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Nicolas Massonnet, Alexandre Carella, Olivier Jaudouin, Patrice Rannou, Gautier Laval, et al.. Improvement of the Seebeck coefficient of PEDOT:PSS by chemical reduction combined with a novel method for its transfer using free-standing thin films. *Journal of Materials Chemistry C*, 2014, 2 (7), pp.1278-1283. 10.1039/C3TC31674B . cea-03961848

HAL Id: cea-03961848

<https://hal-cea.archives-ouvertes.fr/cea-03961848>

Submitted on 29 Jan 2023

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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Improvement of the Seebeck coefficient of PEDOT:PSS by chemical reduction and method for its transfer using free-standing thin films.

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⁵ *Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX*

DOI: 10.1039/b000000x

A simple method for improving the Seebeck coefficient of PEDOT:PSS up to 161 $\mu\text{V/K}$ is presented and combined with a new process for transferring thick ($> 10 \mu\text{m}$) films of PEDOT:PSS on substrates with various shapes, and in particular on flexible substrates. These reduced transferred films have been used in
¹⁰ combination with a nickel ethylenetetrathiolate coordination polymer to fabricate cheap and flexible heat flux sensors.

Cite this: DOI: 10.1039/c0xx00000x

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Introduction

Lately, thermoelectric (TE) materials and systems have focused intensive research efforts, in particular because they enable a direct harvesting and conversion of heat waste into electricity.¹ However, TE systems meet other applications such as heat flux sensors. The Seebeck coefficient, also called thermopower, characterizes the propensity of the material to detect heat flux. It is expressed as the voltage generated by the temperature difference between a cold side and a hot side. Up to now, mainly inorganic materials have been reported for efficient TE conversion.¹ Among them, a few show worthy performances at room temperature, like bismuth telluride based alloys.² Unfortunately tellurium is scarce, toxic, and requires heavy processes to be shaped into thermoelectric elements, thus it is hardly compatible with large-scale production.³ Organic based compounds have been much less studied, but recent studies have revealed their high potential, and further work will certainly lead to high performance TE materials.⁴⁻⁷ These materials possess tunable properties and can eventually be processed through large-area printing techniques. Their TE properties can be enhanced by hybridization with inorganic particles such as nanorods or nanowires,^{8-10,4,11} carbon nanotubes,¹²⁻¹⁵ or other materials.^{16,17} Among eligible conductive polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) has been widely studied and thus can be considered as a good reference material. It is commercially available in the form of aqueous dispersions stabilized with poly(styrenesulfonate) (PSS). Its Seebeck coefficient is generally measured in the 15-20 $\mu\text{V/K}$ range.³ The relationship between the oxidation level of PEDOT:PSS and its TE properties was recently studied by tuning the doping level of the conjugated polymer in an organic electrochemical transistor.¹⁸ This study showed that the Seebeck coefficient of the polymer increases when it is depleted of its charge carriers. Recently, Crispin et al. reported improved TE properties of PEDOT by controlling the oxidation level of polymer thin films. The monomer 3,4-ethylenedioxythiophene (EDOT) was polymerized with iron(III) *para*-toluenesulfonate ($\text{Fe}(\text{Tos})_3$). Then it was exposed to vapours of tetrakis(dimethylamino)ethylene (TDAE) in order to induce a chemical reduction reaction.¹⁹ This series of works proved that the TE properties of polythiophenes can be widely modulated by controlling their oxidation level. Unfortunately, the methods and the materials considered in these studies are not compatible with large-scale production of functional devices.

In this study we investigate an innovative route for processing PEDOT:PSS into TE devices. We also describe a simple wet process that aims at enhancing the Seebeck coefficient of PEDOT:PSS layers. This straightforward method allowed us to increase the Seebeck coefficient of the polymer up to 161 $\mu\text{V/K}$. The combination of the new deposition process and the reducing

method led to the fabrication of flexible heat flux sensors with improved sensitivity.

Experimental section

Fabrication of PEDOT:PSS thick films

Glass substrates (Corning Eagle XG, 2.5 x 2.5 cm², 1.1 mm thick) were washed with de-ionized water, acetone and ethanol. 0.8 mL of a 1.3 %wt. aqueous solution of PEDOT:PSS Clevios PH1000 purchased from Heraeus was drop-casted onto the surface of the glass. Then samples were left drying under a fume hood for 48 h before being transferred in an oven at 80 °C under vacuum for 24 h to complete water removal. These conditions led to homogeneous polymer films with thicknesses in the 10-12 μm range. The reproducibility of the method was assessed on dozens of samples.

Fabrication of PEDOT:PSS thin films

Thin polymer films (~100 nm) were used to perform optical characterizations. They were obtained by spin-coating a solution of PEDOT:PSS Clevios PH1000 at 1600 RPM for 30 s. Samples were annealed on a hot plate at 100 °C for 5 min then fully dried in an oven at 80 °C under vacuum for 24 h. The film thickness was homogeneous, *i.e.* 80 to 100 nm as measured by AFM.

Transfer of the PEDOT:PSS thick films

PEDOT:PSS samples were shaped into 2D TE elements by cutting with a surgical blade. The pre-cut polymer films were immersed in an ethylene glycol (EG) bath for at least 20 min. After 15 min of submersion, the freely floating TE elements were caught with flat tweezers and rinsed with ethanol before being transferred onto their final support.

Chemical reduction of PEDOT:PSS

Sodium sulfite (Na_2SO_3), sodium borohydride (NaBH_4), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), hydrazine monohydrate (NH_2NH_2 , H_2O), tetrakis(dimethylamino)ethylene (TDAE) and ethylene glycol (EG) were purchased from Aldrich and used without further purification (more information are provided in ESI†). Aqueous solutions (10% wt.) of reducing salts were prepared. Organic reducing reagents were used as received. Droplets of the reducing solutions were deposited on the surface of the samples in order to insure a full coverage of the polymer surface. After 10 min, the samples were dipped in an EG bath for 30 min,²⁰ then rinsed with ethanol and stored overnight at 80 °C under vacuum. TE characterizations were carried out rapidly to prevent ageing. The reducing and doping steps were inverted for some samples, as described in Table I.

Thermoelectric characterization

The TE characterization of the samples was performed with a ULVAC ZEM-3 under helium atmosphere. The temperature gradient and the voltage difference on the surface of the samples were monitored by type C thermocouples. A ohmic electrical contact between the polymer and the thermocouples was obtained by depositing two droplets of silver paste on the surface of the sample. Omitting the silver paste contacts induced measurement errors on reduced samples, leading to overestimated Seebeck values. The electrical conductivity was measured with a four-probe system (Loresta-EP MCP-T360).

Water contact angle measurements

The water contact angle measurement was performed with a Krüss DSA10 MK2 drop shape analysis system. Measurements on PEDOT:PSS thick films were carried out before and after transfer.

UV-Vis-NIR spectroscopy

The absorbance spectra of thin films were recorded on a Varian Cary 5000 spectrophotometer. The absorbance of pristine films was systematically recorded before any chemical treatment to insure fair comparability of the results. Ageing characterizations were performed using a cyclic acquisition mode.

Implementation of materials in flexible heat flux sensors

Different types of heat flux sensors were realized: *p*-metal sensors, made of PEDOT:PSS legs linked to each other with gold electrodes, and *p-n* sensors including in addition a *n*-type conductive polymer. Both *p*-metal and *p-n* devices were fabricated in several versions, with either pristine or reduced PEDOT:PSS legs. Polyethylene naphthalate (PEN, Teijin Teonex Q65FA) was used as the supporting flexible layer.

n-type elements were made of nickel ethylenetetrathiolate coordination polymer: Poly[K_x(Ni-ett)], synthesized as described by Sun et al.²¹ The polymer was drop-casted on the PEN sheet using a shadow mask and dried overnight at 80 °C under vacuum.

p-type TE legs were carved on a dried PEDOT:PSS thick layer with a surgical blade. The polymer films still standing on glass substrates were then dipped in EG. They were pinched with tweezers and aligned along metal or *n* junctions on the PEN sheet and dried overnight at 80 °C under vacuum. Once dried, the PEDOT:PSS legs were chemically reduced by a droplet of reducing agent (TDAE or NaBH₄) as previously described, or left as-deposited for the pristine version. When an aqueous NaBH₄ solution was used for the reduction step, the EG dipping and transfer steps were performed after the reduction to insure an optimal thermopower enhancement. The sensors were then washed with ethanol and dried.

Metal electrodes were deposited by sputtering of Ti (30 nm) / Au (100 nm) through a shadow mask at both ends of the sensor (for *p-n* devices) or between the TE legs (for *p*-metal devices). Afterwards, the sensors were encapsulated with 3M FTB3 film.

The device performances were characterized in air under ambient conditions. Sensors were placed between a cold and a hot aluminium blocks. The cold block was thermalized at 15 °C by a water flow while hot block temperature was set by a heater (see Fig. S1 ESI†).

The temperature gradient was measured by a type K thermocouple placed on the surface of the hot block. The measurements were performed after temperature stabilization.

The voltage across the heat flux sensor was monitored by an Agilent 34410A multimeter.

Results and discussion

Transferring free-standing films of PEDOT:PSS

Dipping layers of PEDOT:PSS in an EG bath triggers several noticeable changes. After a 20 min submersion the electrical conductivity, the mechanical resistance and the stability toward water were drastically improved.²² Longer immersions (up to 2 weeks) did not improve further the TE properties of the material, which differs from recently reported observations on thin layers of PEDOT:PSS.²³ After 15 min, a gentle agitation of the bath is sufficient to dissociate the polymer layer from its substrate. Once the polymer floats freely in the solvent bath it can be easily handled. Thick films are solid enough to be extracted from the EG bath and deposited to other substrates without any damage.

Photographs of PEDOT:PSS thick films transferred to various substrates by EG-dipping are available in Fig. S2 (see ESI†). We carried out this technique with various shapes which would have not been achievable using conventional deposition methods. The tested geometrical forms include curves, angles and corners.

When deposited onto flexible materials like PEN films, an excellent conformability of the transferred layer was observed, with a stable electrical conductivity measured at 1200 S.cm⁻¹.

The solvent surrounding the samples became lightly turbid during the first minutes of the treatment. The chemical nature of this phenomenon was not investigated, but it is most likely due to the desorption of PSS from the layer, as stated by Ouyang et al.²⁴ The conductivity improvement resulting from such doping steps is probably due to the removal of a fraction of PSS from the layer, followed by an unfolding of the macromolecular chains and an improvement of the current percolation through the PEDOT network.²⁴

Water contact angle was measured at 57 ° ± 4 ° on transferred PEDOT:PSS films, whereas the droplet was readily absorbed by the pristine polymer layer. Fig. 1 illustrates the effect of a water bath on a pristine polymer layer and an EG-treated polymer layer. While being dipped into water, the untreated polymer rapidly dispersed in the bath, leading to an aqueous dispersion of polymer. On the contrary, the transferred polymer films stayed solid and their physical and electrical properties remained unchanged, no matter the duration of the water immersion. The dipping in EG enhanced the hydrophobic behaviour of the layer, thus preventing its dispersion in water.

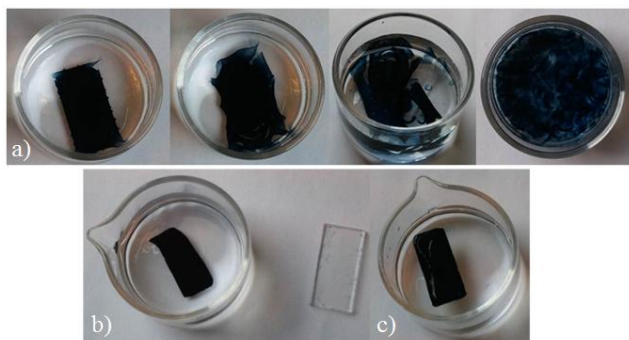


Fig. 1 a) Pictures of an untreated PEDOT:PSS film dipped into water taken at 1 minute interval each b) picture of a treated PEDOT:PSS layer floating freely in an EG bath and c) picture of a treated free standing film put into a water bath for several hours

UV-Vis-NIR absorbance spectroscopy allows a qualitative evaluation of the charge carrier concentration in polythiophenes.²⁵ Pristine PEDOT:PSS films exhibit a large absorption band covering the beginning of the IR domain, from 1250 nm to higher wavelengths. This band is attributed to bipolarons, *i.e.* the dicationic form (DC).¹⁹ These di-cationic charges usually result from the combination of polarons, also named radical cations (RC). UV-Vis-NIR spectroscopic analyses of PEDOT:PSS layers in pristine and EG-doped states show no significant difference as shown in Fig.2. This is because the EG-doping, and secondary doping in general, has no impact on the number of charge carriers in the layer.^{26,27}

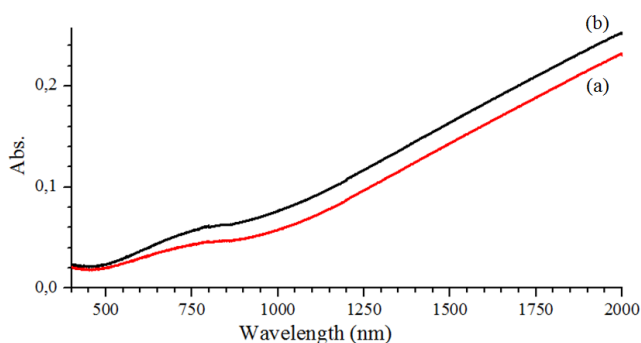


Fig. 2 UV-Vis-NIR absorbance spectra of (a) pristine PEDOT:PSS layer and (b) EG dipped PEDOT:PSS layer

Thermoelectric power improvement through reduction of PEDOT:PSS layers

The method developed in this study consists in treating PEDOT:PSS films by drop-casting of aqueous solutions containing reducing salts or neat organic reducing agents. The resulting Seebeck coefficients are summarized in Table 1. They

show that the thermopower increases significantly upon treatment with reductive species. In entries 2 to 6, after the reduction, PEDOT:PSS thick films were treated by an EG bath as described hereinbefore. This treatment was realized before the reductive step for entries 7 to 11. The EG treatment is a critical step of our reduction method since it strengthens both the chemical stability and the mechanical resistance of the layer. It also washes away reducing species remaining in the polymer layer. The EG bath post-treatment did not modify the oxidation state of our layers. As expected, the highest Seebeck coefficients were obtained with the strongest reducing species. The Seebeck enhancement follows the trend of the redox potentials for aqueous solutions of reducing agents, reaching 104 $\mu\text{V/K}$ for NaBH_4 treated PEDOT:PSS films. Entries 7, 9 and 11 show that performing the EG bath treatment before reduction with aqueous solutions decreased the efficiency of the treatment. The lower thermopower enhancement can be explained by the hydrophobicity of the layer, reducing the diffusion length of aqueous solutions inside the polymer layers. For the same reason, when a non-polar organic reducing agent like TDAE (entry 3) was drop casted onto a pristine PEDOT:PSS layer, the Seebeck enhancement was moderate (43 $\mu\text{V/K}$) whereas polar organic reducing agent like hydrazine (entry 5) led to more efficient reduction with a Seebeck enhancement up to 92 $\mu\text{V/K}$. These results are explained by the limited interactions of hydrophilic PEDOT:PSS layer with non-polar molecules. At the opposite, as observed for entries 8 and 10, hydrophobic EG treated PEDOT:PSS layers have undergone a high Seebeck coefficient improvement (161 and 153 $\mu\text{V/K}$) when treated with organic reducing agents, respectively TDAE and hydrazine. The Seebeck coefficient increase went along with a decrease of the electrical conductivity. Nevertheless, the electrical resistances of the sensors were not critical whatever the reducing agent. Measured electrical conductivities of reduced samples are summarized in Fig. S3 (see ESI†).

We used UV-Vis-NIR absorbance spectroscopy to determine the oxidation level of PEDOT:PSS thin films treated with aqueous and organic reducing agents (Fig. 3). Upon reduction with moderate reducing agents (Na_2SO_3 and $\text{Na}_2\text{S}_2\text{O}_3$), the absorption band around 900 nm attributed to RC increased while we observed a concomitant decrease of the DC contribution (above 1250 nm). Further reduction, obtained with strong reducing agents like TDAE and NaBH_4 , led to the onset of a new band around 660 nm, corresponding to polymeric neutral chains (NC). In accordance with Seebeck coefficient measurements, the reduction level of the PEDOT:PSS measured by UV-Vis-NIR spectrometry increases with the redox potential of the reducing agent.

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Table 1 Thermoelectric power enhancement of PEDOT:PSS films through treatment with aqueous and organic reducing agents

Entry	Reducing agent	Redox potential E° [V/SHE]	EG-dipping	Seebeck coefficient [$\mu\text{V/K}$]
1	None	N/A	a	18
2	$\text{Na}_2\text{S}_2\text{O}_3$	-0.57	a	59
3	TDAE	-0.71 ^c	a	43
4	Na_2SO_3	-0.93	a	70
5	Hydrazine	-1.16	a	92
6	NaBH_4	-1.24	104	
7	$\text{Na}_2\text{S}_2\text{O}_3$	-0.57	b	37
8	TDAE	-0.71 ^c	b	161
9	Na_2SO_3	-0.93	b	39
10	Hydrazine	-1.16	b	153
11	NaBH_4	-1.24	b	53

^a EG dipping performed after the reduction step, ^b EG dipping performed before the reduction step, ^c Electrochemical potential measured in CH_3CN vs the standard calomel electrode

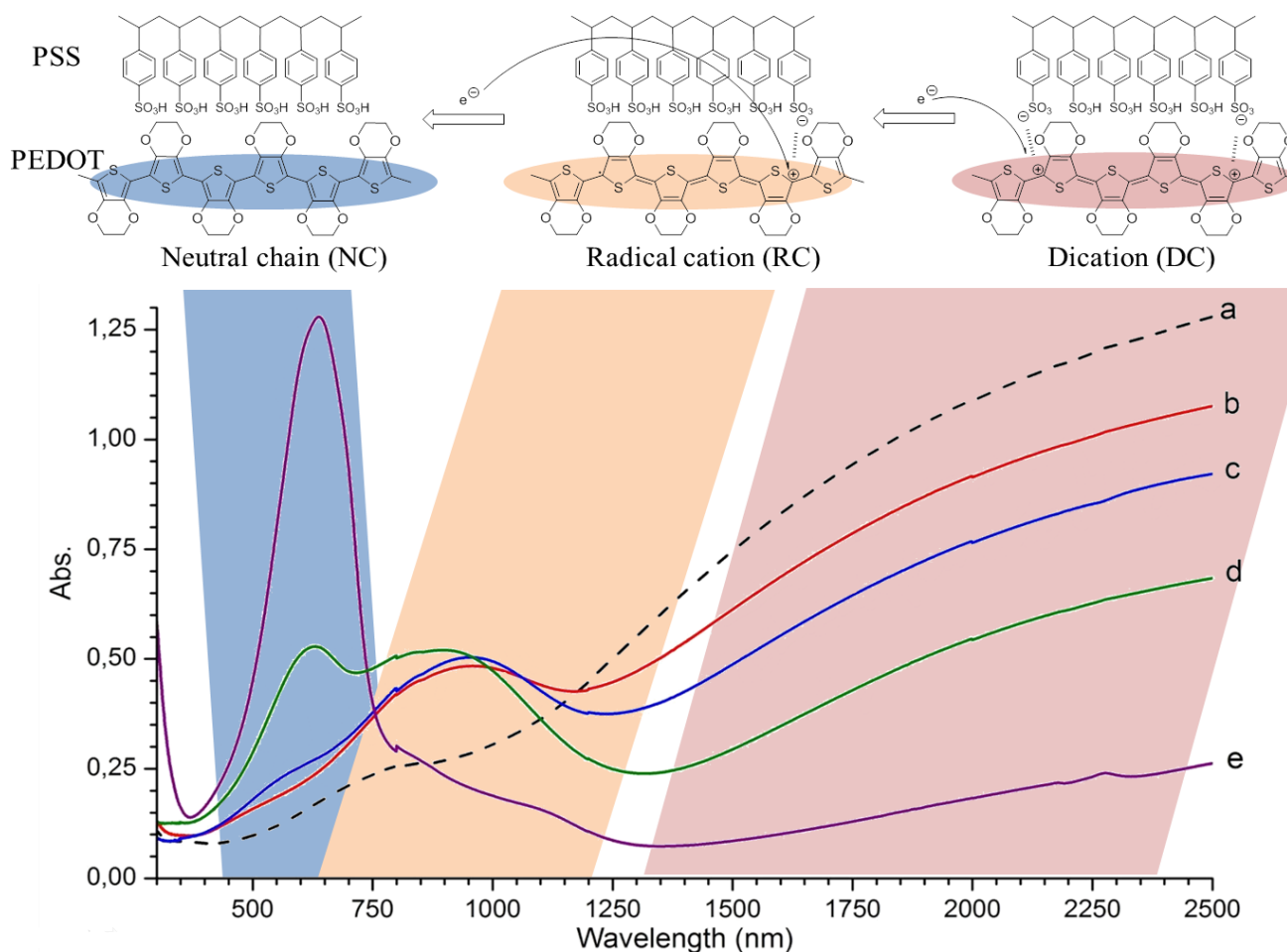


Fig. 3 Top: chemical structures of PEDOT:PSS (left) neutral chain, (center) radical cation charge carrier, (right) dication charge carrier. Bottom: Absorbance spectra of (a) pristine PEDOT:PSS and thin films treated with (b) $\text{Na}_2\text{S}_2\text{O}_3$, (c) Na_2SO_3 , (d) NaBH_4 , (e) TDAE

Cite this: DOI: 10.1039/c0xx00000x

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The thermopower of reduced polymer layers was unstable under ambient conditions (Fig. 4a). Neither encapsulating nor storage under inert atmosphere prevented this phenomenon. A decrease occurred rather quickly until reaching a stable value around 40 $\mu\text{V}/\text{K}$. It is noteworthy that this figure is more than twice the Seebeck coefficient of pristine PEDOT:PSS films. This stable oxidation level was reached after one week of storage in ambient conditions. The underlying oxidation reactions were investigated with UV-Vis-NIR spectrometry. Analysis of the spectra evidences that RC and DC charge carriers are regenerated upon ageing, by the way altering TE properties of the polymer. Fig. 4b shows the evolution of the DC, RC and NC bands as a function of time. NC contribution decreases while RC and DC bands increase due to the regeneration of charge carriers. Sulfonate groups are necessary to stabilize ionic charges on the polymer chains. Consequently the stable oxidation level depends on the amount of PSS still interacting with PEDOT.

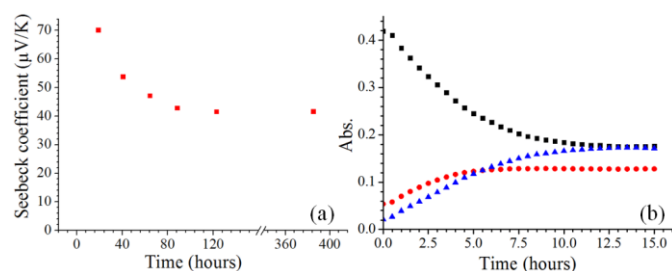


Fig. 4 (a) Evolution of Seebeck coefficient as a function of time for a PEDOT:PSS layer reduced by sodium sulfite and kept in ambient air (b) Evolution of the absorption bands corresponding to NC (638 nm, black square), RC (941 nm, red dot) and DC (2000 nm, blue triangles) with ageing in ambient air.

Morphological and chemical changes of the layers, driven by water and solvent uptake, prevent a completely reversible reduction reaction.²³ The oxidation process occurs faster for the thin layers (100 nm) used for UV-Vis-NIR spectrometry monitoring than for the thick layers (10 μm) used for the monitoring of Seebeck coefficient. The stable oxidation level of thin films is reached after 15 h of exposure to ambient air.

Heat flux sensors characterization

Flexible heat flux sensors working at room temperature were realized as a proof of concept. Functional sensors were fabricated by connecting transferred *p*-type PEDOT:PSS legs onto gold electrodes. Under ambient conditions the Seebeck coefficient of each leg was increased through chemical reduction by a factor 2 regardless of the reducing agent, as presented in Fig. S4 (see ESI†). This enhancement factor matches the stabilized Seebeck coefficient measured on the materials described in the previous paragraphs.

The second type of heat flux sensors included both *p* and *n* type legs. Our transfer method facilitated the positioning of the *p*-type legs of the device while keeping intact the fragile *n*-type legs. The latter were based on nickel ethylenetetrathiolate coordination polymer Poly[$\text{K}_x(\text{Ni-ett})$] reported by Sun et al.²¹ The Seebeck coefficient of the *n*-type material was measured at $-106 \mu\text{V}/\text{K}$. After encapsulation, the *p-n* device did not degrade after dozens of flexions and torsions. The performances of this sensor are reported in Fig. 5. They are compared to our reference device, composed of *p*-metal junctions. The mean thermopower of the *p-n* junctions is 3 times higher when compared to the *p*-metal junctions of the reference. When a reductive treatment is applied to the *p*-type legs of a *p-n* device, the voltage generation is increased by a factor of 4.5 with respect to the reference device.

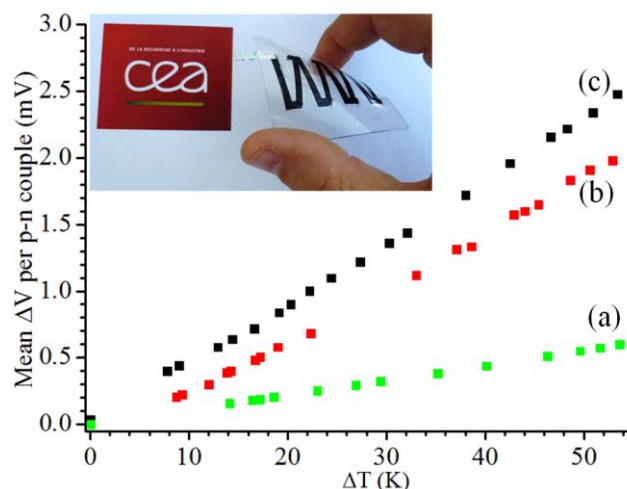


Fig. 5 Bias generation as a function of temperature difference in (a) a *p*-metal device (b) a *p-n* device and (c) a *p-n* device with chemically reduced *p* legs. Inset shows a picture of a *p-n* flexible heat flux sensor on PEN substrate.

Conclusion

A simple reductive treatment has been demonstrated to improve the thermopower of PEDOT:PSS up to $161 \mu\text{V}/\text{K}$. This enhancement of Seebeck coefficient for organic polymers opens the way for various applications like heat flux sensing and more importantly heating/cooling and power generation from waste heat.

We have also developed an innovative method for transferring thick films ($> 10 \mu\text{m}$) of PEDOT:PSS on substrates with various shapes including flexible plastics. This process is complementary to common deposition techniques that would not allow the fabrication of such devices. Reduced transferred thick films have been used to fabricate cheap and flexible heat flux sensors with enhanced thermoelectric properties.

Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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1. T. M. Tritt and M. A. Subramanian, *MRS Bulletin*, 2011, **31**, 188–198.
2. H. J. Goldsmid, *Recent Trends in Thermoelectric Materials Research I*, ed. T. M. Tritt, Elsevier, 2001, vol. **69**, pp. 1–24.
3. M. He, F. Qiu, and Z. Lin, *Energy & Environ. Sci.*, 2013, **17**, 14–17.
4. Du, Y.; Shen, S. Z.; Cai, K.; Casey, P. S. *Progress in Polym. Sci.*, 2012, **37**, 820–841.
5. R. Yue and J. Xu, *Synthetic Met.*, 2012, **162**, 912–917.
6. C. Liu, F. Jiang, M. Huang, B. Lu, R. Yue, and J. Xu, *J. Electron. Mater.*, 2010, **40**, 948–952.
7. D. K. Taggart, Y. Yang, S.-C. Kung, T. M. McIntire, and R. M. Penner, *Nano Lett.*, 2011, **11**, 125–31.
8. K. C. See, J. P. Feser, C. E. Chen, A. Majumdar, J. J. Urban, and R. a Segalman, *Nano Lett.*, 2010, **10**, 4664–4667.
9. Y. Zhang, X. L. Wang, W. K. Yeoh, R. K. Zeng, and C. Zhang, *App. Phys. Lett.*, 2012, **101**, 031909.
10. B. Zhang, J. Sun, H. E. Katz, F. Fang, and R. L. Opila, *ACS Appl. Mater. Interfaces*, 2010, **2**, 3170–8.
11. S. K. Yee, N. E. Coates, A. Majumdar, J. J. Urban, and R. a Segalman, *Phys. Chem. Chem. Phys.*, 2013, **15**, 4024–32.
12. J. Park, A. Lee, Y. Yim, and E. Han, *Synthetic Met.*, 2011, **161**, 523–527.
13. D. Kim, Y. Kim, K. Choi, J. C. Grunlan, and C. Yu, *ACS nano*, 2010, **4**, 513–23.
14. Q. Yao, L. Chen, W. Zhang, S. Liufu, and X. Chen, *ACS nano*, 2010, **4**, 2445–51.
15. C. Yu, K. Choi, L. Yin, and J. C. Grunlan, *ACS nano*, 2011, **5**, 7885–92.
16. M. Culebras, C. M. Gómez, and A. Cantarero, *J. Mater. Sci.*, 2012, **48**, 2855–2860.
17. T.-C. Tsai, H.-C. Chang, C.-H. Chen, and W.-T. Whang, *Org. Electron.*, 2011, **12**, 2159–2164.
18. O. Bubnova, M. Berggren, and X. Crispin, *J. Am. Chem. Soc.*, 2012, **134**, 16456–9.
19. O. Bubnova, Z. U. Khan, A. Malti, S. Braun, M. Fahlman, M. Berggren, and X. Crispin, *Nat. Mater.*, 2011, **10**, 429–33.
20. Y. H. Kim, C. Sachse, M. L. Machala, C. May, L. Müller-Meskamp, and K. Leo, *Adv. Funct. Mater.*, 2011, **21**, 1076–1081.
21. Y. Sun, P. Sheng, C. Di, F. Jiao, W. Xu, D. Qiu, and D. Zhu, *Adv. Mater.*, 2012, **24**, 932–7.
22. C. Liu, B. Lu, J. Yan, J. Xu, R. Yue, Z. Zhu, S. Zhou, X. Hu, Z. Zhang, and P. Chen, *Synthetic Met.*, 2010, **160**, 2481–2485.
23. G.-H. Kim, L. Shao, K. Zhang, and K. P. Pipe, *Nat. Mater.*, 2013, **12**, 1–5.
24. J. Ouyang, Q. Xu, C.-W. Chu, Y. Yang, G. Li, and J. Shinar, *Polymer*, 2004, **45**, 8443–8450.
25. K. Jeuris, L. Groenendaal, H. Verheyen, F. Louwet, and F. . De Schryver, *Synthetic Met.*, 2003, **132**, 289–295.
26. S. K. Jönsson, J. Birgeron, X. Crispin, G. Greczynski, W. Osikowicz, A. Denier van der Gon, W. Salaneck, M. Fahlman, *Synth. Met.*, 2003, **139**, 1–10
27. Q. Wei, M. Mukaida, Y. Naitoh, T. Ishida, *Adv. Mater.*, 2012, **25**, 2831–2836.