Tin Selenide Molecular Precursor for the Solution Processing of Thermoelectric Materials and Devices


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ABSTRACT

In the present work, we report a solution-based strategy to produce crystallographically textured SnSe bulk nanomaterials and printed layers with optimized thermoelectric performance in the direction normal to the substrate. Our strategy is based on the formulation of a molecular ink that can be continuously decomposed to produce a SnSe powder or printed into predefined patterns. The ink formulation and decomposition conditions are optimized to produce pure phase SnSe. The printed layer and the bulk material obtained after hot press display a clear preferential orientation of the crystallographic domains, with the $a$ crystal direction parallel to the pressure axis and normal to the substrate. Such textured nanomaterials present highly anisotropic properties, with best thermoelectric performance in plane, i.e. in the directions parallel to the substrate, which coincide with the crystallographic $bc$ plane of SnSe. This is an unfortunate characteristic because thermoelectric devices are designed to create/harvest temperature gradients in the direction normal to the substrate. We demonstrate that this limitation can be overcome with the introduction of small amounts of tellurium in the precursor ink. The presence of tellurium allows reducing the band gap, increase both charge carrier concentration and mobility, especially cross plane, with a minimal decrease of the Seebeck coefficient. These effects translate into record out of plane ZT values at 800 K.
INTRODUCTION

Solid state thermoelectric (TE) devices offer a direct and solid state means of conversion between thermal and electrical energy, which makes them extremely appealing for a wide range of applications.\textsuperscript{1-6} However, the relatively low energy conversion efficiency and high manufacturing cost of current TE devices, which are in most cases designed for cooling applications, makes them cost-efficient only in few niche markets.\textsuperscript{7} Towards improving cost-efficiency of TE devices, it is imperative to: i) implement lower cost fabrication processes; ii) optimize device parameters for each particular application to maximize efficiency and minimize the amount of used material; iii) develop high performance and lower cost TE materials.

Thermoelectric performance is generally quantified using an adimensional figure of merit, $Z_T = \sigma^2 ST/\kappa$, where $\sigma$, $S$, $T$ and $\kappa$ are the electrical conductivity, Seebeck coefficient, absolute temperature and thermal conductivity, respectively. Among the different families of TE materials proposed, some two dimensional chalcogenides exhibit the best TE performance.\textsuperscript{8-12} Bi$_2$Te$_3$-based alloys provide the highest $Z_T$ values at temperatures around ambient, up to 1.94 at 420 K,\textsuperscript{13} and dominate the TE market.\textsuperscript{14-18} On the other hand, SnSe single crystals have recently achieved unprecedented record $Z_T$ values in the medium-high temperature range, 2.6 at 923K.\textsuperscript{10,19-20} SnSe has a layered crystal structure with weak Van der Waals bonds along the $a$ axis and tight covalent bonds along the $bc$ plane, which results in highly anisotropic transport properties and an impressively low lattice thermal conductivity. Nonetheless, the high production cost and poor mechanical properties of SnSe single crystals limit their use in real applications. All of these have sparked much interest in producing polycrystalline SnSe with TE performance approaching that of SnSe single crystals. Owing to the anisotropic properties of the material, the optimization of polycrystalline SnSe generally requires producing crystallographic textured samples.\textsuperscript{21-32} In this direction, while severe plastic deformation techniques are conventionally used to produce textured polycrystalline materials,\textsuperscript{33-34} spark plasma sintering and hot press approaches, more commonly used to consolidate TE polycrystalline materials, are also able to produce textured materials when using an open dye to induce extrusion or when incorporating a liquid phase in the process.\textsuperscript{12-13,35-39}

Beyond engineering TE materials with improved performance and lower cost, novel strategies to fabricate TE devices that are less labour-intensive and which allow a more rational use of the TE material need to be developed. One potential alternative strategy is ink-
jet printing. The main advantages of printing techniques are low cost, potential to produce shape adaptable or flexible devices, control over the thickness of the TE material and high material use efficiency. While printing strategies are currently well developed and used in a large number of applications, their implementation in new technologies strongly relies on the formulation of proper functional inks.

We report here a thiol-free SnSe molecular ink, which can be used as precursor to produce bulk nanocrystalline SnSe or can be directly printed into SnSe layers. We study the decomposition conditions and demonstrate the possibility to produce pure phase SnSe at moderate temperatures. We further analyse here the processing conditions necessary to obtain crystallographically textured SnSe bulk nanomaterials and layers and characterize their anisotropic TE properties. Finally, the TE performance of the material in the direction normal to the layer substrate is optimized by including small amounts of tellurium within the ink.
**EXPERIMENTAL SECTION**

**Chemicals:** Tin chloride (SnCl\(_2\), 98%) and selenium dioxide (SeO\(_2\), 99.8%) were purchased from Acros Organics. Tri-n-octylphosphine (TOP, C\(_{24}\)H\(_{51}\)P, 97%), oleic acid (OAc, C\(_{18}\)H\(_{34}\)O\(_2\), 90%) and oleylamine (OAm, C\(_{18}\)H\(_{37}\)N, ≥ 98%) were purchased from Sigma-Aldrich. Sodium tellurite (Na\(_2\)TeO\(_3\), 99.5%) was purchased from Fisher. Analytical grade chloroform and ethanol were ordered from various sources. All chemicals were used as received unless specifically noted.

**SnSe ink:** Within an argon-filled glove box, 5.76 g SnCl\(_2\) (30 mmol) and 3.33 g SeO\(_2\) (30 mmol) were weighted and placed inside a glass bottle. Then 150 mL OAm and 20 ml TOP were added inside the bottle. The mixture was subsequently sonicated for 20 min until precursors dissolved completely. Small amounts of OAc were included within the ink to produce dendritic SnSe nanostructures.

**SnSe\(_{1-x}\)Te\(_x\) ink:** To produce SnSe\(_{1-x}\)Te\(_x\) (x = 0.01, 0.02, 0.03) precursor inks, 5.76 g SnCl\(_2\) (30 mmol), 3.33 g SeO\(_2\) (30 mmol) and 6.65x g Na\(_2\)TeO\(_3\) were weighted and placed in a glass bottle, where 150 mL OAm and 20 ml TOP was subsequently added. The mixture was sonicated for 20 min until all precursors dissolved completely.

**SnSe ink decomposition:** The SnSe precursor ink was continuously injected into a preheated glass flask (420 °C), where it immediately decomposed. The flask was naturally cooled down to room temperature (RT) and the crystalline product was collected by dispersion in chloroform and precipitation with ethanol. Dispersion/precipitation steps were repeated three times using chloroform and ethanol aided by centrifugation at 7200 rpm for 5 min.

**Bulk material consolidation:** SnSe particles were thermally annealed at 500 °C (heating rate = 10 ºC/min) for 60 min inside a tube furnace with argon flow to remove organic residues. After cooling to RT, the annealed material was grounded in a mortar and subsequently loaded into a graphite die. The die was then transferred to a custom-made hot press system inside the glove box, where it was heated to 500 °C by using an induction coil. The die was held at this temperature for 5 min under 80 MPa pressure. Afterward, the pressure was released and the die was naturally cooled down to RT. The obtained cylindrical pellets (Ø 8 mm × 12 mm) were cut in rectangular bars in two directions: along the pressure axis (cross-plane direction) and normal to this axis (in-plane direction).
**Printed layers:** The SnSe molecular ink was printed on a graphite foil using an ink jet nozzle. The graphite foil was then annealed on a hot plate at 420 °C for 5 min within an argon-filled glove box. Afterward, the foil was hot pressed at 500 °C for 3 min under 80 MPa pressure.

**Structural and chemical characterization:** The particle size and morphology were characterized by transmission electron microscopy (TEM, ZEISS LIBRA 120), working at 120 kV and field-emission scanning electron microscopy (SEM, Zeiss Auriga) operating at 5.0 kV. High resolution TEM (HRTEM) images and scanning TEM (STEM) studies were conducted on a FEI Tecnai F20 field emission gun microscope operated at 200 kV with a point-to-point resolution of 0.19 nm, which was equipped with high angle annular dark field (HAADF) and Gatan Quantum electron energy loss spectroscopy (EELS) detectors. Elemental analysis was performed using an Oxford energy dispersive X-ray spectrometer (EDX) combined with the Zeiss Auriga SEM working at 20.0 kV. X-ray diffraction analyses (XRD, 20: 5°-80°, scanning rate was set at 5°/min) were carried out on a Bruker AXS D8 Advance X-ray diffractometer with Ni-filtered Cu-Kα radiation (λ= 0.15406 Å), operating at 40 mA and 40 kV. X-ray photoelectron spectroscopy (XPS) was performed on a SPECS system equipped with a Phoibos 150 MCD-9 detector, working at 150 mW with an Al anode XR50 source. Fourier transform infrared spectroscopy (FTIR, Alpha Bruker) was carried out with a platinum attenuated total reflectance single reflection module. The surface topology was measured by atomic force microscopy (AFM, XE 100 Park System Corp.) Scans were conducted in non-contact mode with a silicon Tap300Al-G cantilever (Budget Sensors, spring constant of ~40 N/m and resonant frequency of ~300 kHz). AFM images were analysed in the XEI software (Park System Corp).

**Thermoelectric characterization:** Seebeck coefficients were measured with a static DC method. Electric resistivity data was obtained using a standard four probe method. Electric resistivity and Seebeck coefficients were measured simultaneously in a LSR-3 LINSEIS system in the temperature range from 323 to 803 K under a helium atmosphere. Bearing in mind the measurement precision and system accuracy, an error of ca. 5% in the measurement of Seebeck coefficient and electrical conductivity was estimated. A Xenon Flash Apparatus was used to measure the thermal diffusivities (D) of all samples with accuracies better than 6%. Thermal conductivities were then calculated by the relation κ = C_pDρ, where C_p is the heat capacity that was estimated from the Dulong–Petit law, D is the measured thermal diffusivity and ρ is the mass density that was measured using the Archimedes’ method.
RESULT AND DISCUSSION

To prepare a SnSe molecular ink, the tin and selenium precursors and the solvent were selected taking into account four main parameters: i) minimize cost; ii) direct the crystal morphology toward obtaining planar structures that facilitate posterior assembly into textured nanomaterials; iii) reach a compromise between solvent volatility, which has implications in toxicity and ink stability, and decomposition temperature, which is a key parameters determining production costs; iv) reduce toxicity, avoiding the use of thiols and hydrazine. Taking into account these points, a SnSe ink was prepared by dissolving SnCl$_2$ and SeO$_2$ in a combination of OAm and TOP. OAm played a double role, it reduced Se$^{4+}$ to Se$^0$ and it coordinated to Sn$^{2+}$ to form a Sn-OAm complex, Sn(R-NH)$_2$.$^{40-42}$ TOP coordinated with Se$^0$ to yield TOPSe$_4$ (see Figure S1 in the supporting information, SI).

To analyse the product of its decomposition, the ink was dropped onto a substrate heated at 420 °C. Upon reaching the heated substrate, the ink was rapidly decomposed and a black powder was produced. Large amounts of powder could be obtained by continuously injecting/spraying the ink toward a heated receptacle/support (Figure S1). TEM and SEM characterization of the powder obtained from the decomposition of the ink showed the presence of square-like plates with a lateral size of 4±1 µm and a thickness of 90±20 nm (Figure 1a,b). HRTEM and XRD analyses demonstrated the powder to be highly crystalline and to display a unique crystallographic phase that matched that of orthorhombic SnSe (JCPDS NO. 00-048-1224, Pnma space group, Figure 1c,e). From the XRD pattern, the relatively strong intensity of the 2θ=31.0˚ diffraction peak indexed as (400), indicated a preferential growth in the $bc$ plane, i.e. the plane perpendicular to the [100] crystallographic direction. UV-Vis spectrum showed the SnSe powder to has an indirect band gap at 0.96 eV (Figure S2). XPS analysis of SnSe displayed two Sn 3d peaks at 494.9 eV (Sn 3d$_{3/2}$) and 486.4 eV (Sn 3d$_{5/2}$), which matched well with a Sn$^{2+}$ environment (Figure 1f). Besides, Se 3d$_{3/2}$ and Se 3d$_{5/2}$ peaks located at 54.4 eV and 53.5 eV evidenced the presence of a Se$^{2-}$ oxidation state. EDX chemical analysis showed the SnSe powder to be slightly Sn rich, with a composition ratio Se/Sn = 0.95 (Figure S3). EELS chemical composition maps displayed a homogeneously distribution of both Sn and Se within each particle and from particle to particle (Figure 1d).

To obtain single phase SnSe, the proper adjustment of the nominal element ratio, Sn/Se, and decomposition temperature was fundamental. When increasing the nominal amount of Sn in the ink formulation, a combination of Sn and SnSe phases was obtained upon decomposition.
at 420 °C (Figures 2a). On the other hand, when using a nominal ratio Sn/Se <1, a combination of SnSe and SnSe$_2$ was produced. Using a nominal Sn/Se=0.5 and decreasing the decomposition temperature to 360 °C, pure-phase SnSe$_2$ could be produced (Figure 2a). Figure S4 shows XRD patterns of the materials obtained at different temperatures using a nominal element ratio Sn/Se=1.

Figure 1. a) Representative TEM and b) SEM micrographs of square-like SnSe nanostructures, and a structure model of an individual nanoplate. c) HRTEM micrograph of a SnSe nanoplate, magnified detail of the orange squared region and its corresponding power spectrum. The SnSe lattice fringe distances were measured to be 0.304, 0.207 nm and 0.302 nm, at 43.53, and 87.51 °, which was interpreted as the orthorhombic SnSe phase, visualized along its [100] zone axis. d) EELS chemical composition maps obtained from the red squared area of the STEM micrograph. Individual Sn M4,5-edges at 485 eV (red) and Se L2,3-edges at 1436 eV (green) as well as its composite. e) XRD pattern of SnSe. f) Sn 3d and Se 3d regions of the XPS spectrum of SnSe.

TOP coordinated with Se to yield TOPSe. Without TOP in the precursor solution, SnSe nanostructures could be also obtained, but the ink decomposition required reaction temperatures above 500 °C. Additionally, the aspect ratio of the SnSe nanostructures produced in the absence of TOP was strongly reduced (Figure S5). When adding small amounts of TOP to the solution, the ink decomposition temperature could be reduced down to 420 °C for $V_{TOP}/V_{OAm} > 0.13$, which we associated to the relatively high reactivity of the
formed TOPSe. On the other hand, when replacing OAm by octadecene, SnSe was not formed, probing the important role of OAm in reducing SeO₂ and complexating with Sn²⁺.

Figure 2. XRD pattern of the powder produced from the decomposition at different temperatures of an ink containing different ratios of Sn/Se. A detail of the XRD pattern around 2θ=31º is displayed for clarity. b) SEM micrographs of SnSe plates with orthorhombic structure and SnSe₂ plates with hexagonal phase obtained when decomposing an ink containing Sn/Se=1 at 420 °C and an ink containing Sn/Se=0.5 at 360 °C, respectively.

When adding OAc to the precursor ink, a significant change of the geometry of the produced SnSe particles was observed. Figure 3 shows the evolution of the particle shape with the OAc/OAm ratio. At relatively high OAc concentrations, OAc/OAm>0.2, dendritic structures were produced, which we associate with a selective binding of the carboxylic group in OAc to particular facets during crystal growth. Through AFM analysis, the thickness of plates and dendritic structures supported on a substrate was measured to be in the range 100-150 nm, which is slightly larger than values obtained from SEM statistics (Figure 3e)

The SnSe powder obtained from the ink decomposition was thermally annealed at 500 °C for 60 min inside a tube furnace with argon flow to remove residual organic ligands. The annealed crystals maintained the original plate geometry and showed no appreciable growth. The annealed powder was subsequently loaded into a graphite die and hot pressed at 500 °C for 5 minutes under a uniaxial pressure of 80 MPa. A cylindrical pellet with a relative density of ca. 90% was finally obtained (Figure 4a).
Figure 3. a) Schematic illustration of the shape evolution for square-like and dendritic crystals. b) SEM micrographs of the morphology evolution with increasing OAc/OAm ratios. Dendritic nanostructures were obtained when OAc/OAm > 0.2. Scale bars = 2 µm. c) AFM topography images of a square-like and a dendritic nanostructure and height profiles taken from the displayed red line.

The hot pressed material displayed a clear crystallographic texture, with the SnSe [100] crystal direction oriented along the pressure axis, as shown by XRD analysis of the pellet hold with the diffraction plane coincident and normal to the pressure axis (Figure 4b). This crystallographic orientation is consistent with the [100] being the softer crystallographic direction in SnSe. SEM micrographs showed the pellet to have a layered structure, with layers of material assembling normal to the pressure axis, consistent with XRD results (Figure 4c).

To determine the influence of the shape of the SnSe particles on the crystallographic texture of the consolidated material, we hot pressed SnSe particles with 100 nm average size and 50 nm thickness produced by a reported method\textsuperscript{29} (Figure S8a). The hot press of these less asymmetric particles in the same conditions as the SnSe plates resulted in polycrystalline
materials with no significant texture (Figure S8b,c), proving the influence of the initial particle geometry in the texture of the final polycrystalline material.\textsuperscript{12-13}

\begin{figure}
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\includegraphics[width=\textwidth]{figure4}
\caption{a) Schematic illustration of the process of consolidation of the SnSe powder into a cylindrical pellet. A SEM micrograph of the annealed SnSe nanopowder and an actual image of consolidated pellet are included in the scheme. b) XRD pattern of the SnSe pellet laid along the in-plane and cross-plane directions. c) Representative top view and cross section SEM micrographs of a SnSe pellet,}
\end{figure}

To demonstrate the potential of the SnSe molecular ink to produce printed SnSe layers/patterns, the ink was printed on a flexible graphite foil using an ink jet nozzle. The graphite foil was then annealed on a hot plate at 420 °C for 5 min and additionally hot pressed at 500 °C for 3 min under 80 MPa pressure. SEM and XRD analyses of the printed layer demonstrated it to contain SnSe plates oriented parallel to the substrate (Figure 5, S9).
The TE properties of the polycrystalline SnSe obtained from the ink decomposition were characterized in two directions: cross plane ($//), i.e. parallel to the pressure axis, and in plane ($\perp$), i.e. normal to pressure axis. Electrical conductivities measured in plane ($\sigma_{\perp}$), were higher than those measured cross plane ($\sigma_{//}$), with $\sigma_{\perp}/\sigma_{//} = 3.30$. This result is consistent with the much higher charge carrier mobilities in the $bc$ crystal plane of SnSe when compared with its $a$ direction.

Positive Seebeck coefficients were measured in all the temperature range, consistent with the p-type semiconductor character of undoped SnSe. As expected from the minor dependence of this parameter on scattering, similar values of the Seebeck coefficient were measured in both directions, $S_{\perp} \approx S_{//}$. The slightly higher values systematically obtained cross plane could be ascribed to an energy filtering mechanism at grain boundaries, i.e. a preferential scattering of low energy carriers at the plate interfaces, as previously reported for layered materials.\textsuperscript{12-13}

SnSe nanomaterials displayed very low thermal conductivities in both directions, but slightly higher than those obtained from single crystals, most probably due to a certain degree of oxidation.\textsuperscript{60} Significantly lower thermal conductivities were obtained cross plane when compared with in plane, $\kappa_{\perp}/\kappa_{//} = 1.75$ at 750 K, which was again consistent with the preferential orientation of the plates lying normal to the pressure axis.

Overall, the highest ZT values, up to ZT = 0.5 at 770 K, were obtained in plane. This result is consistent with measurements on single crystals and previous reports,\textsuperscript{10, 21, 23, 46-47} but it is
unfortunate toward the development of printed SnSe-based modules that target the generation/harvesting of cross plane temperature gradient.

To further promote the TE performance of polycrystalline SnSe layers, small amounts of Te were added to the ink in replacement of equivalents amounts of Se. The polycrystalline material obtained from the decomposition of the Te-containing ink, SnSe$_{1-x}$Te$_x$, was characterized by a slightly reduced band gap (Figure S2), a slightly larger charge carrier concentration, $n_H$, and most important a significantly increased charge carrier mobility, particularly cross plane (Figure S11). Best TE performance was obtained from the material containing a 2 at% of Te, SnSe$_{0.98}$Te$_{0.02}$ (Figure 7). This material displayed significantly higher electric conductivities than SnSe without a major reduction of the Seebeck coefficient.
and a minor increase of the total thermal conductivity, associated with the increase of its electronic component. Overall, TE figures of merit up to three-fold larger than those measured for SnSe were obtained. Most important, the highest TE figures of merit were obtained cross plane, reaching $ZT= 1.05$ at 805 K, which is the highest value reported at this temperature and in this direction for polycrystalline SnSe. This excellent performance was related to the presence of Te facilitating charge transport especially cross plane, which translated into a significant increase of the charge carrier mobility.

Figure 7. Temperature dependence of (a) electrical conductivity, $\sigma$; (b) Seebeck coefficient, $S$; (c) power factor, $S^2\sigma$, PF; (d) total thermal conductivity, $\kappa_{total}$; (e) lattice thermal conductivity, $\kappa_L$; and (f) TE figure of merit, $ZT$ of a SnSe$_{0.98}$Te$_{0.02}$ pellet measured in two directions, in-plane (⊥, open symbols) and cross-plane (∥, solid symbols).
CONCLUSION

We detailed a fast solution-based approach to produce crystallographic textured SnSe bulk nanomaterials and printed layers. The molecular precursor solution was prepared directly by dissolving ionic Sn and Se species in a thiol-free and nontoxic solvent. Pure phase SnSe powder was obtained by decomposing the molecular precursor at 420 °C. The composition, crystal phase and shape of the produced SnSe nanostructures could be tuned by modifying the nominal elemental ratio, the decomposition temperature and the use of additional surfactants. Crystallographic textured SnSe bulk nanomaterials and layers were obtained after hot-pressing the ink decomposition products. These materials showed moderate TE performances cross plane which was unfortunate for the design a TE devices that generate/harvest temperature gradients in the direction normal to the substrate. The SnSe TE performance was significantly improved, up to a threefold, by introducing small amounts of Te during ink formulation. The presence of this small amount of Te resulted in an important increase of electrical conductivity cross plane associated to an increase of charge carrier concentration and especially mobility with a minor variation of the Seebeck coefficient. The presence of 2 at% of Te in SnSe$_{0.98}$Te$_{0.02}$ finally translated into record cross plane ZT values at 800 K for polycrystalline SnSe.


