Enhanced Thermoelectric Performance of Ag$_2$S Nanoparticles by Ag-nanoinclusions

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Abstract. We have demonstrated a simple strategy for improvement of thermoelectric performance of Ag$_2$S based composites by modifying reaction conditions in polyol method. The existence of two-phased heterostructure in Ag$_2$S@Ag nanocomposites is confirmed from dual phase Rietveld refinement of its powder X-ray diffraction. The FESEM images confirmed the formation of nanodisks of average thickness 80 nm and width in few hundreds of nm. A systematic reduction in electrical resistivity with increasing Ag-content is observed which leads an enhancement in power factor. The values of Seebeck coefficient are positive or negative depend on fraction of Ag-content in Ag$_2$S matrix. Finally, a significantly high power factor is obtained for Ag$_2$S@Ag nanocomposites synthesized at 245 $^\circ$C. This work open a new way for reduction of electrical resistivity of resistive Ag$_2$S and hence improved its thermoelectric efficiency.

INTRODUCTION

Nowadays around 65 percent of energy is wasted in the form of heat from various sources such as industrial processes, food processing, automobiles and solar radiation. The thermoelectric (TE) materials are special kind of materials which have capability to convert this waste heat into useful electricity silently without producing any harmful by-product. For this high efficiency is needed which determined by a dimensionless figure of merit, $ZT = S^2\sigma T/\kappa - 1$, where $S$, $\sigma$, $\kappa$ and $T$ are the Seebeck coefficient, electrical conductivity, total thermal conductivity and absolute temperature, respectively. Therefore, $S^2\sigma$ (power factor) should be high and $\kappa$ should be low in the TE samples for better efficiency and these can be easily achieved by nanoinclusion in TE host materials [1-4].

Mostly commercially available TE materials contained rare and toxic elements, like Te, Se, Pb etc., and has to be replaced by non-toxic naturally abundant elements. In this direction Ag$_2$S attracts special attention due to its high thermopower and relatively low thermal conductivity [5,6]. It crystallises in monoclinic phase at room temperature and has band gap of 1.1 eV. Faleev et al. [1] proposed metal nanoparticles (NPs) inclusion into semiconducting TE materials can be a useful tool to increase the power factor due to formation of metal-semiconductor interfaces which acts as potential barriers to filter low energy charge carriers. This concept is demonstrated in many reports experimentally [2-4,6]. Sumithra et al. [2] reported 100 % enhancement in $ZT$ value for Bi$_2$Te$_3$ with 2 vol% Bi nanooinclusions. In furthermore, Zhang et al. [3] also demonstrate a 304% enhancement in $ZT$ value of Bi$_2$Te$_3$ with 2% Ag-nanoinclusions due to combine effect of low energy charge carrier filtering and phonon scattering from the metal-semiconductor interface. In our previous work [4], we demonstrated the introduction of 10 vol% of Ag$_2$S NPs in metallic CuS results in an enhancement of $\sim 37$ % in $ZT$ at 300 K due to low energy charge carrier filtering and phonon scattering at Ag$_2$S - CuS interfaces. But single phase pure Ag$_2$S shows very high $\rho$ and consequently not possible to collect Seebeck coefficient data for it. Now with the trending idea of introduction of metal in TE semiconductor [1-3] for better TE performance, we introduced Ag NPs in Ag$_2$S NPs and investigate their thermoelectric properties in range of 80-300 K.
EXPERIMENTAL SECTION

In typical synthesis, 6 millimole (mmol) of AgNO$_3$ (99.9999, Sigma Aldrich) and 4 mmol of thiourea (98%, Merck) were dissolved into 50 mL diethylene glycol (DEG, ≥98.5%, Merck) using magnetic stirrer in round bottom three neck flask (TNF). We have taken little excess quantity of sulphur source in synthesis because sulphur is volatile and can come out in form of gases (SO$_2$/H$_2$S) [7]. An inert atmosphere through continuous flow of Ar-gas was maintained using two outer necks of TNF in stirred solution and heating started at the rate of 6 °C/min using controlled heating mantle. The solution temperature was monitored through thermometer inserted in middle neck of TNF. The reaction was maintained for 2 hrs at 170 °C, 240 °C and 245 °C and products are named as AgS1, AgS9 and AgS10, respectively. The formation of black precipitates (ppt) was started at 160 °C which indicates the production of Ag$_2$S NPs initiated. When temperature reached to 245 °C the boiling of DEG occurred and solution reduced to ~8 mL due to this excess boiling of DEG. This resulting solution with black ppt was washed using steps followed in Ref. 4 for proper removal of DEG. Finally, it was dried at 60 °C in vacuum for 5 hrs to get powder product which was directly used for all characterizations.

To check the phase purity powder X-ray diffraction using Bruker D8 Advance X-ray diffractometer with Cu K$_\alpha$ radiation of wavelength 1.54 Å in 0-20 geometry in the range of 20-80°. Field emission scanning electron microscopy (FESEM) was performed using FEI made Nova Nano field-emission scanning electron microscopy. Temperature dependent electrical resistivity and Seebeck coefficient measurements were performed by four probe and dc-direct methods using home-made system in range 80-325 K, respectively.

RESULTS AND DISCUSSION

For structural information of Ag$_2$S@Ag nanomaterials the X-ray diffraction studies are performed (Fig. 1). In Fig. 1(a) the powder XRD pattern of AgS1 synthesized at 170 °C is shown, in which all peaks are well matched with reference card JCPDS-652356 of monoclinic Ag$_2$S with space group P2$_1$/n confirming the formation of single phase Ag$_2$S. The formation of single phase Ag$_2$S is further confirmed by its Rietveld refinement (Fig. 1(b)) using FullProf software for which initial parameters are taken from Ref. [8]. The obtained cell parameters are tabulated in Table 1 and are very close to that of bulk [8]. Some extra peaks are observed in XRD pattern (Fig. 1(a)) for sample synthesized at 240 °C (AgS9), which are well matched with reference card JCPDS-893722 of face centered cubic (fcc) phase of Ag (space group Fm-3m). The intensities of these extra peaks are intensified (Fig. 1(a)) with increasing reaction temperature up to 245 °C (AgS10). Therefore, the dual phase structural Rietveld refinements of powder XRD of AgS9 and AgS10 are performed (Fig. 1(b)) where initially required parameters are taken from Ref. [8,9]. The obtained parameters are close to their bulk values [8,9] (Table 1). This confirmed the existence of mixed monoclinic phase of Ag$_2$S and fcc phase of Ag NPs in composites. The dual-phase heterostructures of Ag$_2$S@Ag nanocomposites can play special role in its TE performance. The increase in phase fraction of Ag with increasing reaction temperature is due to the volatile nature of sulphur which can come out from Ag$_2$S matrix at high temperature (>220 °C) in the gas form (H$_2$S/SO$_2$) [4,7].

![FIGURE I](attachment:figure1.png)

**FIGURE I**(a) Powder XRD patterns with standard cards and (b) Rietveld refinements of Ag$_2$S NPs synthesized at 170 °C (AgS1), 240 °C (AgS9) and 245 °C (AgS10).
TABLE 1. Obtained parameters from Rietveld refinements of Ag$_2$S@Ag nanocomposites prepared at 170 °C (AgS1), 240 °C (AgS9) and 245 °C (AgS10). Here, fcc (red colour) and M. are used for face centered cubic Ag and monoclinic Ag$_2$S, respectively. The errors in calculation are written in parenthesis.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Ref. 8</th>
<th>AgS1</th>
<th>AgS9</th>
<th>AS10</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å) of Mono. &amp; fcc</td>
<td>4.23</td>
<td>4.226(1)</td>
<td>4.227 &amp; 4.086 (1)</td>
<td>4.226 + 4.086 (1)</td>
</tr>
<tr>
<td>b (Å) of Monoclinic</td>
<td>6.91</td>
<td>6.926(1)</td>
<td>6.927(1)</td>
<td>6.927(1)</td>
</tr>
<tr>
<td>c (Å) of Monoclinic</td>
<td>7.87</td>
<td>7.864(1)</td>
<td>7.866(1)</td>
<td>7.864(1)</td>
</tr>
<tr>
<td>V (Å$^3$) of Mono. &amp; fcc</td>
<td>226.83</td>
<td>226.951</td>
<td>227.07 &amp; 68.232</td>
<td>226.968 &amp; 68.210</td>
</tr>
<tr>
<td>ρ, (g/cm$^3$) of M. &amp; fcc</td>
<td>7.256</td>
<td>7.253</td>
<td>7.249 &amp; 10.286</td>
<td>7.252 &amp; 10.290</td>
</tr>
<tr>
<td>Phase fraction M. + fcc</td>
<td>100%</td>
<td>100%</td>
<td>82.21% + 17.79%</td>
<td>60.54% + 40.46%</td>
</tr>
</tbody>
</table>

The average particle size calculated using Scherer’s formula is 45 nm, 50 nm and 53 nm for AgS1, AgS9 and AgS10, respectively. The particle size of Ag$_2$S@Ag nanocomposites are systematic increase with increasing reaction temperature. For further information of size and shape of NPs, we performed FESEM measurement on consolidated pellet of AgS1 sample, Fig. 2(a), which shows particles are in random sizes and shapes. Most particles are in disk shape of average thickness of 80 nm and width lies in the range of few hundreds of nm. Some bigger particles are also observed which may be due to aggregation of NPs.

![FESEM image of Ag$_2$S (AgS1) NPs (Inset: FESEM image with different magnification)](image)

Figure 2 (a) FESEM image of Ag$_2$S (AgS1) NPs (Inset: FESEM image with different magnification), (b) temperature dependence of thermopower and (c) electrical resistivity of Ag$_2$S@Ag composites (AgS9 &AgS10).

Fig. 2 (b) and (c) showed the temperature dependent thermopower/Seebeck coefficient (S) and electrical resistivity (ρ) of consolidated pellets of Ag$_2$S@Ag nanocomposites in the range of 80-325 K, respectively. Due to very high electrical resistance of Ag$_2$S (AgS1) its S and ρ measurements are not possible. Its high ρ is the main drawback on its TE applications. For reduction of high ρ of Ag$_2$S several efforts have been already done [4-6]. Adelifard et al. [6] achieved low ρ by annealing at high temperature but it may lead to grain growth which is not good for TE. Here, we report a new way to reduce ρ by increasing Ag fraction in composites which is possible by just increasing reaction temperature. In Fig. 2(b), AgS9 possesses very high negative S values ranges from -761 to -892 µV/K, whereas AgS10 showed low and positive S values (0.9 to 3.8 µV/K). The electrical resistivity of resulting AgS10 nanocomposites showed metallic behavior down to 80 K whereas AgS9 shows semiconducting behavior down to 209 K, below which it possesses very high value and was not possible to record (see Fig. 2(c)). This is due to large number of sulfur vacancies formation in Ag$_2$S matrix which leads increase in charge concentration (n) for AgS9 and AgS10 as compared to AgS1(pure Ag$_2$S). As it is well know, S is inversely proportional to electrical conductivity (σ = 1/ρ) or/and charge concentration (n) [1-7]. Consequently, resistive sample (AgS9) possessed high S as compared to conducting sample (AgS10).

Due to very high electrical resistance or very low n of AgS9 it is not possible to collect S values also below 216 K whereas that of AgS10 can be collected down to 80 K (Fig. 2(b)). As the sign of S reflect the sign of majority charge carriers, implies that AgS9 and AgS10 are n-type and p-type semiconductors, respectively. This can be easily understood in terms of formation of core-shell structure of Ag$_2$S-Ag in nanocomposites with increasing reaction temperature. The volatilization of sulfur increases with increasing temperature as clear from refinements (Table 1) the phase fraction of Ag is 0 %, ~18 % and ~41 % in AgS1, AgS9 and AgS10, respectively. This implies initially pure Ag$_2$S nanodisks (highly resistive) are formed at 170 °C (AgS1) then some of sulfur atoms vaporized from surface by increasing reaction temperature up to 240 °C (AgS9). Each sulfur vacancies give two electrons to host...
and hence reduced $\rho$ and showed negative $S$ values. When reaction temperature further increased up to 245 °C (AgS10), a conducting Ag-atomic layers formed on the surface of Ag$_2$S nanodisks and provide a highly conducting path whereas core is still resistive Ag$_2$S. Silver (Ag) is well known a novel metal which possesses only positive thermopower values in the rage of 5-300 K and nearly 1.5 $\mu$V/K at 300 K. However, the $S$ values of AgS10 are positive which is due to fully conducting silver on surface of Ag$_2$S nanodisks. The values of $S$ near 300 K are more than twice of silver (metal) which is due to low-energy charge carriers filtering at metal-semiconductor interfaces of Ag-Ag$_2$S in nanocomposites [1-3]. The highest $S^2\sigma$ (power factor) obtained for AgS10 is 0.95 $\mu$Wm$^{-1}$K$^{-2}$ at 300 K, which is ~ 30 % higher than that of AgS9 (0.72 $\mu$Wm$^{-1}$K$^{-2}$ at 300 K). Although, this value of power factor for Ag$_2$S@Ag nanocomposites (AgS10) is low but it is 31.67 times higher than that of pure Bi$_2$S$_3$ sample hot pressed at 480 °C (0.03 $\mu$W/mK$^2$ at 300 K) [7]. This indicates the important role of introduction of nanoinclusions in nanomaterials TE host. In this work we developed a new strategy for reduction of electrical resistivity of Ag$_2$S and hence enhanced its thermoelectric performance near room temperature.

**CONCLUSIONS**

We have demonstrated an improvement in thermoelectric performance of Ag$_2$S@Ag nanocomposites synthesized by a facile and quick bottom-up approach polyol method. Formation of dual phased-heterostructure Ag$_2$S@Ag was confirmed by Rietveld refinement of its powder XRD. A systematic reduction in electrical resistivity of nanocomposites with increasing Ag-nanooinclusion is observed. Seebeck coefficient of Ag$_2$S@Ag synthesized at 245 °C is positive and showed an enhancement of more than twice of that of pure Ag at 300 K whereas nanocomposites made at 240 °C showed very high negative values. Finally, significantly high power factors, 0.95 and 0.72 $\mu$Wm$^{-1}$K$^{-2}$, are obtained for Ag$_2$S@Ag nanocomposites synthesized at 245 and 240 °C, respectively.

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**REFERENCES**