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Developing Printable Thermoelectric Materials Based on Graphene Nanoplatelet/Ethyl-Cellulose Nanocomposites

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Abstract

Thermoelectric (TE) materials have drawn a lot of attention as a promising technology to harvest waste heat and convert it into electrical energy [1].
Recently, the interest in organic thermoelectrics materials is rapidly increasing because they have benefits such as light weight, low thermal conductivity, and high flexibility. Up to now, most of the attention was on conducting polymers, like P3HT, PEDOT, but these materials have limited stability, which has hindered their widespread applications. [2].
Herein [4], an efficacious processing strategy to fabricate printable TE materials has been developed with Ethyl cellulose (EC), a non-conducting polymer, as the polymer matrix and with Graphene nanoplatelets (GNPs) as fillers. EC, one of the cellulose's derivatives, has been widely used as a binder in the printing pastes [3]. In contrast with conducting polymers, EC is more stable, easy processable, green, and economical.
Conductive pastes with different filler contents have been fabricated. The weight ratio of GNPs and EC were ranged from 0.2 to 0.7. The trend of electrical conductivity as a function of W_{GNPs}/W_{EC} represents percolation behavior. We observed that the Seebeck coefficients of all of the samples were in the range of 15 to 22 µV/K. The highest electrical conductivity and power factor at room temperature (355.4 S/m and 254.0 nW/mK^2, respectively) was obtained for the ratio of 0.7.
Moreover, a 3D structure form (cylindrical pellet) from the highest conductive paste was also fabricated. The proposed technique demonstrates an industrially feasible approach to fabricate different geometries and structures for organic TE modules. So, this approach could provide a good reference for production of high efficiency, low-temperature, lightweight, low-cost, TE materials. So, this approach could provide a good reference for the development of high-efficiency, fast, easy and cost-effective method toward upscaling.

Introduction

Thermoelectric generators (TEG) traditionally are related to well designed semiconductor alloys operating in selected temperature ranges, from medium to very high ΔT.

It is very difficult to simultaneously optimize in the same materials the different phenomena determining the overall TEG capability:

- Seebeck coefficient of the material α
  (as high as possible to generate significant voltage for a given temperature gradient)
- Thermal conductivity λ
  (as low as possible to retain the heat at the junction)
- Electrical conductivity σ
  (as high as possible to minimize Joule heating)

Nanostructured materials can bring to high *ZT* (also at room temperature) because 2D materials and composites tend to accomplish two important phenomena:

1) they tend to significantly increase density of states which increases the Seebeck coefficient in these materials;

and

1) they tend to de-couple the electrical and thermal conductivity allowing quantum well materials to exhibit low thermal conductivities without a corresponding decrease in electrical conductivity

The desirable properties are embodied in the **figure-of-merit:** $Z = \alpha^2\sigma/\lambda$ and the unit of Z is 1/K.

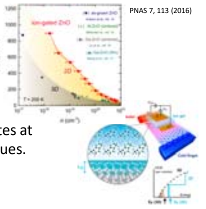
Motivation: Nanostructured Composites

Seeback coefficient based on Mott expression is correlated to changing of σ (or energy-dependent electrical conductivity) near the Fermi level

Effect of DOS function on Seeback coefficient:

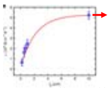
$$S = \frac{\pi^2}{3}\frac{k_B}{q}k_B T\left\{\frac{d\left(\ln\left[\sigma(E)\right]\right)}{dE}\right\}_{E=E_F}$$

σ(E)=n(E)qμ(E)
n(E)=DOS(E) f(E)


PNAS 7, 113 (2016)

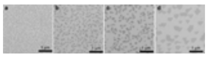
Materials such as lightly doped semiconductors for which the density of states at the Fermi level, changes rapidly with energy are expected to have large S values. However, such materials are generally poor electrical conductors.

PNAS June 7, 2016 vol. 113 no. 23 Enhanced thermopower in ZnO two-dimensional electron gas

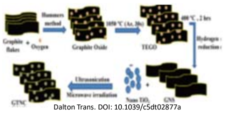


Thermal conductivity (k) Vs grain size (lg)

Influence of grain boundaries (GBs) on the electrical and thermal transport. Different scaling laws of thermal and electrical conductivities of graphene films as a function of grain size.


Nature comms 2017 14486

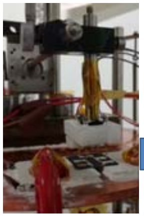
Nanocomposites consisting of highly conductive particles embedded in an insulating matrix. Nano TiO_2 is decorated over 2D graphene sheet and its presence helps to destroy thermally conducted network but allow electrical network to remain intact.

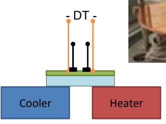


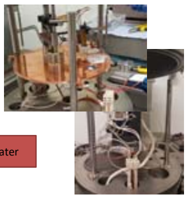
Dalton Trans. DOI: 10.1039/c5dt02877a

Electrical Set-up

Vacuum chamber for device characterization, controlled by Newport 8000 TEC controllers for cooling and heating stages, and Keithley 2420 source meter for resistivity, IV and Seebeck characterization.
Planar or vertical configuration for thin film or pellet characterization.
Dedicated Labview software for the control of thermal stabilization times.

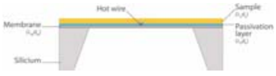






Thermal conductivity:

Measurement based on 3ω method with LINSEIS TFA



differential measurement - covered chip ($\lambda_{meas}t_{meas}$) vs empty membrane

$$\lambda_{measured} \cdot t_{measured} = \lambda_M t_M + (\boxed{\lambda_S t_S} + \lambda_P t_P)$$

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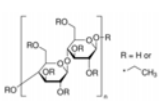
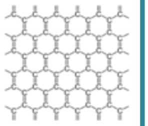
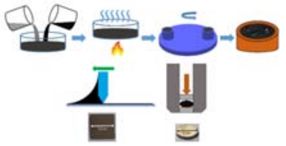
Material Definition and Preparation Technique

Ethyl cellulose is an insulator polymer which has been widely used as a binder for printing different types of films like Titania, and carbon[3]. This polymer is soluble in variety of solvents and, it is green, inexpensive. Here, the paste of Graphene nanoplatelets (GNs) and ethyl cellulose (EC) has been prepared in different ratios between GNs and EC.



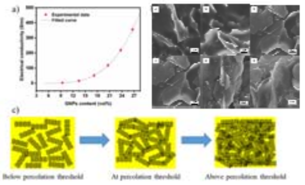


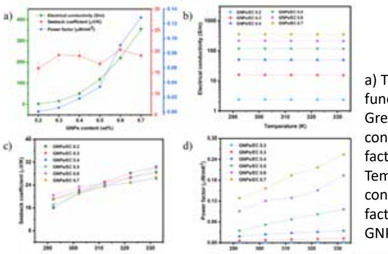


An automated machine implemented with interchangeable blade has been used to deposit the graphene paste on glass 2.5x2.5cm2. Blade coating is based on a doctor blade (knife) that spreads a pre-dosed liquid over the substrate. It guarantees easy construction and operation. Two stripes of silver for thermoelectric measurements were made by silver ink. The thickness of all samples were measured by profilometer (dektak), with thicknesses in the range of 9 to 13 µm. The pellets with thickness about 2-3 mm were make by pellet maker, and after that with high pressure press it became more compact.

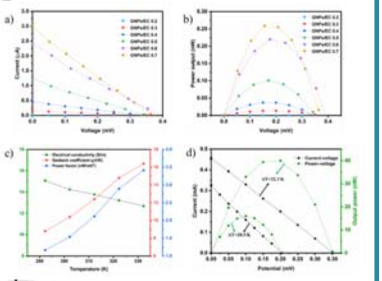
Thermoelectric characterization

Adding the fillers to insulators significantly improves the electrical conductivity and partially increase the thermal conductivity [5].
The electrical conductivity increased by adding the filler, according to percolation model σ=σ0(φ-φ0) t [4]

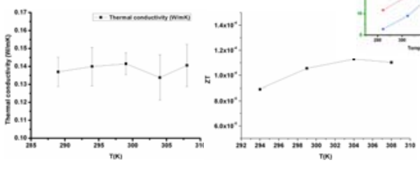




a) TE properties of GNPs/EC nanocomposites as a function of GNPs content at room temperature. Green, red, and blue symbols are electrical conductivity, Seebeck coefficient, and power factor.
Temperature dependence of b) electrical conductivity, c) Seebeck coefficient, and d) power factor of GNPs/EC nanocomposites with different GNPs contents.



a), b) Film:
a) current-voltage and b) power-voltage characteristics of GNPs/EC film with different filler contents at 20 degree temperature difference,
c), d) Pellet:
Temperature dependence of electrical conductivity, Seebeck coefficient, and power factors of GNPs/EC pellets, d) The current-voltage and power-voltage characteristics of GNPs/EC pellets at temperature difference of 20.5 K and 32.3 K



Thermal conductivity and Figure of merit ZT of GNPs/EC nanocomposite film with 0.7 filler contents

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CONCLUSIONS

- Electrical conductivity values of GNPs within an EC matrix have increased based on the percolation model.
- Seebeck coefficient was not dependent on the filler content, and the higher filler content leads to a higher TE performance.
- Pellet from the highest conductive paste was fabricated, showing the potential of the process for achieving higher output power.

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