

Ag₂S–Ag Nanocomposites: A Bottom-Up Approach to Enhance Thermoelectric Power Factor at Near Room Temperature

Anish Kumar*

Abstract

The intrinsic ductility, low toxicity, and naturally occurring abundance of silver sulphide (Ag₂S) have made it a potential thermoelectric material in recent years. However, high electrical resistance severely limits its practical application. Here, we present a thorough analysis of how metallic Ag-nanoinclusions affect the structural, electrical, and thermoelectric characteristics of Ag₂S nanocomposites made using a simple bottom-up polyol approach. (Ag₂S)_{1-x}Ag_x nanocomposites with an Ag content ranging from 0 to 26.1% were produced by controlling the inclusion of Ag nanoparticles by adjusting the proportion of sulfur precursor. X-ray diffraction with Rietveld refinement, FESEM-energy dispersive X-ray (EDX), and X-ray photoelectron spectroscopy were used in structural and phase investigations to confirm the coexistence of monoclinic α -Ag₂S and face-centered cubic Ag phases with uniform interfacial distribution. A semiconductor-to-metal transition controlled by percolative charge transport through Ag-rich grain boundaries is observed together with a consistent decrease in resistivity with increasing Ag concentration, according to electrical transport measurements. Interestingly, for modest amounts of Ag nanoinclusion, improved Seebeck coefficients close to room temperature are seen, which is explained by low-energy charge carrier filtering at semiconductor–metal contacts. The composite comprising approximately 20.1% Ag achieves a maximum figure of merit $ZT = 0.0029$ at 325 K and an optimized thermoelectric power factor of $19.53 \mu W \cdot m^{-1} \cdot K^{-2}$. These findings show that Ag nanoinclusion offers a practical means to separate electrical conductivity and Seebeck coefficient in Ag₂S, creating a feasible route toward mechanically sound, ecologically safe thermoelectric materials that function close to ambient temperature.

Keywords: Ag₂S nanocomposites, Ag nano inclusions, thermoelectric materials, Seebeck coefficient, carrier filtering, electrical transport, power factor

INTRODUCTION

For long-term sustainability, energy production from alternative sources that produce less waste heat, hazardous gases, or noise is crucial. Researchers are interested in thermoelectric (TE) devices because

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of their high-power consumption requirements. TE devices have a long lifespan and require minimal maintenance. They also quietly transform waste heat into power without creating hazardous byproducts. Highly efficient TE materials are required to meet the objective of their compatibility with traditional energy sources. The dimensionless figure of merit $ZT = \alpha^2 T / (\rho \kappa)$ determines the performance of thermoelectric devices, where ρ , κ , and T stand for electrical resistivity, total thermal conductivity, and absolute temperature, respectively [1, 2]. The primary problem is to build

solid materials with high α and σ ($1/\rho$) yet low κ . The best emerging materials for this are semiconductors, where, κ can be reduced in a number of methods, including introducing point defects, nanostructuring, and choosing highly anisotropic layered materials with heavy constituent elements in large unit cells. The reduction of grain size to the nanoscale [1, 3, 4], the introduction of nanocrystals into nanomaterial hosts [5–8], and the introduction of nanoparticles in bulk hosts [2, 9, 10] are the three ways that nanostructuring is recognized as a potential method.

The creation of nanocomposites by introducing nanocrystals in nanomaterials/bulk hosts is a unique strategy for simultaneously reducing κ through combined grain boundary scattering of heat carriers and enhancing power factor (α^2/ρ) induced by low-energy charge carrier filtering [2, 5–11]. Nanostructuring alone can achieve a good ZT value (~ 300 K) [1, 3, 4]. The synthesis of Bi₂Te_{2.7}Se_{0.3}/SnS₂ nanocomposites using the polyol method was demonstrated by Li et al. [8]. They reported an enhanced ZT ~ 0.93 at 450 K for this nanocomposite with 1.47 vol% of SnS₂, which was 2.3 times higher than that of pristine Bi₂Te_{2.7}Se_{0.3}. Mehta et al. [4] showed a readily scalable bottom-up approach to create bulk TE nanomaterials of both n- and p-type pnictogen chalcogenides with ZT >1 at 300 K. They explained the improvement by pointing to the exact control of SnS₂ layer thickness, which drives the low-energy charge carrier filtering effect and phonon scattering from the atomically thin interface of Bi₂Te_{2.7}Se_{0.3}/SnS₂ nanocomposites [8].

In p-type PbTe, Endo axially nanostructured with 4 mol% SrTe, and mesostructured with powder processing and spark plasma sintering, Biswas et al. [2] obtained a ZT value of 2.2 at 915 K. The amplification was ascribed to mesoscale grain boundaries, nanoscale endo-axial precipitates, and point defect scattering phonons on several scales.

Unfortunately, in addition to rare and hazardous materials (Pb, Te, Se, Bi, Sb, etc.), the most promising TE devices now on the market are hard and inflexible with very little ductility or brittleness. Additionally, they can readily break or crack due to careless handling errors, which can result in device failure and ultimately cause environmental issues because of the poisonous compounds in them [12].

This tends to restrict their use in certain contexts, such as automobiles. It is a direct, narrow-bandgap (~ 1.1 eV) layered semiconductor with relatively large absorption coefficients ($\sim 10^6$ cm⁻¹) [13–16], high chemical stability, natural abundance, and negligible toxicity [17]. It is gaining a lot of attention because of its potential uses in resistance switches, nonvolatile memory devices, photocatalysts, solar cells, and thermoelectric devices [18], as well as its good antibacterial qualities [19], photocatalysts, and solar cells [20–22]. Ag₂S has the potential to be a TE material since its electronegativity difference ($\Delta\chi$) among its constituent elements is 0.65, which is very near to the value of <0.5 needed for a greater TE power factor (increased carrier mobility) [23]. For single-phase Ag₂S bulk, this value of α is greatly increased to approximately $\alpha_{400\text{ K}} = -625$ $\mu\text{V/K}$ [13]. Its high electrical resistance ($>10^6$ Ω) has drawn little attention, despite its relatively high α and low κ [13, 21, 22]. By adjusting the atomic ratio of Ag:S and decreasing ρ through crystallite size variation, they propose that the thermoelectric performance of Ag₂S can be enhanced at low temperatures [13, 21, 22].

EXPERIMENTAL SECTION

Method

We simply decreased the amount of thiourea in the aforementioned synthesis processes to insert Ag-NPs into Ag₂S nanomaterials, resulting in the creation of Ag₂S–Ag nanocomposites. While maintaining the same reaction settings and procedures, samples containing varying amounts of thiourea, such as 7.5, 3, 2.85, 2.75, 2.7, 2.65, 2.6, and 2.55 mmol, were produced with a fixed 6 mmol of Ag source. The sequence of (Ag₂S)_{1-x}Ag_x nanocomposites with predicted $x = 0, 0.952, 15.38, 18.18, 20.09, 23.53$, and 21.09 percent was finally produced as a result. The respective codes were ASA0, ASA1, ASA2, ASA3, ASA4, ASA5, ASA6, and ASA7.

RESULTS AND DISCUSSION

X-Ray Diffraction and Energy Dispersive Analysis of X-Ray Studies

The final composite's electrical and thermal conductivity as well as its thermoelectric characteristics will be determined by controlling the phase fractions of metallic Ag-NPs and insulating Ag₂S under the reaction conditions during their production. This has been made possible by methodically altering the amount of thiourea (S-source) to create a range of samples with various Ag:S ratios (section 1.2). Phase purity and crystallinity were initially determined by powder X-ray diffraction (XRD) of the resultant products (Figure 1).

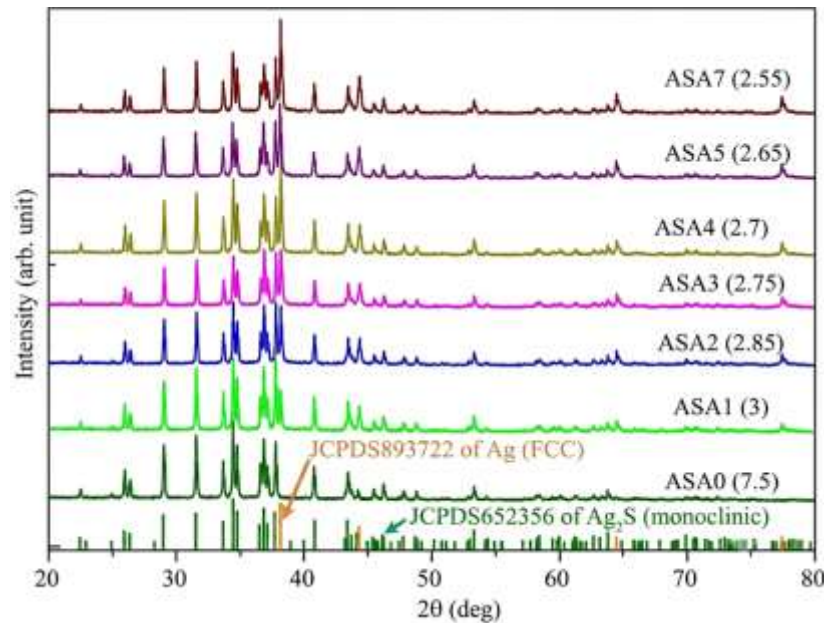
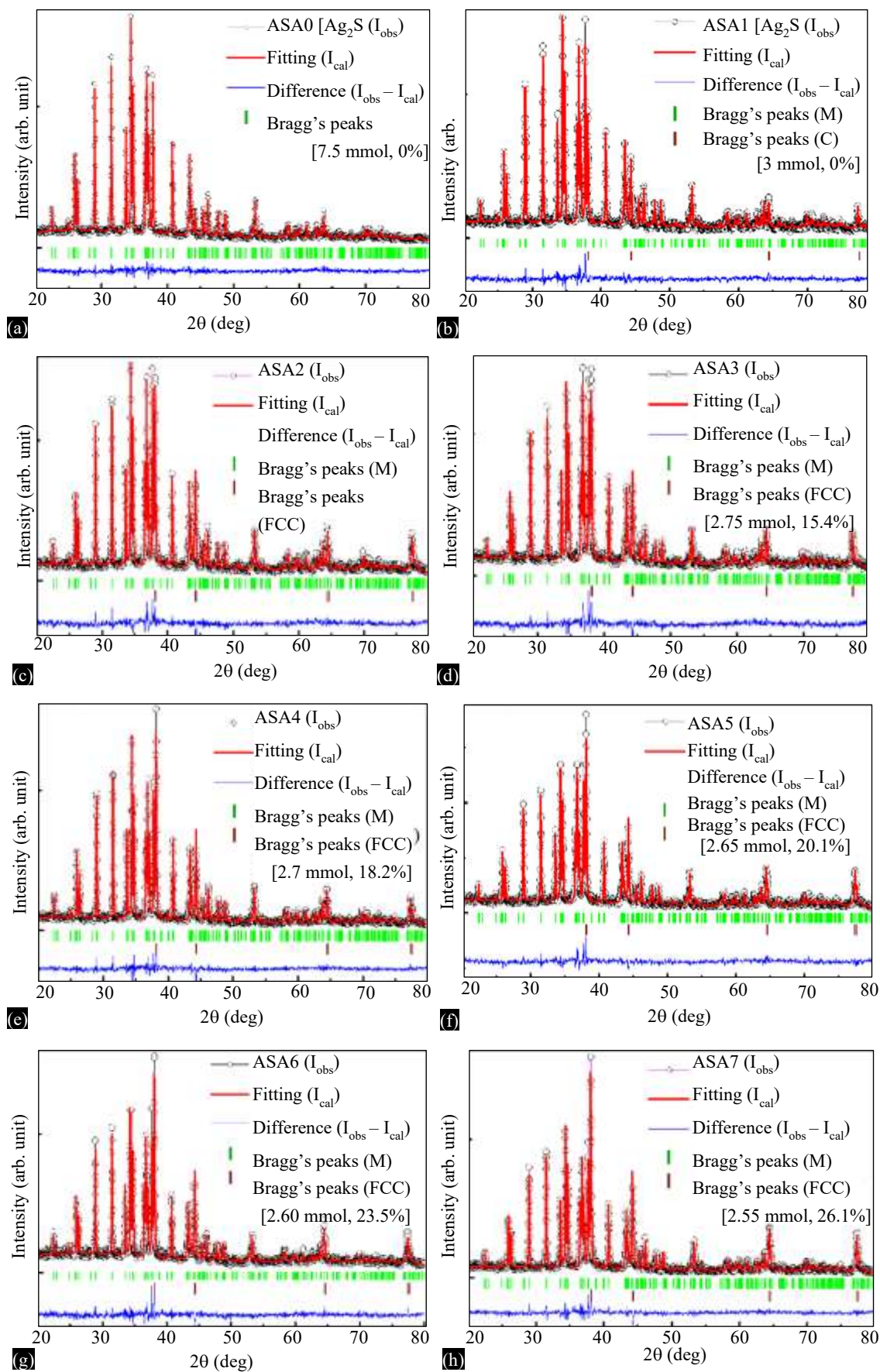


Figure 1. Ag₂S-Ag powder XRD spectra of Ag₂S-Ag nanocomposites made with a fixed Ag source and altering the amount of thiourea from 2.55 to 7.5 mmol (in brackets). Standard reference cards bearing the JCPDS number are placed at the bottom of the spectrum.

Table 1. For both monoclinic (M) Ag₂S and face-centered cubic (FCC) Ag phases, the parameters derived via Rietveld refinement of all samples made with various amounts of thiourea (TU) with fixed AgNO₃ are shown; the errors are indicated in parentheses.

Parameters ↓ (AgNO ₃ :TU) →	ASA0 (6:7.5)	ASA1 (6:3)	ASA2 (6:2.85)	ASA3 (6:2.75)	ASA4 (6:2.7)	ASA5 (6:2.65)	ASA6 (6:2.6)	ASA7 (6:2.55)
a(Å) M	4.227(1)	4.226(1)	4.227(1)	4.227(1)	4.228(1)	4.226(1)	4.226(1)	4.228(1)
FCC		4.087(1)	4.087(1)	4.087(1)	4.087(1)	4.086(1)	4.086(1)	4.087(1)
b (Å)	1.927(1)	1.926(1)	1.928(1)	1.927(1)	1.928(1)	1.926(1)	1.927(1)	1.928(1)
c (Å)	9.533(1)	9.534(1)	9.534(1)	9.533(1)	9.534(1)	9.531(1)	9.532(1)	9.535(1)
V(Å ³) M	227.061	227.028	227.14	227.037	227.10	221.941	227.004	227.165
FCC		68.254	68.276	68.239	68.25	68.211	68.221	68.266
ρ _v (g/cm ³) M	7.230	07.270	07.274	07.272	07.261	07.297	07.251	07.240
FCC		10.284	10.278	10.290	10.284	10.290	10.288	10.283
β (o)	125.576	125.549	125.559	125.566	125.578	125.570	125.565	125.567
f0 (%) M	100	93.45	88.85	87.69	85.77	85.19	84.65	80.99
[nominal]	[100]	[100]	[90.48]	[84.62]	[84.82]	[79.11]	[71.47]	[73.91]
FCC	0	01.55	11.15	12.31	14.23	14.81	15.35	19.01
[nominal]	[0]	[0]	[9.52]	[15.38]	[18.18]	[20.09]	[23.53]	[21.09]
ρ _v measured (g/cm ³)	7.019	7.121	7.434	7.478	7.507	7.547	7.571	7.592



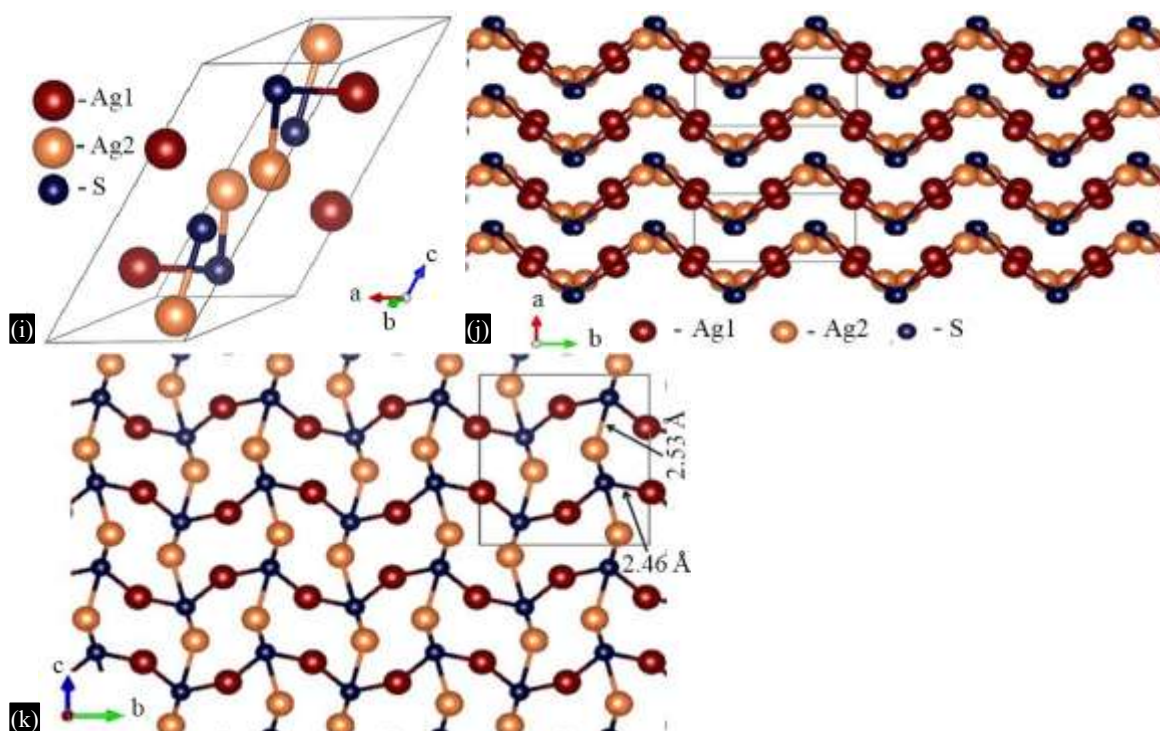


Figure 2. (Ag₂S)_{1-x}Ag_x powder XRD Rietveld refinement (a)–(h), with $x = 0$ –21.1% indicated in square brackets and the amount of thiourea in each graph. The α -Ag₂S crystal structures in (i) three-dimensional unit cells, (j) a-b planes, and (k) b-c planes. The Ag₂S unit cell is shown as a rectangular box with grey lines in Figure 2(a)–(k).

Figure 2(a)–(k) shows a typical atom configuration in monoclinic crystal structures (P21/c) of α -Ag₂S. These structures are created using a crystallographic information file (CIF) file that was acquired following Rietveld refinement of ASA0's XRD using VESTA software. Ag atoms occupy two distinct 4e Wyckoff sites, namely Ag₁ (0.0715, 0.0151, 0.3093) and Ag₂ (0.7264, 0.324, 0.4375), while sulfur atoms occupy one 4e site, S (0.492, 0.2339, 0.1321). This is the unit cell of α -Ag₂S, as shown in Figure 2(i). Figure 2(j) shows clear slipping planes (100) layered along the $\langle 100 \rangle$ direction. For α -Ag₂S, zigzag atomic layers of (100) planes can slip along the $\langle 001 \rangle$ direction. A deformed $4 \times$ Ag-S octagon makes up the Ag-S framework (Figure 2(k)). According to Figure 2(k), the Ag₁-S bond length along the $\langle 010 \rangle$ direction is 2.46676 Å, while the Ag₂-S bond length along the $\langle 001 \rangle$ direction is 2.53358 Å. The development of densely packed stoichiometric Ag₂S nanocrystals is confirmed by the fact that their lengths are less than those of non-stoichiometric silver sulphide Ag_{1.93}S [24–27].

Interestingly, the systematic synthesis of Ag₂S-Ag composites at 160°C requires careful cleaning procedures and appropriate stirring of the solution throughout the precursor process. Furthermore, ASA0, ASA1, ASA3, and ASA5 pellets were subjected to energy dispersive X-ray (EDX) measurements for compositional analysis. Table 1 lists the atomic percentages of the constituent elements in the composites. Here, the elemental ratio of Ag:S was precisely 2:1, as indicated by ASA0. The presence of excess metallic Ag as a second phase is revealed in the instance of ASA1; however, when the Ag component is larger than the nominal value. This is because sulfur is volatile, as shown by the XRD data (Figure 1). The sulfur content in ASA3 and ASA5 was also lower than anticipated (Table 1).

Field Emission Scanning Electron Microscopy

Field emission scanning electron microscopy (FESEM) measurements are used to determine the size and shape of NPs for single-phase Ag₂S (ASA0) and heterostructure Ag₂S-Ag (ASA6). This was done by spreading a fraction of the as-synthesized powder on a conducting carbon tape, which was then

coated with 10 gold (Figure 3(a)–(d)). These images demonstrate the various shapes and sizes of the particles. The majority of the particles are observed in disc forms (circular, cubic, rectangular, or strip-like) with an average thickness of 52 nm and a wide range of lengths and widths between 50 nm and several hundred nanometers (Figure 3(a) and (b)). However, the FESEM images of ASA6 revealed some extra spherical NPs connected to slightly thicker and clearer nanodisks (NDs). These spherical NPs, which range in diameter from 50 to 100 nm, may be Ag-NPs created as a result of the reaction's excess AgNO₃ (Figure 3(c) and (d)). Additionally, some larger particles were observed, which could be the result of smaller NPs aggregating (Figure 3(a)–(d)).

We collected location-specific EDX of ASA6 by concentrating the electron beam on individual ND of Ag₂S (Figure 4(a)) and spherical NPs of Ag (Figure 4(b)) to highlight the production of Ag₂S and Ag heterostructures in ASA6 nanocomposites. The atomic ratio of Ag:S was nearly exactly 2:1 when EDX was performed on crushed pellets of ASA0 (Ag₂S) (Table 2).

Table 2. The nominal values of face-centered cubic (FCC) and monoclinic (M) Ag₂S phases, as well as the elemental compositions of Ag₂S–Ag nanocomposites, were acquired from EDX.

Elements	ASA0	ASA1	ASA3	ASA5
Observed Ag (atm. %) [nominal M+FCC]	61.5 (61.7)	67.6 (61.7)	69.7 (62.9+5.7 = 68.6)	70.4 (61.3+8.1=69.4)
Observed S (atm. %) [nominal M]	33.5 (33.3)	32.4 (33.3)	30.3 (31.4)	29.4 (30.6)

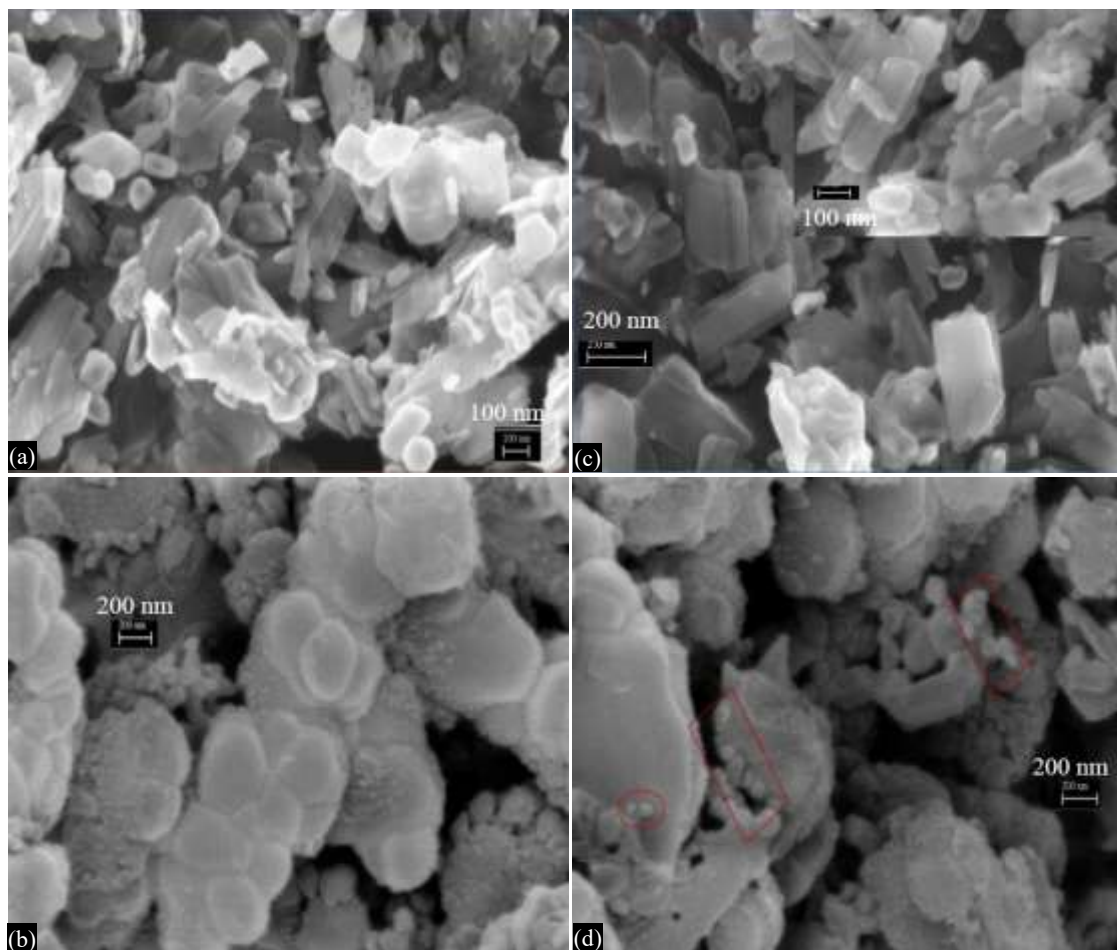


Figure 3. FESEM images of (a) and (b) Ag₂S NPs (ASA0), and (c) and (d) Ag₂S–Ag NCs (ASA6) at different magnifications.

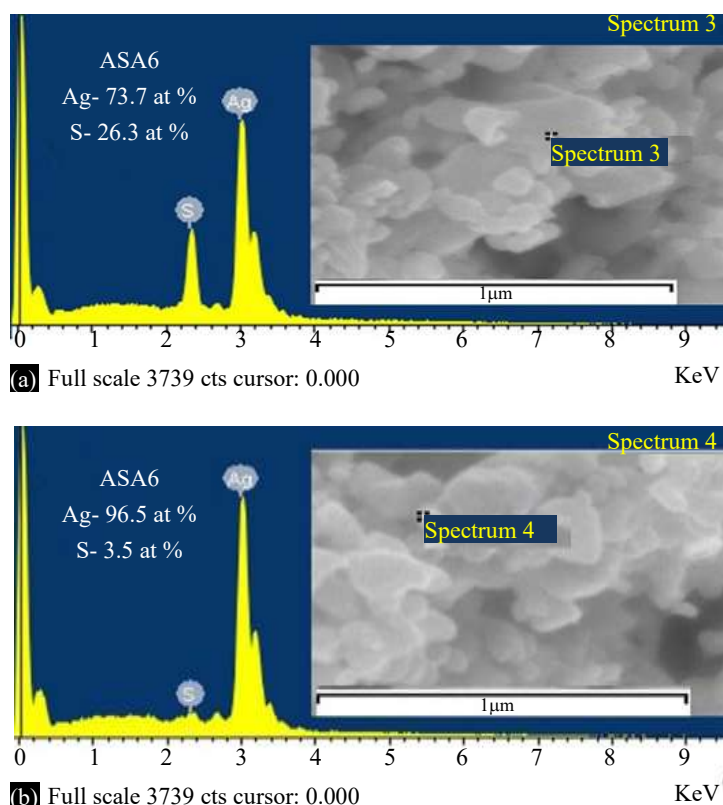


Figure 4. The electron beam size was focused at extremely small sections of (a) a larger nanodisk and (b) a smaller spherical nanoparticle to get the Ag₂S-Ag nanocomposite (ASA6) EDX spectra. Spots of interest are denoted by ":" (four points), and insets show FESEM pictures of matching samples.

However, when examining disk-shaped Ag₂S (Figure 4(a)), the ratio is 73.7:21.3, which is significantly higher than 2:1 and indicates the presence of excess Ag on Ag₂S nanodisks (Figure 3(c) and (d)). To verify this, EDX data were gathered from three distinct spherical NPs. The average atomic ratio of Ag:S was 91.5:3.5, which demonstrates that these spherical NPs may be Ag-NPs. Because the spot size and penetration depth of the electron beam utilized are bigger than the size of the targeted particles, the presence of around 3.5 atomic percent (atm. %) sulfur is expected to arise from larger Ag₂S NPs underneath Ag-NPs. Furthermore, the electron beam could enter Ag₂S ND. This supports our hypothesis that the bigger disk-shaped particles are Ag₂S-coated or bonded to smaller spherical Ag-NPs and/or excess Ag atoms, possibly in an amorphous form [28–37].

Ag content increases in composites when extra Ag atoms begin nucleating and forming smaller Ag metal nanoparticles on the surface of larger Ag₂S nanodisks, according to these FESEM pictures and EDX analysis of Ag₂S-Ag nanocomposites (ASA0 and ASA6). Additionally, as the Ag content of the composites increased, the size of the Ag-NPs also increased. Simultaneously, some of the larger Ag-NPs separated from the Ag₂S disc surface. Consequently, the presence of two types of NPs (Ag₂S and Ag) combined in the composite is demonstrated by FESEM in conjunction with EDX analysis of ASA6. These findings are well supported by the Rietveld XRD improvements mentioned above.

Zeta Potential Study

In NanoPlus 3, 2 mg of synthesized NPs are dispersed in deionized (DI) water at 25°C to determine the zeta potential (ζ) of ASA0 and ASA6. ASA0 and ASA6 had average ζ potentials of -25.4 mV and -11.2 mV, respectively (Figure 5(a)). Ag₂S-Ag nanocomposites are unstable in DI water at 25°C, as indicated by their ζ values, which are smaller than ± 30 mV [6, 37]. The lower ζ value for the comparison of ASA6 with ASA0 indicates that Ag-NPs are joined to Ag₂S NPs, increasing their hydrodynamic size and thus decreasing their mobility (Figure 5(b)).

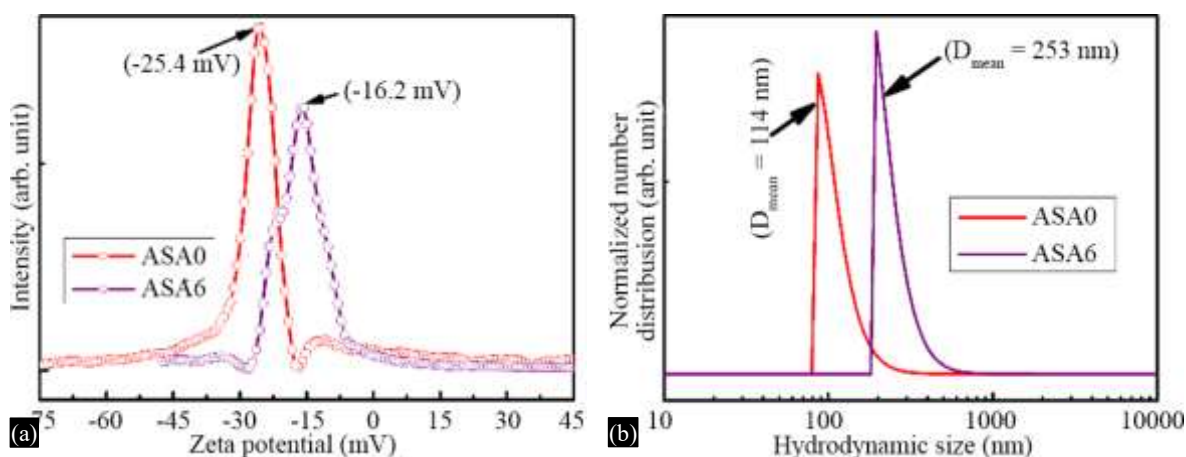


Figure 5. (a) Zeta potential and (b) hydrodynamic diameter spectra of ASA0 and ASA6 NPs dispersed in deionized water.

Since the mobility of NPs in solutions under the applied electric field ($E = 85 \text{ V/cm}$) is directly proportional to the value, the addition of Ag-nano inclusions to Ag₂S NPs alters their surface charge [6, 37]. With a strong correlation to ζ values, the mean hydrodynamic diameters (D_{mean}) for the identical solution of ASA0 and ASA6 as in the related ζ measurements are 114 nm and 253 nm, respectively. This finding implies that Ag-NPs are linked to Ag₂S NPs, increasing the D_{mean} values.

X-ray Photoelectron Spectroscopy

With the ability to probe down to a few nm, X-ray photoelectron spectroscopy (XPS) is used to further examine surface information on Ag₂S–Ag nanocomposites. The lack of impurity elements is confirmed by the survey scan spectrum of ASA1, which was synthesized using the nominally needed quantity of initial precursors and recorded in the region of 0 to 1300 eV (Figure 6(a)). For a thorough investigation of their valence states, high-resolution spectra of C, Ag, S, and O were recorded (Figure 6(b)–(e)). The carbon 1s peak can be deconvoluted into three peaks, which are designated as the C 1s peaks for C–C/C=C, –C–OH, and –C=O [6], respectively. These peaks were centered at 284.6, 281.5, and 288.12 eV (Figure 6(b)).

For the entire spectra, the C 1s peak (284.6 eV) was used as the internal reference. The Ag 3d spectrum was deconvoluted into two peak pairs, as shown in Figure 6(c). The binding energies of Ag 3d_{5/2} and Ag 3d_{3/2} of the Ag⁺ ions in Ag₂S should be attributed to the first pair of peaks, which appear at 367.51 eV and 373.5 eV, respectively [29–32]. Ag 3d_{5/2} and Ag 3d_{3/2} of metal Ag⁰ may be responsible for the smaller components at 368.25 eV and 374.21 eV on the higher energy side [29–32]. The presence of a fraction of Ag⁰ atoms in the composite was validated by the relative spectrum intensities between Ag⁰ and Ag⁺ components (Figure 6(c)). Two peaks that can be attributed to S 2p_{3/2} [31] and S 2p_{1/2} [29, 30] are obtained by deconvolution of the S 2p peak, and they are situated at around 160.8 eV and 162.02 eV, respectively (Figure 6(d)).

UV-visible Absorption and Photoluminescence Spectroscopy

To further validate the existence of Ag₂S and Ag together in the heterostructured nanocomposites, we performed UV-vis absorption spectroscopy for samples synthesized with varying quantities of thiourea (Figure 7(a)–(c)). Ag₂S NPs (ASA0) dispersed in de-ionized water show two obvious absorption edges, first at 260 nm due to the $n \rightarrow \sigma^*$ transition of non-bonding electrons of sulfur in Ag₂S with Ag–S bonds [19, 33]. This result also confirms the absence of unreacted AgNO₃ in the products, for which an absorption peak is expected at 300 nm [34]. Second, its blue-shifted optical band gap [13, 15, 16] is responsible for the absorption peak edge at around 600 (600–700) nm, which is in line with the mode found for Ag₂S NPs [13, 15, 16, 19]. However, as the Ag content increased in all.

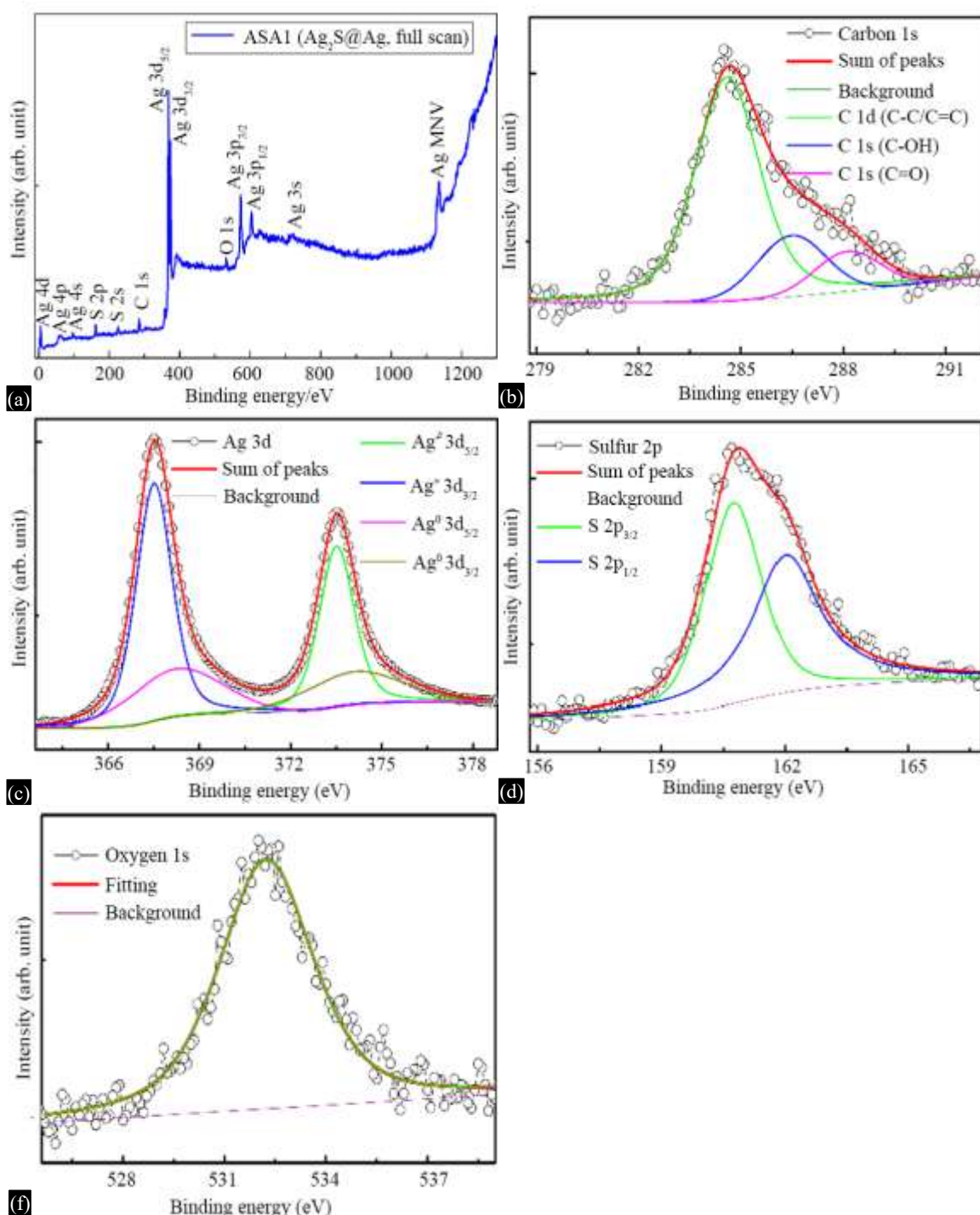


Figure 6. (a) Full survey scan XPS spectrum of ASA1. High-resolution XPS spectra of (b) Carbon 1s, (c) Ag 3d, (d) S 2p and (e) Oxygen 1s. Experimental data are represented by black open circles, and the red curve is the fitting line, which is the summation of all peaks.

In contrast, the Ag₂S nanoparticles' optical absorption edges moved towards the longer wavelength region. The absence of the expected additional broad absorption edge peaks in the visible region (320–500 nm) that would have resulted from the emergence of metallic Ag NP surface plasmon resonance (SPR) in Ag₂S-Ag nanocomposites is explained by the NPs' high sensitivity to aspect ratio [35] and environmental influences [29, 35, 36]. This provides further evidence that Ag-NPs adhere well to the Ag₂S nanodisks, supporting the EDX findings.

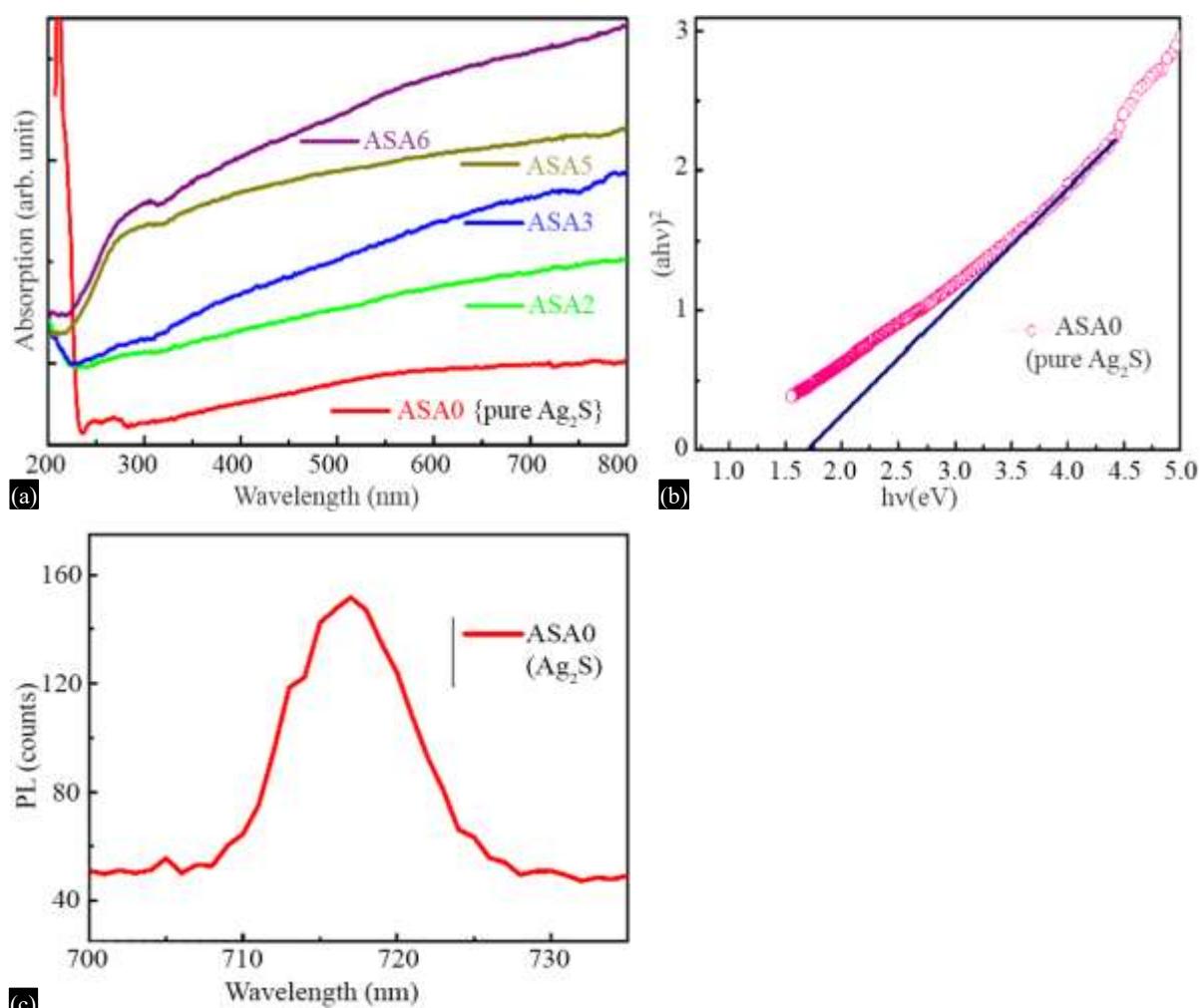


Figure 7. (a) UV-visible absorption spectra of Ag₂S-Ag nanocomposites with Ag-nano-inclusions of 0–23.5% in Ag₂S host and (b) Tauc plots of ASA0. (c) Photoluminescence emission spectra of Ag₂S (ASA0) collected using an exciting wavelength of 476 nm.

In actuality, the bottom of the conduction band of Ag₂S and the Fermi level of metallic Ag are situated at -4.42 eV and -4.26 eV, respectively, from the vacuum level (Figure 8(a)) [29]. The near-Fermi-level conduction electrons of metallic Ag will occupy the empty, low-energy states accessible in Ag₂S when Ag-NPs and Ag₂S NPs come into contact, facilitating electron transfer (Figure 8(b) and (c)). This charge transfer from Ag-NPs to Ag₂S NDs is expected to cause the band bending of the semiconducting side at the interface (Figure 8(b)) since a broad SPR mode that should be present at 320–500 nm is absent (Figure 7(a)). This results in the development of a contact potential barrier that stops additional charge transfer.

This could indicate that many Ag-NPs are unable to fully separate from the host Ag₂S NPs and that, for instance, only a portion of Ag-NPs easily enter solution (water) when they are dispersed in water. This is supported by the zeta potential (ζ) analysis of these composites with very low ζ values in deionized water (Figure 5), which shows that absorption occurs from very small or amorphous NPs in the solution while the majority of the larger crystalline particles settle at the bottom of the cuvette. Furthermore, the Tauc or Bardeen equation [16] was used to determine the optical bandgap of the Ag₂S NPs using UV-visible absorption data (Figure 7(b)). As Ag₂S is a direct band gap semiconductor, the straight line fit to a plot between $(ah\nu)^2$ versus $h\nu$ gives E_g , where a is the absorption coefficient, and $h\nu$ is the photon energy. The band gap obtained for pure Ag₂S (ASA0) was 1.7 eV, in good agreement with previously reported values for NPs [15, 16, 19].

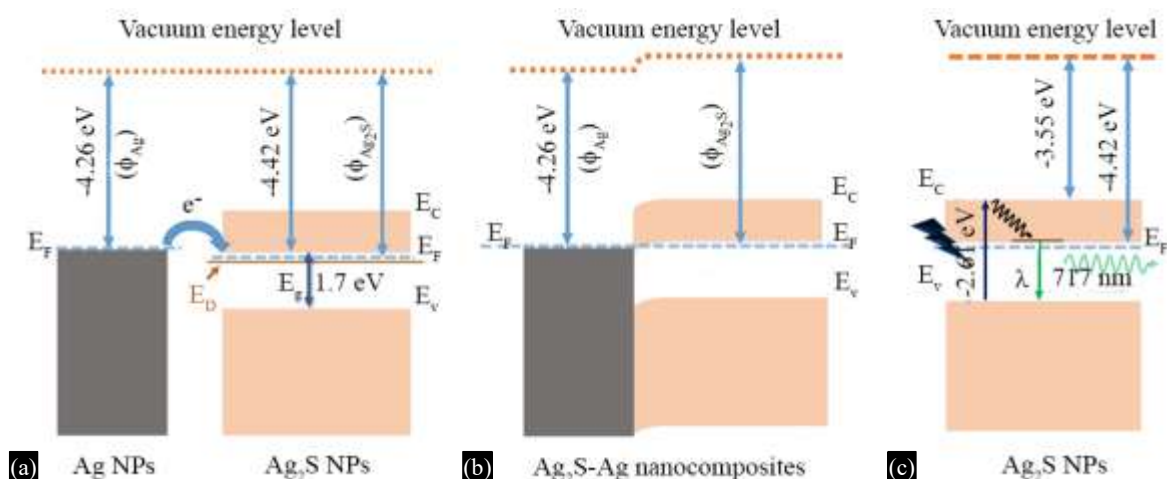


Figure 8. Schematics of (a) band diagram of separate Ag and Ag₂S NPs, (b) band bending in Ag₂S-Ag nanocomposites, and (c) possible mechanism for observation of photoluminescence in Ag₂S NPs.

To justify the above assumption, the photoluminescence (PL) emission spectra are collected for ASA0 (Ag₂S) using a laser excitation source of wavelength 476 nm (2.6047 eV) (Figure 7(c)). The main emission peak of ASA0 (pure Ag₂S) is centered at 717 nm (1.729 eV), which can be ascribed to the band gap recombination of electron-hole pairs [13, 15, 16, 19]. The schematic of the PL phenomenon is shown in Figure 8(c).

Transport Properties

Prior to measuring the transport characteristics, any moisture or adsorbed EG on the powder samples was eliminated, as shown by the XPS results. To do this, pellets of every sample were created using a nominal pressure and placed in a tube furnace set at 200°C for five hours while an Ar-gas flow of 160 cc/min was continuously applied. Following calcination, each pellet was ground into a fine powder, which was then compressed into pellets using a pressure of around 1 GPa for one minute at 25°C. Four-probe electrical resistivity (ρ) measurements were performed on the bar-shaped portion of the pellets, and thermopower (α) data were obtained for the final pellets.

Owing to their high ρ , the ρ data for the ASA0 and ASA1 samples could not be recorded using four-probe ρ measurements. Increasing the Ag content of nanocomposites can reduce their high ρ [22]. The ρ data of the Ag₂S-Ag nanocomposites with different amounts of sulfur sources are displayed in Figure 9(a)–(b). In contrast to ASA1, ASA2 (TU = 2.85 mmol, Thiourea (TU)) exhibits a strong decrease in ρ values, and its sharp exponential rise with decreasing temperature (Figure 9(a)) is explained by semiconducting behavior. Furthermore, down to 225 K, the nanocomposite with 2.75 mmol TU (ASA3) exhibits semiconducting nature; below that, it displays metallic behavior down to 5 K (Figure 9(b)). Other samples created with additional TU reduction show similar patterns, with the semiconducting to metal (SM) transition temperature (TSM) shifting towards the higher temperature side (Figure 9(b)–(d)). The final sample, ASA7 (2.55 mmol TU), showed a fully metallic nature throughout the 5–325 K range, and the SM transition vanished (Figure 9(b)).

The resistivity of ρ_{Ag} decreases linearly with decreasing temperature. These two competing phenomena operate together in these materials, and domination of one over the other in different T regions is thus evident (Figure 9(a)–(b)). All samples (with Ag-nanoinclusions of 0–23.5%), except ASA7, showed semiconducting ρ below 325 K down to about 220 K maximally but with varying ranges because $\rho_{Ag} < \rho_{Ag_2S}$ here since electric current follows the least resistive path; thus, below TSM all samples have to perhaps switch to metallic ρ . Below a particular temperature (TSM), ρ_{Ag} will exhibit lower values as compared to ρ_{Ag_2S} , because ρ_{Ag} goes down linearly and ρ_{Ag_2S} increases exponentially with decreasing T, and exhibits a semiconductor-to-metal transition.

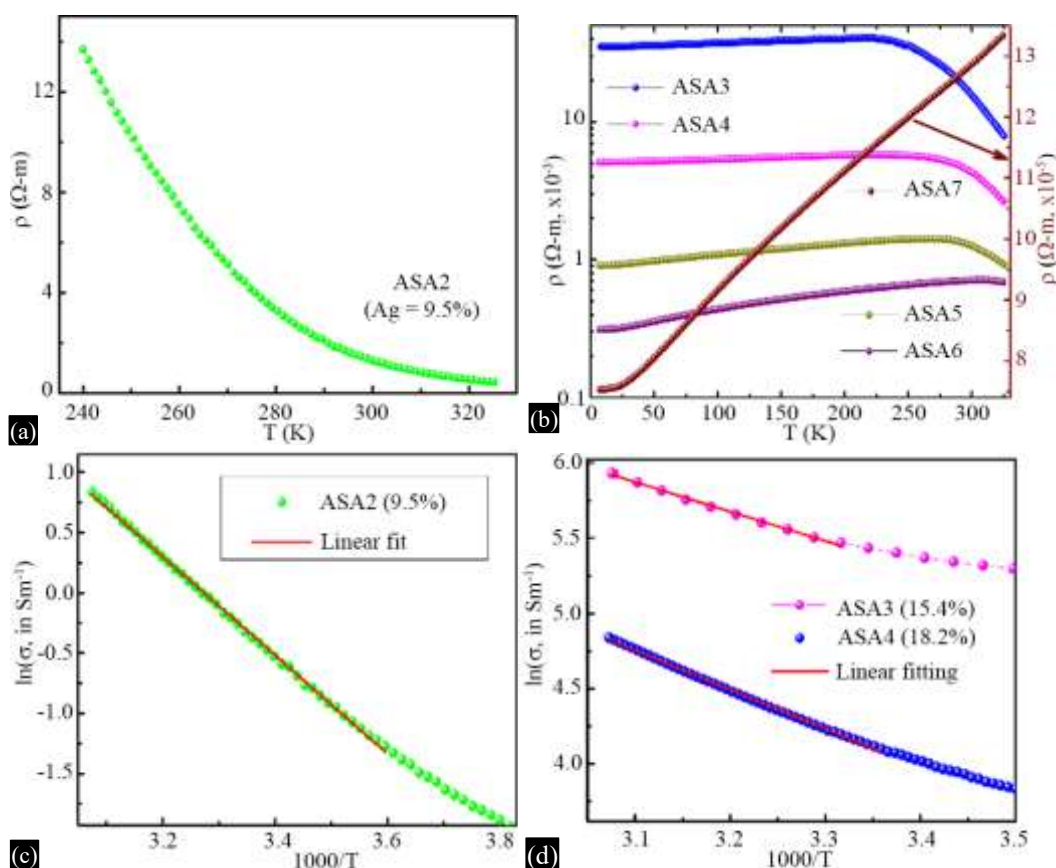


Figure 9. (a)–(b) Temperature-dependent electrical resistivity of Ag₂S–Ag nanocomposites with different % of Ag-nano-inclusions (9.5–23.5%) and (c)–(d) Arrhenius equation fitting of σ data near 300 K for ASA2, ASA3 and ASA4.

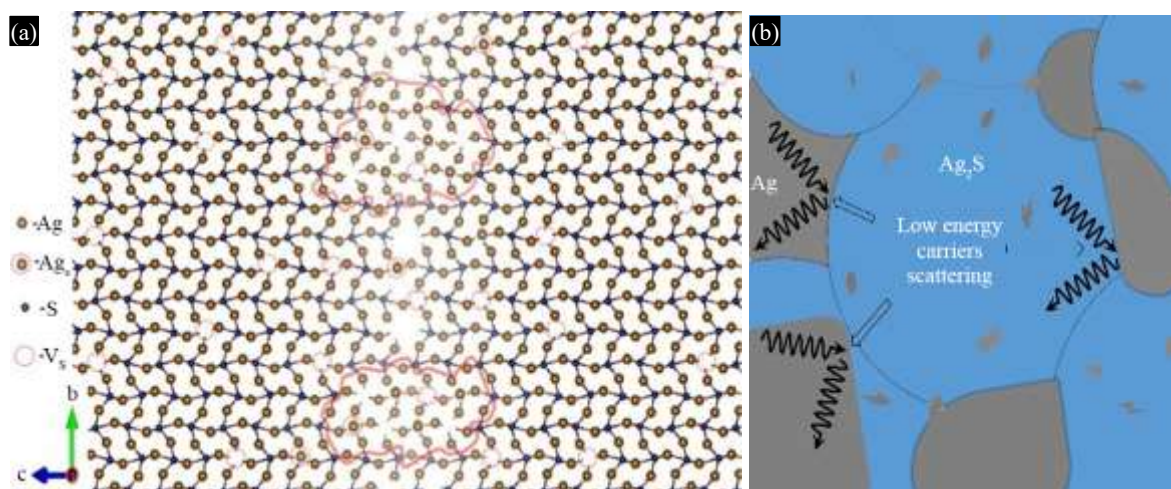


Figure 10. Diagram showing (a) the formation of Ag antisite defects (AgS) and sulfur vacancies (VS) in Ag₂S, as well as the (b) potential scattering of low-energy carriers at the semiconductor-to-metal interfaces in Ag₂S–Ag nanocomposites, and the nucleation centers for Ag-NPs at the Ag-rich grain boundary regions of two neighboring grains (region inside the pink solid line). Ag atom clusters are indicated by very tiny grey patches in (b).

Pure Ag₂S (ASA0) and the first ASA1 nanocomposite are examples of highly resistive samples for which Seebeck coefficient (α) measurements are likewise not feasible (Table 3). As previously mentioned, the ρ of composites decreases as the Ag content increases because of the concurrent

production of crystalline or amorphous Ag-NPs at the grain boundaries and an increase in the number of sulfur defects in the Ag₂S matrix (Figures 9(a)–(b) and 10(a)). As a result, total n rises with Ag in composites, enabling the use of a tiny temperature differential (~ 2 K) to generate detectable voltage. It is commonly known that the Seebeck coefficient α can reflect a relatively tiny change in n and that the inverse relation $\alpha \propto 1/n$ exists [1, 6, 37]. ASA2 (9.5% Ag-NPs) is a more resistive sample with low n and shows very high α values ($-574 \mu\text{V/K}$ at 325 K) with a negative sign. Figure 11(a)–(b) show the temperature dependence of α for ASA2 and all other samples with higher Ag content, respectively. With decreasing T , the magnitude of α decreases, and below 234 K, it exceeds the recordable range of the sensors (Figure 11(a)). These findings indicate that electrons are the majority charge carriers. Based on the ρ analysis, it was determined that ASA2 is an n -type non-degenerate semiconductor. Above their SM transition, the α values of other samples with higher Ag concentration (except for the most recent ASA7) likewise rise with T (Figure 11(a)–(d)).

Table 3. The activation energy (E_{ac}) and energy difference (E_s) between the bottom of the conduction band (E_c) and Fermi level (E_F) obtained from theoretical fitting of ρ and α data. Obtained α , $\alpha_2\sigma$, and TE figure of merit at 325 K for Ag₂S-Ag nanocomposites.

Sample name (Ag %)	E_{ac} (meV)	$E_s = E_c - E_F$ (meV)	α ($\mu\text{V/K}$)	$\alpha_2\sigma$ ($\mu\text{Wm}^{-1}\text{K}^{-2}$)	ZT
ASA2 (9.5)	252.85	178.61	-581.3	0.77	0.15×10^{-3}
ASA3 (15.4)	223.9	164.67	-229.8	1.50	1.03×10^{-3}
ASA4 (18.2)	168.93	162.69	-162.1	9.92	
ASA5 (20.1)		158.42	-134.5	19.53	2.88×10^{-3}
ASA6 (23.5)		55.57	-52.8	4.06	
ASA7 (21.1)			-0.3	0.0006	

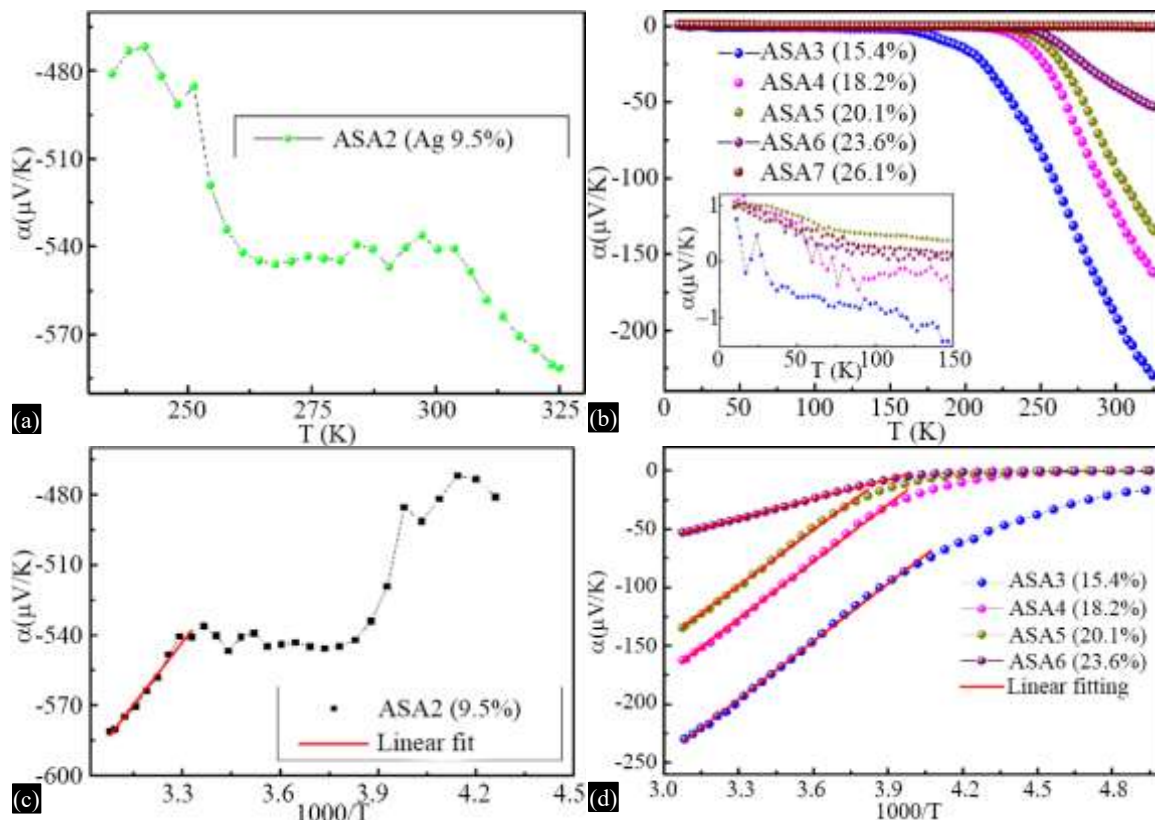


Figure 11. (a)–(b) Seebeck coefficient (α) and (c)–(d) linear fitting of α using Mott's equation for non-degenerate semiconductor of Ag₂S-Ag nanocomposites synthesized with different ratios of initial precursors. Inset in (b) expanded portion of α on a smaller scale.

As the amount of Ag in nanocomposites increases, the magnitude of α at 300 K progressively declines ($\alpha_{\text{ASA3}} > \alpha_{\text{ASA4}} > \alpha_{\text{ASA5}} > \alpha_{\text{ASA6}}$ at ~ 300 K). According to the $\alpha \propto 1/n$ relationship, this is caused by an increase in the carrier density (n) with the Ag content [1, 6, 37]. The number of Ag-NPs nucleation centers (amorphous clusters) in the grain boundary area rises with increasing Ag concentration, and the conjunction of these centers leads to the formation of fully developed Ag NP crystallites. Since conduction electrons are more likely to percolate through Ag grains and effective SM contacts are less common in composites with a higher Ag concentration, α values are suppressed to lower values [11]. Because ASA2 has a low Ag concentration, the Ag-NPs are tiny and may disperse evenly. Because more SM contacts are created, the α values are large ($\alpha_{325\text{ K}} = -575 \mu\text{V/K}$). For ASA3, ASA4, ASA5, ASA6, and ASA7 nanocomposites, the α value at 325 K sequentially decreases to $-229.7 \mu\text{V/K}$, $-162.2 \mu\text{V/K}$, $-134.5 \mu\text{V/K}$, $-52.8 \mu\text{V/K}$, and $-0.3 \mu\text{V/K}$, respectively. These results are in good agreement with both the experimental [7, 24, 25] and theoretical [11, 41] results. They strongly imply that the insertion of metal NPs in semiconducting hosts, which causes the band bending at metal NPs to semiconductor interfaces, can lead to a large improvement in α (Figure 11(a)–(b)).

This exclusively transmits high-energy carriers and can effectively block low-energy charge carriers through an ideal potential barrier height at SM interfaces (Figure 10(b)). Since electrons are the primary charge carriers in both noble metal Ag and sulfur-deficient Ag₂S [22, 28], all nanocomposites should only show negative α values over the whole temperature range of 5–325 K. Although metallic Ag-NPs in bulk have α values ranging from $\alpha_{5\text{ K}} = 0.5$ to $\alpha_{300\text{ K}} = 1.5 \mu\text{V/K}$ but with a negative Hall coefficient, below SM transitions, α values are suppressed to very small values for all samples and switch to positive values at low temperature. This is explained by its intricate Fermi surface with interconnected necks. The Fermi surface curvatures in face-centered cubic (FCC) silver are positive, acute, and just touch the Brillouin zone boundary along each neck axis (111). The Fermi surface produces holes because the density of hole-like states, n_h , connected to the $\langle 111 \rangle$ necks is significantly higher than that of electron-like states, n_e , connected to the $\langle 100 \rangle$ belly. Consequently, the density of thermally excited holes is significantly greater than that of electrons, resulting in a positive α . When a system contains two different kinds of charge carriers, the total thermopower is equal to the sum of α_e (-ve) and α_h (+ve). Thus, the dominance of electrons or holes over one another at a specific temperature range determines the amount and sign of total α (Figure 11(a)–(d)). Different slopes found in the low and high B_z regions yielded different positive RH values below 200 K. These positive RH values below 200 K are due to the complex Fermi surface in Ag₂S–Ag nanocomposites and are well consistent with α data in which very low or positive α values are attained (Figure 11(b)).

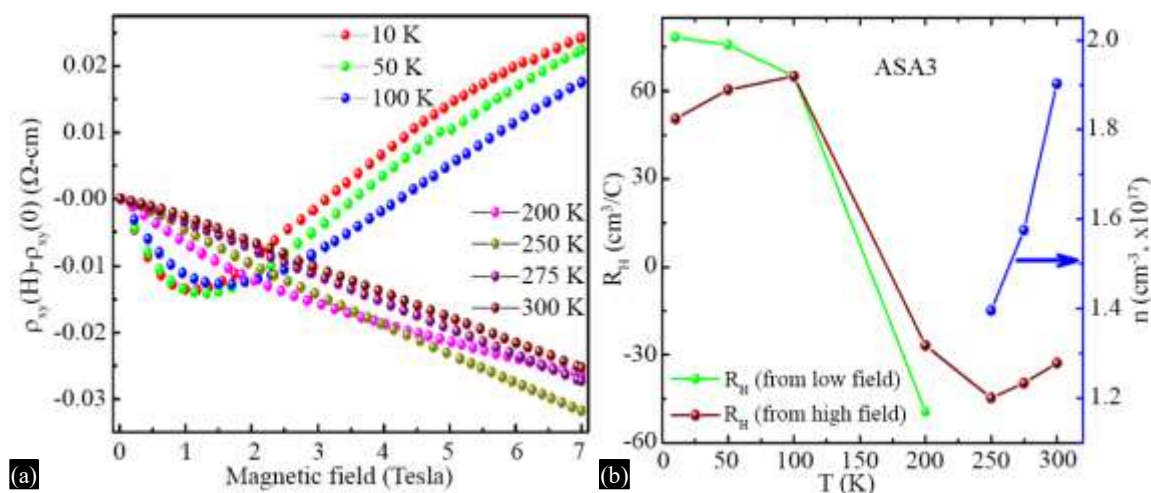


Figure 12. (a) Magnetic field-dependent Hall resistivity p_{xy} and (b) calculated Hall coefficient (R_H = slope of p_{xy} versus B curves) and charge concentration (n) of ASA3 at different temperatures.

The calculated density of defect states (NC) found ($1.38 \times 10^{20} \text{ cm}^{-3}$) using $n = NC_{\text{exp}}(-(\text{EC}-\text{EF})/k\text{BT})$ is greater than $n \sim 1.9 \times 10^{17} \text{ cm}^{-3}$, confirming the non-degenerate semiconducting nature of ASA3 at 300 K (Figure 12(a)–(b)).

CONCLUSIONS

We demonstrated a facile method for the synthesis of Ag₂S-Ag nanocomposites and investigated the effect of Ag-nanoinclusions on their thermoelectric properties. The existence of Ag-NPs as a secondary phase in α -Ag₂S is confirmed by Rietveld refinement of its powder XRD. A substantial reduction in electrical resistivity of Ag₂S with decreasing sulfur content is observed and brings it down to a measurable range. A significantly high Seebeck coefficient and power factor are achieved in 15.4 to 23.5% Ag-nanoinclusions in semiconducting Ag₂S. Hall coefficient (RH) measurements are made for ASA3, and n values are computed to further establish the dominance of various charge carrier types at various T . The slope of the Hall resistivity (ρ_{xy}) vs applied magnetic field (B_z) graphs at various T s would be known as RH. The slopes that are obtained at high temperatures (between 200 and 300 K) are negative, indicating that electrons represent the majority of charge carriers and thus the RH values are negative. The obtained n at 250–300 K are between $1 \times 10^{17} \text{ cm}^{-3}$ and $2 \times 10^{17} \text{ cm}^{-3}$. Nevertheless, a change in the positive slopes with B_z is seen below 200 K, which indicates the presence of two different kinds of charge carriers, with holes in the majority. opens up a new strategy for enhancing the ZT value of this Ag₂S near room temperature and beyond it. The next chapter details trioctylphosphine-induced chalcogenide Bi₂Te₃-BiTe nanocomposites.

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