Multiscale architectures boosting thermoelectric performance of copper sulfide compound

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Abstract Owing to their high performance and earth abundance, copper sulfides (Cu_{2-x}S) have attracted wide attention as a promising medium-temperature thermoelectric material. Nanostructure and grain-boundary engineering are explored to tune the electrical transport and phonon scattering of Cu_{2-x}S based on the liquid-like copper ion. Here multiscale architecture-engineered Cu_{2-x}S are fabricated by a room-temperature wet chemical synthesis combining mechanical mixing and spark plasma sintering. The observed electrical conductivity in the multiscale architecture-engineered Cu_{2-x}S is four times as much as that of the Cu_{2-x}S sample at 800 K, which is attributed to the potential energy filtering effect at the new grain boundaries. Moreover, the multiscale architecture in the sintered Cu_{2-x}S increases phonon scattering and results in a reduced lattice thermal conductivity of 0.2 W·m^{-1}·K^{-1} and figure of merit (zT) of 1.0 at 800 K. Such a zT value is one of the record values in copper sulfide produced by chemical synthesis. These results suggest that the introduction of nanostructure and formation of new interface are effective strategies for the enhancement of thermoelectric material properties.

Keywords Thermoelectric properties; Copper sulfides; Room-temperature synthesis; Nanostructure; Semiconductor

1 Introduction

Thermoelectric (TE) technology, which can directly convert waste heat into useful electricity, plays a crucial part in a global sustainable energy solution for the environmental contamination and energy crisis [1–3]. The efficiency of TE devices is dominated by the performance of selected TE material, which is indexed by the dimensionless figure of merit (zT) = S^2σT/κ, where S, σ, T, and κ are the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively [4–6]. To approach high TE device efficiency, materials with high zT values are desired [7, 8]. A good TE material should simultaneously have a large S as semi-conductors, a high σ as metals, and a low κ as glasses [9–11]. However, these three TE parameters are synergistic with each other. It is hard to combine all these features in a single material [12]. Specifically, σ and S can hardly increase simultaneously as these two parameters are coupled via carrier concentration.
Besides, the reduction of $\kappa$ often degrades the carrier mobility and thus $\sigma$ [15–17]. Conflicts between these properties impede the limitless enhancement of $zT$, where a compromise is necessary to optimize $zT$.

Copper sulfides were identified as a promising TE material since 1827 [18–20]. With low $\kappa$ and high TE performance, copper sulfides attract extensive research interest [21–27]. Currently, the field of copper sulfides is mainly focusing on the reduction of $\kappa$ by designing intrinsically low-dimensional crystalline structures and on the increase of power factor (PF = $S^2\sigma$) by enhancing electron transport properties [28, 29]. Cubic copper sulfide with liquid Cu-ion has intrinsic low lattice thermal conductivity ($\kappa_L$) in high-temperature regions [30, 31], which is the main reason for intrinsically low $\kappa_L$ of copper sulfides [32, 33]. For example, an extremely low $\kappa_L$ below 0.35 W m$^{-1}$ K$^{-1}$ and a high $zT$ of 1.7 at 1000 K has been reported in Cu$_2$S$_{0.52}$Te$_{0.48}$ [34]. Besides, Fe dopants remarkably decrease $\kappa$ without compromising PF, leading to improved $zT$ of 0.8 at 750 K for Cu$_{1.80}$Fe$_{0.048}$S, which is about three times that of Cu$_{1.80}$S [35]. In the aspect of enhancing PF, electron transport abilities play a key role, which can be achieved by tuning the compositions in copper sulfide compound, such as doping, hybridization, and designing mosaic architecture [36–41]. It was demonstrated that Na-doped Cu$_9$S$_5$ shows remarkable low $\kappa$ ranging from 0.68 to 2.3 W m$^{-1}$ K$^{-1}$ due to the weak-binding copper ions in the quasi-molten state, where Na$_{0.01}$Cu$_9$S$_5$ eventually achieves a $zT$ value of 1.1 at 773 K [36]. Se doping was reported to enhance PF of Cu$_2$S by modifying the band structure and a peak $zT$ value of 0.74 was achieved at 723 K in Cu$_{2}$S$_{0.9}$Se$_{0.1}$, which is 131% higher than that of pristine Cu$_2$S [37]. Hybridizing the three-dimensional interface structure of graphene and Cu$_2$S can enlarge $S$. Experiments show that a high $zT$ value and PF reached 1.56 and 1197 W m$^{-1}$ K$^{-2}$ at 873 K in 0.75 wt% G/Cu$_2$S sample [38]. A designed mosaic nanostructured Cu$_{2}$S$_{0.52}$Te$_{0.48}$ shows multiform effects to tune TE properties, where electrons are freely transferred within the quasi-single crystal structural frames while phonons are strongly scattered by lattice strains or interfaces [39]. The optimization of the electron and phonon transport is simultaneously promoted to reach a peak $zT$ value of 2.1 at 1000 K in mosaic nanostructured Cu$_{2}$S$_{0.52}$Te$_{0.48}$. It should be mentioned that controlling and fine-tuning of the mesoscale architectures in nanostructured TE materials can scatter heat-carrying phonons with long mean free paths, leading to the maximum reduction of $\kappa_L$ [42]. This motivates us to design the multiscale architectures in copper sulfides by simultaneously employing nanostructure engineering and grain-boundary engineering. Moreover, it is still necessary to explore low-cost and practical strategies to achieve the reduction of $\kappa_L$ and enhancement of PF, simultaneously.

In this work, the micro- and nano-Cu$_{2-x}$S particles are fabricated by an ambient wet chemical method. The multiscale architecture-engineered Cu$_{2-x}$S is prepared by mechanical mixing of these two kinds of particles and spark plasma sintered (SPS) into pellets. The obvious increase of $\sigma$ in the multiscale architecture-engineered Cu$_{2-x}$S is by 4 times than that of the micro-Cu$_{2-x}$S at 800 K due to the formation of new grain boundaries and carrier mobility. The $\kappa_L$ (below 0.5 W m$^{-1}$ K$^{-1}$) of multiscale architecture-engineered Cu$_{2-x}$S is secured by nanoparticles in the multiscale architecture inducing phonon scattering. A $zT$ value of 1.0 has been achieved at 800 K in the multiscale architecture-engineered Cu$_{2-x}$S, revealing that the design of multiscale architectures improves the TE performance of Cu$_2$S.

**2 Experimental**

**2.1 Chemicals**

Chemical reagents, including Cu nano-powder (25 nm, $\geq 99.5\%$), S powder ($\geq 99.5\%$), 2-Mercaptoethanol ($\geq 99.0\%$), and hydrazine solution (35 wt%), were ordered from Sigma-Aldrich. Cu powder (250–300 mesh, $\geq 99.7\%$), NaOH ($\geq 96.0\%$), and anhydrous ethanol were ordered from Sinopharm Chemical Reagent Co., Ltd.

**2.2 Synthesis of micro-/nano-Cu$_{2-x}$S particles**

In a typical synthesis [43, 44], 7.626 g (0.12 mol) Cu micro-powder or Cu nano-powder, 3.848 g (0.12 mol) S powder, and 200 ml of anhydrous ethanol were added into a 500-ml beaker. Then 25.2 ml (0.36 mol) of 2-mercaptopoethanol and 2 ml of NaOH (7 mol·L$^{-1}$) were added into the beaker with gentle stirring for one day. The formed dark brown precipitates were separated from the solution and redisperssed in the hydrazine solution (200 ml) with stirring for 20 min. The precipitates were filtered, purified with distilled water and ethanol several times, and dried at 50 °C in oven.

**2.3 Synthesis of multiscale architecture-engineered Cu$_{2-x}$S**

The micro- and nano-Cu$_{2-x}$S particles with the ratios of $a$ to $b$ ($a:b = 3:1, 1:1, 1:3$) were mixed by mechanical mixing. Then the mixture particles were annealed under Ar/H$_2$ atmosphere at 700 °C (10 °C·min$^{-1}$) for 2 h. After ground, the mixture particles were sintered by SPS at 420 °C for 5 min in a Φ12 mm graphite die under 70 MPa.
To express expediently in the following content, the multiscale architecture-engineered Cu$_2$-xS with different ratios of $a$ to $b$ were shortly named M/N-3/1-Cu$_2$-xS, M/N-1/1-Cu$_2$-xS, and M/N-1/3-Cu$_2$-xS, respectively.

2.4 Characterization

X-ray diffraction (XRD) patterns for all Cu$_2$-xS samples were detected using Cu K$_\alpha$ radiation ($\lambda = 0.15406$ nm) by a Rigaku D/Max-2550 PC diffractometer (Tokyo, Japan). X-ray photoelectron spectroscopy (XPS) was used to understand the surface chemical composition of the samples. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of all the samples were collected by a Hitachi S-4800 (Japan) microscope and a JEOL JEM-2100F microscope, respectively.

2.5 Thermoelectric measurements

The resultant multiscale architecture-engineered Cu$_2$-xS pellets were cut and polished as cuboids with a size of \(\sim 2 \text{ mm} \times 3 \text{ mm} \times 10 \text{ mm}\) for electrical property measurement and as a disk shape with a diameter of 10 mm and a thickness of 1 mm for thermal diffusion measurement. The \(\sigma\) and \(S\) were measured simultaneously under a He atmosphere by the ZEM-3 (ULVAC-RIKO, Japan). The thermal diffusivity (\(D\)) was measured using a Netzsch LFA427 (Germany). The heat capacity (\(C_p\)) was measured using a NETZSCH DSC 204F1 Phoenix. The test temperature ranges from room temperature to 800 K. The densities (\(\rho\)) were measured by the Archimedes method. The \(\kappa\) was calculated according to the relationship \(\kappa = \rho C_p D\). The carrier concentration (\(n_H\)) and carrier mobility (\(\mu_H\)) at room temperature were measured using the Hall measurement system (Lake Shore 8400).

3 Results and discussion

3.1 Phase and microstructure

Figure 1 illustrates the typical process for fabricating the multiscale architecture-engineered Cu$_2$-xS, in which the micro- and nano-Cu$_2$-xS particles with different ratios were mixed by mechanical mixing and sintered by SPS. The XRD patterns of as-prepared micro, nano Cu$_2$-xS particles, and multiscale architecture-engineered Cu$_2$-xS samples are shown in Fig. 2. The XRD peaks of both as-prepared micro- and nano-Cu$_2$-xS samples can be well assigned to the planes of the orthorhombic Cu$_2$S (JCPDS No. 2–1294). The diffraction peak of the nano Cu$_2$-xS sample is wider than that of the micro-Cu$_2$-xS sample, indicating that the particle size of the micro-Cu$_2$-xS sample is large. After the annealing process, all peaks of the multiscale architecture-engineered Cu$_2$-xS samples consistent with the standard peaks of the tetragonal Cu$_{1.81}$S (JCPDS No. 41–959). An orthorhombic to tetragonal phase transition in the high-temperature annealing process is the intrinsic properties of Cu$_2$-xS [45–49]. Further confirmation of this phase transition was determined by measurement of the \(C_p\) curve, which has a prominent peak at 373 K (Figure S1 in Supporting Information). The tetragonal...
phase was retained after the SPS process and TE measurements, which were confirmed by XRD results (Figure S2).

The typical SEM images and low-resolution TEM images indicate that the micro-Cu$_{2-x}$S sample is irregular particles with a rough surface on the micron scale (Fig. 3a, c), and the nano Cu$_{2-x}$S sample is agglomerating round particles with the diameters ranging from 10 to 20 nm (Fig. 3b, d). The reaction mechanism of Cu$_{2-x}$S is that Cu particles are used as sacrificial templates during the preparation of the micro- and nano-Cu$_{2-x}$S particles [50]. In the reaction, thiol molecules were directionally adsorbed on the surface of Cu particles and S molecules were dissolved in 2-Mercaptoethanol to form thiosulfide, then Cu/thiol groups reacted with thiosulfide to finally form Cu$_{2-x}$S. Thus the particle size of Cu$_{2-x}$S is determined by the size of self-sacrificed Cu template. Employing the M/N-1/3-Cu$_{2-x}$S sample as an example, nanoparticles remained in multiscale architecture-engineered Cu$_{2-x}$S (Fig. 3e) after SPS. The high-resolution TEM (HRTEM) images show the nanoparticles and the interface between nanoparticles in the M/N-1/3-Cu$_{2-x}$S sample. The lattice fringes have a spacing of 1.51 nm (Fig. 3f), which matches well with the (340) planes of the tetragonal phase Cu$_{2-x}$S. The inset fast Fourier transforms (FFT) pattern in Fig. 3f confirms this tetragonal structure.

Due to the Cu$_2$S is easy to oxidize [45], XPS results were used to calculate the ratios of Cu with different valence states in the multiscale architecture-engineered Cu$_{2-x}$S samples (Fig. 4). The XPS spectra of Cu 2p illustrate the presence of both Cu$^+$ and Cu$^{2+}$ in these samples (Fig. 4a). The calculated ratio of Cu$^+/Cu^{2+}$ increases from 8.1, 12.9 to 14.1 as the fraction of nanoparticles increased indicating a reduced amount of Cu vacancies. The S 2p peak from S$^{2-}$ is located around 162.0 eV for all three multiscale architecture of Cu$_{2-x}$S.
Fig. 4 XPS spectra of a Cu 2p and b S 2p of multiscale architecture-engineered Cu$_{2-x}$S (black asterisks in a marking satellite peak of Cu$^{2+}$)

Fig. 5 TE properties of micro-Cu$_{2-x}$S and multiscale architecture-engineered Cu$_{2-x}$S samples in measured temperature (300–800 K): a $\sigma$, b $S$, c $PF$, d $\kappa$, e $\kappa_L$, and f $zT$
samples (Fig. 4b). The Cu/S ratios in the multiscale architecture-engineered Cu$_{2-x}$S samples were calculated being 1.82, 1.83, and 1.85 with increasing the fraction of nanoparticles.

### 3.2 Thermoelectric properties

The temperature-dependent TE properties of micro-Cu$_{2-x}$S and multiscale architecture-engineered Cu$_{2-x}$S samples are

Table 1  Measured and predicted TE parameters for micro-Cu$_{2-x}$S and multiscale architecture-engineered Cu$_{2-x}$S samples

| Samples                | micron Cu$_{2-x}$S | M/N-3/1-Cu$_{2-x}$S | M/N-1/1-Cu$_{2-x}$S | M/N-1/3-Cu$_{2-x}$S |
|------------------------|--------------------|----------------------|----------------------|----------------------|
| $n_H$ at 300 K/(10$^{20}$ cm$^{-3}$) | 0.89               | 2.97                 | 2.53                 | 2.28                 |
| $\rho_H$ at 300 K/(cm$^2$.V$^{-1}$.s$^{-1}$) | 5.95               | 6.85                 | 7.28                 | 8.28                 |
| $m^*$ at 800 K/m$_e$   | 1.4197             | 1.6277               | 1.4515               | 0.2833               |
| $(\zeta T)_{\text{max}}$ at 800 K | 0.91               | 0.78                 | 0.81                 | 1.00                 |
| $\rho/(g$.cm$^{-3})$   | 5.13               | 5.40                 | 5.48                 | 5.50                 |
| $R/%$                 | 91.6               | 96.3                 | 97.8                 | 98.2                 |

*With regard to theoretical density of 5.6 g.cm$^{-3}$

Fig. 6  a Optimized $\mu_H$ of micro-Cu$_{2-x}$S and multiscale architecture-engineered Cu$_{2-x}$S samples in temperature range between 300 and 800 K; b $\zeta T$ as a function of $n_H$ at 800 K, where symbols and solid curves are predicted from SPB model; c $\sigma/\rho$ ratio of micro-Cu$_{2-x}$S and multiscale architecture-engineered Cu$_{2-x}$S samples in temperature range between 300 and 800 K; d presumed carrier and phonon transport paths in multiscale architecture-engineered Cu$_{2-x}$S. Reproduced with permission from Ref. [6]. Copyright 2010, Springer Nature Limited
shown in Fig. 5. The $\sigma$ values of the multiscale architecture-engineered Cu$_{2-x}$S are much higher than that of the micro-Cu$_{2-x}$S sample in the entire measured temperature range (Fig. 5a). Specifically, the $\sigma$ value of M/N-1/3-Cu$_{2-x}$S sample reaches 4.1 $\times$ 10^4 S m$^{-1}$ at 800 K, which is 4 times higher than that of the micro-Cu$_{2-x}$S sample. All samples exhibit positive $S$ with holes as the major charge carriers due to the formation of Cu ion vacancies. The $S$ of the multiscale architecture-engineered Cu$_{2-x}$S samples is lower than that of the micro-Cu$_{2-x}$S sample, with the opposite trend of $\sigma$ curves (Fig. 5b). While PF values of the multiscale architecture-engineered Cu$_{2-x}$S samples are higher than that of the micro-Cu$_{2-x}$S sample and increase with temperature rising after 450 K. M/N-1/3-Cu$_{2-x}$S sample approaches a high PF value of 961 $\mu$W m$^{-1}$K$^{-2}$ at 800 K (Fig. 5c).

The $K$ values of multiscale architecture-engineered Cu$_{2-x}$S samples increase at the low-temperature range and decrease when the temperature is above 600 K (Fig. 5d). $K_L$ is calculated by $K_L = \kappa - \kappa_e$, where $\kappa_e$ is the electronic thermal conductivity [51]. $K_L$ of the M/N-1/3-Cu$_{2-x}$S sample prominently minimizes to 0.2 W m$^{-1}$K$^{-1}$ at 800 K (Fig. 5e). The M/N-1/3-Cu$_{2-x}$S sample possesses an improved $zT$ value of 1.0 at 800 K, which is a 9% enhancement over the micro-Cu$_{2-x}$S sample at 800 K (Fig. 5f).

To understand our improved TE performance of the multiscale architecture-engineered Cu$_{2-x}$S, the introduction of nanostructure and the formation of grain boundaries should be considered. $\sigma$ of the multiscale architecture-engineered Cu$_{2-x}$S samples exhibits an obvious increase comparing to that of the micro-Cu$_{2-x}$S sample (Fig. 5a). To understand this phenomenon, $n_H$ and $\mu_H$ were measured at 300 K and further calculated by using a single parabolic band (SPB) model. The measured $n_H$ and $\mu_H$, the estimated effective mass $m^*$, and predicted maximum $zT$ of all samples are listed in Table 1. The predicted $\mu_H$ curves and the curves of $zT$ in comparison with the experimental points as a function of $n_H$ are shown in Fig. 6a, b, respectively. The results show that $\mu_H$ of the multiscale architecture-engineered Cu$_{2-x}$S samples has been enhanced rather than $n_H$. According to $\sigma = n_H e \mu_H$ (where $e$ is a charge of the electron), the obvious increase of $\sigma$ should be derived from the enhancement of $\mu_H$ (Fig. 6a) [28]. The lower $m^*$ of the M/N-1/3-Cu$_{2-x}$S sample leads to higher $\mu_H$ as well. The $\sigma$ also increases with expanding the fraction of nanoparticles, which is possibly due to the potential energy filtering effect at the micro/nano boundaries [52]. Figure S3 displays that the grain sizes of the annealed multiscale architecture-engineered Cu$_{2-x}$S reduce as the fraction of nanoparticles increasing. The density of samples has a negligible effect on this result since the relative densities for all multiscale architecture-engineered Cu$_{2-x}$S samples are almost the same, as listed in Table 1. In Fig. 6b, $n_H$ of the M/N-1/3-Cu$_{2-x}$S sample is closer to its respective optimum than the micro-Cu$_{2-x}$S sample, which is consistent with the particular M/N-1/3-Cu$_{2-x}$S sample measured having greater $zT$ value than the micro-Cu$_{2-x}$S sample. As shown in Fig. 6c, the $\sigma/\kappa$ ratio of M/N-1/3-Cu$_{2-x}$S sample increases at 700–800 K, which means the reduction of $\kappa$ has more influences than the promotion of $\sigma$ at this temperature region. The presumed phonon (red) and carrier (green) transport paths in the multiscale architecture-engineered Cu$_{2-x}$S are shown in Fig. 6d. The nanoparticles in the multiscale architecture enhancing phonon scattering results in the reduction of $K_L$. The underlying mechanism is that grain boundaries can scatter phonons more effectively than carriers [53]. The presently enhanced $zT$ value at 700–800 K should be mainly attributed to the reduced $K_L$.

4 Conclusion

In conclusion, the multiscale architecture-engineered Cu$_{2-x}$S is fabricated by an optimized ambient wet chemical method combining mechanical mixing and SPS technology. The enhanced TE performance derives from the introduction of nanostructure and the formation of new grain boundaries. The formation of grain boundaries induces the potential energy filtering effect leading to an enhanced $\sigma$ in the multiscale architecture-engineered Cu$_{2-x}$S. Nanostructure and small grain sizes enhance phonon scattering and result in the reduction of $K_L$. The peak $zT$ value of 1.0 at 800 K can be achieved in the M/N-1/3-Cu$_{2-x}$S sample, which is competitive among the reported Cu$_{2-x}$S or its composites at the same temperature. This work indicates our method is low cost and practical for the preparation of the multiscale architecture-engineered Cu$_{2-x}$S, which shows high potential for thermoelectric applications.

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