Doping is an important technique for semiconductor materials, yet effective and controllable doping of organic-inorganic halide perovskites is still a challenge. Here, we present a protocol to dope 2D perovskite (PEA)$_2$SnI$_4$ by incorporating SnI$_4$ in the precursor solutions. We detail steps for preparation of field-effect transistors (FETs) and thermoelectric devices (TEs) based on SnI$_4$-doped (PEA)$_2$SnI$_4$ films. We further describe characterization via conductivity measurement using the four-point probe method, FETs performance, and TEs performance measurements.

Publisher’s note: Undertaking any experimental protocol requires adherence to local institutional guidelines for laboratory safety and ethics.
Protocol

Protocol for doping of an Sn-based two-dimensional perovskite semiconductor by incorporating SnI₄ for field-effect transistors and thermoelectric devices

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SUMMARY

Doping is an important technique for semiconductor materials, yet effective and controllable doping of organic-inorganic halide perovskites is still a challenge. Here, we present a protocol to dope 2D perovskite (PEA)₂SnI₄ by incorporating SnI₄ in the precursor solutions. We detail steps for preparation of field-effect transistors (FETs) and thermoelectric devices (TEs) based on SnI₄-doped (PEA)₂SnI₄ films. We further describe characterization via conductivity measurement using the four-point probe method, FETs performance, and TEs performance measurements.

For complete details on the use and execution of this protocol, please refer to Liu et al. (2022).¹

BEFORE YOU BEGIN

© Timing: 2–4 h

The protocol below describes the specific steps for preparing and characterizing field-effect transistors (FETs) and thermoelectric devices (TEs) based on SnI₄-doped (PEA)₂SnI₄ films.

1. Check the oxygen and moisture level in the glovebox, it should be approximately or less than 0.1 ppm of H₂O and 0.1 ppm of O₂ level.
2. The important materials for making (PEA)₂SnI₄ including phenethylammonium iodide, Tin(II) iodide and Tin(IV) iodide, etc. listed in the key resources table, should be stored in the glovebox preferably for less than three months.
KEY RESOURCES TABLE

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| **Chemicals, peptides, and recombinant proteins** | | |
| Phenethylammonium iodide, ≥ 99.5% | Xi’an Polymer | Cat#PLT5013911 |
| Tin(II) iodide, AnhydroBeads™, –10 mesh, 99.99% trace metals basis | Aldrich | Cat#409308 |
| N,N-Dimethylformamide, anhydrous, 99.8% | Aldrich | Cat#227056 |
| 1-Methyl-2-pyrrolidinone, anhydrous, 99.5%, packaged under argon in resealable ChemSealTM bottles | Alfa Aesar | Cat#043741 |
| Tin(IV) iodide, 95% | Aladdin | Cat#T95042 |
| Octadecyltrichlorosilane, 95% | Acros | Cat# 147400250 |
| Toluene, AR | Innochem | Cat# 100975 |
| Chrome rod, 99.99% | Kurt J. Lesker Co., Ltd | N/A |
| Gold grain, 99.99% | Hezong Xincai Technology Co., Ltd | N/A |
| Glass substrate | Luoyang Guluoglass Co., Ltd | N/A |
| Si/SiO2 substrate | Suzhou EDMICRO Technology Co., Ltd | N/A |
| Scotch magic tape | 3M Technology Co., Ltd | Cat# 810-CQ33 |
| Sodium hydroxide (NaOH), AR, 99% | Innochem | Cat# A36865 |
| Acetone, AR, 99% | Innochem | Cat# 12378 |
| Isopropanol, AR, 99% | Innochem | Cat# A17203 |
| Positive photoresist | Kempur Microelectronics Inc. | Cat# BP212-37S |
| **Other** | | |
| Keithley 4200 semiconductor analyzer | Tektronix Technologies | https://www.tek.com/en/keithley-4200a-scsparameter-analyzer |
| B2912A Precision Source | Keysight | https://www.keysight.com/us/en/product/B2912Aprecision-source-measure-unit-2-ch-10fa-210v-3a-dc-10-5apulse.html?rd=1 |
| ST-100 cryostat | Janis | https://www.lakeshore.com/products/product-detail/jans/st-100-optical-cryostat |
| Model 22C temperature controller | Cryo-con | https://www.cryocon.com/MZ2CProdFolder.php |
| Keithley nano voltmeter model 2182A | Tektronix Technologies | https://www.tek.com.cn/products/keithley/low-level-sensitive-and-specialty-instruments/nanovoltmeter-model-2182a |
| DC stabilized power supply model DP152 | Mestek | http://www.china-nengyuan.com/product/180303.html |
| Single-sided lithography machine model H19-13 | Sichuan Hangyuan Dingsin Technology Co., Ltd | http://www.schdydx.com/pd.jsp?id=33#_pp=2_748 |
| Evaporator model PD-400S | Wuhan PDVACUUM Technology Co., Ltd | http://www.pdvacuum.com/index.php?m=content&c=index&a=show&catid=7&id=61 |
| UV/ozone cleaner | Sunmonde Technology Co., Ltd | http://www.sunmonde.com.cn/ |
| Spin-coater | LEOB science Technology Co., Ltd | http://www.lebioscience.cn/view/id/85.html |
| Analytical balance, model BSA124S | Sartorius Technology Co., Ltd | https://www.sartorius17.cn/files/01/mgh/bas124s.html |
| Glovebox, model Universal | MIKROUNA Technology Co., Ltd | https://www.mikrouna.com/product/index/id/37.html |

STEP-BY-STEP METHOD DETAILS

Device fabrication

» Timing: 16–20 h

» Timing: 5–7 h (for step 1a–1e)

» Timing: 10–11.5 h (for step 2)
The preparation process includes preparing perovskite precursor solutions and spin-coating precursor solutions on cleaned substrates.

1. Bottom-contact electrodes fabrication.
   Define and deposit the bottom-contact electrodes by photolithography and thermal evaporator (<4×10^{-4} Pa), respectively.
   a. Define bottom-contact electrodes by photolithography.
      i. Dissolve 2 g NaOH with 500 mL deionized water as developer.
      ii. Spin the positive photoresist on the desired 4-inch wafer substrate with speed of 3,000 rpm for 30 s and anneal at 105°C for 5 min.
      iii. Expose the substrate under UV light through shadow mask for 7 s.
      iv. Soak the substrate into the developer for 10 s, and dry them with nitrogen gas gun.
   b. For conductivity measurement, Figure 1A shows the electrode structure. Deposit the Cr (2 nm) and Au (30 nm) sequentially on Si++/SiO2 substrates by a thermal evaporator.
   c. For FET devices, Figure 1B shows the electrode structure. Deposit Cr (2 nm) and Au (30 nm) sequentially on Si++/SiO2 substrates by a thermal evaporator.
   d. For TE devices, Figure 2A shows the electrode structure. Deposit Cr (10 nm) and Au (15 nm) sequentially on glass substrates by a thermal evaporator.
   e. Soak the substrates into acetone for 30 min to lift off the photoresist, and dry them with nitrogen gas gun.

Note: For Si++/SiO2 substrates, Si++ refers to heavily doped silicon with low resistivity of 0.01 Ω/cm. The thickness of SiO2 is 300 nm.

2. Preparing perovskite precursor solutions.
   a. Weigh SnI2 (0.1 mmol, 37.3 mg) and PEAI (0.2 mmol, 49.8 mg) in a 1.5 mL glass reagent bottle in sequence.
      i. Add 250 μL 1-Methyl-2-pyrrolidinone (NMP) and 750 μL dimethyl formamide (DMF) into the reagent bottle to form solution A (0.1 M).
   b. Weigh SnI4 (0.1 mmol, 62.6 mg) and PEAI (0.2 mmol, 49.8 mg) in a 1.5 mL glass reagent bottle in sequence.
      i. Add 250 μL NMP and 750 μL DMF into the reagent bottle to form solution B (0.1 M).
   c. Mix solution A and solution B with volume ratio of 1-\text{x}x, where \text{x} represents the doping ratio of SnI4 to obtain 0.1 M (PEAI)$_2$(SnI$_2$)$_{1-x}$(SnI$_4$)$_x$ precursor solutions.
   d. After heating the (PEAI)$_2$(SnI$_2$)$_{1-x}$(SnI$_4$)$_x$ precursor solutions at 60°C for 9 h.
      i. Store the solutions at room temperature (about 25°C here) for 1 h to cool down.

Figure 1. Electrode structures of devices
Scale bar: 200 μm.
(A) Electrode structure of conductivity measurement.
(B) Electrode structure of FET measurement.

© Timing: 1–1.5 h (for step 3)
ii. Filter solutions through 0.45 μm PTFE filters.

△ CRITICAL: The standard mass ratio of SnI₂ and PEAI should be 0.748. The standard mass ratio of SnI₄ and PEAI should be 1.257.

△ CRITICAL: The prepared precursor solutions should not be stored for more than 2 days.

3. Substrate cleaning and spin coating.
   a. Cut the 4-inch wafer substrate into pieces (about 1 cm × 1.5 cm).
   b. For conductivity and FET measurements, ultrasonicate the Si⁺⁺/SiO₂ substrates sequentially in deionized water, acetone and isopropanol for 2 min each.
      i. Blow dry them by a nitrogen gas gun.
      ii. Treat the substrates with UV/ozone for 30 min before spin-coating.
      iii. Cast 30 μL precursor solution in the center of the Si⁺⁺/SiO₂ substrate and spin-coat at 4,000 rpm for 30 s with acceleration of 500 rpm/s.
      iv. Anneal the perovskite films at 100°C for 10 min.
   c. For TEs measurement, pattern the perovskite films as shown in Figure 2.
      i. Ultrasonicate the glass substrates sequentially in deionized water, acetone and isopropanol for 2 min each.
      ii. Blow dry them by a nitrogen gas gun.
      iii. Treat the substrates with UV/ozone for 30 min.
      iv. Spin Octadecyltrichlorosilane (ODTS) solution (5 vol% in toluene) on the glass substrates with at 2,000 rpm for 30 s with acceleration of 1,000 rpm/s.
v. Anneal the substrates at 100°C for 10 min to form an ODTS film on substrate (Figure 2B).
vi. Cover the area except for the hot and cold ends with tape.

vii. Treat the substrates with UV/ozone for 30 min (Figure 2C) before removing the tape (Figure 2D).

viii. Cast 10 μL precursor solution in the center of the glass substrate and spin-coat at 4,000 rpm for 30 s with acceleration of 500 rpm/s.
ix. Anneal the perovskite films at 100°C for 10 min to form patterned perovskite film (Figure 2E).

△ CRITICAL: The area covered by ODTS is hydrophobic, thus the perovskite film can’t form on ODTS covered area.

△ CRITICAL: The time from the end of UV/ozone treatment to the beginning of spin coating should be less than 5 min to avoid weakening of the hydrophilicity. Complete all processes in the glovebox except for the substrate cleaning.

**Device characterization**

**Timing:** 17–23 h

**Timing:** 1–1.5 h (for step 4)

**Timing:** 1–1.5 h (for step 5)

**Timing:** 15–20 h (for step 6)

The characterizations include conductivity, FETs performance, and TE s performance measurements. Due to the instability of perovskite films, conduct all measurements immediately in Ar-filled glovebox in dark after preparation unless otherwise stated.

4. Conductivity measurement.

Measure the conductivity of perovskite film by four-point probe method, Figure 1A shows the electrode structure.

a. Connect the four electrodes with a Keithley 4200 semiconductor analyzer using a probe station.
b. As shown in Figure 1A, the voltages of the four electrodes are named \( V_1 = 0 \) V, \( V_2 \), \( V_3 \) and \( V_4 \), respectively.
c. After the four-point probe measurement, identify the thicknesses of samples by atomic force microscopy (AFM).

△ CRITICAL: The measured \( V_4 \) should be more than 1 V and less than 20 V by adjusting the maximum value of sweep current \( I \).

5. FETs measurement.

Figure 1B shows the electrode structure of bottom-gate bottom-contact FET. Measure the FETs using a B2912A Precision Source.

a. For room-temperature (about 25°C here) measurement, place the samples on the insulated stage of probe station in glovebox.
b. Connect the FETs with a B2912A Precision Source using a probe station in glovebox.
c. Measure the transfer characteristics.
   i. Set the gate voltage (\( V_{GS} \)) sweeps from 40 V to –40 V and back to 40 V (step is –1 V, sweep speed is 25 V s\(^{-1}\)).
   ii. Set the drain voltage (\( V_{DS} \)) as –40 V.
d. Measure the output characteristics.
   i. Set the \( V_{DS} \) sweeps from 0 V to –40 V and back to 0 V (step is –1 V, sweep speed is 20 V s\(^{-1}\)).
ii. Set the $V_{GS}$ as 0, –20 and –40 V, respectively.

△ CRITICAL: Carry out all measurement processes under dark conditions.

△ CRITICAL: Conduct the transfer and output characteristics twice, and save the result of the second measurement, because the light exposure before the test will affect the results of the first measurement.

6. TEs measurement.
To measure the Seebeck coefficients of doped (PEA)$_2$SnI$_4$ films, we use a homemade thermoelectric measurement system, as shown in Figure 2A.²
   a. Connect the pads of on-chip stripe heater, hot end and cold end with probes of Janis ST-100 cryostat in an Ar-filled glovebox.
   b. Close the exhaust valve of the cryostat before transferring it out from the glovebox to protect perovskite from the invasion of air.
   c. Measure the resistances ($R$) of hot end and cold end under 302, 304 and 306 K using B2912A Precision Source and temperature controller.
   d. Link the on-chip stripe heater to a DC stabilized power supply with external wires, and apply a voltage ($V_{heater}$) to the heater.
   e. Change $V_{heater}$ from 4 V to 10 V (step = 1 V).
      i. Measure the corresponding $\Delta V$ using Keithley nano voltmeter.
      ii. Measure the resistances of hot end and cold end by B2912A Precision Source.

Note: The TEs measurement aims to obtain the relationship between temperature difference ($\Delta T$) and thermoelectric potential difference ($\Delta V$), as shown in Figure 2F.

△ CRITICAL: Measure all Seebeck coefficients at RT in a high vacuum (< 10⁻⁵ mbar) using Janis ST-100 in the dark.

EXPECTED OUTCOMES
The important outcomes of the present protocols are illustrated below:

Conductivity measurement: The relationship of $I$ and $V_3 - V_2$ of doped perovskite films can be obtained by four-point probe method (see Figure 3A), and the slope is the conductance ($G$) of
perovskite film. The conductivity \( \sigma = 40 \times 10^{-3} \) cm\(^{-1}\) = 4 \( \times \) G [S]/(1000 \( \times \) d [nm] \( \times \) 10\(^{-7}\)), d (\( \sim \)45 nm) is the thickness of film which is identified by AFM. The doping ratio-dependent conductivity is shown in Figure 3B which directly demonstrates the occurrence of doping.

**FETs measurement:** The measured transfer and output characteristics of FETs based on doped (PEA)\(_2\)SnI\(_4\) films are shown in Figure 4A and 4B. The on/off ratio \( (I_{\text{on}}/I_{\text{off}}) \) can be extracted from Figure 4A, \( I_{\text{on}} \) and \( I_{\text{off}} \) are on-state and off-state currents, which are the maximum and minimum currents of transfer curves, respectively. Here, the \( I_{\text{on}} \) and \( I_{\text{off}} \) are corresponding to the currents at \( V_{\text{GS}} \) of 40V and −40V, respectively. According to the \( I_{\text{DS}}^{0.5} \) versus \( V_{\text{GS}} \) curves (Figure 4C), the mobility (\( \mu \)) and threshold voltage (\( V_{\text{TH}} \)) can be extracted from Figure 4C according to the equations

\[
\mu = \frac{2L}{CW} \frac{\sigma N_{\text{eff}}^{0.5}}{V_{\text{GS}}}
\]

and

\[
I_{\text{DS}} = C \mu \frac{L}{W} (V_{\text{GS}} - V_{\text{TH}})^2,
\]

respectively.\(^3\) \( L \) and \( W \) are length and width of the FETs channel, respectively. The fitted range of \( V_{\text{GS}} \) is from −40V to −30V. The doping ratio-dependent performance parameters are shown in Figure 4D.

**TEs measurement:** The measured temperature-dependent resistances of hot end and cold end are shown in Figure 5A. Temperature coefficient of resistance (TCR) can be extracted by formula: TCR [K\(^{-1}\)] = dR/(R\(_{30K}\)dT). R and T are real-time resistance and temperature, respectively. As shown in Figure 5B, resistances increase with increased \( V_{\text{water}} \), the corresponding temperatures of hot end and cold end can be calculated according to the equation

\[
T = 302 + \frac{R - R_{30K}}{\text{TCR} \times R_{30K}},
\]

\( R \) is the measured resistance.
at temperature of $T$, and $R_{302K}$ is the measured resistance at 302 K. The temperature difference between hot end and cold end can also be calculated (Figure 5B). The measured $\Delta T$ versus $\Delta V$ is shown in Figure 5C, the slope of the fitted line is the Seebeck coefficient ($S = \Delta V/\Delta T$). The power factor ($PF = S^2\sigma$) can be calculated from $S$ (Figure 5C) and $\sigma$ (Figures 3B), these parameters are shown in Figure 5D.

LIMITATIONS
The conductivity of pristine (PEA)$_2$SnI$_4$ film is too low to measure the Seebeck coefficient accurately.

TROUBLESHOOTING

Problem 1
The measured conductivity is much higher than the expected value (device characterization step 4).

Potential solution
The much higher conductivity is contributed to the oxidation of Sn$^{2+}$. The possible reasons are that SnI$_2$, perovskite solution or device is stored too long.

Solution 1: Use newly purchased SnI$_2$.

Solution 2: Prepare new solution.

Solution 3: Measure the devices as soon as possible after fabrication.

Figure 5. Outcomes of TEs measurement
Figures C and D are adopted from ref. 1.
(A) Temperature-dependent resistance of hot end and cold end.
(B) Heater voltage dependent resistance, calculated temperature and temperature difference.
(C) Temperature difference ($\Delta T$)-dependent thermoelectric potential difference ($\Delta V$) of doped TEs.
(D) Doping ratio-dependent Seebeck coefficient, conductivity and power factor. The error bars represent the standard deviation.
Problem 2
The on/off ratio of transfer characteristics is much lower than the expected value (device characterization step 5).

Potential solution
The much lower on/off ratio may be caused by that the actual mass ratio differs greatly from the standard value.

Solution 1: Weigh SnI₂ and PEAI with mass ratio of 0.748 strictly.

Solution 2: Weigh SnI₄ and PEAI with mass ratio of 1.257 strictly.

Problem 3
The Seebeck coefficient of TE does not decrease with the increase of conductivity, or the resistance versus temperature of hot end and cold end (Figure 5A) is not perfectly linear (device characterization step 6).

Potential solution
Solution 1: Reconnect the probes to the electrodes.

Solution 2: Wait 20 min for the temperature to be stable before measuring resistance.

Problem 4
Imperfect perovskite film deposition may be attributed to the dirty atmosphere in glovebox (such as the existence of organic solvent vapor) or the temperature of precursor is much higher than room temperature (about 25°C here) (device fabrication step 3).

Potential solution
Solution 1: Clean the glovebox with fresh Ar gas for at least 10 min.

Solution 2: Place the precursor away from heat for half an hour.

Problem 5
No/flawed measurement (FET measurement) (device characterization step 5).

Potential solution
Solution 1: If the currents of transfer or output measurements are very small, i.e., no FETs current, check the connection between probes and electrodes, and connection between probe station and Precision Source.

Solution 2: If the currents of transfer or output curves are much higher than the typical curves (as shown in Figure 4A and 4B), check that if the measurement environment is dark.

RESOURCE AVAILABILITY

Lead contact
Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Yuanyuan Hu (yhu@hnu.edu.cn).

Materials availability
This study did not generate new unique reagents.

Data and code availability
This study did not produce datasets/code.
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AUTHOR CONTRIBUTIONS
Conceptualization, Y.L., Y.H.; Investigation, Y.L., P.C., X.Q., J.G., J.X., H.W., H.X., S.H., M.H., X.W., Z.Z., L.L.; Writing – Original draft, Y.L., Y.H.; Writing – Review & Editing, Y.L., L.J., Y.H.; Supervision, L.J., Y.H.

DECLARATION OF INTERESTS
The authors declare no competing interests.

REFERENCES
1. Liu, Y., Chen, P.-A., Qiu, X., Guo, J., Xia, J., Wei, H., Xie, H., Hou, S., He, M., Wang, X., et al. (2022). Doping of Sn-based two-dimensional perovskite semiconductor for high-performance field-effect transistors and thermoelectric devices. iScience 25, 104109. https://doi.org/10.1016/j.isci.2022.104109.
2. Wei, H., Chen, P., Guo, J., Liu, Y., Qiu, X., Chen, H., Zeng, Z., Nguyen, T., and Hu, Y. (2021). Low-cost nucleophilic organic bases as n-dopants for organic field-effect transistors and thermoelectric devices. Adv. Funct. Mater. 31, 2102768. https://doi.org/10.1002/adfm.202102768.
3. Liu, Y., Chen, P.-A., and Hu, Y. (2020). Recent developments in fabrication and performance of metal halide perovskite field-effect transistors. J. Mater. Chem. C Mater. 8, 16691–16715. https://doi.org/10.1039/D0TC03693E.
4. Haque, M.A., Kee, S., Villalva, D.R., Ong, W.-L., and Baran, D. (2020). Halide perovskites: thermal transport and prospects for thermoelectricity. Adv. Sci. 7, 1903389. https://doi.org/10.1002/advs.201903389.