sup>

where  $v_g$  is the group velocity of phonons,  $\hbar$  is the reduced Planck's constant,  $x$  is the reduced phonon energy,  $\theta$  is the Debye temperature, and  $\tau$  is the phonon scattering, while the subscript c represents 'combined', U represents 'Umklapp', A represents 'alloy', and N represents 'normal'.

The experimental and calculated lattice thermal conductivities are plotted in Fig. 5(c) (calculation details are described in the ESI†) The phonon scattering by embedded C<sub>60</sub>s was considered to be defect scattering. The calculation was only based on the 0.7 mol% C<sub>60</sub>/Cu<sub>2</sub>Se nanocomposite sample. The volume fraction of C<sub>60</sub> is derived from the mole fraction and size of C<sub>60</sub>. The calculation results fit well with the experimental results of the 0.7 mol% C<sub>60</sub>/Cu<sub>2</sub>Se nanocomposite. To fit the experimental data, 8 nm was used as the diameter of the clustered C<sub>60</sub> nanoparticles, which is consistent with TEM results shown in Fig. 2. The samples with other C<sub>60</sub> amounts (0.03, 0.3, 0.5 mol%) also had low lattice thermal conductivities that were similar to that of the 0.7 mol% sample. These data indicate that additional phonon scattering can drastically reduce lattice thermal conductivity when C<sub>60</sub> is embedded in Cu<sub>2</sub>Se. For example, correlated scattering between scattered phonons by multiple C<sub>60</sub> nanoparticles could additionally reduce lattice thermal conductivity.<sup>4</sup> M. Brewster and C. Tien<sup>37</sup> suggested that when  $c/\lambda < 0.3$ , where  $c$  is the interparticle distance and  $\lambda$  is the phonon wavelength, the correlated scattering effect should be considered, as interference between scattered phonons becomes important. A rough estimation (as described in the ESI†) suggests that the interparticle distances for the 0.3, 0.5, and 0.7 mol% C<sub>60</sub>/Cu<sub>2</sub>Se nanocomposites were around 5.3, 4.5, and 4.0 nm, respectively. As shown in Fig. 2, the experimentally observed value for interparticle distances was also on the few-nm scale. Considering that the dominant phonon wavelength is around 1–10 nm, some portion of phonon waves could have a  $c/\lambda$  value below 0.3, indicating the importance of the correlated scattering effect. Therefore, the observed lattice thermal conductivity is lower than the theoretical estimate, as shown in Fig. 5(c). Because of significant phonon scattering, the lattice thermal conductivity was around 0.25 W m<sup>−1</sup> K<sup>−1</sup> which is similar to the minimum thermal conductivity.<sup>2</sup>

$$\kappa_L = \frac{k_B}{2\pi v_g} \left( \frac{k_B T}{\hbar} \right)^3 \left\{ \frac{\theta}{\int_0^{\frac{\theta}{T}} \frac{\tau_c x^4 e^x}{(e^x - 1)^2} dx} + \frac{\left[ \int_0^{\frac{\theta}{T}} \frac{\tau_c}{\tau_N} \frac{x^4 e^x}{(e^x - 1)^2} dx \right]^2}{\int_0^{\frac{\theta}{T}} \frac{1}{\tau_N} \left( 1 - \frac{\tau_c}{\tau_N} \right) \frac{x^4 e^x}{(e^x - 1)^2} dx} \right\} \quad (3)$$

$$\frac{1}{\tau_c} = \frac{1}{\tau_N} + \frac{1}{\tau_D} + \frac{1}{\tau_U} + \frac{1}{\tau_A}$$



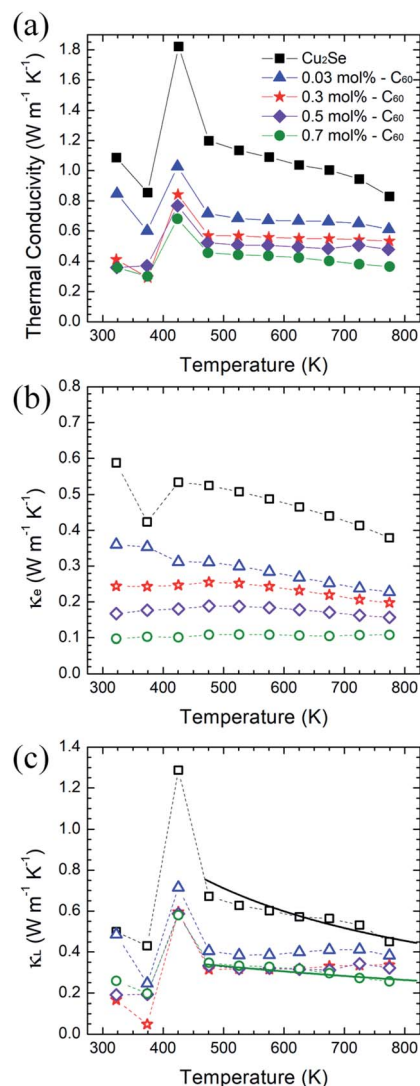


Fig. 5 Thermal properties of  $C_{60}/Cu_2Se$  nanocomposites. Experimental (markers) and calculated (solid lines) (a) total thermal conductivities, (b) electron thermal conductivities, and (c) lattice thermal conductivities.<sup>38</sup>

As shown in Fig. 6, the maximum  $zT$  was around 1.4 at 773 K for the 0.7 mol%  $C_{60}/Cu_2Se$  nanocomposite. The enhancement of  $zT$  was mainly caused by the synergetic effect of phonon scattering and carrier localization. The strong phonon scattering by embedded  $C_{60}$  significantly reduced lattice thermal conductivity by 40–50% over the entire tested temperature range. The energy-dependent electron scattering by potential well of  $C_{60}$  significantly reduces electrical conductivity, resulting in the reduction of electronic thermal conductivity. Through these mechanisms, incorporation of  $C_{60}$  decreases the total thermal conductivity by around 60%. Moreover, the Seebeck coefficient is enhanced by the carrier localization. By the synergetic effect of the carrier localization and phonon scattering by the embedded  $C_{60}$ s,  $zT$  is enhanced by 20–30% in  $C_{60}/Cu_2Se$  nanocomposites compared to that of pure  $Cu_2Se$ .

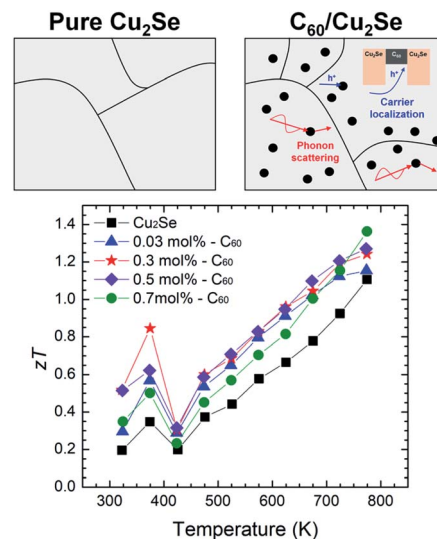


Fig. 6 Schematic comparing pure  $Cu_2Se$  and a  $C_{60}/Cu_2Se$  nanocomposite and the thermoelectric figure of merit  $zT$  as a function of temperature.<sup>38</sup>

## Conclusion

$C_{60}$  incorporated  $Cu_2Se$  nanocomposites were synthesized using a simple solid-state reaction. The microstructure of the  $C_{60}/Cu_2Se$  nanocomposites was different from that of pure  $Cu_2Se$ . Grain growth was suppressed in  $C_{60}/Cu_2Se$  nanocomposites because of the Zener pinning effect, showing that the nanocomposites contain more grain boundaries than pure  $Cu_2Se$ . The dispersed  $C_{60}$ s are clustered in the fullerite form around 10 nm size. They act as phonon scatterers and potential wells for holes. Due to the phonon scattering by the embedded  $C_{60}$  nanoparticles, the lattice thermal conductivity of the  $C_{60}/Cu_2Se$  nanocomposite is reduced by around 40–50% compared to that of pure  $Cu_2Se$ . The reduction of lattice thermal conductivity was analyzed quantitatively using a phonon scattering model. The Seebeck coefficient was enhanced by carrier localization caused by  $C_{60}$ . Due to the difference in Fermi level between  $C_{60}$  and  $Cu_2Se$ ,  $C_{60}$  can act as a potential well for carriers (holes), resulting in carrier localization (energy filtering). Through quantitative analysis using the Boltzmann transport equation, it was found that the  $C_{60}/Cu_2Se$  nanocomposites have an additional scattering process for carriers that is caused by the  $C_{60}$  nanoparticles. The additional scattering process increased the Seebeck coefficient by 43%. Through the synergetic effect of phonon scattering and carrier localization in  $C_{60}/Cu_2Se$  nanocomposites, the thermoelectric figure of merit was enhanced by 20–30% compared to that of pure  $Cu_2Se$ .

## Experimental<sup>38</sup>

### Synthesis

The precursor materials, namely, copper powder (Cu, <425  $\mu m$ , 99.5%), selenium pellets (Se, <5 mm, >99.99%), and fullerene powder ( $C_{60}$ , 98%) were obtained from Sigma-Aldrich. The mixture of raw materials was sealed in a quartz tube and loaded



in a furnace, where the temperature was slowly increased to 673 K in 6 hours and then held for 2 hours. The reaction was carried out at a temperature of 1073 K for 5 days, and the samples were naturally cooled to 298 K. Subsequently, the resultant ingots were ground into a powder. The fullerene ( $C_{60}$ ) was added to the as-synthesized  $Cu_2Se$  powder through a simple mechanical alloy method. Fullerenes and hand ground  $Cu_2Se$  were weighed to produce accurate  $C_{60}$  contents of 0.03, 0.3, 0.5, and 0.7 mol%. Then, the mixed powders were mechanically ground using planetary ball milling for 2 hours. The pure  $Cu_2Se$  hand ground powder was also ground again using ball milling for 2 hours. In order to obtain high density samples for measurement, the ball-milled powders were consolidated into pellets by spark plasma sintering (SPS) at 723 K and under a high pressure of 85 MPa. The relative densities of  $C_{60}$ -incorporated  $Cu_2Se$  samples were 98.6–99.9% of the theoretical density.

### Characterization

The crystal structures of the ball-milled products and sintered pellets were characterized by powder X-ray diffraction (PXRD), recorded on X-ray diffractometer equipment using a  $Cu-K\alpha$  radiation wavelength of 1.5418 Å at 40 kV and 30 mA. The diffraction data were collected at a scan rate of  $2^\circ \text{ min}^{-1}$  with the angle ranging from  $10^\circ$  to  $80^\circ$ . The microstructures of samples were obtained by scanning electron microscopy (SEM) using a JEOL JSM-6700F at an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) and high resolution TEM (HR-TEM) images were recorded on a JEOL JEM-F200 instrument.

The electrical conductivity ( $\sigma$ ) and Seebeck coefficient ( $S$ ) were measured simultaneously on a ZEM-3 (Ulvac-Riko ZEM-3). The thermal conductivity ( $\kappa$ ) was obtained through  $\kappa = D \times C_p \times \rho$ , where  $D$ ,  $C_p$  and  $\rho$  are the thermal diffusivity, heat capacity, and mass density, respectively. The thermal diffusivity ( $D$ ) was measured using an LFA 457 (NETZSCH). The heat capacity ( $C_p$ ) was obtained from the literature.<sup>36</sup> The Archimedes method was performed to calculate the mass density ( $\rho$ ). The Hall coefficient was obtained using a physical property measurement system (PPMS 16T, Quantum Design) with magnetic field ranging from  $-9$  T to  $9$  T.

### Calculation of Seebeck coefficient and lattice thermal conductivity

The calculation of the Seebeck coefficient is based on eqn (2) in the main text. The temperature-dependence of the Fermi level position is used as fitting parameter to calculate the Seebeck coefficient of pure  $Cu_2Se$ . The Seebeck coefficient for  $C_{60}/Cu_2Se$  nanocomposites is fitted by changing the scattering parameter.

The calculation of lattice thermal conductivity is based on the Callaway model, as described in eqn (3). The relaxation time for the defect (embedded  $C_{60}$ ) is obtained by methods reported in the literature.<sup>3</sup> (A detailed process is described in the ESI†)

### Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

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