Efficient p-Type Doping of Tin Halide Perovskite via Sequential Diffusion for Thermoelectrics

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Metal halide perovskites (MHPs) hold great potential in thermoelectric (TE) applications, thanks to their regular and soft lattice in nature. However, the poor electrical conductivity caused by low charge carrier density \(<10^{14} \text{ cm}^{-3}\) for lead-based MHPs strongly impedes its TE development. In this scenario, tin halide perovskites (THPs) emerge as promising TE candidates owing to their high background hole densities \( (>10^{19} \text{ cm}^{-3}) \). However, further electrical doping remains challenging, originating from the limited capability of accommodating heterogeneous dopants and the heavy compensation in THPs. Herein, a novel diffusion-mediated doping approach is demonstrated to prominently increase the p-type doping level of THPs by a sequence of air exposure and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) surface treatments. In paradigm photovoltaic THP materials—CH(NH3)2SnI3 (namely FASnI3), the electrical conductivity is dramatically increased by \( 300 \times \) from 0.06 to 18 S cm\(^{-1}\) in thin films, leading to a remarkable enhancement of power factor by \( 25 \times \) up to 53 \( \mu \text{W m}^{-1}\text{K}^{-2}\). In contrast, only a slight variation of thermal conductivity is observed after F4TCNQ deposition, which is in accordance with the increase in electrical conductivity, indicating that the lattice structures of FASnI3 remain intact after doping. This study paves an illuminating way to ameliorate TE properties in halide perovskites.

1. Introduction

Rapid development has been witnessed in the past decade on metal halide perovskites (MHPs), particularly in the field of optoelectronics on account of their uniquely high defect tolerance, long exciton diffusion length, bandgap tunability, and low-cost solution processability.\[^3\] The chemical formula of MHPs is denoted as ABX\(_3\), where A represents the monovalent organic or inorganic cation, B is a metal cation such as Sn\(^{2+}\) or Pb\(^{2+}\), and X is a halide anion.\[^4\] MHPs structurally consist of the corner-sharing metal \([BX_6]^{4-}\) octahedra and the interstitial A-site cations, which jointly endow them with intrinsically high carrier mobility \( (\mu) \) and attenuated heat transport, resulting in electron-crystal-like and phonon-glass-like behavior, respectively, thereby holding broad prospects for thermoelectric (TE) applications.\[^5\]

Typically, the performance of TE materials is determined by the mutually coupled characteristics of electrical conductivity \( (\sigma, \text{ S cm}^{-1}) \), Seebeck coefficient \( (S, \mu \text{V K}^{-1}) \), and thermal conductivity \( (\kappa, \text{ W m}^{-1}\text{K}^{-1}) \), which collectively contribute to the dimensionless figure of merit \( (\text{zT}) \) in the form of \( S^2\sigma T/\kappa \)

where \( T \) is the absolute temperature and \( S^2\sigma \) is also defined as power factor \( (PF, \mu \text{W m}^{-1}\text{K}^{-1}) \).

Although the electrical and thermal characteristics of lead-based MHPs have been widely studied, the TE performance is still far from satisfactory because of their intrinsically low \( \sigma \).\[^7\] Tin halide perovskites (THPs) recently stood out with an inherently higher carrier concentration than their lead counterparts due to the characteristic self-doping effect, which is conducive to superior electrical conductivity and hence renders them considerably favorable for TE applications.\[^11,12\] However, the carrier density of THPs is still constrained by the limited capability of accommodating heterogeneous dopants and the heavy compensation from intrinsic defects, both of which severely undermine their TE performances. The studies of THP-based TE materials are rarely reported and have just come to burgeon in recent years.\[^13–16\] most of which were centered upon diversified doping strategies. Among them, all-inorganic CsSnX\(_3\) perovskites have attracted enormous attention, thanks to their relatively high \( \sigma \).\[^13\]

To exemplify it, single-crystal CsSnI\(_3\) nanowires yielded a superior \( \sigma \) of 282 S cm\(^{-1}\) without optimization.\[^17\] A further study reported an encouraging increase in \( \sigma \) by one order of magnitude via air doping the thermally vapor-deposited CsSnI\(_3\) films with a chlorine-rich capping layer.\[^18\] Nevertheless, these fabrication
methods of all-inorganic perovskites are costly and complex, which would be unsuitable for scalable production. Meanwhile, inorganic halide perovskites were revealed to possess higher $\sigma$ than their organic/inorganic counterparts, which is mostly ascribed to the organic cation dynamic disorder.[19] Early studies were focused on CH$_3$NH$_3$SnI$_3$ (namely, MA$_2$Sn$_2$I$_6$)-based crystals[20,21] and showed the extrinsic doping of Sn$^{4+}$ ions as an efficient method to increase the carrier concentration by fivefolds yet failed to achieve a satisfactory $\sigma$ in THPs. In addition, the thermal instability of the MA component impaired long-term stable operation. More recently, another benchmark family of hybrid THPs—CH(NH$_2$)$_2$SnI$_3$ (i.e., FASnI$_3$), which delivered the highest photovoltaic efficiency in THP-based solar cells,[22–26] also emerged as promising TE candidates. For instance, Gong et al. mixed a classic electron acceptor, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F$_4$TCNQ), into the FASnI$_3$ precursor solution and reported a noticeable improvement of $\sigma$ up to 13.65 S cm$^{-1}$; however, the doping level is still constrained because the insufficient dopants were incorporated purposely to ensure the desired film morphology.[27] Although the aforementioned strategies have manifested as direct avenues to elevating $\sigma$ of THPs, a lack of in-depth understanding of interactions between dopants and perovskite lattices results in the uncontrollable and restrained doping level along with poor reproducibility across research laboratories.

In this study, we demonstrate for the first time an effective and facile surface treatment of combined air oxidation and F$_4$TCNQ diffusion to significantly enhance the doping efficiency in FASnI$_3$ films while enabling to unveil their distinct roles in THPs. First, we investigate the oxidation-assisted doping process of Sn$^{4+}$ in the FASnI$_3$ film and confirm its favorable impacts by exhibiting a 50× increase in $\sigma$. Then, it is validated that the increased $\sigma$ accounts for the major part of PF improvements, which highlight the priority of $\sigma$ modulation to $S$ when improving the PF of THPs. To prevent FASnI$_3$ from the over air exposure, which leads to the lattice decomposition and hence worse performance, F$_4$TCNQ is further exploited by surface deposition and then diffuses into the THP bulk, as verified by the time-of-flight secondary-ion mass spectrometry (TOF-SIMS). Surprisingly, it is observed that F$_4$TCNQ realizes a superimposed p-doping effect upon the as-oxidized thin film. Joint analysis of Fourier-transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) distinguishes the doping mechanisms of F$_4$TCNQ and oxidation by charge and atomic transfer, respectively, which underpins the origin of the accumulated doping effect in FASnI$_3$. Consequently, a striking increase in $\sigma$ by $\times 300$ is obtained, which leads to an outstanding PF of 53 $\mu$W m$^{-1}$ K$^{-2}$, accompanied also by remarkably enhanced electrical stability.

2. Results and Discussion

The FASnI$_3$ thin films were fabricated by the facile spin-coating method (refer to Experimental Section for details) with a thickness of ≤250 nm, which is comparable with previous literatures.[27,28] Time-dependent electrical measurements were conducted to explore the air-doping effect of FASnI$_3$ thin film. As shown in Figure 1a, when the thin film was exposed to air, $\sigma$ is increased tremendously by 50× in the first 15 min as a result of p-type doping by O$_2$, showing a peak value of 2.6 S cm$^{-1}$ at 15 min, which is presumably attributed to the dramatically enhanced carrier concentration. Further air exposure however leads to deteriorated electrical transport owing to the decomposition of the perovskite lattices. On the other hand, a sharp decrease is observed in $S$ from 607 to $\approx 126 \mu$V K$^{-1}$ in the first 60 min and then $S$ tends to be steady with air exposure due to the gradually saturated carrier concentration. Compared with the variation of $\sigma$, the change of $S$ is too flattened to play a dominant role in determining the PF. Consequently, the trend of the time-dependent PF is similar to $\sigma$, suggesting that the optimized PF can be achieved by direct control of the oxidation level, which can be estimated from $\sigma$. As a result, the highest PF of 10 $\mu$W m$^{-1}$ K$^{-2}$ is obtained upon air exposure for 15 min. Moreover, it is reported that the degradation of the perovskite lattice is also in intimate correlation with ambient humidity.[29,30] As shown in Table S1 in the Supporting Information (SI), we tested the optimal oxidation time and highest $\sigma$ for FASnI$_3$ films at room temperature with different relative humidities (RHs) of 20% and 65%. At a higher RH, the time required to achieve the peak $\sigma$ is shortened, while the $\sigma$ value is decreased from $\approx 2.50$ to $\approx 1.34$ S cm$^{-1}$, presumably

![Figure 1](https://www.advancedsciencenews.com)

Figure 1. a) Electrical characteristics of FASnI$_3$ thin film as a function of air exposure time. b) XRD patterns of FASnI$_3$ thin film in air with lattice plane indices.
attributable to the moisture-induced structure decomposition especially in the presence of oxygen.

To characterize the air stability of FASnI3 film, X-ray diffraction (XRD) was used to probe the perovskite crystal structure. Figure 1b displays the time-dependent XRD patterns of FASnI3 thin films in air, which are consistent with previous studies.\textsuperscript{28,31} The peak intensity declines, while the full-width-half-maximum (FWHM) of peaks is raised without additional signals during 120 min of aging, indicating that the structural components of FASnI3 remain relatively stable without the generation of obvious impurity phases, in spite of slightly decreased crystallinity. During the thin-film fabrication process, SnF\textsubscript{2} additive was added into the perovskite precursor solution to promote the crystallization of FASnI3 while acting as an antioxidant to stabilize the perovskite bulk phase against air exposure.\textsuperscript{[32]} As the reaction with oxygen originates from the surface, SnF\textsubscript{2} shows a merit of reducing the oxidation rate to better tune the doping level.

Nevertheless, the oxidation rate of the perovskite film varies with the environmental effects such as light illumination, temperature, humidity, and so on, rendering it difficult to attain an optimal doping level precisely. Moreover, the lattice degradation caused by the excessive O\textsubscript{2} doping impairs the stability of electrical characteristics, as shown in Figure 1, which will be discussed later. To tackle these issues, F\textsubscript{4}TCNQ, which is one of the most widely adopted and effective p-type dopants due to its strong electron-withdrawing ability and the extended $\pi$-system, was exploited to further p-dope the oxidized perovskite. As shown in Figure 2a, F\textsubscript{4}TCNQ possesses a deep lowest unoccupied molecular orbital (LUMO) energy level ($\approx -5.2$ eV) that is energetically in the vicinity of the highest occupied molecular orbital (HOMO) energy level of FASnI\textsubscript{3} ($\approx -5.0$ eV) and hence doping is facilitated by electron transfer from the HOMO of FASnI\textsubscript{3} to the LUMO of F\textsubscript{4}TCNQ.\textsuperscript{[33,34]} To acquire the best $\sigma$ without overexposing the thin film in air, F\textsubscript{4}TCNQ was immediately solution spray deposited onto the FASnI\textsubscript{3} thin film that approaches the peak electrical characteristics. The detailed sequential doping process of the FASnI\textsubscript{3} thin film is illustrated in Figure 2b. The as-spin-coated FASnI\textsubscript{3} film was first transferred into air, during which the resistance of the film was continuously recorded for a rough estimate of the doping level. Next, F\textsubscript{4}TCNQ dissolved in chlorobenzene was spray coated on the surface of the oxidized FASnI\textsubscript{3}, followed by a thermal annealing process, during which F\textsubscript{4}TCNQ dopants tended to diffuse through the grain boundaries and subsequently into the bulk of thin film, as verified by TOF-SIMS in Figure 2c. The F element is detected with the sputter time to signify the existence of F\textsubscript{4}TCNQ molecules at the different depths of the FASnI\textsubscript{3} thin film that was prepared in

![Figure 2. a) Schematic energy level diagram of FASnI3 and F4TCNQ. b) Illustrative thin-film fabrication process during which F4TCNQ molecules enter the film by solid diffusion. c) TOF-SIMS spectra of the film deposited with two and eight layers of F4TCNQ, showing a variation of F-element content at different depths. The inset shows the 3D render overlay of F and I in FASnI3 films after deposition of two layers of F4TCNQ. d) Summary of electrical characteristics of FASnI3/F4TCNQ films with various numbers of F4TCNQ layer.](image-url)
the absence of SnF₂ additive. Although the intensity of F₄TCNQ is slightly decreased throughout thin films, the overall trend indicates that F₄TCNQ molecules diffuse uniformly to realize additional p-doping, which is also illustrated in the inset of Figure 2c when compared with the distribution of I element. More importantly, such diffusion doping from the surface enables efficient incorporation of the adequate molecular dopants into the FASN₁₃ thin films without adversely affecting perovskite crystallization during film fabrication.

Given the limited solubility of F₄TCNQ in chlorobenzene, we fabricated the FASN₁₃/F₄TCNQ films that were deposited with various numbers of doping layers to modulate the dopant contents and measured the electrical characteristics accordingly. As shown in Figure 2d, σ exhibits a sequence of positive and then negative trends as the number of F₄TCNQ layers progressively increased from 0 to 4, which ultimately reached a maximum value of 18.0 S cm⁻¹ with double layers of F₄TCNQ. According to the TOF-SIMS spectra in Figure 2c, excessive dopants continue to penetrate into the thin film instead of residing on the surface and thus deteriorate charge transport as they act as impurities/traps, leading to a decrease in σ value. In addition, F₄TCNQ-doped samples present a slight decrease in S, similar to the oxidation process shown in Figure 1a, which is ascribed to the increased carrier concentration. As a consequence, the enhancement of σ leads to the prominently improved PF from 10 to 53 µW m⁻¹ K⁻².

Moreover, it is demonstrated that the doping effect of F₄TCNQ on σ places a superposition on that of O₂. Based on the equation of \( \sigma = \frac{nq}{l} \) where n is carrier concentration and q is elementary charge, the carrier concentration before and after doping can be evaluated by characterizing the carrier mobility of as-prepared films. According to the grazing-incidence wide-angle X-ray scattering (GIWAXS) pattern in Figure S1 in Supporting Information, the isopropy of FASN₁₃ film allows to estimate the in-plane mobility by the out-of-plane mobility. Then, the space–charge-limited-current (SCLC) method was adopted extract the charge mobility. As shown in Figure S2 in Supporting Information, the peaks at 1395, 1341, and 1598 cm⁻¹ represent the b₁u mode of \( \nu_{C\cdots C} \) as well as b₂u and b₁g modes of \( \nu_{C\cdots C} \) respectively. Note that the C–F signals are too weak to be identified when compared with the signals of halogenated hydrocarbons.

To distinguish the respective role of F₄TCNQ and O₂ during the sequential doping processes, the XPS profiles were acquired for neat, oxidized, as well as successive oxidized and F₄TCNQ-doped FASN₁₃ with the Sn-3d and I-3d binding energy spectra displayed in Figure S5 (Supporting Information), where the peaks at 1395, 1341, and 1598 cm⁻¹ represent the b₁u mode of \( \nu_{C\cdots C} \) as well as b₂u and b₁g modes of \( \nu_{C\cdots C} \) respectively. The full FTIR spectra are shown in Figure S5 (Supporting Information), where the peaks at 1395, 1341, and 1598 cm⁻¹ represent the b₁u mode of \( \nu_{C\cdots C} \) as well as b₂u and b₁g modes of \( \nu_{C\cdots C} \) respectively. The full FTIR spectra are shown in Figure S5 (Supporting Information), where the peaks at 1395, 1341, and 1598 cm⁻¹ represent the b₁u mode of \( \nu_{C\cdots C} \) as well as b₂u and b₁g modes of \( \nu_{C\cdots C} \) respectively. The full FTIR spectra are shown in Figure S5 (Supporting Information), where the peaks at 1395, 1341, and 1598 cm⁻¹ represent the b₁u mode of \( \nu_{C\cdots C} \) as well as b₂u and b₁g modes of \( \nu_{C\cdots C} \) respectively. The full FTIR spectra are shown in Figure S5 (Supporting Information), where the peaks at 1395, 1341, and 1598 cm⁻¹ represent the b₁u mode of \( \nu_{C\cdots C} \) as well as b₂u and b₁g modes of \( \nu_{C\cdots C} \) respectively. The full FTIR spectra are shown in Figure S5 (Supporting Information), where the peaks at 1395, 1341, and 1598 cm⁻¹ represent the b₁u mode of \( \nu_{C\cdots C} \) as well as b₂u and b₁g modes of \( \nu_{C\cdots C} \) respectively.

During this process, O₂ scavenges two electrons from Sn²⁺ ion and therefore two holes are released into the matrix to achieve p-type doping, as shown in Equation (2).

\[
\text{Sn}^{2+} + O_2 \rightarrow \text{SnO}_2 + 2h^+
\]
octahedral lattice as well as the formation of SnI$_4$ and SnO$_2$ at the grain boundaries, which can be defined as main atom transfer process. On the other hand, only electron transfer occurs in the case of F$_4$TCNQ between the [SnI$_6$]$^{4-}$ octahedra and dopants, wherein the I$^{-}$ anions also contribute to charge transfer due to the strong electron-withdrawing capabilities of —C≡N and —F radical groups. As a consequence, Sn$^{2+}$ remains within the lattices instead of generating Sn vacancies and causing atom transfer. Such an assumption is also evidenced by the morphological variation of the samples after treatments by both dopants, as shown in the field-emission scanning electron microscopy (FESEM) images in Figure 3d, wherein the film features pinholes (as highlighted in the yellow circles) upon air exposure, while remaining compact and homogeneous when doped by F$_4$TCNQ, suggestive of the structural decomposition in the former yet the lattice integrity in the latter. Moreover, the XRD patterns of FASnI$_3$ films with and without F$_4$TCNQ treatment shown in Figure S6 (Supporting Information) also verify the intact crystal structure with almost no peak shift or additional peak after doping, indicating that F$_4$TCNQ molecules do not penetrate into the perovskite lattice or cause structural decomposition during p-doping.

As the air exposure is accompanied by the degradation of lattice structure, it retards charge transport through thin films. Thus, the time-dependent PF variations were recorded to evaluate the durability of as-prepared perovskite thin films at room temperature and in Ar atmosphere without encapsulation, as shown in Figure 4. Here, $T_{90}$ represents the time required for PF to drop down to 90% of the original sample. The over-oxidized samples, in which the collapse of crystal structure is predominant in influencing charge transport, show the worse stability among others with a considerable PF decrease in 120 h, further highlighting the critical importance of controlling the oxidization degree of FASnI$_3$. When exposed in air, a large amount of O$_2$ ions tend to adsorb on the surface of the perovskite thin film or penetrate through grain boundaries. The excessive O$_2$ or the incompletely bonded O$^{2-}$ ions continue to extract the Sn$^{2+}$ ions from the perovskite lattice after being transferred backward to Ar atmosphere, thus leading to the additional p-type doping during storage. This is also suggested by the slight increase in PF for FASnI$_3$ and FASnI$_3$/F$_4$TCNQ.

Figure 3. a) FTIR spectra of neat F$_4$TCNQ and FASnI$_3$/F$_4$TCNQ films in $\nu$C≡N region. b) Sn 3d$_{5/2}$ and I 3d$_{3/2}$ XPS spectra of FASnI$_3$ with various oxidation levels and after F$_4$TCNQ doping. Fitted Gaussian components are also shown. c) Schematic illustration of the doping process in the case of O$_2$ and F$_4$TCNQ, respectively. d) FE-SEM images of the neat, oxidized and F$_4$TCNQ-doped FASnI$_3$ thin films.
shown in Figure 4. However, F$_4$TCNQ will compete to shield the lattice from O$_2$ molecules or O$^-$ ions due to the stronger electronegativity and meanwhile passivate the defects at the grain boundaries, which exert a positive effect on preventing the crystal structures from rapid degradation. Consequently, the FASnI$_3$/F$_4$TCNQ hybrid film delivers the best electrical stability among others.

It is generally acknowledged that MHPs possess an ultralow κ due to both low-phonon group velocities and short-phonon lifetimes. It is therefore essential to distinguish the diffusion doping process in this study from the other bulk doping strategies in literatures with regard to their impacts on κ. An accurate measurement of κ however affords a big hurdle for THP thin films due to the limited capability of available methods to characterize the in-plane thermal diffusion in such nonself-supporting thin films as well as the ambient instability of THPs as discussed earlier. Consequently, the thermal transport property of THP films has been barely studied. Moreover, it remains obscure whether the inclusion of F$_4$TCNQ results in an increase in κ, which possibly counteracts its benefits on PF. Here we exploited scanning thermal microscopy (SThM) to investigate the effect of F$_4$TCNQ doping on the κ$_{\text{total}}$ of FASnI$_3$. In the SThM method, an atomic force microscopy platform is used to detect the change of thermal resistance based on which the κ$_{\text{total}}$ can be calculated (refer to the details in SI). The κ$_{\text{total}}$ of as-oxidized FASnI$_3$ is estimated to be $0.286 \pm 0.007$ W m$^{-1}$K$^{-1}$ at $\sigma \approx 2.6$ S cm$^{-1}$ (room temperature), which is even lower than the reported value of MAPbI$_3$ perovskite films ($\approx 0.3$ W m$^{-1}$K$^{-1}$). Further surface diffusion of F$_4$TCNQ dopants slightly increases the κ$_{\text{total}}$ to $0.296 \pm 0.007$ W m$^{-1}$K$^{-1}$ at $\sigma \approx 18.0$ S cm$^{-1}$, which is comparable with a literature value of F$_4$TCNQ bulk-doped FASnI$_3$ films at $\sigma = 13.65$ S cm$^{-1}$ by the same measurement. Although a sixfold enhancement in κ is observed upon F$_4$TCNQ deposition on air-oxidized FASnI$_3$, the increase in κ$_{\text{total}}$ is relatively insignificant ($\approx 0.01$ W m$^{-1}$K$^{-1}$). Note that κ$_{\text{total}}$ comprises electron contribution (κ$_e$) and phonon/lattice contribution (κ$_l$), of which κ$_e$ follows Wiedemann–Franz’s law:

$$\kappa_e = L \sigma T$$

(3)

where $L$ is the Lorentz number. Based on Equation (3), κ$_e$ can be calculated as approximately $0.01$ W m$^{-1}$K$^{-1}$ for the F$_4$TCNQ-doped film, for which we attribute this subtle increase in κ$_{\text{total}}$ to the enhanced $\sigma$, suggesting that F$_4$TCNQ penetration imposes negligible effects on the lattice structures of FASnI$_3$ while merely residing the grain boundaries and thus leads to fairly stable κ$_{\text{total}}$, which plays a decisive role in κ$_{\text{total}}$. As a result, the $T$ value of the optimal F$_4$TCNQ-doped sample is estimated to be $\approx 0.05$ at room temperature.

3. Conclusions

In conclusion, we have successfully demonstrated a sequential strategy by combining the oxidation-assisted optimal doping and diffusion doping via F$_4$TCNQ surface treatment to achieve continuous elevation of the doping level in FASnI$_3$ thin films, leading to a dramatically increased $\sigma$ of $18$ S cm$^{-1}$ and hence a remarkable PF of $53$ $\mu$W m$^{-1}$K$^{-2}$, accompanied by greatly improved electrical stability. Such a diffusion-mediated doping strategy not only allows for the facile and noninvasive inclusion of dopants into FASnI$_3$ films but also underpins the significance of the two-step doping method with an interesting superimposed effect on elevating the doping level by distinct mechanisms. Unsatisfactorily, it is worth noting that $S$ in our work is constrained by the increased carrier concentration. Most recently, high $S$ and excellent thermal stability were realized in 2D tin-based perovskites because of their quantum confinement effect and organic ligands, respectively. We therefore envision that the surface doping strategy demonstrated in this work, when applied to low-dimensional THPs, may further boost the TE performance.

4. Experimental Section

**Materials and Reagents:** FAI (99.9%) and SnF$_2$ (99.9%) were purchased from Maituwai Ltd. (China) while SnI$_2$ (99.9%) was from Alfa Aesar (China). All other chemicals were purchased from J&K Scientific, Ltd. (China). All the reagents were used as received.

**Thin-Film Fabrication:** The pristine FASnI$_3$ precursor solution (1M) was prepared by mixing SnI$_2$, FAI, and SnF$_2$, at a stoichiometric ratio of 10:10:1 in mixed DMF:DMSO (4:1 vol%) solvent. Then, the precursor solution was stirred under room temperature at $600$ rpm for 1 h. For film fabrication, the FASnI$_3$ solution was first spin coated on an indium tin oxide (ITO)-patterned glass substrate at $5000$ rpm at room temperature for 60 s, during which toluene was deposited as antisolvent to accelerate the crystallization of the FASnI$_3$ film. The as-prepared films were heated at $70^\circ$C in an argon (Ar) atmosphere for $20$ min to remove residual solvent and then transferred into air at ambient temperature ($26^\circ$C) and at RH of $25 \pm 5\%$ with an oxygen concentration of $\approx 20.8\%$, during which the resistance of the film was continuously recorded for a rough estimate of the doping level. Next, F$_4$TCNQ was dissolved in chlorobenzene solvent as saturated solution ($1.5$ mg mL$^{-1}$) and subsequently spray coated on the oxidized FASnI$_3$, followed by the thermal annealing process. All samples were prepared in argon (Ar) atmosphere ($\text{H}_2\text{O} < 0.1$ ppm, O$_2 < 0.1$ ppm) glovebox.

**Characterization and Measurements:** Electrical properties of thin films were measured at room temperature using a custom-built apparatus according to our previous report. A four-probe technique was used to measure electrical conductivity on a multimeter (Keithley 2010) and the Seebeck coefficient was measured by heating one resistor block while simultaneously measuring the generated temperature gradient ($\Delta T$) and TE voltage ($\Delta V$).
measurements were performed on the electron-only and hole-only devices with configurations of ITO/SnO$_2$/THPs/PC$_{61}$BM/Au and ITO/PEDOT: PSS/THPs/PTAA/Au, respectively, in which a bias was scanned from 0 to 3 V with a step of 0.01 V. The obtained electrical characteristics were plotted in logarithmic coordinates with the vertical axis representing $J$ and the horizontal axis the electric field intensity ($F$) in V cm$^{-1}$. The plots were then fit to calculate electron and hole mobilities.

XRD pattern data for 2θ values were collected with a Bruker AX D8 Advance diffractometer with nickel-filtered Cu Kα radiation (λ = 1.5406 Å). GIWAXS experiments were carried out at the Shanghai Synchrotron Radiation Facility (SSRF). The samples were prepared on glass substrates and the data were obtained with an area CCD detector of 3072 × 3072 pixels resolution (225 mm × 225 mm) at beamline BL14B1. The monochromated energy of the X-ray source was 10 keV, while the X-ray wavelength was 1.2378 Å and the incidence angle was set at 0.3°. FESEM images were acquired on ZEISS Gemini 300 at an accelerating voltage of up to 30 kV. XPS analysis was conducted with X-ray photoemission spectroscopy (PHI5300). All the peaks were calibrated by C1s. TOF-SIMS measurements were obtained by TOFSIMS 5 (IONTOF).

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.

Keywords

air doping, diffusion doping, electrical conductivity/thermoelecrtics, F$_2$TCNQ, FASnI$_3$

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