



# Flexible and thermostable thermoelectric devices based on large-area and porous all-graphene films



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## ABSTRACT

Thermoelectric (TE) generators, being able to convert temperature gradients into electricity, are an appealing eco-friendly energy harvesting technology. In order to broaden the applications of TE materials, many researchers have focused their efforts towards flexible TE materials to substitute the commercial rigid TE devices. Most of these works used polymers as flexible TE materials, but their lower efficiency and melting point in comparison to inorganic TE materials are limiting factors for many applications. Here, we report the fabrication of a flexible and thermostable TE generator based on porous all-graphene films. The output power of the generator is up to 0.43  $\mu\text{W}$  for a temperature gradient of 75 K. In addition, it runs at 550 K higher temperature than current flexible TE devices, which allows its application at much higher temperatures than conventional flexible TE.

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## 1. Introduction

As an attempt towards sustainable development thermoelectric (TE) materials have been explored to harvest electrical energy from industrial waste heat [1,2]. Significant efforts have been pursued towards crystalline semiconductor materials with high TE figure of merit (ZT) and low thermal conductivity [3]. Up to now, it is undeniable that the state-of-the-art TE materials are inorganic semiconductors, such as lead and bismuth telluride [4], skutterudites-cobalt antimonide et al. [5]. However, due to their toxicity (such as Pb, Sb and Se), high cost of raw materials, scarcity of natural resources (such as Te), limited processability, potential for heavy metal pollution, and more importantly, their rigidity, restrict the broad application of TE technology in curved, rugged and complicated surface of industrial environment to a great extent [6]. Therefore, substantial attention has been given to organic TE materials due to their non-toxicity, availability, and excellent flexibility, such as polyaniline [7], polyacetylene [8],

polypyrrole, polythiophenes [9], PEDOT and PEDOT: PSS [10,11]. Unfortunately, these organic TE materials are still inferior to conventional inorganic TEs due to their low conductivity and Seebeck coefficient [12–14]. Therefore, several studies also pursue the combination of inorganic materials and polymers through the fabrication of flexible TE nanoscale composites. For instance, Carroll's group has reported a CNTs/PVDF composite based thermoelectric fabrics [15]. Yu's group has reported many works on energy harvesting by using flexible TE composites, such as polyaniline/CNTs [16], MWCNT:DOC/PVAc [17], MWNT/(PEDOT:PSS)/TCPP [18], and CNTs/PEI:DETA [19]. However, the use of organic materials also constrains the implementation of flexible TE for high temperature applications. Thus, the implementation of more practical and cost-effective devices for harvesting electricity from industrial waste heat, it still a challenge unless materials with excellent thermoelectric performance, high mechanical flexibility, and good heat resistance could be fabricated.

Lately, a lot of attention has been placed on well-known 2D carbon material, graphene, due to its exceptional electronic transport properties (a suspended single-layer graphene has a record carrier mobility of above 200000  $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ), high Seebeck coefficient ( $\sim 80 \mu\text{V K}^{-1}$ ) and mechanical properties (highest reported

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Young's modulus of ~1100 GPa and fracture strength of 130 GPa) [20–25]. Systematic theoretical study of the thermoelectric properties of nanoscale thin stripes of graphene have been reported [26,27]. Grossman et al. first predicted theoretically that the graphene with suitable chemical functionalization (hydrogen and pentane) can reach its maximum ZT ~3 at room temperature [28]. Hossain et al. reported an enhancement of ZT of the monolayer graphene nanoribbons by introducing nanopores at the nanoribbons structure and tuning the pores to their optimal dimension [29]. To the best of our knowledge, however, there have been few reports concentrating on thermoelectricity of macroscopic graphene films and device assembly [30,31].

In the present study, we describe the fabrication of flexible TE device based on free-standing graphene films with a porous three-dimensional (3D) structure prepared by blade coating method.

## 2. Experimental

### 2.1. Synthesis of the PGOFs

All the reagents were of analytical grade and ultrapure water (18.2 M $\Omega$  resistance) was used in all experiments. The graphene oxide (GO) gel was prepared as previously reported by our group [32]. Briefly, 0.75 g of as-purchased graphite oxide (SE2430 purchased from The Sixth Element Changzhou Materials Technology Co., Ltd.) were dispersed in water (100 mL) to obtain a homogeneous dispersion. Next, the dispersion was subject to 1 h ultrasonication using an Ultrasonic Cleaner (Branson 3510, 350 W, Emerson) followed by 30 min of probe ultrasonication (FS-300, 300 W, Sonix Ultrasonic Instrument) for exfoliation of graphite oxide into GO. To remove any unexfoliated graphite oxide and larger graphene sheets, the resultant brown dispersion was then centrifugated for 30 min at 4000 r.p.m (centrifuge 5702, Eppendorf). The resulting supernatant was concentrated to form viscous gels for blade coating by further rotary evaporation at 50 °C under ~0.09 MPa for about 1 h (see Supplementary Fig. S1).

The wet films were fabricated via blade-coating with an automatic coater (AFA-III, MTI Corporation) by spreading the gels out on prewashed (with alcohol) emery paper (as shown in Fig. 1a and Table S1). The emery paper was used for the substrate because of the rough surface which helps films to be easily peeled off. The thickness was accurately controlled (in the range of 0–100  $\mu\text{m}$ ) by adjusting the concentration of GO suspension and the distance of scraper to substrate in order to form a uniform wet film. After dried halfway under ambient conditions, the film was peeled off from the substrate and quick-frozen in liquid nitrogen (as shown in Fig. 1b, the film with the area of 25 cm  $\times$  11 cm). Lastly, the film was freeze-drying for 24 h to obtain the thoroughly dried porous graphene oxide films (PGOFs). As shown in Fig. S8, relatively uniform PGOFs can be fabricated through this procedure. For comparison, compact graphene oxide films (CGOFs) were also prepared by drying the wet film for about 8 h at ambient conditions.

### 2.2. Fabrication of thermoelectric devices

To synthesize *p*-type porous graphene films (PGFs) iodine ion doping is used as previously reported [30]. In brief, the as-prepared PGOFs were horizontally immersed in HI (55 wt%) at room temperature for 1 h in order to reduce the pristine PGOFs. The obtained films were then alternately washed with water and ethanol several times to completely remove HI, and then were kept in water at room temperature for about 12 h. The films were then freeze-dried during 48 h for further characterization and devices fabrication. This procedure of chemical reduction endows the porous graphene

films (PGFs) with a high conductivity, also realized the *p*-type doping by iodine dopant [33,34]. The reduction and doping of the as-prepared PGOFs was carried out in a tubular reactor. After flowing NH<sub>3</sub> (highly purified, 40 mL min<sup>-1</sup>) for about 5 min, the furnace was slowly heated (3 °C/min) up to 600 °C. After 1 h at 600 °C, the furnace was cooled down in ammonia atmosphere. The films were removed from the tube reactor after the oven temperature was below 40 °C. The pure PGOFs were annealed in NH<sub>3</sub> (as the protective atmosphere) in order to obtain the *n*-type modules [35,36]. The *n*- and *p*-type compact graphene films (CGFs) were obtained similarly but instead of freeze-drying the films, they were vacuum dried at 60 °C for 6 h. As-prepared *n*- and *p*-type PGFs were cut into ten stripes (80 mm long  $\times$  7 mm wide). The TE modules were made by alternatively connecting *n*- and *p*-type PGFs mounted over a polyimide substrate (150 mm long  $\times$  90 mm wide). Each stripe was electrically connected in series by using silver wires (diameter 0.2 mm) as electrical contacts, and at each side of the PI substrate five couples were placed. A fine layer of conductive silver paint was applied to the contact regions between the silver wire and the PGFs stripes to reduce the electrical resistance of the interconnection, while copper foils tape was used for reinforcing the modules.

### 2.3. Characterization and measurements

The morphologies and the structure of the PGFs were observed using a scanning electron microscopy (SEM, Phenom G2 Pro, FEI) at 10.0 kV. Chemical analysis of the distribution and efficiency of doping process was obtained through an SEM (Quanta-250, FEI) equipped with an energy dispersive spectrometer (EDS) detector (Oxford Instruments). Raman spectroscopy measurements were carried out on a Laser Raman Spectrometer (inVia Reflex, Renishaw) at an excitation wavelength of 633 nm. The conductivities were calculated according to the following equation:  $\sigma = (L/WT) \times (1/R)$ , where L, W and T correspond to the length, width and thickness, respectively. The thickness of the films were acquired by SEM and the electrical resistance of the doped PGFs were performed by the two-probe method using a Zahner electrochemical workstation (Zennium CIMPS-1, Zahner), which is the average value of multiple measurement results. The Hall measurements were performed with the Hall effect measurement system (HMS-3000, Ecopia). The temperature distribution images of the device were obtained in real-time by an infrared (IR) camera (A300, FLIR). The TE voltage ( $V_T$ ) and current were recorded with the high power system sourcemeter instrument (2657A, Keithley). Temperature of the hot surface was controlled by a micro-heater, while the cold surface was assured through a copper ingot heat sink to ambient. The Seebeck coefficient was measured at room temperature along the in-plane direction of the film and carried out as shown at the schematic diagram in Fig. S9. The thermal conductivity was measured at room temperature using a self-heating method (the results and the calculation are shown in Fig. S10). All of the photographs were captured using a charge-coupled device (CCD) video camera (PowerShot G10, Canon).

## 3. Results and discussion

The maximum speed of blade coating (Fig. 1a) to form a uniform wet film was 6 m min<sup>-1</sup>, which is extremely favorable for industrialization, while the width of the film can be magnified with a larger machine. Fig. 1b–f demonstrate the high flexibility of the PGOFs films after NH<sub>3</sub> annealing and HI reduction. For demonstrating the flexibility of the *n*- and *p*-type modules (called legs), the rectangular stripes of the films were rolled around a ~5 mm diameter PTFE stick, thus enabling its application on curved

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