High-performance, air-stable, n-type thermoelectric films from a water-dispersed nickel-ethenetetrathiolate complex and ethylene glycol

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COMMUNICATION

High-performance, air-stable, n-type thermoelectric films from a water-dispersed nickel-ethenetetrathiolate complex and ethylene glycol

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An efficient solution-based process for the fabrication of air-stable n-type thermoelectric films is reported. A nickel-ethenetetrathiolate complex was synthesized in dimethyl formamide and used to produce a dispersion in an aqueous medium. The film, fabricated via a simple drop-casting method with ethylene glycol, exhibited a remarkably high thermoelectric n-type power factor of 33 μW m^{-1} K^{-2}.

Flexible thermoelectric generators, which convert waste heat into electricity, are convenient and low-cost energy-harvesting devices that have recently received an increasing amount of attention.[1] The performance of thermoelectric materials can be evaluated using the figure of merit $ZT = S^2\sigma T/\kappa$ or the power factor $PF = S^2\sigma$, where S, σ, T, and κ are the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively. Organic and organometallic semiconducting materials are particularly suited for the use as thermoelectric materials due to their very low thermal conductivity, which offers significant advantages not only in realizing high efficiencies, but also in generating a temperature gradient in thermoelectric films.[2] Moreover, relatively large such films can be fabricated easily using a low-cost solution-based process. p-Type and n-type organic semiconducting materials are of vital importance for the generation of flexible thermoelectric modules. Over the past decade, solution-processable high-performance p-type organic materials made from poly(3,4-ethylenedioxythiophene) (PEDOT) derivatives have been intensively studied.[3] However, the development of n-type materials, which are equally important for the advancement of flexible thermoelectric modules, has been hampered partially due to their instability upon doping with an n-dopant under atmospheric conditions.[4]

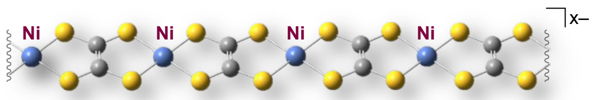

Fig. 1 Structure of nickel-ethenetetrathiolate (Ni-ETT) with a planar π-conjugated backbone (carbon: grey, sulfur: yellow, and nickel: blue).

One promising example of an n-type organometallic semiconductor that can be used as a thermoelectric generator are nickel-ethenetetrathiolate (Ni-ETT) complexes (Fig. 1).[5,6] Ni-ETT possesses a one-dimensional polyanionic π-conjugated system and, although it exhibits high air-stability and n-type thermoelectric behavior, it is insoluble in virtually all common organic solvents. Thus, methods to efficiently process Ni-ETT in solution in order to produce films have remained scarce until recently.[7-9] Toshima and co-workers reported a method to prepare dispersed Ni-ETT in *N*-methyl-2-pyrrolidone (NMP) by adding the surfactant dodecyltrimethylammonium bromide during the synthesis of Ni-ETT. The dispersed solution of Ni-ETT can then be drop-cast with poly(vinyl chloride) to give an n-type composite film (PF = 4.7 × 10^{-4} μW m^{-1} K^{-2} at room temperature).[8] Yee and co-workers carefully optimized the conditions of the synthesis of Ni-ETT and subsequently generated a dispersion by mechanically mixing polyvinylidene difluoride (PVDF) and Ni-ETT in dimethyl sulfoxide (DMSO) using a ball-mill. The resulting dispersion can then be drop-cast to furnish an n-type composite film that exhibits a high power factor (PF = 23 μW m^{-1} K^{-2}) at room temperature.[9] However, n-type composite films fabricated via these solution-based processes tend to suffer from the impact of the insulating properties of the additives that are used. Thus, we envisioned that a solution-processed film based on Ni-ETT where any insulating additives have been removed would be more suitable for the fabrication of high-performance thermoelectric films.

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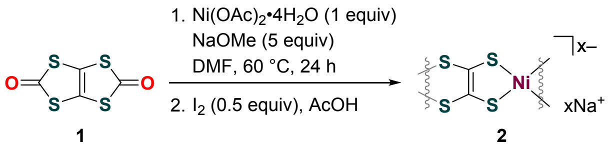
Herein, we report our results on the development of an efficient solution-based process that affords n-type Ni-ETT films with a remarkably high thermoelectric power factor (PF = 33 μW m^{-1} K^{-2}) and high stability under atmospheric conditions.



Scheme 1 Synthesis of Ni-ETT **2** in DMF.

First, we examined the reaction conditions for the synthesis of Ni-ETT **2** (Scheme 1). Even though methanol is usually used as the standard solvent for this reaction,[6] we chose dimethylformamide (DMF) as the corresponding low-molecular-weight complexes exhibit good solubility in DMF and because the reactivity of methoxide ions may potentially be enhanced in DMF.[5,10] When we examined the reaction of monomeric precursor **1** with sodium methoxide in DMF under a nitrogen atmosphere, the solution gradually turned black without noticeable formation of insoluble aggregates, even after a partial oxidation with iodine. In contrast, the reaction performed in methanol almost quantitatively generates insoluble solids including sub-millimeter precipitates of **2**.[9] The Ni-ETT product **2**, obtained following the reaction in DMF, was carefully purified via repeated decanting with methanol, water, and DMSO. The resulting solid was subsequently sonicated in water to give a black aqueous dispersion (Fig. 2a). Dynamic light scattering (DLS) measurements demonstrated that **2** is well-dispersed in water and that the average particle size is ~190 nm. In contrast, the reported average particle size for the dispersion of PVDF/**2** in DMSO, which was prepared with a ball mill, is 650 nm.[7]

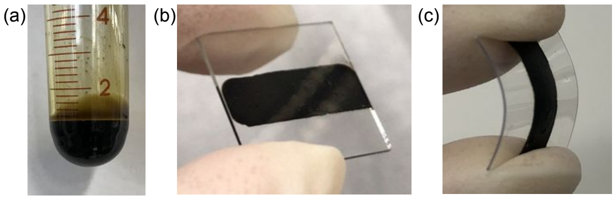


Fig. 2 Images of (a) an aqueous dispersion of **2** as well as the drop-cast films on (b) glass and (c) PET substrates.

With the aqueous dispersion of **2** in hand, we next examined the formation of films under atmospheric conditions. For that purpose, the dispersion of **2** was drop-cast onto a glass substrate, dried at 70 °C, and further annealed at 210 °C (30 min) to give a black film with a thickness of 6.8 μm (Fig. 2b). For comparison, **2** was also synthesized in methanol and a composite film of PVDF/**2** was fabricated via a mechanical process.[9] When compared with the composite film of PVDF/**2** (σ = 24 S cm^{-1}), conductivity measurements demonstrated that the film fabricated from **2** (σ = 39 S cm^{-1}) exhibits enhanced conductivity in the in-plane direction. However, due to the S-σ trade-off relationship,[1] the absolute value of the Seebeck coefficient of the film made from **2** (S = –50 μV K^{-1}) is smaller than that of PVDF/**2** (S = –64 μV K^{-1}). In other words, the films exhibit comparable n-type power factors (PF = 10 μW m^{-1} K^{-2}) at room temperature.

We then explored a new additive to impart excellent thermoelectric n-type properties to the film made from **2**. Solution-processed films of doped PEDOT with poly(4-styrenesulfonate) (PEDOT:PSS) are known to exhibit remarkable performance for a variety of applications when ethylene glycol (EG) is used as an additive.[11] Inspired by these reports, we examined EG as an additive for the fabrication of films of **2**. We prepared a film by drop-casting a mixture of the aqueous dispersion of **2** and EG (10:1, v/v) on a glass substrate, followed by annealing at 210 °C (30 min). While EG (boiling point: 198 °C) should evaporate during the annealing process, we noticed that the surface of the obtained film is smoother than the film prepared without EG. The thermoelectric performance measured in the in-plane direction is summarized in Table 1. The results indicate that the use of EG increases the electrical conductivity (σ = 52 S cm^{-1}). Moreover, the absolute value of the Seebeck coefficient (S = –79 μV K^{-1}) is also higher, which results in a remarkably high n-type power factor (PF = 33 m^{-1} K^{-2}) at room temperature. It should be emphasized here that the film was prepared entirely under atmospheric conditions. This stands in stark contrast to n-doped thermoelectric polymers, which are usually fabricated under an inert atmosphere to avoid contact with O$_2$ and water.[4] The film of **2** exhibits a highly stable power factor, which remains largely undiminished after 10 days under atmospheric conditions (for details, see the ESI). Moreover, the film can be prepared on a flexible polyethylene terephthalate (PET) substrate, which affords a comparably high performance that persists after bending the film five times (Fig. 2c). The PF of the film of **2** achieved here is, to the best of our knowledge, the highest hitherto reported for an air-stable solution-processed n-type thermoelectric film.[4]

Table 1 Thermoelectric performance[a] of n-type films prepared by drop-casting an aqueous dispersion of **2** with or without EG

Entry	Additive	σ [S cm^{-1}]	S [μV K^{-1}]	PF [μW m^{-1} K^{-2}]
1	EG	52	–79	33
2	–	39	–50	10

[a] Measured in the in-plane direction.

In order to obtain deeper insight into the impact of EG on the film-formation process, alternative polar additives such as NMP (boiling point: 202 °C) and diethylene glycol (245 °C) were studied. However, when using these additives, the drop-casting did not produce a smooth film of **2**. Grazing-incidence wide-angle X-ray diffraction (GIWAXD) analysis using synchrotron radiation revealed the ordering of the structures of **2** within the films. Similar results were obtained regardless of whether EG was used as an additive (Fig. 3a). A diffraction halo was observed mainly along the $\mathbf{q}_z$ axis (out-of-plane) at a distance (d_π) of ~3.3 Å. This is indicative of the formation of π-stacking in the vertical direction (face-on) relative to the film (Fig. 3b).

Next, the surface roughness of the thermoelectric films was observed using laser microscopy (Fig. 4). The results indicate that the addition of EG significantly improves the smoothness of the surface of the film, i.e., the obtained root-mean-square height (Sq = 0.107 μm) is smaller than that of the film fabricated without EG (Sq = 0.198 μm). According to these results, we tentatively concluded that the solubility of **2** is slightly increased by the reversible coordination of EG to the sodium ions, which partially fuses the interface between the particles. Given the boiling point of EG (198 °C), it should evaporate almost quantitatively from the surface of the film at 210 °C to yield a high-performance n-type film.[12]

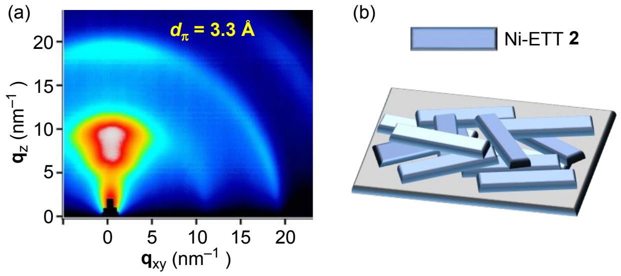


Fig. 3 (a) GIWAXD image of the drop-cast film fabricated from **2** in the presence of EG and (b) schematic illustration of the face-on orientation of **2** within the film.

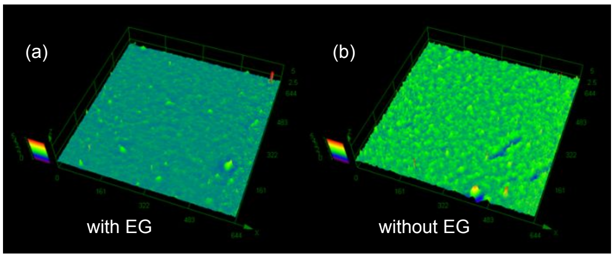


Fig. 4 Laser microscopy Images of the solution-processed films of **2** fabricated (a) with and (b) without EG (6.4 μm × 6.4 μm).

Conclusions

In summary, we have demonstrated that a high-performance n-type thermoelectric film can be fabricated via a simple solution-based process using a water-dispersed nickel-ethenetetrathiolate (Ni-ETT) complex (**2**) and ethylene glycol (EG). The obtained thermoelectric film exhibited a remarkably high n-type power factor (PF = 33 m^{-1} K^{-2}) that persists under atmospheric conditions. This environmentally benign process should contribute to the advancement of flexible thermoelectric modules. Studies to develop further efficient solution-based processes as well as novel π-conjugated metal complexes are currently in progress in our laboratory and the results will be reported in due course.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

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12 Based on NMR and MS measurements of extracts of the films, these should be almost free from residual EG after annealing.

A table of contents entry

A high-performance n-type thermoelectric films were fabricated via an environmentally benign process using a water-dispersed nickel-ethenetetrathiolate (Ni-ETT) and ethylene glycol.