



Cite this: DOI: 10.1039/d6mh00095a

Received 18th January 2026,
Accepted 15th April 2026

DOI: 10.1039/d6mh00095a

rsc.li/materials-horizons

Ag₂Se/conjugated polyelectrolyte heterojunction films for high-performance flexible thermoelectrics

Yu-Chi Peng,^a Chih-Wei Hsu,^a Haim Kwon,^b Po-Shen Lin,^a Moon Sung Kang,^c
Han Young Woo^d and Cheng-Liang Liu^d    ^e

Silver selenide (Ag₂Se) has emerged as a promising room temperature thermoelectric material due to its intrinsically high performance, tunable electronic structure, and environmental compatibility. To further enhance its thermoelectric performance, a heterojunction engineering strategy is implemented herein by introducing a conjugated polyelectrolyte (CPE) at the Ag₂Se surface. The resulting ion-electron coupling forms an electron-rich interfacial channel that serves as a highly conductive charge transport pathway. Consequently, the planar heterojunction (PHJ) composite film delivers an electrical conductivity (σ) of $2209.7 \pm 226.9 \text{ S cm}^{-1}$ and an impressive power factor (PF) of $2629.3 \pm 291.0 \text{ } \mu\text{W m}^{-1} \text{ K}^{-2}$ at 303 K, representing the highest reported values among Ag₂Se-based composite films. Moreover, flexible thermoelectric generators (TEGs) fabricated from the PHJ film exhibit excellent mechanical flexibility, with only minor resistance changes after repeated bending at 35% curvature. These findings highlight the strong potential of the Ag₂Se/CPE heterojunction film as a high-performance platform for flexible thermoelectric power generation in next-generation wearable electronics.

1. Introduction

The rapid expansion of artificial intelligence (AI) technology has led to a surge in global energy demand, thereby propelling advancements in energy technologies such as photovoltaics, fuel cells, and thermoelectric devices. Among these, thermoelectric technology is particularly attractive because it enables the direct and reversible conversion between thermal and

New concepts

Conventional organic-inorganic thermoelectric composites are predominantly fabricated as bulk-mixed systems, in which electrical optimization is intrinsically coupled to structural disorder, interfacial randomness, and mechanical fragility. In such architectures, reported performance enhancements are largely governed by effective carrier concentration modulation through chemical doping or compositional averaging, rather than by deliberate control over carrier separation or transport directionality. Here, we introduce a fundamentally different thermoelectric design paradigm based on layer-resolved electrostatic programming. By constructing a precisely engineered bilayer architecture in which a conjugated polyelectrolyte is spatially segregated from the inorganic thermoelectric host, we decouple charge redistribution from bulk chemical modification. This well-defined planar heterojunction generates a directional interfacial electrostatic field that induces heterojunction-mediated carrier separation, rather than homogeneous doping. As a result, charge carriers are selectively accumulated and transported along an interfacial pathway without introducing compositional disorder into the thermoelectric bulk. To our knowledge, this work provides the first experimental demonstration that carrier separation in inorganic thermoelectrics can be induced and sustained through electrostatically programmed interfaces, rather than through bulk dopant incorporation or compositional tuning. This planar heterojunction concept establishes a new route for interface-driven thermoelectric design, in which transport efficiency, mechanical compliance, and electronic functionality can be simultaneously optimized through architectural control rather than chemical complexity.

electrical energy, thus offering a solid-state and maintenance-free pathway for waste-heat recovery.^{1–4} In this context, flexible thermoelectric generators (TEGs) that can harvest low-grade heat such as body heat have emerged as promising power sources for next-generation wearable electronics. Their ability to combine continuous energy harvesting with mechanical flexibility makes them well suited for seamless integration with the human body.^{5–9}

Among various thermoelectric materials, silver selenide (Ag₂Se) has attracted considerable attention due to its intrinsically high thermoelectric performance near room temperature, along with its favorable electronic structure and environmental

^a Department of Materials Science and Engineering, National Taiwan University, Taipei 10617, Taiwan. E-mail: liucl@ntu.edu.tw

^b Department of Chemistry, Korea University, Seoul 02841, Republic of Korea. E-mail: hywoo@korea.ac.kr

^c Department of Chemical and Biomolecular Engineering, Sogang University, Seoul, 04107, Republic of Korea. E-mail: kangms@sogang.ac.kr

^d Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan

^e Advanced Research Center for Green Materials Science and Technology, National Taiwan University, Taipei 10617, Taiwan

compatibility.^{10–13} However, despite these advantages, further improvements in both thermoelectric performance and mechanical flexibility remain as critical challenges for practical applications.^{14–16} For example, Jiang *et al.*¹⁷ have reported the *in situ* synthesis of a polyvinylpyrrolidone (PVP)/Ag₂Se composite film on a nylon membrane to achieve excellent flexibility along with an ultrahigh power factor (PF) of $\sim 1910 \mu\text{W m}^{-1} \text{K}^{-2}$ at 300 K. This performance was attributed to coherent interfacial contact and high crystallinity of the Ag₂Se grains, which significantly enhanced the electrical conductivity and, hence, the PF. More recently, Hu *et al.*¹⁸ demonstrated the *in situ* growth of an Ag₂Se/single-walled carbon nanotube (SWCNT) composite film with a PF of $\sim 987.4 \pm 104.1 \mu\text{W m}^{-1} \text{K}^{-2}$ at 300 K. In this system, the incorporation of SWCNTs induced additional interstitial Ag, thus leading to an increased electron concentration and improved thermoelectric performance. However, although such Ag₂Se composites can deliver enhanced thermoelectric performance, conventional bulk-mixed architectures often suffer from severe phase separation. In these systems, inorganic fillers tend to aggregate into localized domains while the polymer matrix segregates elsewhere, thereby resulting in limited interfacial contact, poorly defined transport pathways, and increased charge carrier scattering.^{52,53} These structural limitations restrict the further optimization of charge transport. To overcome these challenges, a planar heterojunction (PHJ) architecture in which polymer and inorganic layers are spatially separated but intimately interfaced offers a compelling alternative. This vertically stratified configuration enables continuous and well-defined electron transport pathways while minimizing the interfacial disorder and scattering that are commonly observed in bulk heterojunction (BHJ) composites.

Once a PHJ structure has been established, the choice of interfacial polymer becomes a decisive factor in governing the charge transport behavior. Thus, while neutral conjugated polymers have been widely explored as passive structural or dispersing components in TEG applications due to their tunable molecular structures, solution processability, low toxicity, and intrinsically low thermal conductivity,^{19–21} conjugated polyelectrolytes (CPEs) provide an additional degree of freedom *via* their charged functional groups, which can actively modulate the interfacial energetics and promote charge carrier separation at the polymer–inorganic interface.^{22–24} These features make the CPEs particularly attractive for precisely engineered heterojunction systems.

In the present study, poly(3,4-ethylenedioxythiophene)-*co*-(2,2'-bithiophene)-*co*-(3-thienyl-4-sodiumsulfonate) (PCPDTBTSeO₃Na) is used as a CPE along with Ag₂Se to construct a PHJ architecture designed to simultaneously enhance the electrical conductivity and mechanical flexibility. Due to the interfacial modulation enabled by the ionic CPE layer, the Ag₂Se/CPE PHJ composite achieves a high electrical conductivity of $2209.7 \pm 226.9 \text{ S cm}^{-1}$ and an exceptional PF of $2629.3 \pm 291.0 \mu\text{W m}^{-1} \text{K}^{-2}$ at 303 K, representing the highest reported values among Ag₂Se-based composite films to date. Furthermore, flexible TEGs fabricated from this composite exhibit excellent durability under repeated bending at a curvature of 35%. Overall, this work presents a

previously unexplored heterojunction engineering strategy that simultaneously enhances the thermoelectric performance and mechanical flexibility of Ag₂Se-based composites, thereby highlighting their strong potential for next-generation wearable and room-temperature thermoelectric applications.

2. Methods

2.1. Materials

Selenium dioxide (SeO₂, >99%) and β -cyclodextrin (β -CD, >98%) were obtained from Shanghai Macklin Biochemical Co. L-Ascorbic acid ($\geq 99\%$), polyvinylpyrrolidone (PVP, $M_w \approx 40\,000$), ethylene glycol (anhydrous, 99.8%), silver nitrate ($\geq 99.0\%$), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, 99%), were purchased from Sigma-Aldrich. The ionic conjugated polymer PCPDTBTSeO₃Na (CPE, $M_w \approx 25\,000$) was supplied by 1-Material. The conjugated polymer PCDTBT-C16 (CP) was synthesized according to a previously reported method, with $M_n = 5290 \text{ g mol}^{-1}$ and $M_w = 13\,400 \text{ g mol}^{-1}$, respectively. All chemicals and solvents were used as received without further purification.

2.2. Synthesis of Ag₂Se nanowires

Selenium nanowires (Se NWs) were first synthesized following a modified literature method.²⁵ The synthetic procedure is illustrated in Fig. S1a. Briefly, 1 g SeO₂ and 1 g β -CD were dissolved in 200 mL of distilled water under magnetic stirring until a clear solution was obtained. Separately, 8 g L-ascorbic acid was dissolved in 50 mL of distilled water and added dropwise slowly into the SeO₂ solution under continuous stirring. The reaction continues for 4 h, the solution turned with a reddish-brown precipitation. The product was collected *via* centrifugation and washed thoroughly with distilled water and ethanol. The obtained Se intermediate precipitate was redispersed in ethanol using tip sonication for 10 min and then aged for 12 h prior to vacuum drying, affording Se NW powders. For the conversion to Ag₂Se NWs, 0.3 g PVP was dissolved in 200 mL of ethylene glycol to form a homogeneous solution. An appropriate amount of the Se NWs was sonicated in the PVP solution for 20 min to ensure uniform dispersion, followed by dropwise addition of an aqueous AgNO₃ solution slowly. The reaction proceeded for 4 h under constant stirring. The resulting Ag₂Se NWs were collected by centrifugation, washed repeatedly with distilled water and ethanol, and dried under vacuum to obtain black Ag₂Se NW powders.

2.3. Preparation and thermoelectric characterization of heterojunction films

The overall fabrication process is schematically presented in Fig. S1b. As-prepared Ag₂Se NWs were dispersed in HFIP and ultrasonicated at 28 kHz for 40 min to form a uniform ink. The dispersion was then drop-cast onto polyimide (PI) membranes and dried at 40 °C until solvent evaporation was complete. The dried layer was cold pressed under a load of 196 kN for 10 min and subsequently annealed at 498 K in vacuum, forming dense

Ag₂Se NW films. A top polymer layer was then prepared *via* drop-casting a dilute polymer solution (5, 10, 15 wt% of CPE) onto the Ag₂Se film, forming a PHJ composite. For comparison, BHJ films were fabricated by co-dispersing Ag₂Se NWs and polymer in HFIP *via* tip-sonication followed by film deposition. The in-plane Seebeck coefficient (*S*) and electrical conductivity (σ) of the nanocomposite samples were measured using a commercially available thermoelectric tester ZEM-3 (Advance Riko). All measurements were performed under a helium atmosphere at a controlled temperature of 303 K to minimize thermal and environmental fluctuations.

2.4. Preparation and measurement of flexible thermoelectric generators

Flexible TEGs based on the PHJ composite films were fabricated following the same procedures described above. The devices were assembled by electrically interconnecting four n-type thermoelectric legs using copper wires. Silver paste was applied at the junctions to ensure low-resistance electrical contacts, forming a four-leg TEG configuration. The performance of the flexible TEGs was evaluated using a custom-built measurement system under ambient conditions. The hot-side temperature was adjusted to establish different temperature gradients (ΔT), while the cold side temperature was maintained at approximately 295 K (Fig. S19). Device temperatures were monitored using thermocouples attached to the film surfaces, with signals recorded by a Keithley DAQ 6510 data acquisition system. The output voltage and short-circuit current were measured using a Keithley 2182A nanovoltmeter and a Keithley 2400 sourcemeter, respectively.

3. Results and discussion

3.1. Structure and composition of Ag₂Se/conjugated polyelectrolyte composites

As shown schematically in Fig. 1a, two representative polymers were incorporated into Ag₂Se, namely CPE and CP. These polymers

were selected because their contrasting electronic structures enable fundamentally different charge carrier transport behaviors in Ag₂Se-based thermoelectric composites.²⁶ To elucidate the interfacial mechanisms responsible for enhancing the thermoelectric properties of Ag₂Se, PHJ and BHJ refer to heterojunction structures formed between Ag₂Se and CPE, in a planar and bulk configuration, respectively. As shown in Fig. S2, the cyclopentadithiophene (CPDT) backbone of the CPE undergoes spontaneous single-electron transfer (SET) upon protonation to generate radical cations (positive polarons or holes) along the conjugated polymer chain. These charge carriers are stabilized by the tethered sulfonate (SO₃[−]) counterions *via* long-range coulombic interactions, thus enabling stable self-doping and enhanced electronic functionality of the CPE.^{27,28} After formation of polarons on the polymer backbone, Na⁺ counterions are no longer required for charge compensation and are likely dissolved in the processing medium.²⁹ When Ag₂Se is interfaced with the CPE, the high density of SO₃[−] groups establishes a strong and spatially negative electrostatic potential at the heterointerface.^{30,31} This interfacial potential gradient serves as a driving force that enhances the charge carrier separation within the adjacent Ag₂Se layer, thereby effectively promoting electron–hole dissociation. The holes are then stabilized *via* electrostatic interaction with the SO₃[−] groups, while the released electrons are injected into the Ag₂Se conduction band, thereby strengthening the n-type transport.³² Thus, the interfacial electrostatic environment created by the CPE actively modulates the electronic structure of Ag₂Se. Thus, as shown in Fig. 1b, both the PHJ and BHJ structures incorporating the CPE exhibit characteristic polaron and bipolaron absorption features due to the self-doping effect. By contrast, the neutral CP fails to generate a comparable interfacial electric field or induce significant charge carrier redistribution due to the absence of ionic functionalities, and no polaron or bipolaron absorption features are observed.³³ Overall, the ionic nature of the CPE provides a stronger and more stable interfacial potential gradient than does the neutral CP, thereby enabling more effective regulation of the electronic

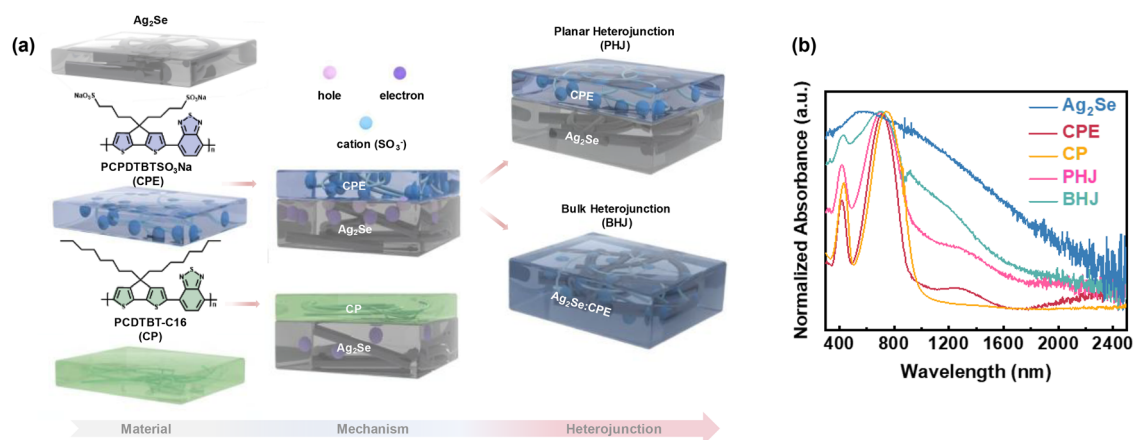


Fig. 1 (a) The schematic overview of this report integrates material selection, mechanistic insights, and the design of the interfacial heterojunction structure. (b) UV-vis absorption spectra of Ag₂Se, PCPDTBT-SO₃Na (CPE), PCDTBT-C16 (CP) and the heterojunction films (PHJ and BHJ).

environment in Ag_2Se . This interfacial engineering establishes the foundation for efficient charge transfer and charge carrier management, which is expected to contribute to an enhanced thermoelectric performance in the $\text{Ag}_2\text{Se}/\text{CPE}$ heterojunction composite.

The effects of CPE incorporation on the crystal structure and chemical composition of Ag_2Se are revealed by the X-ray diffraction (XRD) patterns in Fig. 2a and Fig. S3a, b. The as-synthesized Se and Ag_2Se nanowire (NW) powders in Fig. S3a and b can be indexed to hexagonal Se (PDF#42-1425) and orthorhombic Ag_2Se (PDF#24-1041), respectively, with no observable impurity phases or peak shifts, thereby confirming complete chemical conversion and negligible lattice distortion during synthesis. In the case of the CPE-containing composite films, however, both the PHJ and BHJ configurations exhibit a weak broad feature at $\sim 9^\circ$ due to amorphous polymer matrix, thereby confirming successful incorporation of the CPE. Notably, compared to the BHJ film, the Ag_2Se phase in the PHJ composite exhibits significantly enhanced diffractions due to the (002), (004), (013), and (014) crystal planes. This suggests a stronger preferential alignment of Ag_2Se NWs along these planes within the PHJ structure, which may facilitate more efficient directional electron transport.^{14,34,35}

The functional groups in the various samples are identified by the Fourier-transform infrared (FTIR) spectra in Fig. 2b. Thus, compared with the pristine Ag_2Se , the CPE-containing composite films exhibit additional peaks at 1038 and 1134 cm^{-1} due to the respective symmetric and asymmetric stretching vibrations of SO_3^- groups, along with an adsorption at 1281 cm^{-1} attributed to the asymmetric C–C stretching of the CPDT unit, and a band at 1500 cm^{-1} due to the stretching vibration of the C=N ring in the conjugated backbone.²⁴ In the pristine Ag_2Se sample, weak absorption bands are observed in the aliphatic regions, such as those at 1366 and 1424 cm^{-1} , and those at 2928 and 2855 cm^{-1} . Such peaks are generally associated with the respective bending and stretching vibrations of aliphatic CH_2 and CH_3 groups, and do not originate from the Ag–Se lattice. Rather, these features are attributed to trace organic residues, probably the

remnants of compounds used during synthesis (e.g., ethanol or PVP), which may remain weakly adsorbed on the Ag_2Se surface after washing and drying. Such residual organic signatures are commonly observed in solution-processed metal chalcogenides and are generally regarded as having negligible impact on the intrinsic crystal structure of Ag_2Se .

The morphologies and spatial elemental distributions of the as-synthesized Se and Ag_2Se nanostructures are revealed by the scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) results in Fig. S3c–j. Here, both samples exhibit uniform NW-like morphologies that are consistent with previous literature reports,²⁵ while the EDS elemental maps of the Ag_2Se confirm the homogeneous distributions of Ag and Se without any impurity segregation. Top-view and cross-sectional SEM images of a dense pristine Ag_2Se film that was prepared by cold-pressing followed by vacuum-annealing are presented in Fig. S4a and b. This film exhibits a relatively continuous morphology with retained needle-like features and no noticeable cracks or structural damage, thereby demonstrating that the densification process effectively produces a uniform and dense Ag_2Se layer.

Representative surface morphologies of the PHJ and BHJ structured composite films are presented in Fig. 3a and b, respectively. Here, the PHJ film exhibits a polymer-like, semi-transparent top surface corresponding to the deposited Ag_2Se layer, whereas the BHJ film displays a mixed microstructure in which needle-like Ag_2Se NWs are uniformly dispersed throughout a soft, translucent polymeric matrix. Moreover, the distinct structural configurations of these two types of composites are further highlighted by the cross-sectional SEM analyses in Fig. 3c, d and in Fig. S5. Here, the PHJ film clearly displays a bilayer arrangement consisting of an upper CPE layer ($\sim 1\text{ }\mu\text{m}$) on top of a dense Ag_2Se layer ($\sim 10\text{ }\mu\text{m}$), whereas the BHJ film exhibits a homogeneous structure with Ag_2Se NWs uniformly embedded throughout the polymer phase. The corresponding EDS elemental mapping images of the PHJ and BHJ samples are presented in Fig. 3e and j, where the expected elements are confirmed and no extraneous impurities are detected.

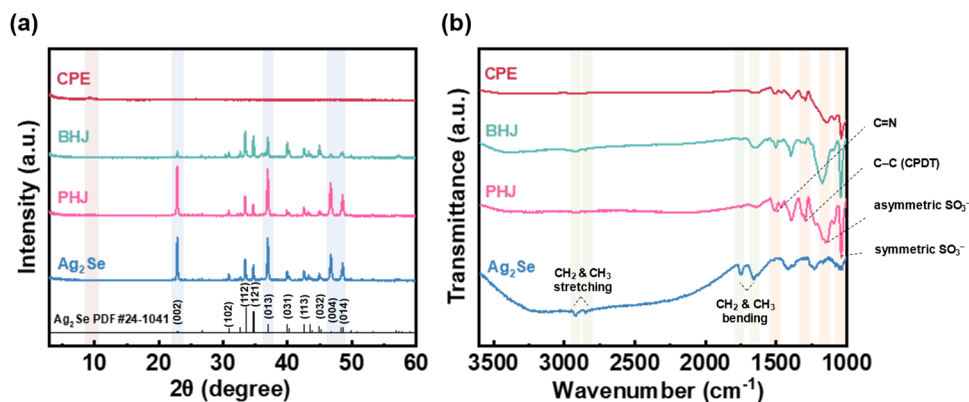


Fig. 2 (a) X-ray diffraction (XRD) patterns of Ag_2Se , PHJ, BHJ and CPE. All diffraction peaks can be indexed to orthorhombic Ag_2Se (PDF#24-1041), indicating preservation of the Ag_2Se crystal structure after heterojunction formation. (b) Fourier transform infrared (FTIR) spectra of Ag_2Se , heterojunction films (PHJ and BHJ) and CPE.

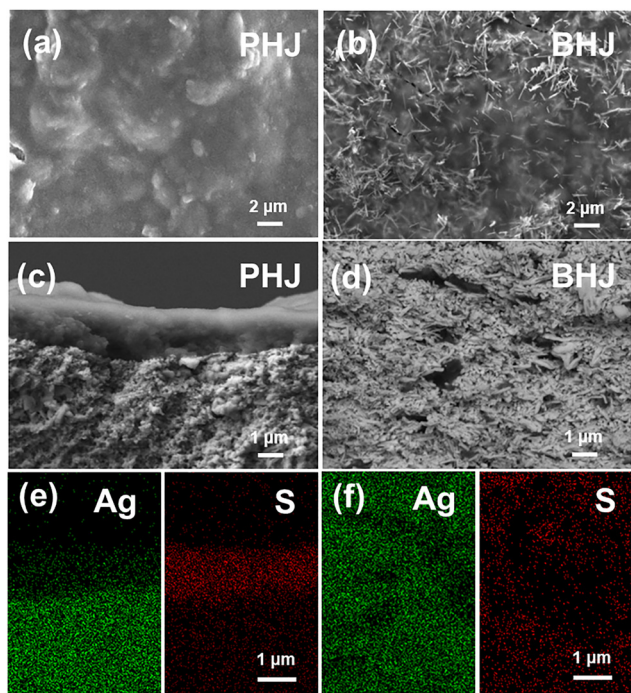


Fig. 3 Top-view scanning electron microscope (SEM) images of the heterojunction films (a) PHJ and (b) BHJ, respectively. Cross-sectional SEM images of (c) PHJ and (d) BHJ films. Energy dispersive spectrometer (EDS) elemental mapping images showing the spatial distributions of Ag and S in (e) PHJ and (f) BHJ films, respectively.

Additional insights into the nanoscale structures of the various samples are provided by the transmission electron microscopy (TEM) images and the associated fast Fourier transform (FFT) patterns in Fig. S6. These results indicate that

the incorporation of CPE does not induce any detectable changes in the local crystal structure of Ag_2Se , so that similar features are observed both here and in the pristine Ag_2Se (Fig. S4c and d). These results are also consistent with the XRD analysis in Fig. 2a above. Collectively, these observations demonstrate that both the PHJ and BHJ composite architectures preserve the intrinsic crystallinity of Ag_2Se while modulating the film microstructure through controlled polymer distribution.

The overall elemental compositions of the pristine Ag_2Se , the pristine CPE, and the corresponding BHJ structured composite film are revealed by the wide-scan XPS spectra in Fig. S7a–c. In addition, more detailed analyses of the pristine Ag_2Se and CPE samples are provided by the corresponding high-resolution spectra in Fig. S7d and e, while the interfacial interactions and chemical-state evolution between the Ag_2Se and CPE in the BHJ structured composite film are examined in detail in Fig. 4. Here, the Ag 3d core-level spectrum of the composite film exhibits two well-resolved peaks at 366.7 and 372.8 eV, corresponding to the respective $3d_{3/2}$ and Ag $3d_{5/2}$ levels, which are characteristic of Ag^+ species in orthorhombic Ag_2Se .³⁶ Meanwhile, the Se 3d spectrum of the composite displays doublets at 52.5 eV (Se $3d_{5/2}$) and 54.3 eV (Se $3d_{3/2}$), which are consistent with Se^{2-} in the Ag–Se lattice.³⁷ In addition, the S 2p spectrum of the composite can be deconvoluted into two distinct sets of doublets. Here, the peaks with lower binding energies at 163.7 and 165.1 eV correspond to the thiophene sulfur atoms in the conjugated backbone, thereby indicating the coexistence of both covalent and ionic sulfur environments within the composite. Meanwhile, the components with higher binding energies at 168.1 and 169.4 eV are attributed to the S $2p_{3/2}$ and S $2p_{1/2}$ levels of the SO_3^- groups, in which the electronegative

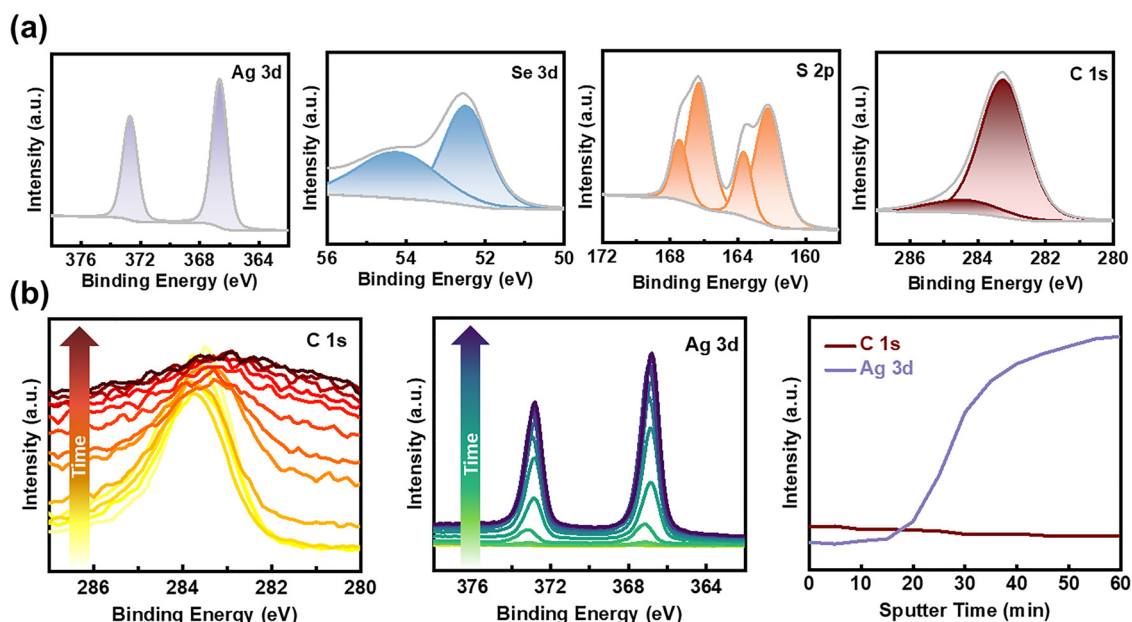


Fig. 4 High-resolution X-ray photoelectron spectroscopy (XPS) spectra of (a) BHJ films. (b) XPS depth-profile analysis of the PHJ film, showing the spectra of Ag and C elements and their signal intensity variation as a function of sputtering time from left to right.

oxygen atoms are attached to the sulfonate moiety, and are consistent with the chemical structure of the CPE.³⁸ Further, the C 1s spectrum exhibits a dominant peak at 283.3 eV associated with C=C bonds in the conjugated polymer backbone, along with a weaker component at 284.4 eV arising from residual aliphatic C-C functionalities.³⁹

The variation in composition with depth in the PHJ structured composite film is elucidated by the XPS depth profile in Fig. 4b. In this configuration, the CPE constitutes the top layer and Ag₂Se is the underlying layer. Thus, as the sputtering time increases, the intensity of the C 1s signal originating from the CPE is seen to decrease gradually, while the Ag 3d signal from Ag₂Se concomitantly increases. These opposite depth-dependent trends confirm a clear vertical stratification and a well-defined interface between the CPE and Ag₂Se layers, thereby indicating the structural integrity of the PHJ configuration.

3.2. Thermoelectric performance

To examine the modulation of charge transport in the flexible n-type thermoelectric materials consisting of Ag₂Se integrated with either the neutral CP or the ionic CPE with the PHJ or BHJ architectures, the charge carrier concentration (n) and mobility (μ) of the various composite systems are compared in Fig. 5a. Here, the PHJ structured composite incorporating the CPE achieves the highest charge carrier concentration of $(17.2 \pm 6.1) \times 10^{18} \text{ cm}^{-3}$, along with a high mobility of $3474.5 \pm 547.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This mobility can be attributed to the continuous and well-defined interface between the CPE layer and the needle-like Ag₂Se grains, which minimizes any transport interruptions by the heterojunction.^{40,41} By contrast, the CP-containing PHJ structure (PHJ (CP)) exhibits a significantly poorer electrical performance, as the neutral CP lacks any ionic functionalities and therefore cannot generate a strong interfacial electrostatic field in order to promote charge carrier activation or accumulation. Meanwhile, the BHJ configuration exhibits comparatively poor charge carrier concentration and mobility because the random polymer distribution within the Ag₂Se matrix disrupts the conductive pathways, introduces energetically mismatched interfaces, and increases charge carrier scattering.^{40,41}

To strengthen the influence of different CPE contents on material structure and performance, The ratio depending

results (Fig. S11) indicate that the 10 wt% CPE sample delivers the best thermoelectric performance. At this composition, an optimal balance between interfacial modulation and charge transport is achieved, leading to the maximum power factor. Consequently, 10 wt% was chosen as the representative composition for detailed characterization and mechanistic analysis. When the polymer content is too low, it cannot induce a sufficient increase in electron concentration to effectively enhance the electrical conductivity. In contrast, when the polymer content is excessively high, the polymer phase which being intrinsically non-conductive acts as a transport barrier. As a result, no further improvement in thermoelectric performance can be achieved. Then, combine the above trends are reflected in the electrical conductivity data in Fig. 5b. Due to simultaneously high charge carrier concentration and mobility, the 10 wt% PHJ structured Ag₂Se/CPE composite exhibits the highest electrical conductivity (σ) of $2209.7 \pm 226.9 \text{ S cm}^{-1}$, which exceeds the majority of previously-reported values for Ag₂Se-based thermoelectric composites. As expected for n-type Ag₂Se-based systems, all the measured Seebeck coefficients (S) are negative. While heterojunction formation inevitably leads to a reduction in the absolute value of S due to increased charge carrier concentration, the PHJ composite maintains a reasonably high Seebeck coefficient of $-104.1 \pm 226.9 \mu\text{V K}^{-1}$. Despite the decrease in $|S|$, the substantial enhancement in σ yields an excellent PF of $2629.2 \pm 291.0 \mu\text{W m}^{-1} \text{ K}^{-2}$. Further, the measured temperature-dependent electrical conductivity of each sample in the range of 303 to 383 K is presented in Fig. 5c. Here, all samples exhibit a monotonic increase in electrical conductivity with increasing temperature, which is consistent with the intrinsic semiconducting behavior of Ag₂Se and indicates that thermally activated charge carrier transport dominates in this temperature range.⁴² In Fig. S12, The temperature-dependent Seebeck coefficient exhibits a trend consistent with that observed at room temperature. Specifically, pristine Ag₂Se shows the highest Seebeck coefficient, followed sequentially by the PHJ and BHJ structures. Regarding the power factor, Ag₂Se and PHJ demonstrate comparable performance within this temperature range. However, at elevated temperatures, the polymer component in the heterojunction structures may experience partial performance degradation, which can adversely affect charge transport stability. As a result,

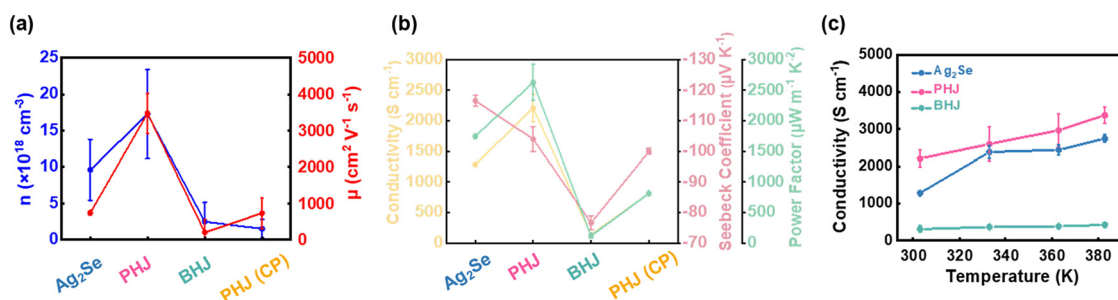


Fig. 5 (a) Carrier concentration (n) and mobility (μ), (b) thermoelectric performance, and (c) temperature-dependent electrical conductivity (σ) of Ag₂Se and composite films (PHJ, BHJ, PHJ(CP)). All measurements were at a controlled temperature of (303 K).

pristine Ag₂Se exhibits the highest power factor under high-temperature conditions.

3.3. Mechanism of thermoelectric composite

To elucidate the origin of the enhanced thermoelectric performance, the underlying charge transport mechanism of the Ag₂Se/CPE system is analyzed in the following paragraphs. As noted in the Introduction, Ag₂Se is widely recognized as a high-performance thermoelectric semiconductor due to its intrinsically high electrical conductivity and favorable electronic structure for charge carrier transport. Meanwhile, as a self-doped material, the CPE can serve as an effective interfacial electrostatic activator that promotes charge transport *via* ionic-electronic coupling.³² In this work, we propose a core argument that applies to both planar heterojunction (PHJ) and bulk heterojunction (BHJ) structures both involve direct contact between CPE and Ag₂Se. The primary difference lies in the extent of contact: the BHJ structure corresponds to an almost completely mixed state, whereas the PHJ structure refers to a well-defined interfacial contact between two distinct layers. For reaction mechanism between these two heterojunctions, namely that SO₃[−] groups in the CPE establishes a strong and spatially negative electrostatic potential at the Ag₂Se/CPE interface. This interfacial field acts as a driving force that enhances electron-hole separation within the adjacent Ag₂Se film. Based on this mechanism, an efficient charge carrier transport model is illustrated in Fig. 6a. Thus, the SO₃[−] groups electrostatically stabilize positive charges while facilitating the dissociation of electron-hole pairs, thereby releasing additional electrons into the conduction pathway. As the XPS results in Fig. S9 and Table S2, we tried to use BHJ represent the contact between CPE and Ag₂Se. The Ag 3d and Se 3d peaks in the BHJ film shift slightly toward lower binding energies compared to pristine Ag₂Se, while the S 2p peak associated with the CPE shifts toward higher binding energy. Such complementary shifts indicate charge redistribution at the Ag₂Se/CPE interface. Further energy level characterization *via* AC-2 and UV-vis measurements (Fig. S9c) reveals a distinct band realignment. Both PHJ and BHJ structures demonstrate a convergence of the electrochemical potential to approximately 0.74 eV, indicating the establishment of interfacial electrostatic equilibrium. The superior thermoelectric performance of PHJ compared to BHJ arises from the fact that, in the PHJ configuration, the entire modulation

effect is concentrated at a well-defined interface. Specifically, the interfacial electric field induces electron accumulation at the heterointerface and attracts intrinsic electrons from the Ag₂Se bulk toward this region. This process results in the formation of an electron-rich interfacial channel that serves as a highly efficient charge carrier transport pathway. The cooperative enhancement of charge carrier concentration and mobility arising from this interfacial modulation directly leads to the observed increase in electrical conductivity. In contrast, the BHJ structure, due to its fully mixed and homogeneous morphology, exhibits a more disordered spatial arrangement of Ag₂Se and CPE domains. As a result, the contact interfaces are randomly distributed, leading to a less well-defined and more tortuous charge carrier transport pathway. This structural disorder increases carrier scattering and energy dissipation during transport, thereby reducing the probability of efficient charge conduction across the film. Consequently, the overall thermoelectric performance of the BHJ structure is inferior to that of the PHJ configuration. For the measurement setup of the electrical properties, since the CPE's conductivity is several orders of magnitude lower than that of Ag₂Se, it acts as an electrically insulating layer in this framework. The model is supported by transport anisotropy measurements (Fig. S13), showing that out of plane resistance is significantly higher than in-plane resistance. This confirms that the measured transport properties primarily reflect lateral carrier flow within the Ag₂Se layer, specifically modulated by the interfacial electrostatic interaction with the CPE.

Single parabolic band (SPB) analysis elucidates the distinct transport behaviors in PHJ and BHJ configurations (Fig. S10). In the PHJ system, the increased effective mass ($\sim 0.34m_0$) and concurrent rise in carrier concentration and Seebeck coefficient signify a unique interfacial modulation. This is attributed to the ordered planar interface acting as charge reservoir, where interfacial injection outweighs filtering-induced depletion. Despite the higher effective mass, the PHJ structure achieves superior mobility by suppressing scattering and enhancing relaxation time. Conversely, the BHJ structure exhibits a drastically reduced effective mass ($\sim 0.068m_0$) and lower carrier concentration, indicating that structural disorder and neutral impurity scattering in the bulk-heterojunction hinder effective interfacial modulation.

For the neutral CP lacks any ionic functionalities and therefore cannot generate a comparable interfacial electrostatic

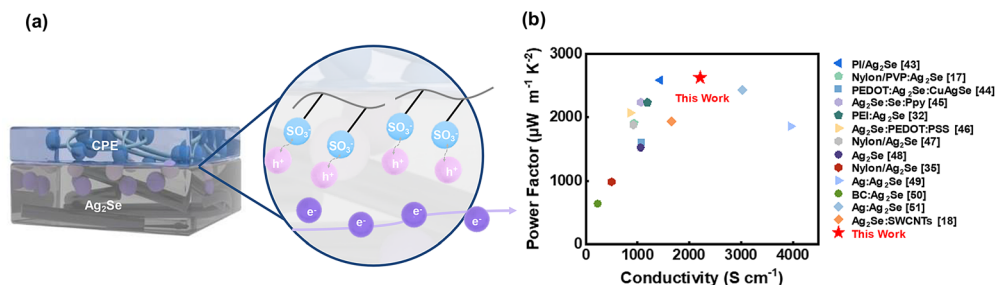


Fig. 6 (a) Schematic illustration of the thermoelectric enhancement mechanism in the PHJ structure. (b) Comparison of conductivity and power factor of the PHJ composite film in this work with reported values for Ag₂Se-based thermoelectric films in the literature (see Table S1).^{17,18,32,35,43–51}

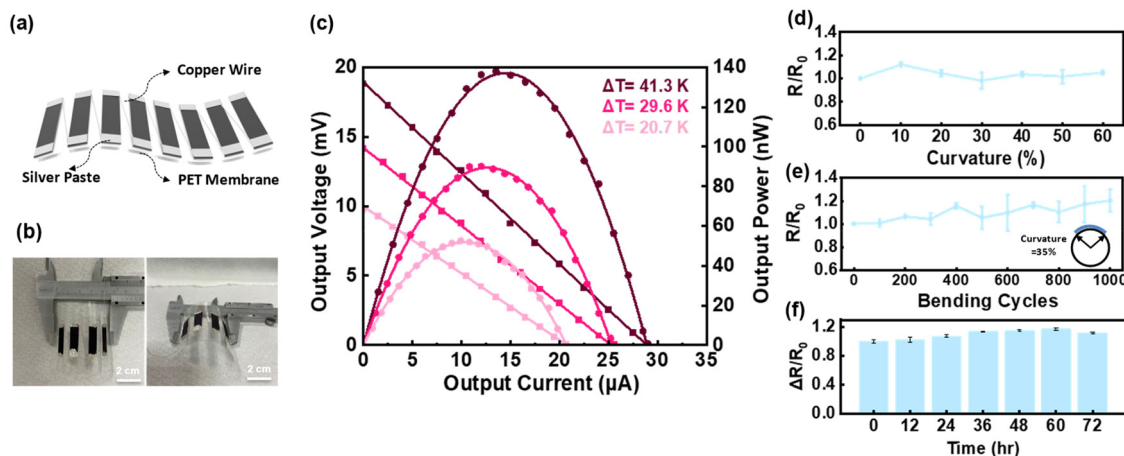


Fig. 7 (a) Schematic illustration and (b) optical photograph of the in-plane PHJ film-based flexible thermoelectric generator (TEG). (c) Output voltage and power of the PHJ film-based flexible TEG as a function of load current at different temperature differences (ΔT). R/R_0 of PHJ films (d) under different curvature and (e) after 1000 cycles bending with 35% curvature. (f) Long-term environmental stability of the PHJ-based TEG device.

field. As a result, even when a planar heterojunction architecture is employed, the CP-based system fails to form an efficient charge carrier transport pathway and exhibits limited improvements in thermoelectric performance. Overall, the CPE-based PHJ represents the most effective strategy among the examined approaches, providing efficient interfacial interactions and significantly improved charge transport characteristics. This interfacial design enables the simultaneous enhancement of charge carrier concentration and mobility, thereby serving as the primary mechanism for improving the thermoelectric properties of the Ag_2Se composite.

The room-temperature electrical conductivity and PF values of the PHJ structured composite film are compared with those of previously reported Ag_2Se -based thermoelectric systems in Fig. 6b and Table S1. Here, the CPE-based PHJ exhibits a superior PF along with a comparatively high electrical conductivity, which can be attributed to the ion-induced interfacial modulation and the formation of an efficient charge carrier transport pathway through the PHJ architecture. These results highlight the $\text{Ag}_2\text{Se}/\text{CPE}$ heterojunction structure as a highly effective platform for achieving high performance n-type thermoelectric materials, thereby indicating its strong potential for next-generation flexible thermoelectric applications.

3.4. Thermoelectric generator

To assess the practical applicability of the optimized composite, a four-legged TEG was fabricated using the PHJ film as the active material. Each thermoelectric leg measured $2.5 \text{ cm} \times 0.6 \text{ cm}$, and conductive silver paste was applied to both ends to ensure low-resistance electrical contact. Copper wires were then attached using silver adhesive to serve as electrodes for performance evaluation. A schematic illustration of the measurement setup and a photographic image of the device under bending are provided in Fig. 7a and b, respectively. Meanwhile, the output characteristics of the PHJ-based TEG under different temperature gradients (ΔT) are presented in Fig. 7c (Fig. S15). The output voltage decreases linearly with increasing current,

which follows Ohm's law, while the corresponding output power displays a quadratic dependence on ΔT . As the ΔT increases from about 20 to 40 K, the maximum output power rises from $53.1 \mu\text{W}$ to $137.9 \mu\text{W}$, demonstrating an approximately proportional relationship between ΔT and power generation. This behavior confirms the efficient conversion of thermal energy into electrical power within the PHJ-based device with a comparison (Table S3) existing literature highlights the superior thermoelectric conversion performance of our system.

Mechanical reliability is a critical factor for flexible thermoelectric devices. As shown in Fig. 7d and e, the device retains excellent electrical stability under mechanical deformation, with only a 5.1% increase in resistance as the bending curvature is gradually increased to 60%. Moreover, under continuous bending at a fixed curvature of 35%, the device exhibits only a 20% increase in resistance after 1000 bending cycles, thereby indicating the outstanding mechanical durability and structural robustness of the PHJ film. To evaluate long-term reliability, Fig. 7f shows the electrical resistance in an ambient atmosphere over a 72 hour period maintains a highly stable resistance profile with minimal deviation, demonstrating well done environmental stability and consistent performance for practical applications. Overall, the PHJ-based flexible TEG combines high thermoelectric output with exceptional mechanical flexibility and stability, thereby indicating its strong potential for integration into next-generation wearable and portable thermoelectric energy-harvesting systems.

4. Conclusion

Herein, a conjugated polyelectrolyte (CPE) was used to modulate the thermoelectric properties of silver selenide (Ag_2Se) composites *via* interfacial engineering. The intrinsic self-doping of the selected CPE *via* its SO_3^- groups was shown to establish a strong and spatially negative electrostatic potential,

which acted as a driving force for enhanced charge carrier separation in the Ag_2Se . The resulting electron accumulation at the heterointerface formed a highly conductive transport channel, thereby significantly improving the charge transport and electronic conductivity. Due to this interfacial modulation, the planar heterojunction (PHJ) composite achieved a high electrical conductivity of $2209.7 \pm 226.9 \text{ S cm}^{-1}$ and a power factor (PF) of $2629.3 \pm 291.0 \mu\text{W m}^{-1} \text{ K}^{-2}$ at 303 K, which represents the highest reported PF among Ag_2Se -based composite films to date. In addition, a flexible thermoelectric generator fabricated from the PHJ film exhibited excellent mechanical robustness, retaining stable electrical properties after repeated bending cycles, thereby confirming its excellent mechanical flexibility and durability. Overall, this study has demonstrated an effective interfacial-engineering strategy that combines high electrical conductivity, record-level PF, and outstanding flexibility. These results highlight the strong potential of this heterojunction platform for next-generation room-temperature flexible thermoelectric applications.

Author contributions

Conceptualization: Y.-C. Peng, C.-W. Hsu, C.-L. Liu. Methodology: Y.-C. Peng, P.-S. Lin. Investigation: Y.-C. Peng, C.-W. Hsu. Visualization: Y.-C. Peng, C.-W. Hsu. Supervision: M.-S. Kang, H.-Y. Woo, C.-L. Liu. Resources: H.-Y. Woo. Writing – original draft: Y.-C. Peng. Writing – review & editing: Y.-C. Peng, C.-W. Hsu, C.-L. Liu.

Conflicts of interest

The authors declare that they have no conflict of interest.

Data availability

The data supporting this article have been included in the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d6mh00095a>.

Further information is available from the corresponding author upon reasonable request.

Acknowledgements

This work was funded by the 2030 Cross-Generation Young Scholars Program from the National Science and Technology Council (NSTC) in Taiwan under grant numbers 114-2628-E-002-005, the Academic Research-Career Development Project (Sprout Research Projects) from National Taiwan University (114L7817) and the Advanced Research Center for Green Materials Science and Technology under the Featured Area Research Center Program as part of the Higher Education Sprout Project funded by the Ministry of Education (114L9006). The authors gratefully thank Ms Su-Jen Ji and Ms Chia-Ying Chien for the assistance in SEM, EDS and TEM experiments of the Instrumentation Center at National Taiwan University, supported by

the NSTC. The authors acknowledge Mr. Han-Pang Chen from Instrument Center, College of Science, National Taiwan University/NSTC for providing assistance in XPS measurements.

References

- 1 W.-N. Wu, K. Nishiyama, C.-Y. Chen, J.-M. Lin, S.-H. Tung, T. Higashihara and C.-L. Liu, *J. Mater. Chem. A*, 2025, **13**, 31542–31552.
- 2 D. Liu, D. Wang, T. Hong, Z. Wang, Y. Wang, Y. Qin, L. Su, T. Yang, X. Gao, Z. Ge, B. Qin and L.-D. Zhao, *Science*, 2023, **380**, 841–846.
- 3 Y. Huang, X. Shen, G. Wang, B. Zhang, S. Zheng, C.-C. Yang, X. Hu, S. Gong, G. Han, G. Wang, X. Lu and X. Zhou, *Energy Environ. Sci.*, 2023, **16**, 1763–1772.
- 4 M. Massetti, F. Jiao, A. J. Ferguson, D. Zhao, K. Wijeratne, A. Würger, J. L. Blackburn, X. Crispin and S. Fabiano, *Chem. Rev.*, 2021, **121**, 12465–12547.
- 5 T. Cao, X.-L. Shi, B. Hu, S. Liu, W. Lyu, M. Li, S. Wang, W. Chen, W.-D. Liu, R. Moshwan, T. Tesfamichael, J. MacLeod and Z.-G. Chen, *Adv. Sci.*, 2025, **12**, 2500364.
- 6 Y.-X. Chen, X.-L. Shi, J.-Z. Zhang, M. Nisar, Z.-Z. Zha, Z.-N. Zhong, F. Li, G.-X. Liang, J.-T. Luo, M. Li, T. Cao, W.-D. Liu, D.-Y. Xu, Z.-H. Zheng and Z.-G. Chen, *Nat. Commun.*, 2024, **15**, 8356.
- 7 L. Zhang, X.-L. Shi, Y.-L. Yang and Z.-G. Chen, *Mater. Today*, 2021, **46**, 62–108.
- 8 S. Hou, Y. Liu, L. Yin, C. Chen, Z. Wu, J. Wang, Y. Luo, W. Xue, X. Liu, Q. Zhang and F. Cao, *Nano Energy*, 2021, **87**, 106223.
- 9 Y. Deng, M. Wei, Y. Lei, J. Lu, P. Peng, Y. Zhang and Z. Zheng, *CrystEngComm*, 2025, **27**, 1055–1077.
- 10 T.-R. Wei, P. Qiu, K. Zhao, X. Shi and L. Chen, *Adv. Mater.*, 2023, **35**, 2110236.
- 11 S. Y. Tee, X. Y. Tan, X. Wang, C. J. J. Lee, K. Y. Win, X. P. Ni, S. L. Teo, D. H. L. Seng, Y. Tanaka and M.-Y. Han, *Inorg. Chem.*, 2022, **61**, 6451–6458.
- 12 H. Wu, X.-L. Shi, J. Duan, Q. Liu and Z.-G. Chen, *Energy Environ. Sci.*, 2023, **16**, 1870–1906.
- 13 M. Zhu, X.-L. Shi, H. Wu, Q. Liu and Z.-G. Chen, *Chem. Eng. J.*, 2023, **475**, 146194.
- 14 D. Yang, X.-L. Shi, M. Li, M. Nisar, A. Mansoor, S. Chen, Y. Chen, F. Li, H. Ma, G. X. Liang, X. Zhang, W. Liu, P. Fan, Z. Zheng and Z.-G. Chen, *Nat. Commun.*, 2024, **15**, 923.
- 15 W. Chen, M. Li, X. Wang, J. Otte, M. Zhang, C. Zhang, T. Cao, B. Hu, N. Li, W.-D. Liu, M. Dargusch, J. Zou, Q. Sun, Z.-G. Chen and X.-L. Shi, *Nat. Commun.*, 2025, **16**, 7579.
- 16 N.-H. Li, Q. Zhang, X.-L. Shi, J. Jiang and Z.-G. Chen, *Adv. Mater.*, 2024, **36**, 2313146.
- 17 C. Jiang, P. Wei, Y. Ding, K. Cai, L. Tong, Q. Gao, Y. Lu, W. Zhao and S. Chen, *Nano Energy*, 2021, **80**, 105488.
- 18 Q.-X. Hu, W.-D. Liu, L. Zhang, W. Sun, H. Gao, X.-L. Shi, Y.-L. Yang, Q. Liu and Z.-G. Chen, *Chem. Eng. J.*, 2023, **457**, 141024.
- 19 S. Xu, X.-L. Shi, M. Dargusch, C. Di, J. Zou and Z.-G. Chen, *Prog. Mater. Sci.*, 2021, **121**, 100840.

- 20 Z. Ji, Z. Li, L. Liu, Y. Zou, C.-A. Di and D. Zhu, *Adv. Mater. Technol.*, 2024, **9**, 2302128.
- 21 W.-N. Wu, Q.-B. Zheng and C.-L. Liu, *Synth. Met.*, 2024, **307**, 117682.
- 22 D. Tsokkou, L. Peterhans, D. X. Cao, C.-K. Mai, G. C. Bazan, T.-Q. Nguyen and N. Banerji, *Adv. Funct. Mater.*, 2020, **30**, 1906148.
- 23 B. H. Lee, I. H. Jung, H. Y. Woo, H.-K. Shim, G. Kim and K. Lee, *Adv. Funct. Mater.*, 2014, **24**, 1100–1108.
- 24 Y. Jiang, R. J. Vázquez, S. R. McCuskey, B. R. P. Yip, G. Quek, D. Ohayon, B. Kundukad, X. Wang and G. C. Bazan, *ACS Appl. Mater. Interfaces*, 2024, **16**, 19968–19976.
- 25 D. Park, H. Ju and J. Kim, *J. Ind. Eng. Chem.*, 2021, **93**, 333–338.
- 26 X. Dai, Q. Meng, F. Zhang, Y. Zou, C.-A. Di and D. Zhu, *J. Energy Chem.*, 2021, **62**, 204–219.
- 27 C.-K. Mai, R. A. Schlitz, G. M. Su, D. Spitzer, X. Wang, S. L. Fronk, D. G. Cahill, M. L. Chabinye and G. C. Bazan, *J. Am. Chem. Soc.*, 2014, **136**, 13478–13481.
- 28 J. Tang, Y.-H. Pai and Z. Liang, *ACS Energy Lett.*, 2022, **7**, 4299–4324.
- 29 D. X. Cao, D. Leifert, V. V. Brus, M. S. Wong, H. Phan, B. Yurash, N. Koch, G. C. Bazan and T.-Q. Nguyen, *Mater. Chem. Front.*, 2020, **4**, 3556–3566.
- 30 S. Kee, M. A. Haque, Y. Lee, T. L. Nguyen, D. Rosas Villalva, J. Troughton, A.-H. Emwas, H. N. Alshareef, H. Y. Woo and D. Baran, *ACS Appl. Energy Mater.*, 2020, **3**, 8667–8675.
- 31 D. Zhao, A. Würger and X. Crispin, *J. Energy Chem.*, 2021, **61**, 88–103.
- 32 Q.-X. Hu, W.-D. Liu, L. Zhang, H. Gao, D.-Z. Wang, T. Wu, X.-L. Shi, M. Li, Q.-F. Liu, Y.-L. Yang and Z.-G. Chen, *Adv. Energy Mater.*, 2024, **14**, 2401890.
- 33 S. Wang, G. Zuo, J. Kim and H. Sirringhaus, *Prog. Polym. Sci.*, 2022, **129**, 101548.
- 34 T. Cao, X.-L. Shi, B. Hu, Q. Yang, W.-Y. Lyu, S. Sun, L.-C. Yin, Q.-Y. Liu, W. Chen, X. Wang, S. Liu, M. Li, W.-D. Liu, T. Tesfamichael, Q. Liu, J. MacLeod and Z.-G. Chen, *Nat. Commun.*, 2025, **16**, 1555.
- 35 Y. Ding, Y. Qiu, K. Cai, Q. Yao, S. Chen, L. Chen and J. He, *Nat. Commun.*, 2019, **10**, 841.
- 36 J. Xie, M. Han, X. Zeng, D. Mao, H. Li, X. Zeng, R. Liu, L. Ren, R. Sun and J. Xu, *Chem. Eng. J.*, 2022, **435**, 135172.
- 37 Z. Zhang, Y. Yang, J. Gao, S. Xiao, C. Zhou, D. Pan, G. Liu and X. Guo, *Mater. Today Energy*, 2018, **7**, 27–36.
- 38 E. Jin Bae, Y. Hun Kang, K.-S. Jang and S. Yun Cho, *Sci. Rep.*, 2016, **6**, 18805.
- 39 C. L. Chiang and J. M. Yang, in *Novel Fire Retardant Polymers and Composite Materials*, ed. D.-Y. Wang, Woodhead Publishing, 2017, pp. 295–312.
- 40 K. Zhang, S. Wang, X. Zhang, Y. Zhang, Y. Cui and J. Qiu, *Nano Energy*, 2015, **13**, 327–335.
- 41 L. Zhang, X.-L. Shi, H. Shang, H. Gu, W. Chen, M. Li, D. Huang, H. Dong, X. Wang, F. Ding and Z.-G. Chen, *Nat. Commun.*, 2025, **16**, 5002.
- 42 H. Wang, X. Liu, Z. Zhou, H. Wu, Y. Chen, B. Zhang, G. Wang, X. Zhou and G. Han, *Acta Mater.*, 2022, **223**, 117502.
- 43 Y. Lei, R. Qi, M. Chen, H. Chen, C. Xing, F. Sui, L. Gu, W. He, Y. Zhang, T. Baba, T. Baba, H. Lin, T. Mori, K. Koumoto, Y. Lin and Z. Zheng, *Adv. Mater.*, 2022, **34**, 2104786.
- 44 Y. Lu, Y. Qiu, K. Cai, X. Li, M. Gao, C. Jiang and J. He, *Mater. Today Phys.*, 2020, **14**, 100223.
- 45 Y. Li, Q. Lou, J. Yang, K. Cai, Y. Liu, Y. Lu, Y. Qiu, Y. Lu, Z. Wang, M. Wu, J. He and S. Shen, *Adv. Funct. Mater.*, 2022, **32**, 2106902.
- 46 R. Wang, R. Sun, Y. Ren, Y. Ma and L. Ma, *J. Mater. Sci.: Mater. Eng.*, 2025, **20**, 31.
- 47 C. Jiang, Y. Ding, K. Cai, L. Tong, Y. Lu, W. Zhao and P. Wei, *ACS Appl. Mater. Interfaces*, 2020, **12**, 9646–9655.
- 48 D. Lee, W. Park, Y. A. Kang, H. T. Lim, S. Park, Y. Mun, J. Kim and K.-S. Jang, *ACS Appl. Mater. Interfaces*, 2023, **15**, 3047–3053.
- 49 Q. Gao, W. Wang, Y. Lu, K. Cai, Y. Li, Z. Wang, M. Wu, C. Huang and J. He, *ACS Appl. Mater. Interfaces*, 2021, **13**, 14327–14333.
- 50 D. Palaporn, W. Mongkolthanaruk, K. Faungnawakij, K. Kurosaki and S. Pinitsoontorn, *ACS Appl. Energy Mater.*, 2022, **5**, 3489–3501.
- 51 X. Li, Y. Lu, K. Cai, M. Gao, Y. Li, Z. Wang, M. Wu, P. Wei, W. Zhao, Y. Du and S. Shen, *Chem. Eng. J.*, 2022, **434**, 134739.
- 52 S. Jindal, G. S. S. Saini, R. Kumar and S. K. Tripathi, *J. Appl. Phys.*, 2022, **132**, 235303.
- 53 Q. Jiang, J. Yang, P. Hing and H. Ye, *Mater. Adv.*, 2020, **1**, 1038–1054.