

General Syntheses of High-Performance Thermoelectric Nanostructured Solids without Post-Synthetic Ligand Stripping

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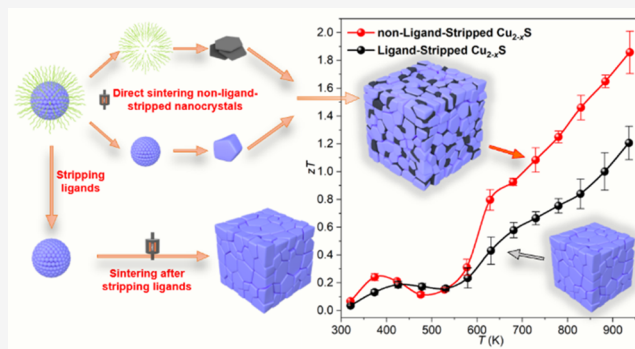
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Supporting Information

ABSTRACT: Ligand-assisted wet chemical synthesis is a versatile methodology to produce controllable nanocrystals (NCs). The post-treatment of ligands is significant for the performance of functional devices. Herein, a method that retains ligands of colloidal-synthesized nanomaterials to produce thermoelectric nanomaterials is proposed, which differs from the conventional methods that strip ligands using multistep cumbersome processes. The ligand-retention method can control the size and dispersity of nanocrystals during the consolidation of the NCs into dense pellets, in which retained ligands are transformed into organic carbon within the inorganic matrices, establishing clear organic–inorganic interfaces. Characterizations of the nonstripped and stripped samples confirm that this strategy can affect electric transport slightly but reduce the thermal conductivity largely. As a result, the materials (e.g., SnSe, Cu_{2-x}S, AgBiSe₂, and Cu₂ZnSnSe₄) with ligands retained achieve higher peak zT and better mechanical properties. This method can be applied to other colloidal thermoelectric NCs and functional materials.

KEYWORDS: Thermoelectric, Colloidal nanocrystals, Ligands, Metallic chalcogenides



Colloidal synthesis shows great potential in many applications, including optoelectronics, biolabeling, catalysis, and thermoelectrics (TEs).^{1–6} The synthesized colloidal nanocrystals usually consist of inorganic crystalline cores with layers of organic molecule ligands (e.g., oleic acid, trioctylphosphine oxide, alkanethiols, etc.) attached to their surfaces. The choice of ligands is of utmost importance for the colloidal stability NCs and the function of NC-based devices. The size, chemical composition, structure, and morphology of the nanocrystal cores are regulated by ligands during the nucleation and growth process, determining the physiochemical properties.^{7,8} The interparticle distance, colloidal dispersion, and packing density of an NCs assembly determined by the ligand nature/coverage strongly affect the charge carrier transport property, thermal conductivity, and chemical reactivity.^{9–13} For example, Wang et al. proposed a novel ligand-cross-linking process to increase the thermal conductivity of NC solids by overcoming the thermal-transport bottleneck between adjacent colloidal NCs.¹⁴ Zheng et al. demonstrated that the unique ligand system could modify the active sites and improve the catalytic capability of PdAu bimetallic nanocluster catalysts.¹⁵

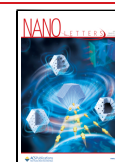
For TE materials, the performance is evaluated by the dimensionless figure of merit zT ($zT = S^2\sigma T/\kappa$, where S , σ , T , and κ are the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively).^{10,16,17} A good TE material requires a high power

factor ($PF = S^2\sigma$) and low κ . An effective strategy to achieve depressed κ is to sinter ligand-assisted wet-chemistry-synthesized nanoparticles into dense nanostructured blocks, which enhance phonon scattering at numerous grain boundaries.¹⁸ During assembly into semiconducting solids, the surface ligands are readily lost by thermally decomposing the organic ligands, chemically removing them, or replacing long organic ligands with shorter organic or inorganic ligands before sintering.^{19–21} For instance, Yu et al.²² removed organic ligands of large-scale colloidal Cu₂ZnSnSe₄ NCs by dealing with hydrazine before NCs consolidation. With this strategy, various materials such as Cu₂SnSe₃,²³ Bi₂Te₃,²⁴ Cu₂CdSnSe₄,²⁵ and Cu₃FeS₄²⁶ were sintered into pellets by spark plasma for TE applications. Maria Ibáñez et al.²⁷ removed ligands by heating the nanoparticle powders under inert gas before the hot press procedure. Talapin et al. investigated surface ligand exchange by metallic cation, halide anions, metal chalcogenide, and halide perovskites for NCs–ligand interface modification and optimized TE performance.^{3,28–30} In addition, ligand

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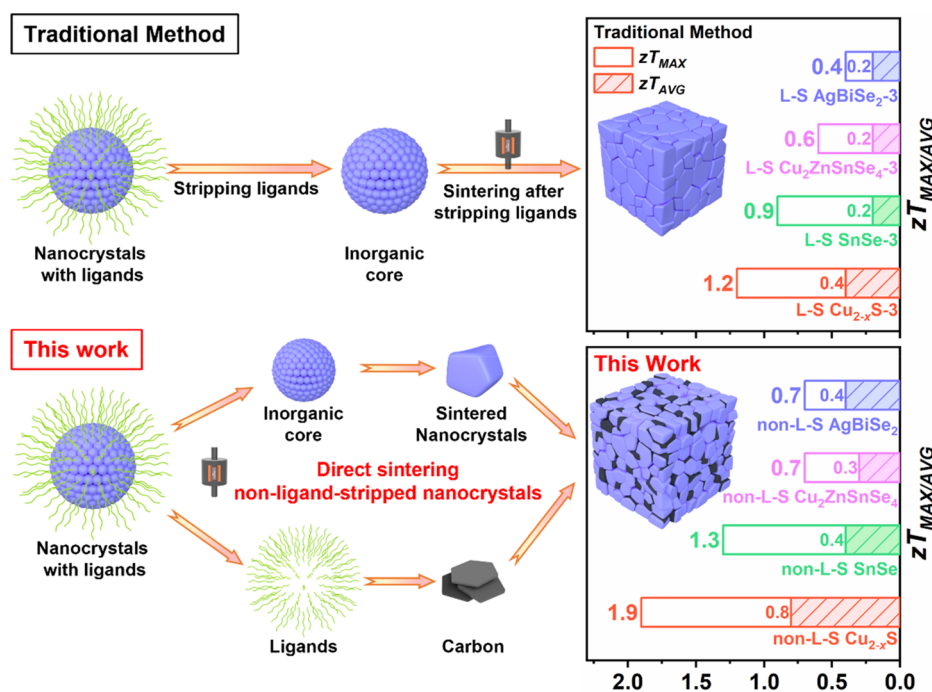


Figure 1. Schematic diagram of improving TE performance of the nanocrystals (SnSe, Cu_{2-x}S, AgBiSe₂, and Cu₂ZnSnSe₄) through retaining organic ligands.

exchange in commercial quantum dot light-emitting diodes frequently enhance charges transfer between quantum dots to improve quantum efficiency.^{31–36} However, all these post-ligand treatments are multistep processes, which are cumbersome and costly.^{4,9,37} Also, they often need expensive hydrazine or thiols, which are toxic or flammable. On the contrary, without stripping the organic ligands, the structure of the ligands can influence the assembled semiconductor nanocrystals and achieve their interfacial modification at the surfaces of NCs, which has rarely been studied and remains a challenge. This motivated us to delve into how ligand retaining can regulate the TE properties of colloidal NCs.

Herein, a new strategy to retain the ligands of TE nanomaterials is demonstrated in SnSe, Cu_{2-x}S, AgBiSe₂, and Cu₂ZnSnSe₄ NCs, in contrast to the traditional methods that strip the ligands. Ligand coatings can be partially retained and used as controllable molecular solders, simultaneously acting as precursors for forming secondary carbon phases during NCs consolidation. Calculations indicate that the introduced high-density organic–inorganic semiconductor interface suppresses the κ of the materials. As a result, compared with control samples (with ligand stripping), the samples without ligand stripping show higher peak and average zT values. In addition to excellent TE performance, Cu_{2-x}S without ligand stripping shows improved mechanical properties, which provide the potential for device applications. The preparation method without ligand stripping reduces solvents and toxic reagents, enabling the cost-effective fabrication of efficient TE materials, a practical example of atom economy and green chemistry.

Figure 1 shows the synthesis processes, comparing the ligand-stripping and ligand-retaining methods. First, the nanoparticles are synthesized by a colloidal synthesis approach, which forms a layer of ligand molecules on the nanoparticle surfaces. Hydrazine, as a Brønsted base, traditionally removes the original capping ligands from the nanocrystal surfaces. Whether these nanoparticles are treated with hydrazine to

remove ligand molecules or not, the process is named the ligand-stripping or ligand-retaining process. The nanoparticles are sintered into dense nanostructured blocks using Spark Plasma Sintering (SPS). As a proof of concept, we select SnSe (the record-high zT TE material), phonon-liquid electron-crystal Cu_{2-x}S, diamond-like structured AgBiSe₂, and multi-ary Cu₂ZnSnSe₄ with the commonly used long-alkyl-chain organic ligands (oleylamine (OAm), oleic acid (OA), and dodecanethiol (DDT)) as examples. The sintering and molding of as-synthesized nanocrystals lasted for 30 min in a closed die during SPS, preventing the volatilization of ligands. Therefore, the remaining organic ligands thermally decompose and transform into organic carbon as a secondary phase within the matrices, forming the inorganic NCs-organic carbon interface (Figures 1 and S1). Reduced κ in the non-L-S samples is attributed to residual carbon at the grain boundaries and the slightly smaller crystal domains than in the L-S samples. The well-developed surface chemistry of colloidal NCs by retained ligands offers the opportunity to engineer the interfaces and microstructures of the assembled solids, resulting in a high average zT and excellent mechanical properties. In this study, NCs treated with hydrazine hydrate for 0, 1, and 3 time(s) are referred to as non-L-S sample, L-S sample-1, and L-S sample-3, respectively.

The atomic structures of the samples are characterized through several techniques. The representative X-ray diffraction (XRD) patterns (Figure S2) demonstrate the crystalline structure of the SnSe, Cu_{2-x}S, AgBiSe₂, and Cu₂ZnSnSe₄ NCs, which are indexed to the orthorhombic $Pnma$ phase, tetragonal $P4_32_12$ and monoclinic $P2_1/c$ phase, hexagonal $P\bar{3}m1$ phase, and cubic $F\bar{4}3m$ phase, respectively. The hydrazine treatment does not change the crystal structure of the materials. Table S4 in the Supporting Information shows the cell parameters of the above materials. The transmission electron microscopy (TEM) images of the SnSe, Cu_{2-x}S, AgBiSe₂, and Cu₂ZnSnSe₄ NCs characterize the size distribution and morphology of as-

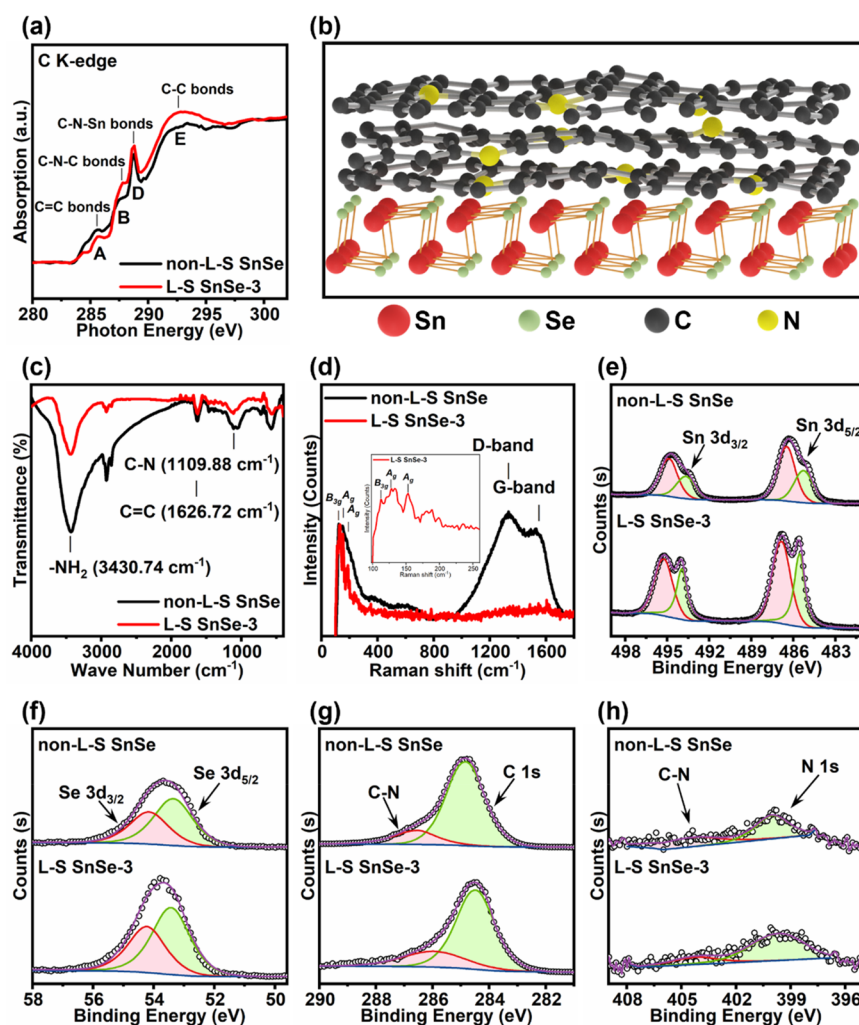


Figure 2. (a) C K-edge soft X-ray absorption near-edge spectroscopy (XANES) normalized spectra. (b) Schematic diagram of NCs surface morphology structure. (c) Fourier transform infrared (FTIR) and (d) Raman spectra of non-L-S SnSe and L-S SnSe-3. The XPS peak areas of (e) Sn $3d_{3/2}$ and Sn $3d_{5/2}$, (f) Se $3d_{3/2}$ and Se $3d_{5/2}$, (g) C 1s, and (h) N 1s of the non-L-S SnSe and L-S SnSe-3.

synthesized NCs (Figures 3a and S4). Disk-like, small sphere-like, irregular, and cubic shapes with average sizes of around $336 (\pm 65)$ nm, $18 (\pm 3)$ nm, $19 (\pm 4)$ nm, and $13 (\pm 2)$ nm are obtained for these four materials, respectively. The high-resolution (HR) TEM of SnSe, Cu_{2-x}S , AgBiSe_2 , and $\text{Cu}_2\text{ZnSnSe}_4$ are shown in Figures 3b and S4.

To identify the chemical environment of the organic surfactant shell surrounding the TE materials before and after ligand stripping, we perform Fourier transform infrared (FTIR) spectroscopy for dried samples. As shown in Figure 2c, the presence of the OAm molecules is identified by the symmetric and asymmetric stretching vibrations of $-\text{NH}_2$ at 3430.74 cm^{-1} , the bending vibrations of $\text{C}=\text{C}$ bonds at 1626.72 cm^{-1} , and the bending vibration of the $\text{C}-\text{N}$ bond at 1109.88 cm^{-1} . These features are weaker in the L-S SnSe-3 sample compared with the nonstripped samples. The L-S SnSe-3 sample also shows the removal of ligands from the surface of colloidal nanoparticles by exchange with hydrazine. This result is in good accordance with Raman spectra (Figures 2d and S3), in which the carbon peaks of the samples are calibrated relative to the characteristic B_{3g} and A_g Raman modes of SnSe at 109 , 128.5 , and 150 cm^{-1} .^{38,39} Two dominant carbon peaks of SPSed SnSe samples without ligand stripping at around 1334 and 1526 cm^{-1} correspond to the D

and G bands, respectively (Figure 2d). The D band is assigned to the breathing mode of A_{1g} symmetry or sp^3 -rich phase for the disordered graphite. The G band corresponds to the E_{2g} mode of 2D graphite, which is related to the vibration of sp^2 -hybridized carbon. The D and G bands indicate that the surface ligands are turned into organic carbons during sintering. The relatively high intensity of the D-band and G-band (I_D/I_G) (1.11) for non-L-S SnSe indicates a high degree of carbon disorder, which is beneficial for enhancing phonon scattering and reducing thermal conductivity.^{40–42} For SPSed L-S SnSe-3, the intensity of the D and G bands are significantly decreased due to the ligand stripping and the elimination of carbon during the annealing process.^{41,42} This is also proved by carbon composition analysis. The carbon content (1.23 wt %) for SPSed non-L-S SnSe pellets was much higher than that (0.264 wt %) of L-S SnSe-3 pellets. In addition, the N atom in oleylamine ligands will incorporate into the nanostructure solids during the bulk consolidation step to provide a large density of point defects, facilitating the reduction of thermal conductivities (Figure 2b). To test the formation of the carbon-heteroatom bond, soft X-ray absorption near-edge structure (XANES) measurements are used to detect the K-edge excitation of elemental C (Figure 2a) to investigate the electronic structure and the nature of the carbon defect of the

SnSe-Carbon sample. Four peaks at ~ 285.5 , 287.8 , 288.7 , and 292.1 eV are denoted as A, B, D, and E, respectively. The absorption peak A corresponds to π^* excitations of C=C bonds at the defect sites,⁴³ and the peak E corresponds to the σ^* structure of C-C bonds.⁴⁴ The strong π^* and σ^* bands structures show that the carbon is graphitized.⁴⁵ The weak shoulder peaks B and D exist between π^* and σ^* features, ascribed to the π^* excitation of C-N-C bonds in the g-C₃N₄ structure and C-N-Sn bridging bonds, respectively, demonstrating a stronger interfacial interaction between N-doped carbon and SnSe nanoparticles and the defective characteristics of the carbon layer.^{43–45}

X-ray photoelectron spectroscopy (XPS) analysis further proves this phenomenon (Figure 2e–h). The Sn peaks of non-L-S SnSe are slightly shifted to lower binding energies (BEs) compared to the reported SnSe (~ 0.33 eV),⁴⁶ demonstrating the bonding of C-N-Sn. The same phenomenon has also occurred in the Se 3d spectra, shifting about 0.12 eV to lower BE. The fitting result of the N 1s peak shows that two peaks at 400.5 and 404.2 eV correspond to pyridinic-N and graphitic-N, and pyridinic-N is the dominant species.^{44,45,47} The C 1s spectrum can be divided into two peaks at 284.8 eV and a higher BE of 286.6 eV, corresponding to the sp^2 hybridized graphitic carbon and C-N species.⁴⁸

TEM images (Figure 3c,d) demonstrate that the Cu_{2-x}S NCs are embedded in the nanostructured solids, and the ligands are carbonized as a carbon coating on the grain of Cu_{2-x}S. Figure 3d shows the *d*-spacing of carbon is approximately 0.41 nm.⁴⁹ The carbon is mainly distributed along with the marginal area of Cu and S elements, as depicted in the EDS elemental mapping in Figure 3g–j. The carbon coating of Cu_{2-x}S is rarely observed in the ligand-stripped samples (Figure 3e), consistent with the FTIR, Raman, and carbon-content analysis results as discussed above. In addition, elemental mappings are performed to identify Sn, Se, Ag, Bi, Cu, and Zn elements in nanoparticles for SPSed SnSe, SPSed AgBiSe₂, and SPSed Cu₂ZnSnSe₄ (Figures S6–S8).

The TE properties of Cu_{2-x}S are measured in the temperature range from 300 to 937 K (Figure 4). The dependence of the σ and the *S* on the temperature of non-L-S samples is similar to that of L-S samples. The electrical conductivity shows two peaks because of the phase transition, which is similar to the reports in the literature.^{50,57} For non-L-S Cu_{2-x}S, the two peaks are 21.5×10^3 and 32.2×10^3 S m⁻¹ at 323 and 650 K, respectively. Relatively high electrical conductivities were obtained for the ligand-stripped samples, and the carbon capping layer slightly affects the electric transport of the nonligand-stripped sample. The value of the *S* obtained for the Cu_{2-x}S samples increases with temperature and decreases with increasing ligand stripping throughout the entire temperature. For example, as shown in Figure 4d, the room-temperature *S* for the non-L-S Cu_{2-x}S, L-S Cu_{2-x}S-1, and L-S Cu_{2-x}S-3 samples are 79.1, 74.5, and 58.3 $\mu\text{V}\cdot\text{K}^{-1}$, respectively. Such difference is largely related to the n_{H} (Figure 4b), derived from the copper vacancy and the residual carbon at the grain boundaries. The non-L-S Cu_{2-x}S with more carbon components have lower n_{H} , and alkaline hydrazine hydrate treatment can lead to the etching of the surface of NCs, in which the generation of metal vacancies will increase their n_{H} . Finally, the PF of all the samples is shown in Figure 4e. At 937 K, the PF of non-L-S Cu_{2-x}S (0.97 mW m⁻¹ K⁻²) is higher than that of the L-S samples (0.90 mW m⁻¹ K⁻²) due to its higher *S*.

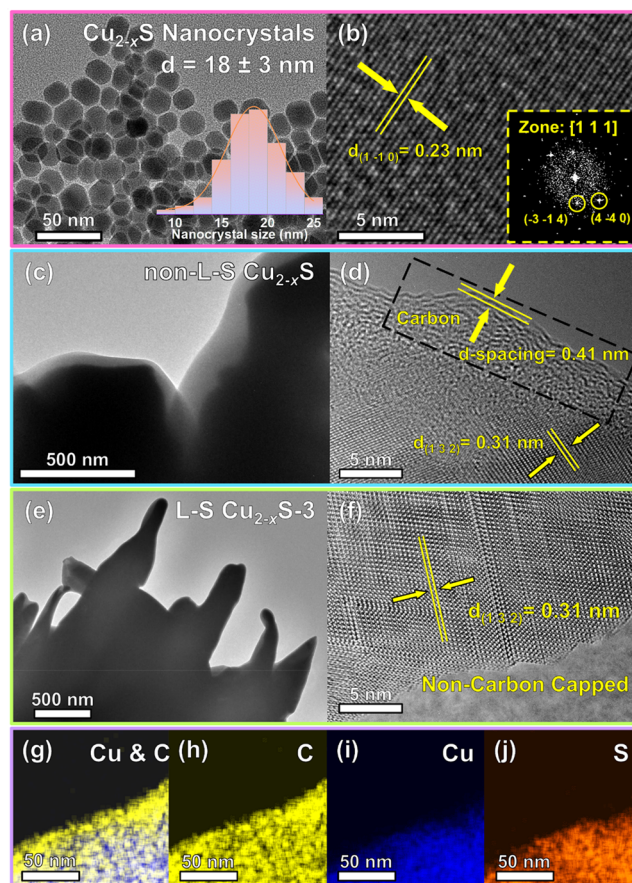


Figure 3. Morphology characterizations of Cu_{2-x}S samples. (a) The TEM images with the grain size distribution histograms of the synthesized sphere-like Cu_{2-x}S nanoparticles. (b) The HRTEM image of Cu_{2-x}S nanoparticles. (inset) The corresponding FFT pattern. (c, d) TEM and HRTEM images of the non-L-S Cu_{2-x}S sample, the carbon is marked in the black dashed box. (e, f) TEM and HRTEM images of the L-S Cu_{2-x}S-3. (g–j) The energy-dispersive spectroscopy (EDS) elemental mapping of C (yellow), Cu (blue), and S (orange) for non-L-S Cu_{2-x}S sample.

The κ_{tot} (Figure 4g) of the non-L-S Cu_{2-x}S pellet is 0.63 W m⁻¹ K⁻¹ at 323 K, which is lower than those of L-S Cu_{2-x}S-1 (0.73 W m⁻¹ K⁻¹) and L-S Cu_{2-x}S-3 (0.83 W m⁻¹ K⁻¹). According to the Wiedemann–Franz law, the electronic thermal conductivity can be calculated via $\kappa_{\text{ele}} = L\sigma T$, where $L = (1.5 + \exp(-|S|/116)) \times 10^{-8}$ is the Lorenz number. After subtracting κ_{ele} from κ_{tot} , we obtain the lattice thermal conductivity κ_{lat} , as shown in Figure 4f.^{16,58} It is found that the κ_{lat} decreased by as much as 43% (from 0.35 to 0.20 W m⁻¹ K⁻¹) upon retaining the ligands. Due to the slightly enhanced PF and much-reduced κ_{tot} , a high zT_{max} of 1.9 (at 937 K) is achieved for non-L-S Cu_{2-x}S (Figure 4h). Figure 4i compares the zT values achieved in this work with the state-of-the-art peak zT in Cu_{2-x}S compounds, indicating that the method of retaining ligands in this work positively impacts improving the TE properties. In addition, the theoretical maximum efficiency of 10% for the non-L-S Cu_{2-x}S and a theoretical maximum figure of merit ZT of a TE device of the 0.5 for 320–930 K temperature range was calculated using the method provided by Snyder et al. (Figure S10).⁵⁹

To understand the decreased lattice thermal conductivity with retaining ligands (or increasing amorphous carbon content), we conducted theoretical analyses using Cu_{2-x}S as

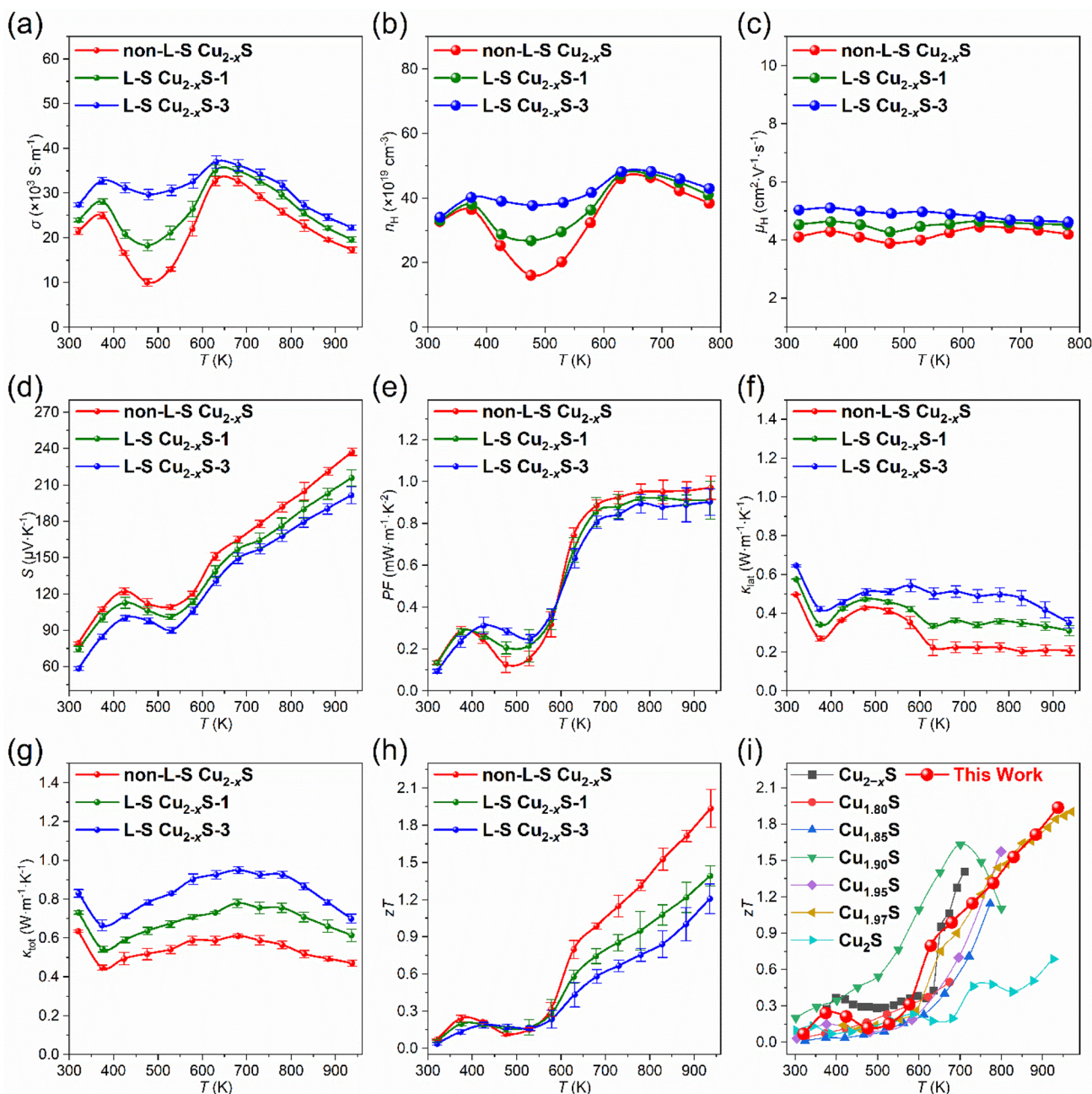


Figure 4. Temperature-dependent (a) electrical conductivity (σ), (b) carrier concentration (n_H), (c) carrier mobility (μ_H), (d) Seebeck coefficient (S), (e) power factor (PF), (f) lattice thermal conductivity (κ_{lat}), (g) total thermal conductivity (κ_{tot}), and (h) zT of Cu_{2-x}S TE materials.^{50–56} Reprinted with permission from ref 50. Copyright [2021] [Wiley]. Reprinted with permission from ref 51. Copyright [2021] [ACS publications]. Reprinted with permission from ref 52. Copyright [2020] [Elsevier B.V.]. Reprinted with permission from ref 53. Copyright [2015] [RSC]. Reprinted with permission from ref 54. Copyright [2011] [RSC]. Reprinted with permission from ref 55. Copyright [2021] [Elsevier B.V.]. Reprinted with permission from ref 56. Copyright [2016] [Wiley].

an example. To estimate the interfacial thermal resistance (R_K) between Cu_2S and amorphous carbon, we calculated the phonon density of states (DOS) of Cu_2S by density functional theory (DFT). We collected the phonon DOS of different forms of carbon,^{60,61} as shown in Figure 5b. It is found that they exhibit a great mismatch: Cu_2S has extremely high DOS below 10 THz, where the DOS of carbon is minimal, indicating that R_K should be very large. To estimate whether R_K can play a role in reducing the thermal conductivity of Cu_2S , we estimated R_K using the diffusive mismatch model

(DMM)⁶² (See page 7 of Supporting Information for detailed calculations).

Owing to the reduced κ and the increased PF, higher zT values of non-L-S Cu_{2-x}S are achieved as 1.9 at 937 K, 1.6-fold of the value obtained by L-S Cu_{2-x}S -3 ($zT = 1.2$), indicating our strategy of retaining ligands affects improving TE performance (Figure 4f). To validate the potential of the described procedure to prepare nanomaterials with enhanced performance, in addition to Cu_{2-x}S , we obtained the TE properties of SnSe, AgBiSe₂, and $\text{Cu}_2\text{ZnSnSe}_4$ pellets (Figures S11–S13). Lower κ of non-L-S samples indicate the scattering

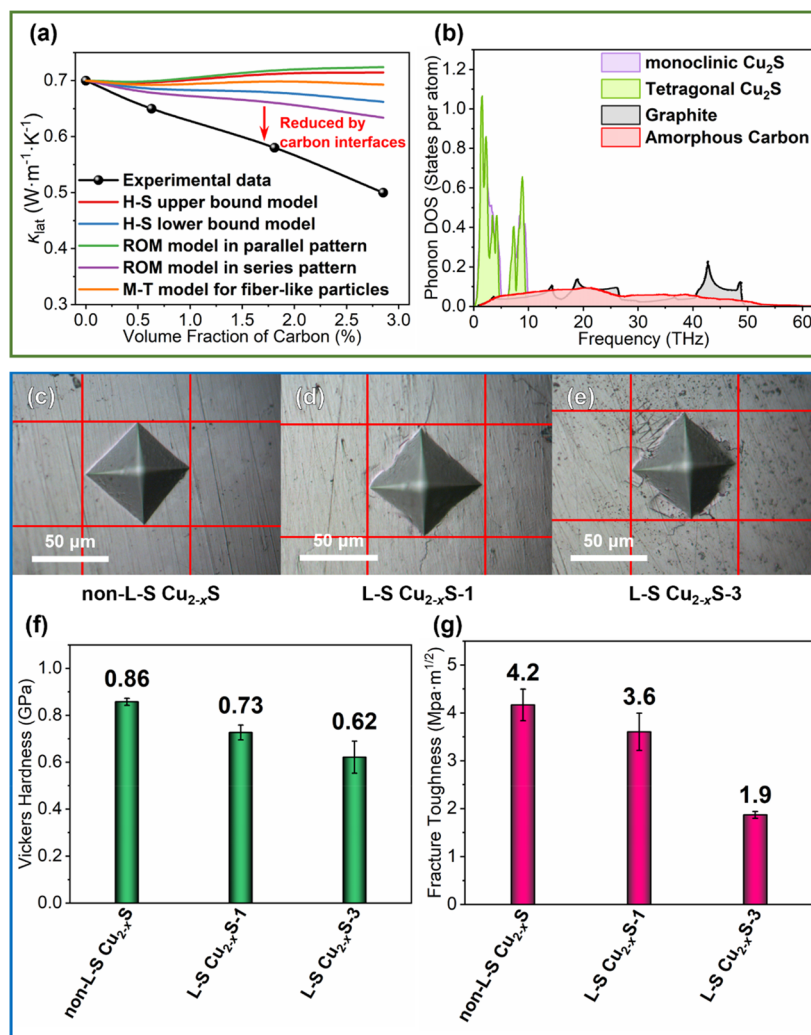


Figure 5. (a) Lattice thermal conductivity (κ_{lat}) at 323 K with different volume fractions of carbon. The thermal conductivities are predicted by the Hashin-Shtrikman bound model (H–S ub and H–S lb), the rule of mixture (ROM) model in parallel and series patterns, and the Mori-Tanaka (M-T) model for fiber-like particles. (b) The mismatch in phonon density of states between Cu₂S and different forms of carbon.^{60,61} Reprinted with permission from ref 60. Copyright [2004] [Elsevier Ltd.]. Reprinted with permission from ref 61. Copyright [2018] [Informa UK Limited]. The microscopic appearance of indentation of the (c) non-L-S Cu_{2-x}S, (d) L-S Cu_{2-x}S-1, and (e) L-S Cu_{2-x}S-3. (f) Micro Vickers hardness and (g) fracture toughness of the non-L-S Cu_{2-x}S, L-S Cu_{2-x}S-1, and L-S Cu_{2-x}S-3.

of phonons at interfaces in these nanocrystalline alloy composites.

Finally, the zT values of the above non-L-S samples prepared by the retained ligands route are all higher than those of L-S sample-3 due to reduced κ_{tot} without deterioration of the electrical transport performance. As shown in Figure 1, the highest zT for the L-S SnSe-3, L-S Cu_{2-x}S-3, L-S AgBiSe₂-3, and L-S Cu₂ZnSnSe₄-3 are 0.9, 1.2, 0.4, and 0.6, respectively, while the highest zT for non-L-S samples are 1.3, 1.9, 0.7, and 0.7, respectively, and the average zT has a similar trend. We believe that the surface-ligand influence on properties is related to the effect of surface treatment on the final surface composition and structure. The inorganic NCs-organic carbon interfaces effectively scatter long mean-free-path electrons and phonons, which is beneficial to reducing the κ . Although the carbon-nano grain interfaces slightly, there is a decrease of the σ due to the insulating capping layer of carbon. Under certain conditions, they also play an important role in enhancing the S . Therefore, the zT can be improved by balancing the electronic

and thermal properties by regulating the amount of retained organic ligands.

After we achieved an improved zT value, we also evaluated the fracture toughness to understand the effect of retained ligands on the mechanical properties (take the Cu_{2-x}S system, for example). The Vickers hardness (H_v) and fracture toughness (K_{IC}) are measured on the polished surface according to the equations $H_v = 1854.4 \cdot F/D^2$ and $K_{\text{IC}} = A \cdot (E/H_v)^{0.5} \cdot (F/c^{1.5})$, where F is the applied load, D is the length of the diagonal of the resultant impression, the calibration constant is a value of 0.01,^{63,64} c is the radial crack length of Vickers indentation, and E is Young's modulus of the Cu_{2-x}S samples.⁶⁵ We use nanoindentation to measure Young's modulus. Figure 5f,g shows that the hardness and the fracture toughness of L-S Cu_{2-x}S-3 are about 0.62 GPa and 1.9 MPa·m^{1/2}, respectively. In contrast, the hardness and fracture toughness of the non-L-S Cu_{2-x}S can reach as high as 0.86 GPa and 4.2 MPa·m^{1/2}. Ligands used as controllable molecular solders can generate a bridging effect between Cu_{2-x}S grains

and improve their stronger interaction, resulting in optimized mechanical durability.

In conclusion, we develop a general synthesis method to avoid complex ligand stripping procedures and introduce controlled amounts of secondary carbon phases. We have demonstrated that residual carbon between grain boundaries suppresses thermal conductivity and enhances the mechanical properties of NC solids. Furthermore, the convenience and potential of the strategy are demonstrated with SnSe, Cu_{2-x}S, AgBiSe₂, and Cu₂ZnSnSe₄ NCs, which possess higher *zTs* as compared to control samples with ligand stripping. Our result provides a general route for suppressing thermal transport in organic/inorganic hybrid materials. Beyond the above metallic chalcogenides in this work, the strategy will likely be broadly applicable to other colloidal nanomaterials. It should help to expand interface engineering to other device applications, such as photovoltaics, electronics, and light-emitting diodes.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.nanolett.3c01438>.

Details of the experimental section, density functional theory calculation (Tables S1–S3), additional X-ray diffraction patterns (Figure S2), additional transmission electron microscopy, and scanning electron microscopy analyses (Figures S4–S9 and S14), and TE properties of SnSe, AgBiSe₂, and Cu₂ZnSnSe₄ (Figures S10–S13) (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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