Supporting Information

Fully Printed Organic-Inorganic Nanocomposites for Flexible Thermoelectric Applications

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S1: Flexible PEDOT:PSS-based Thermoelectric Nanocomposite Fabrication

In this work, flexible PEDOT:PSS-based thermoelectric nanocomposites were fabricated with the combination of in-house developed and optimised thermoelectric inks and our advanced printing techniques. A wide-area and fine-feature Optomec Aerosol Jet Printing (AJP) 200 System was installed in our lab that can allow for a high-resolution rapid prototyping of multilayer electronic and structural patterns for circuits and devices onto various substrates. The concept of AJP is transferring functional material inks directly onto a substrate under the effect of confined air flow. The user-defined pattern can be directly drawn from the AutoCAD software and be edited and modified as desired, which provides large design flexibility and is extremely useful for fabricating made-to-order devices that have unique features. Figure S1 shows the AutoCAD-designed pattern and the experimentally printed thermoelectric nanocomposite pattern onto a polyimide (PI) sheet (75 μm thick, Goodfellow).

Figure S1. (a) Schematic of the AutoCAD-designed thermoelectric pattern for the AJP process, and (b) photo of the experimentally printed 5-layer thermoelectric nanocomposite pattern.

Our AJP 200 system supports two different atomisation methods: ultrasonic atomiser (UA) and pneumatic atomiser (PA), where the UA works better with small amount printing and lower viscosity ink, while the PA prefers large volume printing and has a larger ink viscosity capacity. For the atomisation mechanism of UA as demonstrated in Figure S2a, the UA
atomised the liquid ink with the help of high-frequency pressure waves generated by an ultrasonic transducer. Then, the droplets were transported within an N₂ carrier gas and directly fed towards the deposition print head.¹ However, the atomisation mechanism of PA is quite different to UA as illustrated in Figure S2b. The PA utilised a high-velocity N₂ gas flow to shear the ink into small droplets. As the pressure in the atomiser chamber building up, it could be seen that there were a large amount of ink droplets impacting the sidewall and draining back into the liquid ink, while smaller particles remained suspended in the mist.² Then, the created mist flow was connected to a virtual impactor to concentrate the aerosol stream, where an exhaust pump was applied to remove excess atomised droplets from the system. Finally, the output gas flow from the virtual impactor was directed to the deposition print head.²

After atomisation, the aerosol mist was fed through a fine hollow nozzle tip and then deposited onto the substrate by moving the motorised platen beneath the nozzle tip as demonstrated in Figure S2c. In our AJP 200 system, the fine-feature nozzle tip size ranges from 100 to 300 μm. The printing speed can achieve up to 200 mm/s, and the stand-off height can be up to 5 mm.² Moreover, a mechanical process shutter was used to interrupt the flow of the focused aerosol stream to pause or stop the deposition process. The minimum printed feature that can be achieved is 10 μm onto virtually any surface, planar or non-planar, while the single pass layer thickness can be 100 nm to 2 μm.² Within the deposition print head illustrated in the enlarged view of Figure S2c, an innovative aerodynamic focusing technology was utilised here to realise the printing. There were two gases flowing co-axially through the nozzle and out of the tip,¹ where the atomiser gas flow (Q_{atm}) generated by the atomiser was surrounded by a continue annular N₂ sheath gas flow (Q_{sh}) that could focus and accelerate the aerosol stream. Then, the resulting high-velocity aerosol droplets were jetted toward the substrate.¹²
Finally, a 200mm x 200mm heated vacuum platen controlled by a motion-control system is utilised for the pattern printing, as seen in Figure S2d. The motion system includes two motorised axes, and the motion accuracy can achieve ± 6 µm for each axis. The platen can also be heated up from 20 to 120 °C so that the mounted substrate can be heated to a desired temperature. It is worth mentioning that the substrate temperature is crucial for creating a fin-feature line, as higher temperature can reduce the coffee-ring effect and quickly cure the newly-deposited wet line so as to avoid the overspray issue. However, the temperature cannot be too high, since high temperature can cause the solvent evaporating too quick, producing a poor quality line or causing the clogging of the nozzle tip. Moreover, a vision system equipped with an optical digital camera is employed here for the alignment and online process monitoring during printing, which enables a better control of the line width, density, continuity, edge smoothness, etc.
Figure S2. Schematic of the atomisation process of (a) ultrasonic atomiser (UA) and (b) pneumatic atomiser (PA), where the inset illustrates the detailed atomisation mechanism. (c) Annotated photo of the fine-feature deposition print head. Inset: the mechanism of aerosol jet printing. (d) Annotated photo displaying the motion system. Inset: the printing process.

S2: Surface Treatment on the Printed PEDOT:PSS Films

In order to investigate the feasibility of enhancing the thermoelectric performance of PEDOT:PSS-based nanocomposites, the pristine printed PEDOT:PSS films were surface treated with different solvent: H$_2$SO$_4$ (20 vol.%, Sigma Aldrich), ethylene glycol (EG, 99.8%, Sigma Aldrich) and dimethyl sulfoxide (DMSO, 99.9%, Sigma Aldrich). Among them, as compared in Figure S3, the EG treated samples with 5-layer printing exhibited the best performance, with the
$S \sim 14.8 \ \mu V/K$, $\sigma \sim 96.9 \ \text{S/cm}$, and $PF \sim 2.1 \ \mu W/mK^2$. Furthermore, different PEDOT:PSS polymer solvent from different suppliers were also compared. It is found that the $\sigma$ of the PEDOT:PSS from Heraeus Clevios™ PH1000 surpassed the one from Sigma-Aldrich, which was more than 5 times higher as compared in Figure S3a and Figure 4b.

**Figure S3.** (a) Seebeck coefficient and electrical conductivity, and (b) power factor of the printed PEDOT:PSS films with different surface treatments.

**S3: Printed PEDOT:PSS-based Nanocomposite Quality Comparison**

Our AJP 200 system is compatible with a large variety of inks, pastes or other materials that can be deposited, with a wide viscosity capacity ranging from 1 up to 1000 cP. With respect to a good ink, it should be not too viscous (preventing atomisation), no shear-thickening behaviour, not too thin or too low viscosity (overspray). Since the atomisation and printing conditions have great influence on the printed line profile and morphology, it is essential to find out the optimum conditions for different ink formulations. Therefore, for the investigation of the printed line quality, 85 wt.% (nominal) $\text{Sb}_2\text{Te}_3$ nanoflakes were printed with 1, 5, and 10 layers...
for more detailed comparison. It was found that denser and more uniform nanocomposite with fewer noticeable pores or cracks on the surface was obtained with increasing printed layers, leading to homogeneous nanocomposites with thickness of ~2 µm as shown in Figure S4. The reproducibility of our printed nanocomposites was assessed on at least four samples under the same condition. As compared in Figure S5, the σ, S and PF increased with increasing number of printed layers. Considering the printing process time, 5-layer printing was chosen as the optimum condition for the printed nanocomposite investigation in this paper.

Figure S4. Profilometer thickness measurement of (a) 1-layer, (b) 5-layer, and (c) 10-layer printed PEDOT:PSS-based nanocomposites loaded with 85 wt.% (nominal) Sb₂Te₃ nanoflakes.

Figure S5. (a) Seebeck coefficient & electrical conductivity and (b) power factor measurements of different layers of printed PEDOT:PSS-based nanocomposites loaded with 85 wt.% (nominal) Sb₂Te₃ nanoflakes.
S4: Characterisation and Measurement of Printed PEDOT:PSS-based Nanocomposites

This section discussed the width and thickness measurement and morphology characterisation results of different printed PEDOT:PSS-based nanocomposites. Figure S6 shows that wider and thicker printed lines were obtained with increasing wt.% of loaded particles.

**Figure S6.** Width and thickness measurement of 5-layer printed PEDOT:PSS-based nanocomposites loaded with different wt.% of (a) Bi₂Te₃ nanoparticles and (b) Sb₂Te₃ nanoflakes, respectively. (c) Morphology comparison of 5-layer printed PEDOT:PSS-based nanocomposites with different loading ratio of Bi₂Te₃ nanoparticles and Sb₂Te₃ nanoflakes.
S5: Thermoelectric Measurement of Flexible PEDOT:PSS-based Thermoelectric Nanocomposites

This section discussed the in-plane Seebeck coefficient and electrical conductivity measurement on the printed PEDOT:PSS-based thermoelectric nanocomposites by an in-house built measurement setup, as illustrated in the detailed schematic drawing in Figures S7 a-c. As shown in Figure S7b, since the printed thermoelectric patterns were too small and too thin to be directly measured, the silver paint (Electrolube) was hand-deposited onto both edges of the sample as metallic pads so that better thermal and electrical contact between the sample and inner Seebeck probes could be achieved, thereby reducing the measurement error on the Seebeck voltage and the sample resistance. Although the added silver electrodes may slightly change the effective length of the thermoelectric legs being tested, there should be no difference on the measured Seebeck coefficient or electrical conductivity values. A bespoke test bench was built by reversibly installed two temperature-controlled Peltier modules (RS Components), one operating as a heat source while the other as a heat sink to create a small temperature difference in between (-60 to +60 °C). A DC source (Thurlby) was employed to control the temperature of Peltier modules by varying the applied power. Additionally, the whole test bench was placed in a N2-filled chamber and tested at room temperature so that the ambient electrical and thermal noise could be minimised and the condensation of ambient water vapour on the cold Peltier module could be prevented during the measurement. As illustrated in Figures S7 b & c, the sample was mounted in the middle by using copper tapes so that a stable temperature gradient could be created across the sample. A pair of commercial platinum resistance thermometers (Pt-100, Farnell) served as thermocouples were taped down by Kapton tapes onto the surface of sample to detect their local real-time temperatures, where a silicone thermal grease (Servisol heat sink
compound, Farnell) was employed for better thermal contact. The generated voltage across both sides was measured using four enamelled conducting copper wires as electric leading wires, where the resistance of sample was also measured for the electrical conductivity measurement.

Figure S7. (a) Schematic drawing of the in-plane Seebeck coefficient and electrical conductivity measurement technique. (b) Enlarged view of the printed thermoelectric pattern and measurement setup. (c) Annotated photo of our in-house designed thermoelectric measurement setup, where the enlarged image showing more details of the setup. (d) Linear fitting curve for the Seebeck coefficient calculation.
A custom-designed hardware and software data acquisition system was developed here for the semi-automatic data acquisition and analysis. As the resistance of the Pt-100 thermometer was directly proportional to the temperature, the resistance of both Pt-100 thermometers were recorded simultaneously by two Keithley 196 digital multimeters for the temperature measurement. While a Keithley 2000 digital multimeter was used for the Seebeck voltage ($\Delta V$) and sample resistance ($R$) measurements. These multimeters were all connected to the computer with the GPIB interface, and the collected raw data was then processed via a LabVIEW program. By varying the temperature across the thermoelectric legs, the temperature gradient $\Delta T$ was measured by the resistance thermometers, while the generated voltage difference $\Delta V$ was measured by a voltmeter. The Seebeck coefficient were calculated by the equation: $S = -\Delta V / \Delta T$. The linear fitting for the plot of $\Delta V$-$\Delta T$ was computed and averaged to find the best possible fit with the aid of Origin software. The Seebeck coefficient was calculated by analysing the linear regression slope of the $\Delta V$-$\Delta T$ curve (see Figure S7d). The electrical conductivity was determined via a pseudo four-point probe configuration to eliminate the effect of contact electrodes resistance and the leadouts resistance,$^4$ using the same measurement set-up discussed above. The $\sigma$ was calculated by the equation: $\sigma = L / (R \cdot A)$, where $L$ is the length between two ends of the sample, $R$ is the resistance, and $A$ is the cross-section area of printed nanocomposite.

**S6: Finite-element Modelling of Printed Thermoelectric Nanocomposites**

A finite element analysis based COMSOL Multiphysics has been conducted to simulate the thermoelectric performance on the printed thermoelectric nanocomposite. To define heat throughout the printed thermoelectric nanocomposite, the *Heat Transfer in Solids* physics interface has been used. The *Electric Currents* physics interface has also been applied to calculate the electric field, current, and potential distribution. Finally, in order to couple the
thermal and electrical behaviour of the model, the *Thermoelectric Effect* multiphysics has been utilised for the modelling of the thermoelectric generation. Figure S8a illustrates that temperature at the top and the base of the model were set to 320 K and 260 K respectively to have 60 K temperature difference. An open-circuit voltage of ~2 mV was generated across the nanocomposite as displayed in Figure S8b. Furthermore, the simulation of the temperature and electric potential distribution in the microscale of nanocomposite has also been conducted as shown in Figures S8 c & d, with the matrix set to PEDOT:PSS polymer and in-filled spheres set to Bi$_2$Te$_3$ nanoparticles.

**Figure S8.** (a) Temperature profile and (b) the generated voltage of the 5-layer printed thermoelectric nanocomposite in the macroscale, and (c) the temperature and (d) electrical potential distribution in the microscale.
S7: Fabrication and Measurement of Flexible Thermoelectric Generators

Two different prototypes of flexible printed thermoelectric generators (TEGs), as illustrated in Figure S9, were fabricated with the ink blended with PEDOT:PSS polymer and Sb$_2$Te$_3$ particles via our AJP method. For the parallel-connected mode shown in Figures S9 a & b, 340 $p$-type Sb$_2$Te$_3$-PEDOT:PSS nanocomposite arrays were printed onto a 15cm x 15cm flexible polyimide sheet as thermoelectric legs, while two silver circular lines were printed onto both edges of the thermoelectric legs as metal interconnects to connect them electrically in parallel. For the series-connected mode presented in Figures S9 c & d, silver lines were printed in between each printed thermoelectric leg to join the 50 printed thermoelectric legs electrically in series. For a working thermoelectric module, it should be continuous electrical contact and good thermal contact. Thus, silver nanoparticle ink was chosen and printed via our AJP method as electrical connections due to its high electrical and thermal conductivity, low sintering temperature, and good physical and chemical stability over a large operating temperature range.\textsuperscript{6}

In order to investigate the practical thermoelectric performance of these printed thermoelectric nanocomposites, they were cut and assembled with a tin can into a simple prototype of TEG, as illustrated in Figures S9 e & f. To improve their overall output power, two identical printed TEGs were stacked up and electrically connected in series. The copper tape was also employed as the thermal conducting medium between the heat source (i.e. tin can) and thermoelectric legs. Then, the tin can was filled with boiled hot water (~100 °C) to create a temperature gradient between the inner and outer of the printed thermoelectric legs, where the temperature difference was found to be ~20 °C with the aid of a pocket-sized infrared thermal imaging camera (FLIR). The parallel-mode TEG with 340 thermoelectric legs and $R_{\text{int}}$ of ~58 $\Omega$ generated $V_{oc}$ of ~0.6 mV, $I_{sc}$ of ~0.7 mA, and $P_{\text{max}}$ of ~0.42 $\mu$W at $\Delta T$ of ~20 °C, while the
series-mode TEGs with 50 thermoelectric legs and $R_{\text{int}}$ of ~2700 $\Omega$ produced $V_{\text{oc}}$ of ~40 mV, $I_{\text{sc}}$ of ~0.6 mA, and $P_{\text{max}}$ of ~24 $\mu$W. The series-connected mode exhibited much higher voltage and power output, while the parallel-connected mode gave a slightly higher current. Importantly, these flexible printed TEGs could overcome the limitations that their rigid counterparts have, and the challenge of assembling many individual legs into one module without using solders can be solved with the help of our large-area printing technique. The thermoelectric performance of these printed TEGs can be further improved through stacking up several of them. Although these polymer-based thermoelectric devices can only be operated in low-temperature environment due to the thermal stability nature of polymer, with respect to wearable TEGs, the thermal stability is not a major issue to be considered.
Figure S9. Photo of the 5-layer printed (a) parallel and (c) series connected thermoelectric nanocomposite arrays for thermoelectric generator fabrication, and the schematic representation of AutoCAD-designed patterns for (b) parallel and (d) series-connected modes. The prototype of the printed thermoelectric generator in (e) parallel and (f) series mode.
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