Solution-Processed Wafer-Scale Ag₂S Thin Films: Synthesis and Excellent Charge Transport Properties

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Monoclinic α-Ag₂S is an intriguing member of transition metal sulfides with great potential for all-inorganic flexible optoelectronics and thermoelectrics. Fabrication of large-area, high-quality α-Ag₂S thin films and understanding their charge transport properties are critical for device operations yet have remained largely unexplored. Here, a novel two-step, the solution-processed approach is reported to produce wafer-sized, highly crystalline α-Ag₂S thin films. Ultrafast terahertz (THz) conductivity measurements reveal that photogenerated charge carriers undergo efficient band transport, with room-temperature mobility of ≈150 cm² V⁻¹ s⁻¹ and a diffusion length exceeding 500 nm. Furthermore, introducing poly(vinyl alcohol) (PVA) as the rigid component into the aqueous silver thiolate precursor enables the synthesis of free-standing α-Ag₂S thin films with a mobility of ≈35 cm² V⁻¹ s⁻¹, demonstrating their potential for flexible optoelectronics. This study provides a facile synthesis route for high-quality, large-area α-Ag₂S thin films with good charge transport properties, relevant for their integration into optoelectronics and wearable electronics.

1. Introduction

Monoclinic α-Ag₂S is a representative transition metal sulfide (TMS) with extraordinary ductility resembling metals due to the high cleavage energy between the adjacent crystal planes.[1] The unique combination of its metal-like ductility and relatively high intrinsic mobility (over 100 cm² V⁻¹ s⁻¹)[2] renders α-Ag₂S as potential active components for flexible optoelectronics. For instance, Jo et al.[2] pioneered the solution-processed synthesis of ductile semiconducting Ag₂S thin films with remarkable stretchability as high as 14.9%, enabling wrinkled Ag₂S-based memory devices with excellent mechanical stretchability and their further integration with motion sensors to form self-powered healthcare monitoring systems. Furthermore, α-Ag₂S has also attracted considerable attention for thermoelectrics due to the high Seebeck coefficient.[3]

Besides its great potential for flexible electronics and thermoelectrics, α-Ag₂S has been long considered as promising light absorbers for low-cost and efficient optoelectronics, including thin-film solar cells, since the first research surge of TMSs for photovoltaics in the 1980s.[4] The advantage of α-Ag₂S for optoelectronics is that it combines fascinating properties, including non-toxic elements, a suitable direct bandgap (with an energy gap of 0.9–1.1 eV)[5] for photovoltaics, and an extremely high absorption coefficient.[7] Within the theoretical framework developed by Shockley and Queisser, the maximum efficiency of a single junction solar cell based on α-Ag₂S can reach up to ≈30%.[8] Despite its great promise, α-Ag₂S has attracted little research attention compared to other TMS materials such as pyrite, and the conversion efficiency of Ag₂S-based photovoltaic devices remains quite moderate with the state-of-the-art value of around 3%.[9] The origin for the relatively low energy conversion efficiency of α-Ag₂S solar cells may be attributed to relatively high defect densities, as reported for some of other TMS materials.[10]

Therefore, to realize the full potential of α-Ag₂S for the above applications, producing high-quality thin films with relatively low defect density and excellent charge transport properties (e.g., high carrier mobility) is mandatory. Over the past decades, several methods have been developed to prepare Ag₂S thin films, such as chemical bath deposition (CBD)[11] epitaxial growth,[12] chemical vapor deposition,[13] spray pyrolysis,[14] and electrodeposition.[15] Despite these efforts, the production of high-quality, large-scale α-Ag₂S thin films in a facile manner remains challenging, impeding the development of relevant devices and applications. Furthermore, understanding the charge transport properties in α-Ag₂S is essential for device operations, yet has remained largely unexplored.

Here we develop a two-step, solution-processed wafer-scale deposition of α-Ag₂S thin films with high charge carrier mobility and long charge carrier diffusion length (over 500 nm). We employ water-soluble silver thiolate (i.e., Ag-3-mercaptopropionic acid (Ag-MPA)) as the precursor, which can be easily...
processed into uniform silver thiolate films with a controllable thickness (from 30 to 200 nm). Following the pyrolysis of the silver thiolate, a continuous and highly crystalline Ag\(_2\)S film is readily obtained. We perform time- and frequency-resolved photoconductivity measurements by ultrafast THz spectroscopy to investigate their charge transport properties. The results reveal high mobility of \(\approx 150\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}\), and a charge carrier diffusion length over 500 nm, exceeding the optical penetration depth that determines the photogenerated charge carrier distribution (e.g., \(\approx 300\ \text{nm}\) at 3.1 eV). The latter condition ensures that the majority of charge carriers can circumvent the trapping process to reach the electrodes for thin-film photovoltaic applications following light absorption. Intriguingly, the photoconductivity of \(\alpha\)-Ag\(_2\)S is found to increase strongly with decreasing temperature. This indicates a band-like charge transport mechanism in our samples and suggests a minor role of defect scattering in determining the charge carrier conductivity (and thus the high quality of our sample). Finally, we show that our synthetic method can be further extended to synthesize free-standing \(\alpha\)-Ag\(_2\)S thin films with satisfactory mobility of \(\approx 35\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}\), demonstrating their great potential for flexible optoelectronics. Our study provides a facile strategy for fabricating high-quality (i.e., low defect density and high carrier mobility) and large-area \(\alpha\)-Ag\(_2\)S thin films. The efficient charge transport in \(\alpha\)-Ag\(_2\)S paves the way for the integration of Ag\(_2\)S thin films toward optoelectronics and wearable electronics.

2. Results and Discussion

As schematically shown in Figure 1a, we realize the solution-processed synthesis of \(\alpha\)-Ag\(_2\)S by using Ag-MPA as the precursor. Firstly, Ag(NO\(_3\)) was mixed with MPA in ethylene glycol (EG) and diethylene glycol (DEG). Following a purification step, the synthesized Ag-MPA can be further dispersed into water to form Ag-MPA aqueous solution.\(^{[16]}\) The Ag-MPA precursors were then spin-coated on the substrate of interest to form an Ag-MPA thin film (Figure 1b), which converts into monoclinic \(\alpha\)-Ag\(_2\)S thin film upon pyrolysis (Figure 1c).

The X-ray diffraction (XRD) pattern of Ag-MPA films (with a thickness of 500 nm) shows periodic diffraction peaks at 2\(\theta\) = 4°, 8°, and 12° (Figure 1d), which correspond to the (010), (020), and (030) facets, respectively. This indicates that Ag-MPA comprises lamellar structures with an interlayer spacing of \(\approx 2\ \text{nm}\) between the adjacent Ag-S layers. To shed light on the structure of Ag-MPA, we conducted solid-state NMR spectroscopy (see Figure S1, Supporting Information). We found that around 50% MPA ligands are distributed perpendicular to the Ag-S layers in the trans conformation, whereas the other half of MPA ligands are distributed almost parallel to the Ag-S layers in the gauche conformation (as shown in Figure 1b). The terminal carboxyl group of MPA ligands coordinates with the hydroxyl group of EG or DEG by hydrogen bonding. The hydroxyl groups contribute to the excellent water-solubility of the silver thiolate precursor.

Upon heating the Ag-MPA thin film at 180 °C for 15 min, the characteristic peaks of Ag-MPA disappear with the emergence of the crystalline peaks of monoclinic \(\alpha\)-Ag\(_2\)S (Figure 1d). Based on thermogravimetric (TG) measurement, we show that the decomposition from the Ag-MPA to \(\alpha\)-Ag\(_2\)S starts from \(\approx 170\ \text{°C}\) (see Figure S2, Supporting Information). In addition, based on the XPS study (see Figure S3, Supporting Information), we can conclude that over \(\approx 90\%\) of the sulfur belongs to Ag\(_2\)S, indicating a relatively complete transformation. Further effort in controlling annealing conditions (e.g., time and temperature) to optimize the crystallization process and further decrease the MPA residuals is required. Based on the Tauc plot analysis, we estimate the bandgap of \(\alpha\)-Ag\(_2\)S thin film (Figure 1e) to be \(\approx 1.3\ \text{eV}\), close to the theoretically predicted bandgaps ranging from 0.9 to 1.1 eV.\(^{[5,6]}\)

The formation and morphology of \(\alpha\)-Ag\(_2\)S were further examined by high-resolution transmission electron microscopy (HRTEM) (Figure 1f), atomic force microscopy (AFM) (Figure 1g and Figure S4, Supporting Information), and scanning electron microscopy (SEM) (Figure S5, Supporting Information). The HRTEM image (Figure 1f) reveals lattice fringes with an interplanar spacing of 2.4 Å, which matches well with the distance between the adjacent (013) planes of \(\alpha\)-Ag\(_2\)S (PDF 14-0072). Thanks to the high solubility of Ag-MPA and the mild crystallization process, AFM images of \(\alpha\)-Ag\(_2\)S thin film (Figure 1g and Figure S4, Supporting Information) exhibits a relatively smooth surface with a root mean square (RMS) surface roughness of 11 nm (for a film of 200 nm thick), and a lateral diameter of \(\approx 2.5\ \text{cm}\), demonstrating their potential for device-relevant applications. The top and cross-section SEM images (Figure S5, Supporting Information) reveal that the samples are pinhole-free, and have relatively smooth surfaces. The thickness of the Ag\(_2\)S thin film can be readily increased by repeating the spin-coating and heating processes (at least up to \(\approx 1.5\ \text{μm}\) as shown in Figure S6, Supporting Information). We find that increasing the film thickness does not impact on the photoconductivity amplitude and dynamics (see Figure S7, Supporting Information).

To shed light on microscopic charge transport properties of Ag-MPA and \(\alpha\)-Ag\(_2\)S thin films, we employed ultrafast optical pump–THz probe (OPTP) spectroscopy to probe their time- and frequency-resolved photoconductivity. As an all-optical technique, OPTP spectroscopy accesses the conductivity of materials of interest in a contact-free fashion, and thus is particularly powerful for exploring the nature of charge transport in nanomaterials.\(^{[17]}\) In a typical OPTP measurement, an ultrafast (\(\approx 100\ \text{fs}\) duration) laser pulse of 3.1 eV optically injects charge carriers into Ag-MPA (as a control measurement) and \(\alpha\)-Ag\(_2\)S thin films (with a thickness of \(\approx 200\ \text{nm}\); see Figure S4, Supporting Information) following the interband excitation. Subsequently, a single-cycle THz pulse (\(\approx 1\ \text{ps}\) duration) drives the conduction of photogenerated free charge carriers by the oscillating THz electric field \(E\). This leads to THz attenuation due to free carrier absorption. The relative change of the THz electric field \((-\Delta E/E)\) is proportional to the photoconductivity \(\Delta\sigma\) following the thin-film approximation (Equation (1)).\(^{[18]}\)

\[
\Delta\sigma = \frac{n + 1}{Z_0 l} \cdot \frac{\Delta E}{E}
\]

where \(n = 1.95\) represents the refractive index of the fused silica substrate in the measured THz range (0.5–2 THz), \(Z_0 = 377\ \text{Ω}\) is the impedance of free space, \(l\) is the optical penetration depth.

Figure 2a compares the photoconductivity dynamics of Ag-MPA and \(\alpha\)-Ag\(_2\)S thin films at the same absorbed photon
density of $\approx 3.4 \times 10^{14}$ cm$^{-2}$. Upon excitation, the optically injected charge carriers in Ag-MPA thin films exhibit poor photoconductivity of $\approx 20$ S m$^{-1}$ in the peak, followed by a fast decay process within $\approx 1$ ps. The rapid photoconductivity decay may be tentatively assigned to the charge localization process (e.g., by trapping). By contrast, photogenerated charge carriers in $\alpha$-Ag$_2$S thin films possess much higher photoconductivity of $\approx 6000$ S m$^{-1}$ ($\approx 300$ times higher than that of Ag-MPA) and a substantially longer lifetime (as shown below), demonstrating their potential for photovoltaic and optoelectronic applications.

To further elucidate their charge transport properties, we measured the frequency-resolved complex photoconductivity for $\alpha$-Ag$_2$S (Figure 2b) and Ag-MPA (Figure 2c) thin films at $\approx 1$ ps after their maximum photoconductivity. The frequency-resolved complex photoconductivities can be phenomenologically described by the Drude-Smith (DS) model. In the model, the motion of charge carriers in the samples is subject to backscattering (e.g., at grain boundaries), following (Equation 2)\cite{17,19}:

$$
\Delta\sigma(\omega) = \frac{\omega_p^2}{2\pi}\frac{\varepsilon_0\varepsilon_r\tau}{1-i\omega\tau}\left(1 + \frac{c}{1-i\omega\tau}\right)
$$

where $\omega_p$, $\tau$, $\varepsilon_0$ denote the plasma frequency, effective carrier scattering time, and vacuum permittivity, respectively. The
parameter $c$ parameterizes the probability of backscattering, with values spanning from 0 (for isotropic scattering) to −1 (for preferential scattering). The DS fit to the data yields $\tau$ of $39 \pm 2$ and $42 \pm 4$ fs, and $c$ parameters of $-0.49 \pm 0.01$ and $-0.92 \pm 0.02$ for $\alpha$-$\text{Ag}_2\text{S}$ and Ag-MPA thin films, respectively. Given the inferred scattering time $\tau$ and $c$, together with the effective charge carrier mass obtained from reference $\text{(m})^{20}$, we estimate the mobility ($\mu$) of $\alpha$-$\text{Ag}_2\text{S}$ thin film to be $\approx 150 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the dc limit following $\mu = \frac{\varepsilon \tau}{m^*}(1 + c)$, where $\varepsilon$ is the elementary charge. The estimated $\mu$ is in good agreement with the reported device-relevant mobility,$^{[20]}$ representing one of the highest values for chalcogenide-based inorganic semiconducting materials (all quantified by THz spectroscopy, see Table S1, Supporting Information). Furthermore, THz measurements at four different sample spots show similar peak photoconductivities and lifetimes (Figure S8, Supporting Information), demonstrating the uniformity of the film.

Along with the remarkably high charge mobility, another figure of merit of a material for photovoltaic applications is the long charge carrier lifetime, or equivalently, low decay rate. To unveil the charge decay rates associated with different recombination channels (trapping, bimolecular recombination, and Auger recombination) in $\alpha$-$\text{Ag}_2\text{S}$, we measured photoconductivity dynamics for its thin film under various incident pump fluences ranging from 4.4 to 82.5 $\mu\text{J cm}^{-2}$. As shown in Figure 3a, the photoconductivity decays faster at elevated pump fluences, as a result of the increasing contributions from the higher-order decay channels (e.g., bimolecular and Auger recombination)$^{[21]}$. To clarify the dependence of decay rates on the charge carrier density, we globally fit the pump fluence-dependent photoconductivity dynamics with the coupled rate equation (Equation (3)):

$$\frac{dn(t)}{dt} = -k_1n - k_2n^2 - k_3n^3$$

where $n(t)$ is the charge carrier density at the pump-probe delay $t$, $k_1$ represents the monomolecular recombination rate coefficient accounting for the trapping-related process, $k_2$ stands for the bimolecular recombination rate coefficient originating from the recombination of electron–hole pairs, and $k_3$ denotes the Auger recombination rate coefficient. Based on the fitting, $k_1$, $k_2$, and $k_3$ are extracted to be $2.08 \times 10^8 \text{ s}^{-1}$, $7.13 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and $1.19 \times 10^{-29} \text{ cm}^6 \text{ s}^{-1}$, respectively. This gives rise to the total decay rate ($R_{\text{total}}$), by weighting the contribution of different recombination channels, as shown in Figure 3b (black line) as a function of absorbed photon density. By knowing the high charge mobility $\mu$ and the recombination rate $R_{\text{total}}$, we can further calculate the diffusion length $L$ in $\alpha$-$\text{Ag}_2\text{S}$ thin film following (Equation (4)):

$$L(n) = \frac{D}{\sqrt{R_{\text{total}}(n)}} \text{ with } D = \frac{\mu k_B T}{\varepsilon}$$

Figure 2. THz photoconductivity of $\text{Ag}_2\text{S}$ and Ag-MPA thin films. a) Time-resolved THz photoconductivity of $\text{Ag}_2\text{S}$ thin film (black line) and Ag-MPA thin film (red line, multiplied by 50). Samples are excited by a 3.1 eV laser pulse with the same absorbed photon density of $3.4 \times 10^{14} \text{ cm}^{-2}$, and their photoconductivity is probed by a single-cycle THz pulse under $\text{N}_2$ atmosphere. Frequency-resolved THz photoconductivity of b) $\text{Ag}_2\text{S}$ thin film and c) Ag-MPA thin film measured at $\approx 1$ ps after the maximum photoconductivity. The solid and dashed lines represent the Drude-Smith model describing the real and imaginary components of the complex THz photoconductivity, respectively.

Figure 3. Charge carrier dynamics of $\text{Ag}_2\text{S}$ thin films at various initial charge carrier concentrations. a) Fluence-dependent THz photoconductivity dynamics of $\text{Ag}_2\text{S}$ thin film following 3.1 eV excitations, with incident pump fluences ranging from 4.4 to 82.5 $\mu\text{J cm}^{-2}$. The solid lines represent global fitting to the recombination rates equation as discussed in the main text. The recombination rates $k_1$, $k_2$, and $k_3$ are extracted to be $2.08 \times 10^8 \text{ s}^{-1}$, $7.13 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, and $1.19 \times 10^{-29} \text{ cm}^6 \text{ s}^{-1}$, respectively. b) Charge carrier recombination rates of $\text{Ag}_2\text{S}$ thin films at varied charge carrier concentrations. Here $\varphi$ stands for the photon-to-charge conversion ratio representing the number of charge carriers created per absorbed photon. c) Charge carrier diffusion length of $\text{Ag}_2\text{S}$ thin films as a function of charge carrier concentration.
where $k_B$ and $T$ stand for the Boltzmann constant and temperature, respectively. Figure 3c plots the lower bound limit of $L$ as a function of carrier density by assuming the photon-to-charge branching ratio $\phi = 1$. We found that the lower bound limit of $L$ is already around 500 nm, following a relatively low excitation fluence that is relevant for practical applications ($<10^{17}$ cm$^{-2}$).

To demonstrate their potential in optoelectronic applications, here we compare the characteristic charge carrier properties of $\alpha$-Ag$_2$S with the state-of-the-art solution-processed materials for photovoltaics (e.g., organic-inorganic hybrid perovskites; see Table S2, Supporting Information). While $\alpha$-Ag$_2$S shows an unfavorably (1–2 orders of magnitude) higher recombination rate than those of perovskites, it possesses an order of magnitude larger charge carrier mobility. By balancing these two parameters for charge transport, the charge carrier diffusion length of $\alpha$-Ag$_2$S is found to be close to those of perovskites ($\approx 1$ μm). More importantly, the inferred carrier diffusion length, in spite of being underestimated, is already much longer than the penetration depth ($\approx 300$ nm at 3.1 eV) of excitation photons for $\alpha$-Ag$_2$S. This favorable condition indicates that for thin-film $\alpha$-Ag$_2$S devices, e.g., with a thickness of 500 nm (see Figure S9, Supporting Information), the majority of photogenerated charge carriers can be collected by electrodes without significant trap-mediated carrier loss, mainly thanks to the high charge carrier mobility and high absorption coefficient of the $\alpha$-Ag$_2$S. Figure S10 (Supporting Information) demonstrates that the Ag$_2$S film thickness can be increased to 1 μm to guarantee absorption exceeding 95% at the band-edge. Given that our inferred lower limit of the diffusion length of 500 nm is already close to 1 μm, our studies seem relevant for the photovoltaic community.

To provide more insights into the charge transport mechanism, we record temperature $(T)$-dependent photoconductivity dynamics for $\alpha$-Ag$_2$S thin film from 350 to 78 K. In principle, the measured photoconductivity is proportional to the product of the density $(n)$ and mobility $(\mu)$ of photogenerated charge carriers. Thanks to the high absorption of $\alpha$-Ag$_2$S (over 80% at 3.1 eV), $n$ is expected to change little in the temperature-dependent measurements for $\alpha$-Ag$_2$S. Therefore, the charge carrier mobility (and thus charge scattering time) plays a dominant role in dictating the photoconductivity. As shown in Figure 4a, the photoconductivity increases with decreasing temperature, revealing a negative temperature coefficient of conductivity (and thus charge carrier mobility), i.e., $\frac{d\mu}{dT} < 0$.

This suggests that photogenerated charge carriers are conducted in $\alpha$-Ag$_2$S thin films following band-like transport. The power-law fitting ($\Delta\sigma \propto T^\alpha$) between the maximum photoconductivity and temperature (Figure 4b) yields a power index $\alpha = -1$. The obtained strong temperature dependence of conductivity in our sample suggests that phonon scattering dominates the charge transport, and that defect scattering plays a relatively minor role in determining the charge carrier mobility of $\alpha$-Ag$_2$S. Overall, the observed high charge carrier mobility and band-like transport underline the high quality of our samples with relatively low defect density.

Finally, we demonstrated that our synthesis strategy can be readily extended to fabricate flexible, freestanding $\alpha$-Ag$_2$S thin films with potential applications in flexible (opto-)electronics. For that, we introduced poly(vinyl alcohol) (PVA) to the aqueous Ag-MPA solution. The reasons for choosing PVA in the synthesis are twofold: PVA can be well-blended with the precursor solution, maintaining the solution-processed feature of the approach; and it can host Ag$_2$S while introducing its flexible mechanical nature to the thin film. Upon pyrolysis, the XRD pattern of Ag$_2$S-PVA exhibits a broad halo at $2\theta = 19^\circ$ stemming from the amorphous PVA and crystalline peaks originating from $\alpha$-Ag$_2$S (Figure 5a). The resulting Ag$_2$S-PVA thin film shows a flat surface with an extremely low surface roughness of $\approx 635$ pm (Figure 5b), a large lateral size of $\approx 3$ cm $\times$ 2 cm (Figure 5c), and outstanding structural integrity during bending (Figure 5d). Frequency-resolved complex photoconductivity for the freestanding Ag$_2$S-PVA thin film can also be well-described by the Drude-Smith model as discussed above, yielding $\tau$ of $42 \pm 4$ fs and $c$ of $-0.92 \pm 0.02$, respectively. Compared to the supported $\alpha$-Ag$_2$S film, the addition of PVA leads to an increase in the absolute value of $c$ parameter, while $\tau$ remains almost the same within the experimental error. This gives rise to mobility of $\approx 35$ cm$^2$ V$^{-1}$ s$^{-1}$ in the dc limit, still exceptional for conducting polymers typically used for flexible electronics.[22] The reduced mobility may arise from the disturbed crystallization process of $\alpha$-Ag$_2$S and separation of conducting $\alpha$-Ag$_2$S domains, as a consequence of introducing

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**Figure 4.** Temperature-dependent THz photoconductivity of Ag$_2$S thin films. a) Temperature-dependent time-resolved THz photoconductivity dynamics of Ag$_2$S thin films following 3.1 eV excitation with a fixed incident pump fluence of 1.8 μJ cm$^{-2}$. b) The maximum THz photoconductivity as a function of temperature. The dashed line represents a power-law description of the data.
PVA. Further tailoring the relative ratio between the aqueous Ag-MPA solution and PVA and optimizing the crystallization conditions may help to increase the mobility of freestanding Ag$_2$S-PVA thin films. In addition, composition tuning also offers us a powerful knob to improve the surface quality of Ag$_2$S layers loaded on the substrate. For instance, we show that one can substantially reduce the surface roughness over 50% from 11 (with no PVA) to ≈3 nm (see Figure S11, Supporting Information) by adjusting the Ag-MPA/PVA ratio (to, e.g., 0.2).

Finally, to (i) investigate the effect of bending on the optoelectronic properties of PVA-Ag$_2$S films, we perform in situ THz photoconductivity measurements on free standing PVA-Ag$_2$S thin films (≈25 mm × 15 mm), by controlling the extent of the bending and the number of bending cycles. The measurement is achieved by mounting the two edges of the free-standing PVA-Ag$_2$S onto a home-designed sample holder, and tuning the lateral distance between the clamps via a translation stage, as schematically shown in Figure S12a (Supporting Information). Figure S12b,c (Supporting Information) shows two images of the free-standing PVA-Ag$_2$S thin film without and with bending load, respectively. Figure S12d (Supporting Information) demonstrates the photoconductivity dynamics, while their peak values at different bending degrees are summarized in Figure S12e (Supporting Information). As we can see, no obvious photoconductivity change is noticed during the bending (up to ≈25% compression load). This indicates that bending plays a minor role in affecting the optoelectronic properties of the free-standing PVA-Ag$_2$S thin film. In Figure S12f,g (Supporting Information), we show that over 100 times of bending cycles, no clear drop is seen in the THz photoconductivity. In addition, no obvious crack is noticed after 100 times bending (see Figure S13, Supporting Information), indicating the robustness of PVA-Ag$_2$S thin film for flexible electronics. Based on these data, we conclude that the PVA-Ag$_2$S composite is a promising candidate for flexible electronics, which uniquely combines excellent mechanical and electrical properties.

3. Conclusion

In conclusion, we report the solution-processed synthesis of wafer-scale, highly crystalline α-Ag$_2$S thin films by employing aqueous Ag-MPA as the precursor and investigate their charge transport properties by ultrafast THz spectroscopy. THz photoconductivity measurements reveal that the photogenerated charge carriers migrate in α-Ag$_2$S thin films by band-like transport with exceptional mobility of ≈150 cm$^2$ V$^{-1}$ s$^{-1}$, and a long diffusion length over 500 nm. The synthesis can be further extended to fabricate free-standing α-Ag$_2$S thin films with decent mobility of ≈35 cm$^2$ V$^{-1}$ s$^{-1}$, promising for flexible electronics and optoelectronics. Our study not only provides a facile synthesis route for large-scale, high-quality α-Ag$_2$S films, but also sheds light on the charge transport mechanism of α-Ag$_2$S, relevant for potential applications in optoelectronics and wearable electronics.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.
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