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ABSTRACT

Organic materials have attracted great interest for thermoelectric applications due to their tuneable electronic properties, solution processability and earth-abundance, potentially enabling high-throughput realization of low-cost devices for low-power energy harvesting applications. So far, organic thermoelectricity has primarily focused on materials development, with less attention given to integrated generators. Yet, future applications will require the combination of efficient generators architectures and scalable manufacturing techniques to leverage the advantages of such promising materials. Here we report the realization of a monolithic organic micro-thermoelectric generator (μ-OTEG), using only direct writing methods, embedding the thermoelectric legs within a plastic substrate through a combination of direct laser writing and inkjet printing techniques. Employing PEDOT:PSS for the p-type legs and a doped fullerene derivative for the n-type ones, we demonstrate a μ-OTEG with power density of 30.5 nW/cm^2 under small thermal gradients, proving the concrete possibility of achieving power requirements of low-power, distributed sensing applications.

1. Introduction

The thermoelectric effect enables the generation of sustainable energy by converting heat flux into electric power. Unfortunately, the high costs of the most advanced technologies [1–5], as the ones based on Bi-chalcogenides, have limited its fields of application [6,7]. Nevertheless, there is a wide range of possible applications for this technology in waste-heat energy harvesting, from industrial/automotive heat recovery to the emerging wearable electronics and Internet-of-Things (IoT) [8–10]. In particular, due to technological advances as well as components downscaling, the power demand for distributed wireless sensors has drastically reduced, to the μW level [11,12]. Therefore, the implementation of a low-cost thermoelectric device, capable of delivering μW over cm^2 areas when operating at limited temperature difference (ΔT), offers the opportunity to replace or complement batteries for powering IoT sensors. Indeed, these devices will have to work within limited temperature differences, going from 2 K, for wearable applications, to around 10 K, for integrated sensors networks [13]. Compact and thin thermoelectric generators (TEG) composed by thermocouples with lateral dimensions in the order of tens/hundreds of μm (μ-TEG), are ideal candidates for the TEG integration into sensors platforms.

There has been a growing interest in doped organic semiconductors [14–18] to substitute Bi-based chalcogenides, which, albeit offering record thermoelectric properties, contain rare and toxic elements [6,19]. Organics, in that respect, represent a more sustainable approach and their solution-processability could be exploited to develop high-throughput, room-temperature processes based on printing techniques to manufacture cost-effective organic μ-TEG (μ-OTEG) on flexible substrates.

However, developing generators reaching μW, with only cm^2 devices, under small ΔT, not exceeding few tens of K, is still a challenge with organic semiconductors. The main obstacle is represented by

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achieving compact, printed μ-OTEG with monolithic architectures. In fact, most of the studies conducted in the field of organic thermoelectricity have been focused on the improvement of the thermoelectric performances [20–29], to fill the gap with inorganic technologies, while the development of suitable processing methods and devices architecture lagged behind. Consequently, most of the OTEG reported to date are simple demonstrators of the thermoelectric properties [30], having either thermoelectric elements with dimensions in the order of millimiters, therefore compromising density and the achievement of a suitable output voltage over a limited area [31–34] or a planar geometry, i.e. thermocouples parallel to the flexible substrate, thus inherently characterized by a limited number of low-density thermocouples [35–39]. Indeed, so far, there has been no demonstration in literature of μ-OTEGs and of the possibility of employing scalable manufacturing techniques to realize conformable and compact thermoelectric devices.

To address this limit, here we propose and demonstrate a monolithic μ-OTEG embedded in a plastic film, minimizing the heat losses through the substrate, and fabricated only by means of direct-writing digital processes, paving the way to mass manufacturing of cost-effective harvesters. Our strategy combines femtosecond-pulse laser ablation of micro-cavities and their filling with p- and n-type organic conductors by inkjet printing. By adopting printable formulations of PEDOT:PSS for p-type legs and of a doped fullerene derivative for n-type ones, we realize the first example of an integrated μ-OTEG adopting scalable processing and based on printed conductive organic materials. We achieve a maximum power density of 30.5 nW/cm^2 with a $\Delta T = 25$ K around room temperature (RT, 303 K). This result, obtained on a proof-of-concept device, demonstrates the possibility of delivering μW to a load with only a few cm^2 μ-OTEG just by geometrical tailoring.

2. Experimental

2.1. Materials

The p-type semiconductor is a commercial formulation of PEDOT:PSS (PJ700) supplied by Heraeus. The Ag-nanoparticles ink (ANP DGP 40LT-15C) was purchased from Sigma-Aldrich. PTEG-1 was synthesized according to a previously published procedure [40].

2.2. Femtosecond laser writing

All μ-TEGs have been realized using only direct writing techniques on flexible commercial PEN substrates with different thicknesses (25, 50 and 125 μm) which have been supplied from DuPont Teijin Films. The thermocouples area was defined on the substrates using Femtosecond Micromachining to realize 3D conical cavities passing throughout the PEN film. The micromachining system is equipped with a regenerative amplified mode-locked femtosecond laser source based on Yb:KGW active medium (Light Conversion, Pharos) whose amplified pulses at the fundamental wavelength (1030 nm) are characterized by duration of 240 fs, repetition rate up to 1 MHz and pulse energy up to 0.2 mJ. In order to create the holes array, the following writing parameters were set: 2nd harmonic $\lambda = 515$ nm, 100 kHz repetition rate and average power 120 mW. Each hole was obtained through the irradiation of 150 pulses on the exact same position. The laser light was statically focused on the substrate surface through a telecentric microscope objective (10X, Mitutoyo) and the 2D structure is achieved moving the sample. Computer-controlled, 3-axis air-bearing translation stages (ABL-1000, Aerotech) with maximum resolution of few tens of nm over a wide range, interfaced by CAD-based software (ScaBase, Altechna) were used to translate the sample relative to the desired laser irradiation patch and energy density pulse deposition.

2.3. Inkjet printing of materials

The p-type PEDOT:PSS ink was deposited using Fujifilm Dimatix Materials Printer DMP-2831 at a plate temperature of 40 °C. For the n-type doped semiconductor PTEG-1, a 10 mg/ml solution in o-xylene was prepared and printed in the same conditions as its p-type counterpart. The electrical contacts and the connections were printed using ANP DGP 40LT-15C ink, supplied by Sigma Aldrich, printed at RT. Once all the materials were printed, the devices were annealed overnight in N_2 atmosphere at 120 °C, to evaporate all the solvents residuals, promote dopant diffusion and to sinter the silver nanoparticles into a compact film. Finally, the devices were capped for protection and electrical insulation purposes using a thin poly(methyl methacrylate) (PMMA) layer, spin coated from a solution of 120 mg/ml in N-butyl-acetate.

2.4. TEGs characterization

A home-build set-up [41] was used to measure the performances of the devices. The measurements were performed in combination with a variable resistor as load in order to evaluate the presence of non-Ohmic effects.

3. Results

3.1. μ-OTEG architecture and fabrication

In order to drastically reduce thermal losses inherent to the use of a flexible and insulating plastic substrate, we designed a device architecture embedded into a PEN foil, realizing a compact and monolithic μ-OTEG. To this end, through holes had to be fabricated into the plastic foil in correspondence of the thermoelectric legs. Such architecture presents a challenge when it comes to filling the holes with the thermoelectric ink, since the fluid can spill from the opposite side.

Therefore, we devised a layout of the through holes to solve this problem. Instead of fabricating a single hole for each leg, we created arrays of micro-cavities covering the leg footprint (Fig. 1a), which in the proposed device is a square with 200 μm lateral dimension. To this aim, we adopted fs-laser writing, a direct-writing yet highly parallelizable technique [42,43]. The fs-laser writing allows depositing energy in the matter in a very controlled way thanks to highly non-linear processes (multiphoton absorption) that arise only at high optical energy density. By focusing an ultra-short pulsed laser (fs) inside the material through a high aperture numerical objective, the “cold” processing of the material takes place only within the volume of the focused spot, normally a few μm^2, obtaining a micron controlled ablation of the plastic. The fabricated cavities have a truncated cone shape with a larger top diameter, around 20 μm, and smaller bottom diameter, of about 6 μm (Fig. 1b). This peculiar shape has the advantage of allowing the penetration of the thermoelectric inks inside the cavities from the larger diameter side due to capillary effect, while blocking their exit from the other owing to the rheological properties of the fluid.

After the ablation of the cavities, the p- and n-type materials are deposited by inkjet printing in correspondence of the top openings (Fig. 1c). An example of a micro-cavity filled with an inkjet-printed thermoelectric material is reported in Fig. 1d. Following the printing of the active materials, bottom and top side electrical interconnections are fabricated, by inkjet printing first a thin PEDOT:PSS interlayer followed by a silver-based ink (Fig. 1e and f). Such a double-layer improves contact to the active legs and make them more mechanically robust (Fig. SI1). Finally, the devices are capped on both sides using a PMMA layer with a thickness of about 1 μm for electrical insulation. The resulting flexible μ-OTEG is a matrix of 16 × 16 thermoelectric legs, realizing 128 thermocouples, and occupies an area of 0.36 cm^2 (Fig. 1g). The devices realized are proof-of-concepts and therefore the thermocouples geometry was kept as simple as possible, but the flexibility of the employed digital processes ensures the possibility to realize far more compact geometries, to maximize the fill factor [44], and to match the thermoelectric properties of the p- and n-type legs.

Overall, the process that we developed combines, as never done

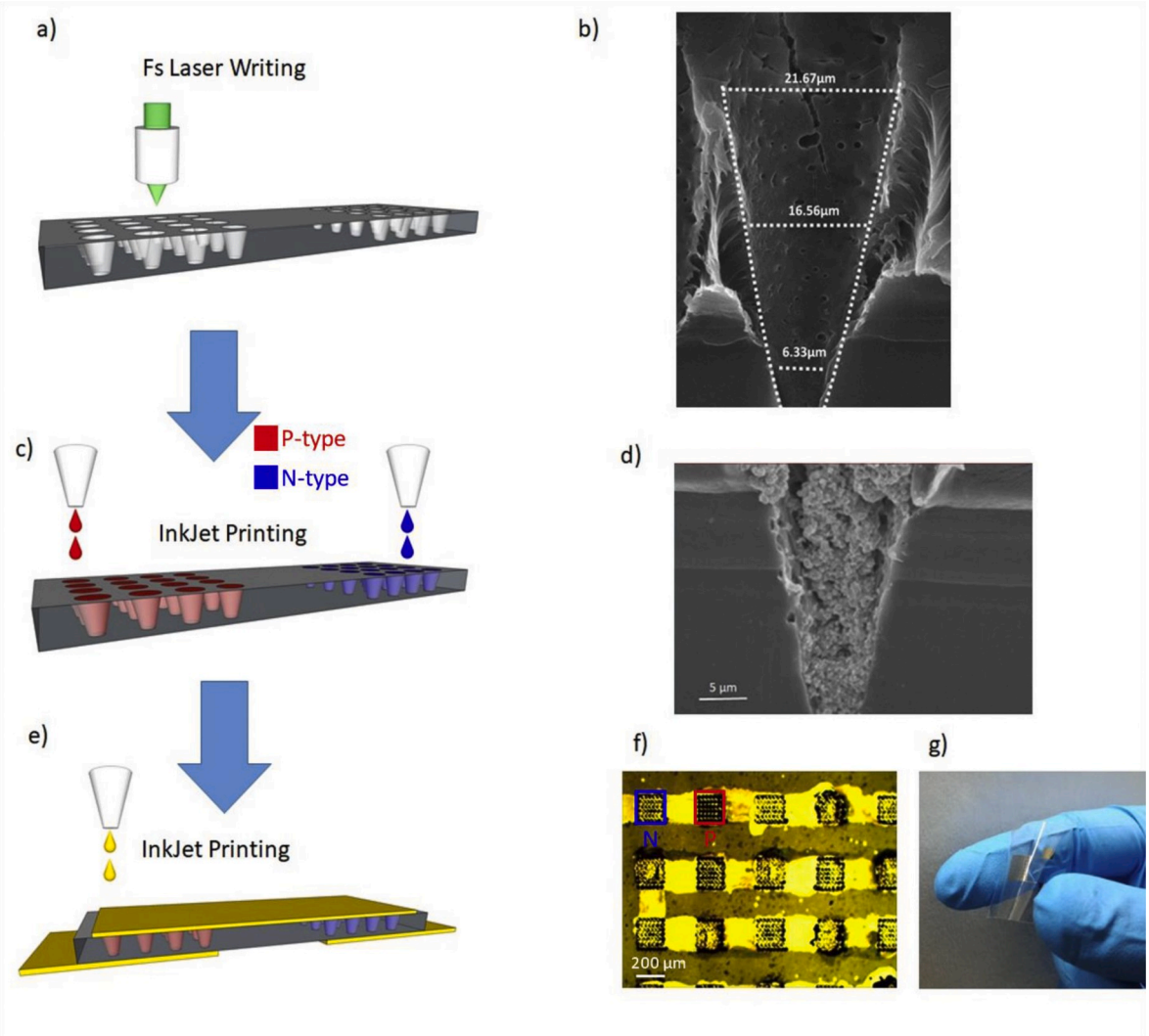

Fig. 1. µ-OTEG fabrication: a) fs-laser writing of micro-cavities defining the embedded thermocouples within the PEN film. b) SEM cross-section of a single cavity in a 50 µm thick PEN substrate. c) Inkjet printing of the thermoelectric materials within the cavities. d) SEM cross-section of a single cavity after the printing of the PEDOT:PSS ink. e) Inkjet printing of the electrical contacts using a silver nanoparticle-based ink. f) Optical microscope image of the final layout comprising the thermocouples. g) Photograph of the complete flexible device.

before, fs-laser patterning and inkjet printing to fabricate a 3D structured organic device and possesses three main advantages: a highly compact device structure, the possibility of easily changing the 3D geometry of the thermocouples to maximize the power output, depending on the thermoelectric properties of the materials, and better thermal coupling due to the removal of the plastic substrate. Such important features are obtained by renouncing to part of the active area, as the micro-cavities occupy only a fraction of the whole leg footprint. Nevertheless, since the minimum resolution of the adopted direct-writing techniques is well below what implemented in this demonstration, such aspect, as well as the square size of the legs and relative distances can be largely engineered to achieve a much denser configuration.

3.2. *P-type only generators*

At first, to validate the process and our device architecture, we opted for a simplified generator. P-type only legs are printed and n-type ones, more challenging to be realized because of the present limits with stable and printable n-type doped organic semiconductors [45], are substituted by a metallic interconnection, short-circuiting the device top and bottom sides. For the p-type legs we adopted an inkjet printable formulation of PEDOT:PSS (Heraeus PJ700). Such material at 303 K delivers a Seebeck coefficient (α) of ~11 µV/K, an electrical conductivity in the out-of-plane direction ($\sigma_{\perp}$) of ~1 S/cm and an out-of-plane thermal conductivity ($k_{\perp}$) of 0.5 W/mK [46]. The selected formulation represents a good model p-type material to assess the quality of the proposed device architecture.

The vertical metallic interconnections have been realized by inkjet printing a silver nanoparticles-based ink (ANP DGP 40LT-15C). We chose to limit the printed ink volume below 1 nl, compared to hundreds of nl for the p-type semiconductor. With such volume, the ink covers only the cavity walls without filling them completely (Fig. SI2), granting an interconnection but limiting the negative effect of Ag high thermal conductivity on the harvesting performances of the device.

The first p-type only µ-OTEG was embedded in a 25 µm thick substrate, thus defining thermocouples of an equivalent height, with a total internal resistance of 1.6 kΩ. Such µ-OTEG, as well as all devices reported in this work, was characterized with an home-built set-up [41], measuring the thermopower around room temperature (~303 K) and under small temperature gradients (from 5 to 25 K), thus under plausible conditions of actual use. Fig. 2a displays the power density (P_d) as a function of the load current (I_{Out}): a parabolic dependence, with a maximum of ~3 nW/cm^2 ($\Delta T = 25$ K), as function of the circuit current

can be observed, as expected from equation (1):

$$P_d \propto \frac{R_{TEG} I_{Out}}{V_{TEG}} - \frac{R_{TEG}^2 I_{Out}^2}{V_{TEG}^2} \quad (1)$$

where R_{TEG} represents the TEG resistance and V_{TEG} represents the thermovoltage generated. Therefore, the p-type only device fabricated according to the proposed architecture behaves as an ideal thermoelectric generator (V_{Out} vs. I_{Out} is shown in Fig. SI3), thus providing a first proof that the process we implemented is indeed suitable for the fabrication of integrated TE devices.

The limited P_d, besides suffering from the use of p-type only conductors, depends also on the relatively short legs adopted. Indeed, higher values of thermovoltage are expected to be generated by increasing thermocouples height as an effect of a higher effective temperature difference across the active material [13]. This can be simply obtained by embedding the devices into thicker plastic foils.

To assess the increase of the generated output power with thickness, we fabricated devices by employing substrates of 50 and 125 μm thickness (Fig. SI4). The p-type thermocouples embedded in the substrates have a resistance that increases linearly as a function of the height (Fig. SI5). The corresponding generators have a thermovoltage that linearly depends on the external temperature, and have a power density scaling quadratically with ΔT. Interestingly, such dependence nicely matches what predicted by a 1D heat-transfer model [13] (Fig. 2b, Fig. SI6 and Supplementary Note 1). Therefore, it is possible to conclude that the process and architecture are flexible towards geometrical optimizations in order to improve the thermopower output of the device as a function of a given set of thermoelectric materials.

3.3. OTEGs integrating inkjet-printed p-type and n-type materials

After the validation of the μ-OTEG fabrication process through the realization of devices using only a p-type doped organic semiconductor, a complete thermoelectric generator integrating both p- and n-type doped materials was realized. Clearly, the addition of n-type legs, in electrical series and thermal parallel with the p-type ones, can improve the output power by addition of a thermovoltage component and by increasing the device thermal insulation, thus intercepting a larger effective temperature gradient across the active materials.

The device architecture is identical to the one previously demonstrated, where, instead of Ag, an n-type leg was realized by inkjet printing a suitable n-type doped organic semiconductor. Achieving good organic n-type thermoelectric materials that are both printable and stable to ambient processing is still a challenge [47–49]. Here we adopted a fullerene derivative, a [60]fulleropyrrolidine, with an additional polar triethylene glycol ether side chain, dubbed PTEG-1, that is able to reach a power factor of 16.7 μW/mK^2 and an electrical conductivity of 2.05 S/cm, both amongst the highest values ever obtained for a doped n-type organic semiconductor [50,51].

The final P/N μ-OTEG generator comprises 48 integrated thermocouples, embedded in a 25 μm thick plastic film, with an internal resistance of 60 kΩ. The device voltage output and power density as a function of the load current are reported in Fig. 3a and b, respectively. A linear dependence of the generated voltage (~32 mV for $\Delta T = 25$ K) and a parabolic shape of the power density (maximum of 30.5 nW/cm^2 for $\Delta T = 25$ K) are observed also in this case. The voltage and power density output as a function of the external temperature difference are shown in Fig. 3c and d respectively. The voltage scales linearly with increasing ΔT, while the power density output shows a quadratic dependence. This data further confirms the ideality of the device (electrical scheme of an ideal TEG in Fig. SI7). Compared to the P-type only μ-OTEG with the same thickness, an increase by more than a factor of 10 in the power density was obtained.

Therefore, as expected, the introduction of an n-type doped semiconductor led to a significant improvement in the thermoelectric performances both in terms of voltage and power output, now reaching an remarkable power density for a fully organic thermoelectric generator [31,32], here achieved in a compact μ-TEG integrating printed p-type and n-type legs. The versatility of the proposed architecture and process will make it possible to further improve the thermoelectric performances in future. For example, by increasing the thermocouple height up to a value of 200 μm, the power output can be predicted to reach values in the order of 200 nW/cm^2 already with the reference materials here adopted. Such power density would enable delivering μW electrical power, as required by low-power distributed sensors, at $\Delta T = 25$ K with a device of only few cm^2.

4. Conclusions

We have presented a novel architecture and process for the fabrication of a vertical μ-OTEG embedded in a plastic substrate, employing only direct writing techniques, such as inkjet printing for all active

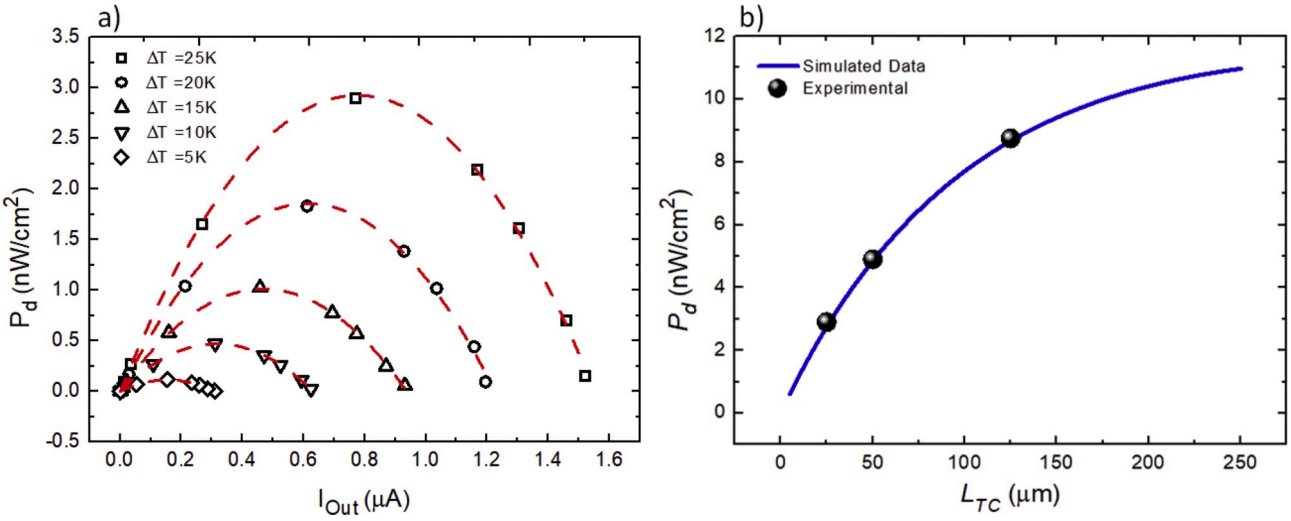

Fig. 2. Thermoelectric characterization of the p-type only μ-OTEG integrating 128 thermocouples: a) Power density (P_d) as a function of the load current (I_{Out}): its shape is an indication of the fully ohmic behaviour of the TEG. b) Thermocouple power density as a function of the thermocouple height (L_{TC}): the experimental values (black symbols) are compared with the simulated data (blue line). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

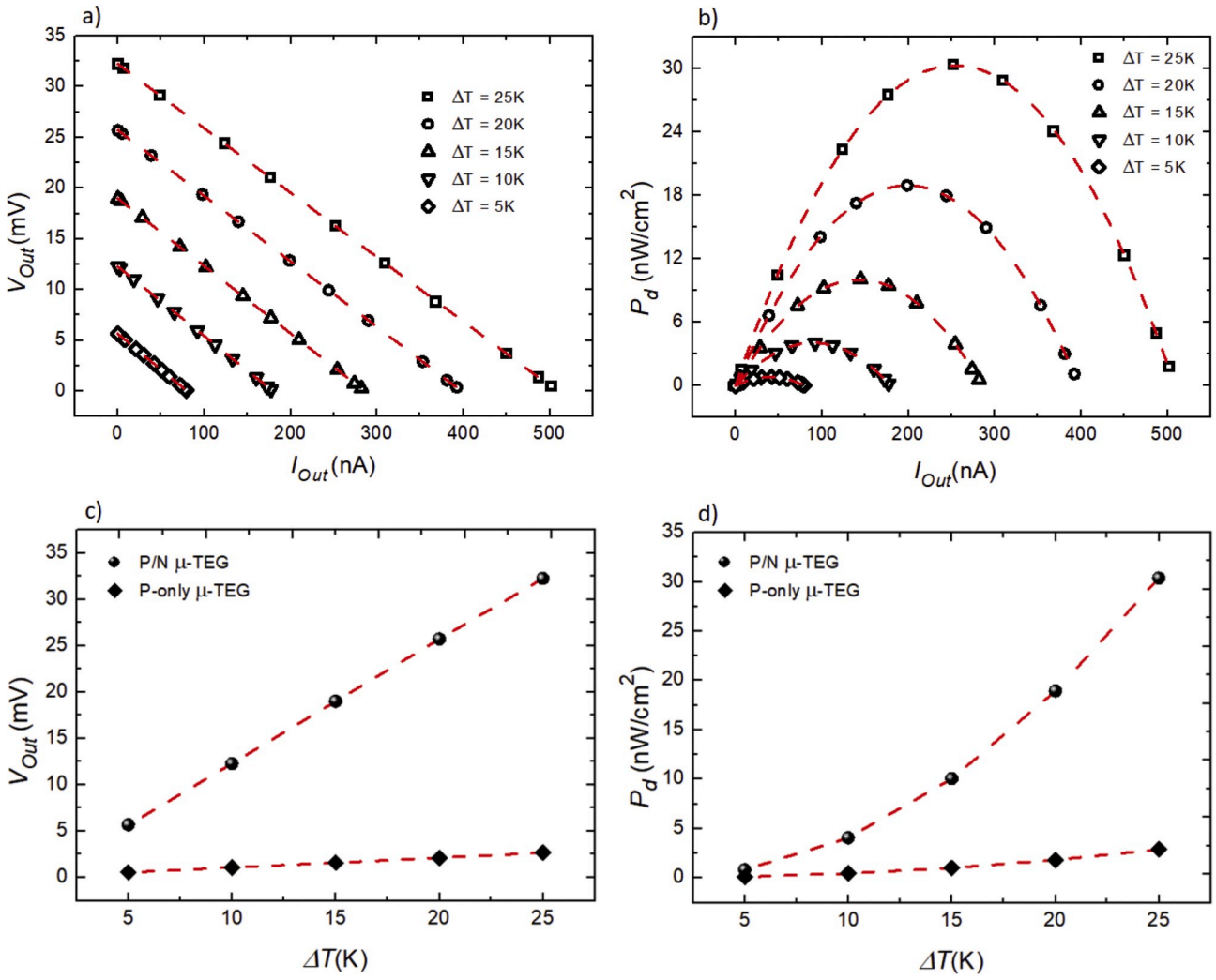

Fig. 3. Thermoelectric characterization of the P/N μ-OTEG with 48 thermocouples. a) Voltage (V_{Out}) and b) power density (P_d) output of the μ-OTEG as a function of the load current. c) V_{Out} and d) P_d output as function of the external temperature difference (ΔT). In c) and d) data for the P-only device are reported for comparison. Devices height is 25 μm.

materials and interconnections, and fs-micromachining for definition of high resolution leg cavities in the substrate. Our approach provides flexibility in the control of the 3D geometrical parameters of the thermocouples and allows to create highly dense structures in order to maximize the devices performances. The architecture and process were validated at first by fabricating a P-type only generator, demonstrating the ideal increase of power density with thermocouple height, simply achieved by adopting thicker substrates, up to 125 μm. Following such validation, we introduced an n-type fullerene derivative to realize a P/N μ-OTEG, delivering a record power density for fully organic micro-generators, in the order of 30 nW/cm^2 at $\Delta T = 25$ K.

The presented μ-OTEG qualifies as a platform to deliver real case applications of organic thermoelectric materials. If we consider the possibility of employing, as p-type semiconductor, a DMSO treated PEDOT:PSS [52] ($S = 80$ μV/K, $\sigma = 900$ S/cm and $k_\perp = 0.25$ W/mK) and the same fullerene derivative employed in this work, which is currently one of the best n-type TE semiconductors, power density values around the μW/cm^2 are theoretically reached already at $\Delta T = 25$ K and even lower temperature gradients (Fig. SI8). Moreover, the potential of the presented architecture goes beyond organic devices, as it is compatible with any solution processable thermoelectric material. Power density values around 10 μW/cm^2 are achievable employing already existing composites such as, for example, SeSn nanosheets (NS) and PEDOT:PSS [53] ($S = 100$ μV/K, $\sigma = 300$ S/cm and $k_\perp = 0.3$ W/mK) blends and a solution printable hybrid ink made by TiS_2 NS and fullerene [54] ($S = -100$ μV/K, $\sigma = 380$ S/cm and $k_\perp = 0.6$ W/mK), as shown in Fig. SI9. Such values, potentially reachable with already available materials thanks to our architecture, would allow to further expand the range of applications served by cost-effective thermoelectric harvesters. Therefore, the proposed μ-OTEG has the potential to pave the way for a new generation of mass-produced and cost-effective, highly compact organic-based TEG serving real-life, low-power applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

M. Massetti: Conceptualization, Methodology, Validation, Investigation, Writing - original draft, Writing - review & editing, Visualization. **S. Bonfadini:** Investigation. **D. Nava:** Investigation. **M. Butti:** Investigation. **L. Criante:** Investigation, Supervision, Writing - review & editing. **G. Lanzani:** Conceptualization, Supervision, Resources, Writing - review & editing. **L. Qiu:** Investigation. **J.C. Hummelen:** Conceptualization, Supervision, Resources, Writing - review & editing. **J. Liu:**

Investigation. **L.J.A. Koster:** Conceptualization, Supervision, Resources, Writing - review & editing. **M. Caironi:** Project administration, Conceptualization, Methodology, Supervision, Resources, Writing - original draft, Writing - review & editing.

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Appendix A. Supplementary data

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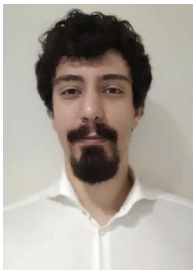

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