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# Thermoelectric Nanocarbon Ensembles

**Principal Investigator: D.M. Gruen**

**Argonne National Laboratory**

**2009 U.S. Department of Energy Hydrogen Program and Vehicle Technologies**

**Annual Merit Review and Peer Evaluation Meeting, May 18-22, 2009, Arlington, VA.**

# Collaborators at ANL

**P. Bruno, J. Routbort, D. Singh**
**R. Arenal*, M. Xie**

**L. Curtiss, P. Redfern**

*** ONERA-CNRS, Paris, France**

# Overview

## Timeline

- Start- Oct 2007
- Continuing Development Program
- Progressive Series of Optimization Steps

## Budget

- Funding received for FY08 500K
- Funding received for FY09 400K

## Partners

- DOE/BES/Materials Science
- Michigan Technological University

  *(Graduate Student, Dept. of Physics)*
- ONERA-CNRS, Paris, France *(HRTEM, HREELS, MWRaman)*
- ORNL

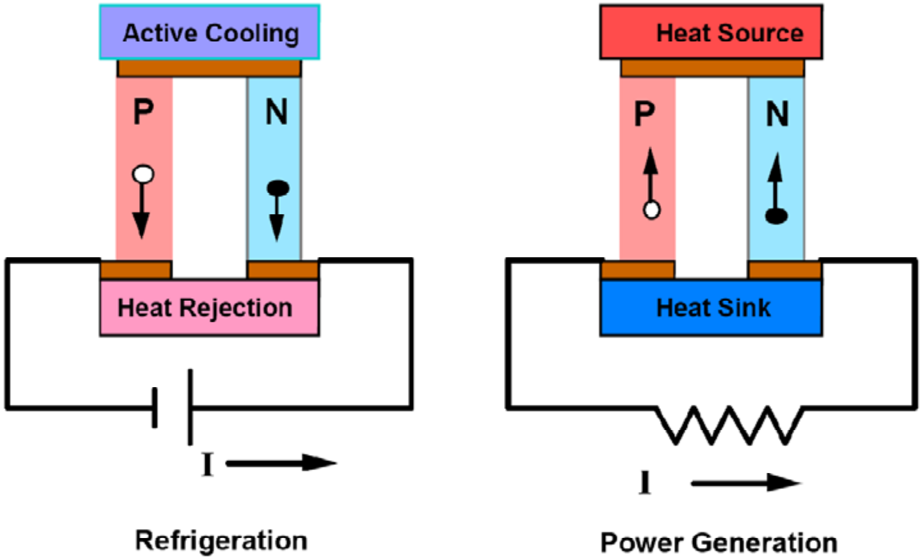
  *(Thermal Conductivity)*
- Naval Surface Weapon Research Center

  *(High Temperature Annealing)*

# Barriers

- Need higher ZT materials operating at high temperatures
- Must be environmentally benign, readily abundant, and cost effective
- Must be manufacturable in bulk amounts
- Must be mechanically and thermally stable

$$ZT = \sigma S^2 T / \kappa$$



# Objectives

- **Create a new class of high-efficiency, high-temperature thermoelctric materials based on highly entropic nanocarbon ensembles.**
- **The materials are designed to increase fuel efficiency by 3-10% through automotive and truck waste heat recovery.**
- **If substantial increases in ZT can be achieved these materials would also lend themselves to applications such as solar thermal energy conversion.**

# Milestones

- **2008 - Proof of Principle**

  **Bulk, thermally and mechanically stable p-type nanocarbon ensembles were successfully synthesized**

  *(D. Gruen, P. Bruno, M. Xie, APL 2008, 92 (143118) )*

- **2009 – 20 to 40 fold increase of Power Factor to 1 $mW/K^2cm$ after equilibrium annealing at 2500K**

  *(D. Gruen, P. Bruno, R. Arenal, J. Routbort, D. Singh, M. Xie, JAP in press)*

# Milestones cont.

- **2009 – Density functional calculations show that boron doping creates a high density of states within thermal energies of the Fermi level**

  *(P. Redfern, D. Gruen, L. Curtiss, Chem. Phys. Lett., in press)*

- **2009 – Further increase in Power Factor by quench annealing**

# Approach

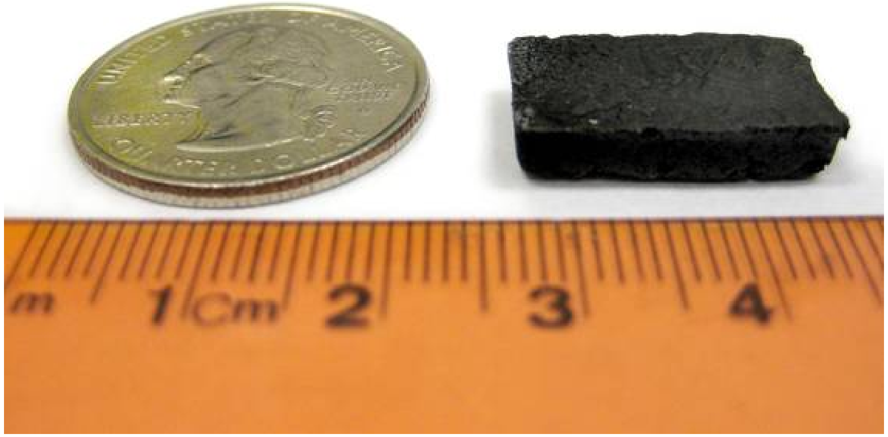
**The search for a new class of potentially high ZT materials focuses on the following characteristics:**

- **Preservation of nano-crystallinity at high temperatures**
- **Potential for high electronic entropy**
- **Potential for p and n-type doping**
- **Not resource limited**
- **Environmentally benign**
- **Scalable fabrication, low cost production**

***Nanocarbons Ensembles have been found to possess all the above properties*** **and have been chosen as a model system on which to study thermoelectric performance. In addition they lend themselves to**

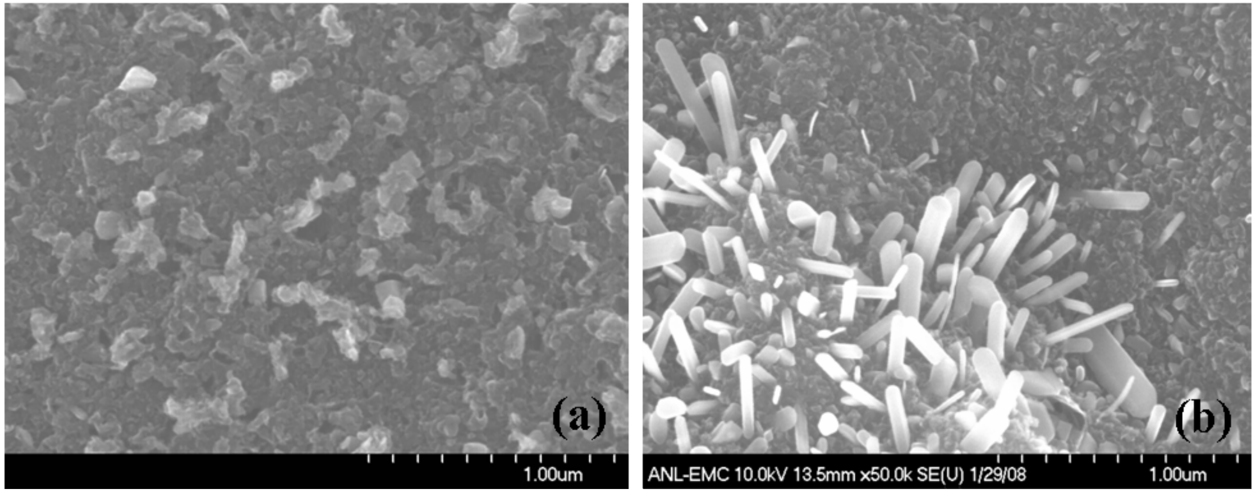
- **Rigorous density functional theoretical calculations.**

# Results/Accomplishments




**Photograph of the nanocarbon ensemble (NCE) as synthesized.**

**Scanning Electron Microscope (SEM) micrographs for (a) NCE and (b) boron-doped NCE**



# Technical Accomplishments

## In-house apparatus for measuring Seebeck coefficient and electrical conductivity on the nano-ensembles

- 1800K, single-zone tube furnace and controller
- Keithley 2700 Multimeter/Data Acquisition System
- Keithley 6220 Current Source
- Computerized data acquisition

# Technical Accomplishments

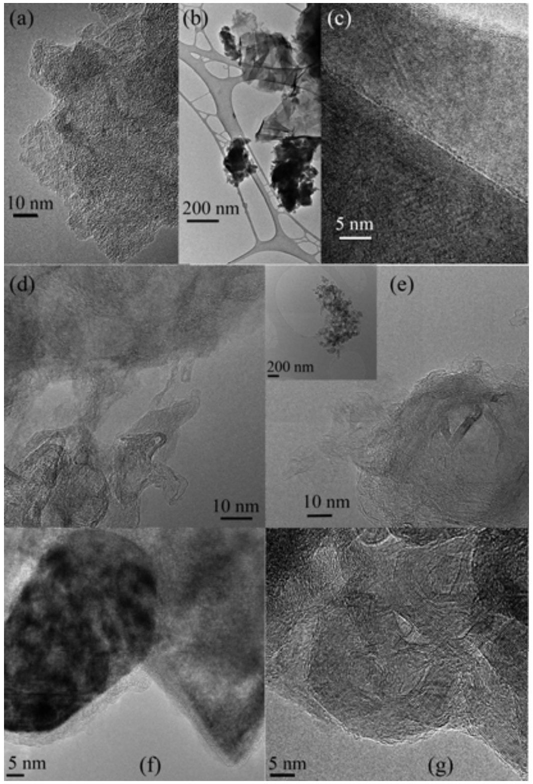
## Induction furnace


- Model SI-7KWHF induction heater
- Omega IR optical pyrometer
- 2000K, RF furnace
- Helium quenching capability

Quenching ramp:
1600C→1000C in 25s
1000C→ Troom in 150s

# Results

## TEM micrographs of boron doped NCE

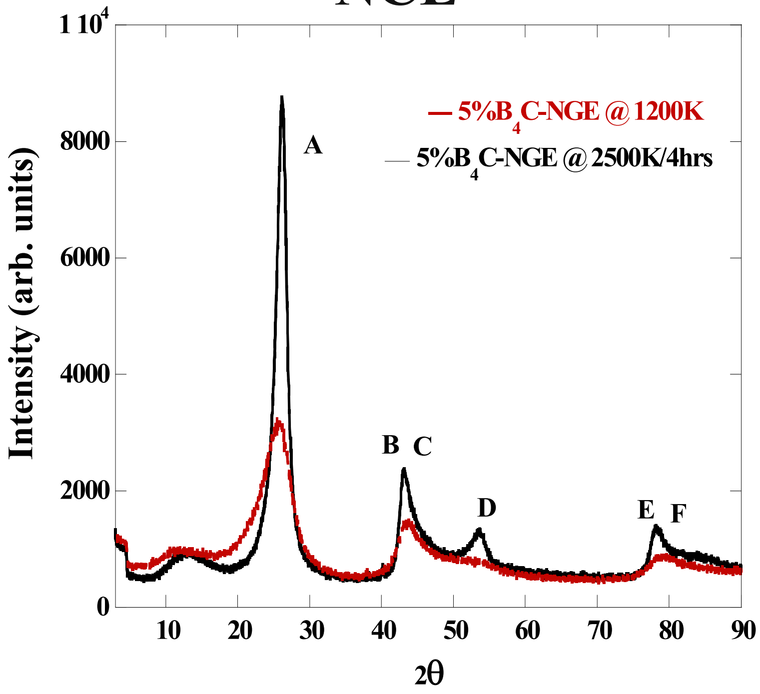



As- fabricated

Annealed at 1700K

Annealed at 2100K

## XRD spectra of boron doped NCE

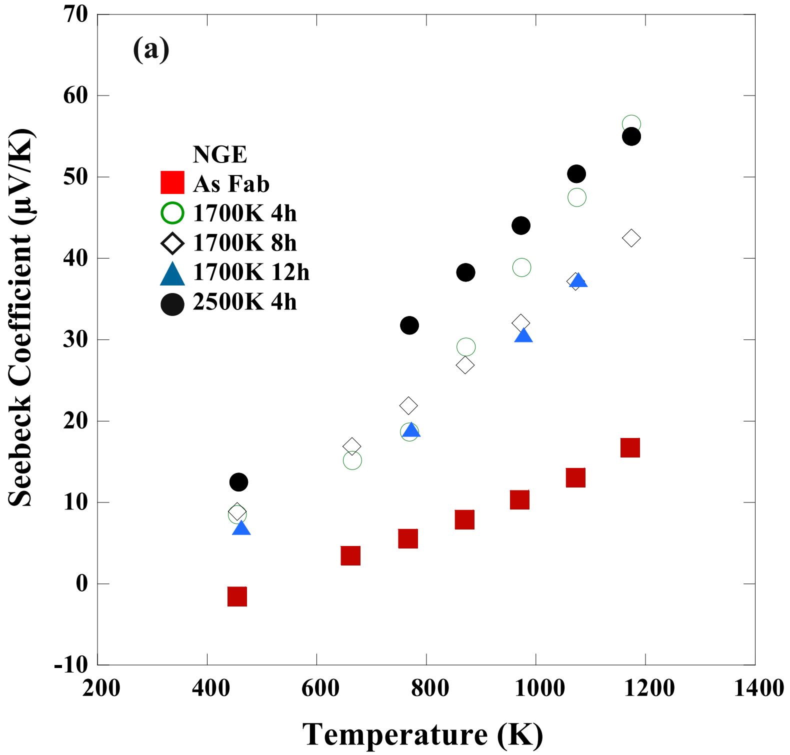


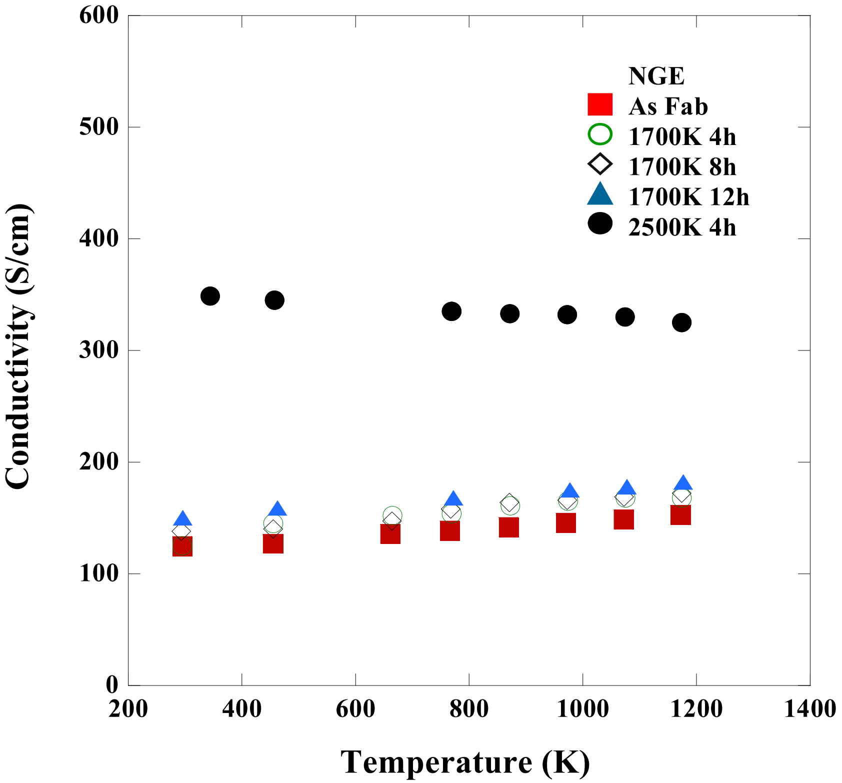

as fabricated and after annealing at 2500K

**The thermal treatment reduces the amount of unorganized (disordered) carbon in the material**

# Results

**Seebeck coeff. (left) and Electrical conduct. (right) results for a boron doped NCE sample as a function of temperature and annealing times.**

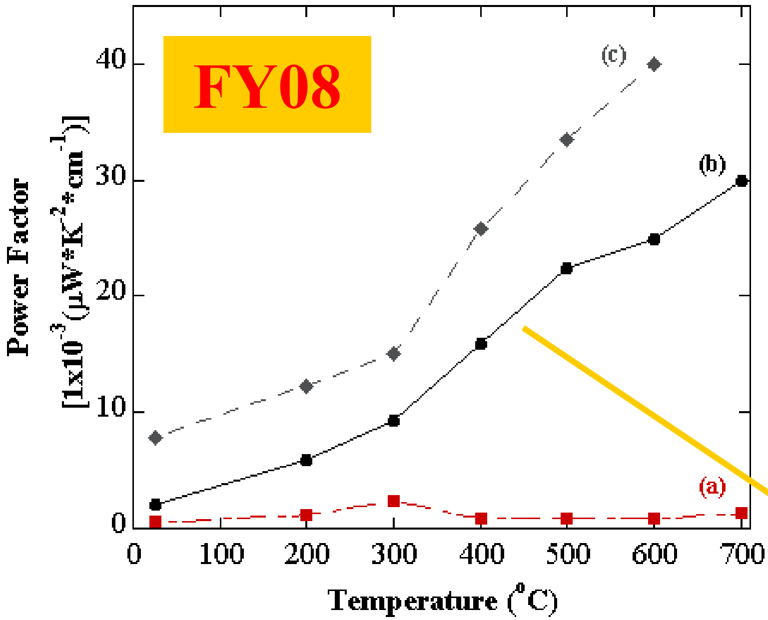


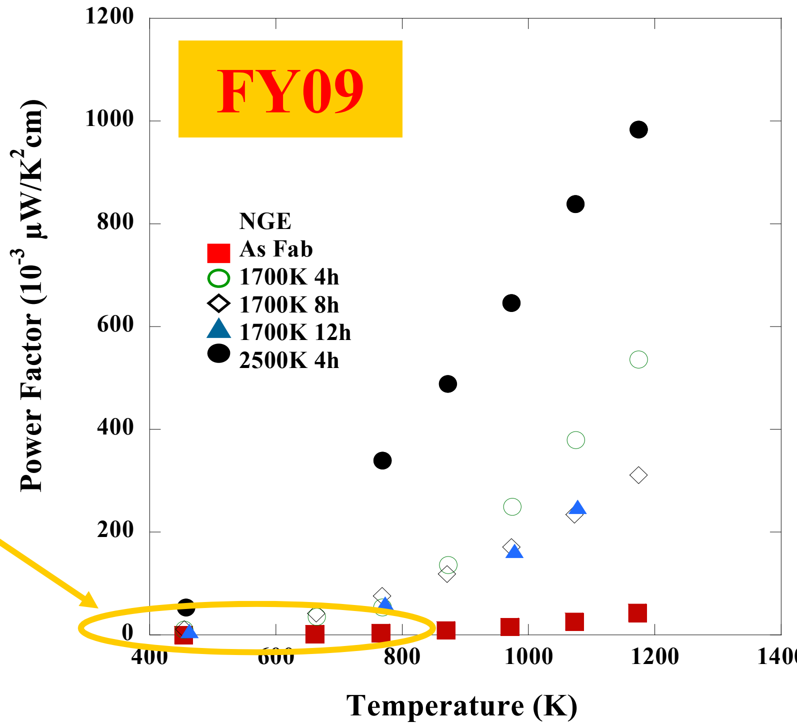




**Seebeck coeff. and electrical conductivity increase with the annealing temperature and time**

# Results & Progress

## Power factor (PF): effect of the doping (left) and annealing (right)

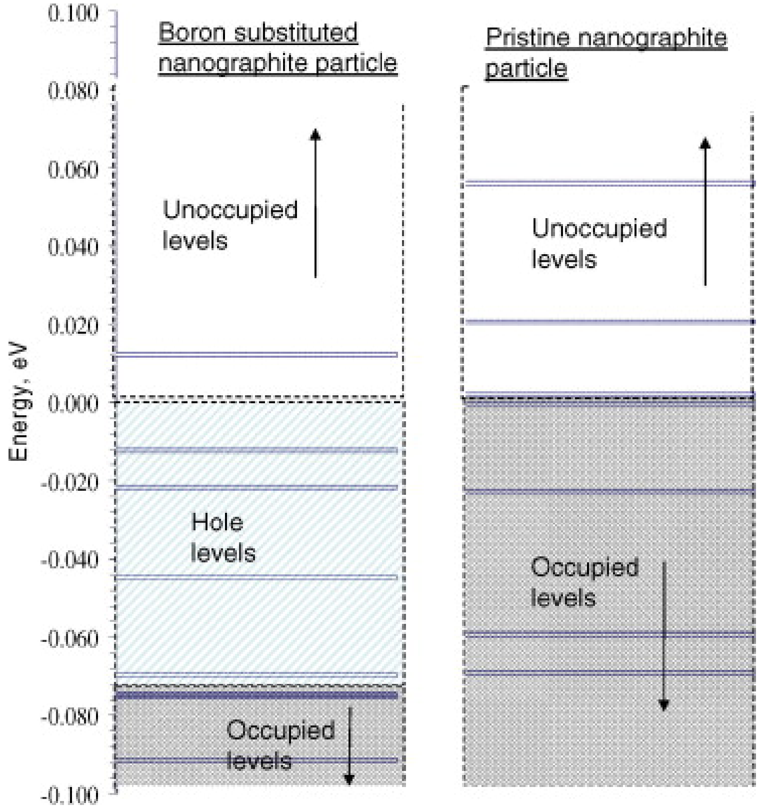



- PF increases about 30-40 times with boron doping
- PF increases about 3 orders with annealing temp and time

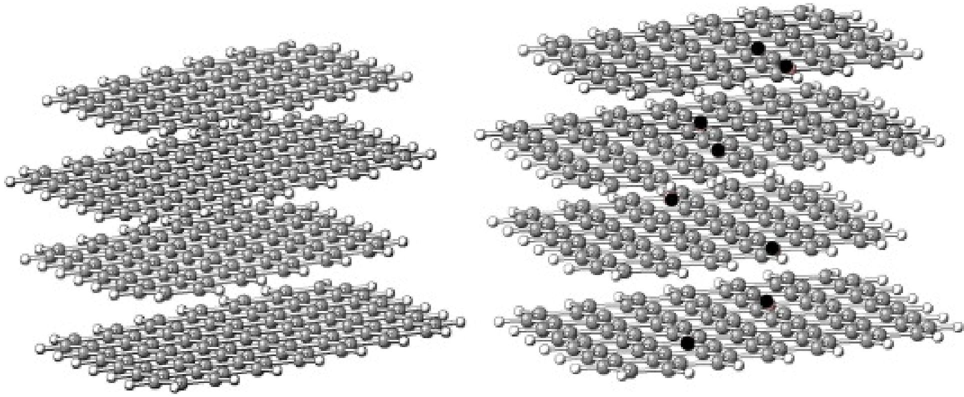
**A value of 1 $\mu$W/K$^2$cm for the power factor has recently been attained with compacts annealed at 2500K**

# Results/Theory



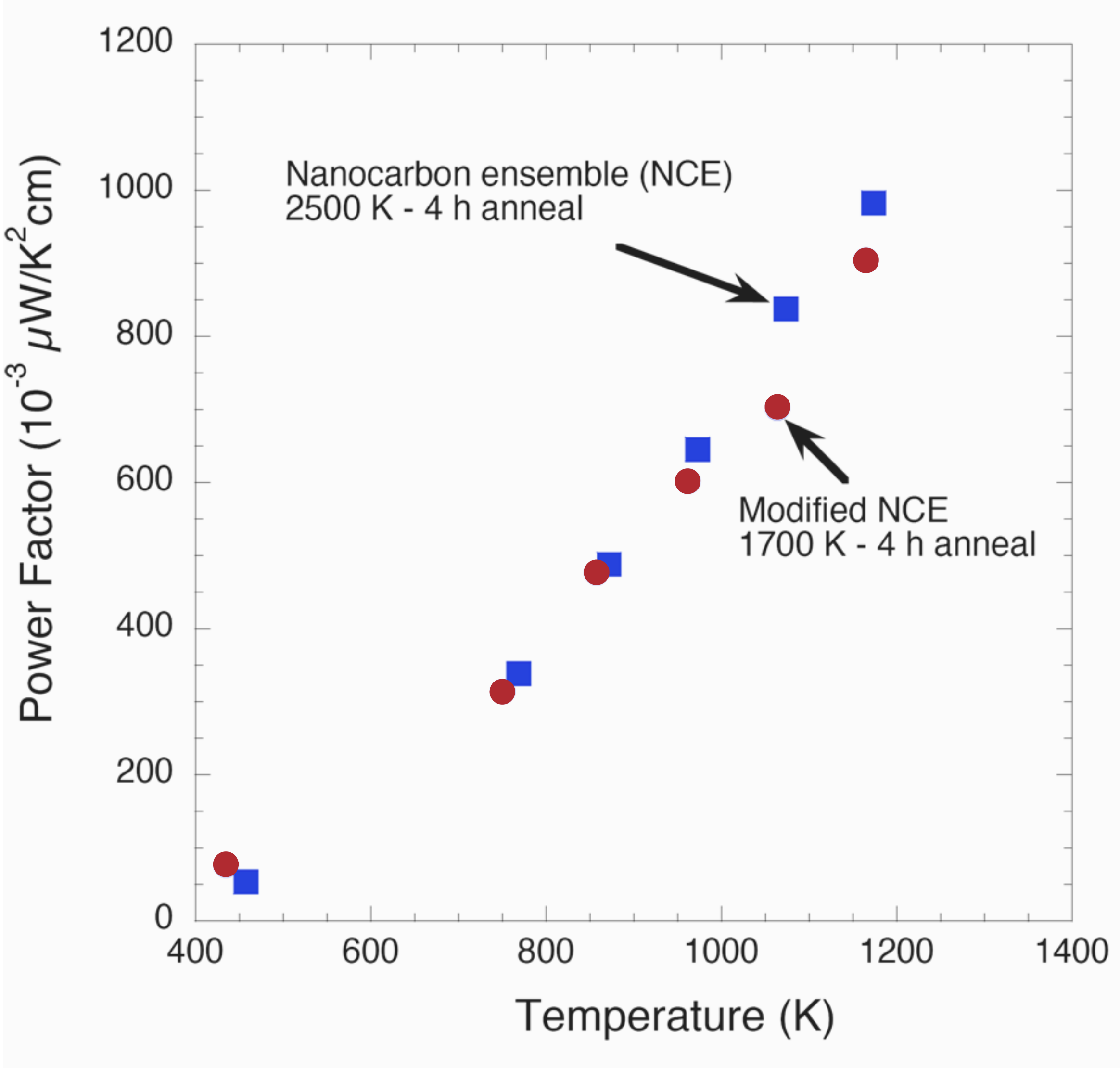

**Results from Density Function Tight Binding calculations.**

**Energy levels for pristine and boron substituted nanographite particles with four layers of graphene sheets.**



**Structure of 4-layer nanographite particles with and without boron substitutions (filled black circles).**

# Results & Progress




- Modified NCE has the same PF after 1700K anneal as the NCE after 2500K.
- We expect that the PF of the modified NCE will be strongly enhanced after 2500K anneal.

# Future Work

- **Increase Seebeck Coefficient**
  - ✓ **Modification of nano-ensemble composition by inclusion of high Seebeck coefficient nano-materials**
  - ✓ **High temperature annealing followed by quenching**

- **Increase the electrical conductivity**
  - ✓ **Optimize polyhedral graphene structures by 'templating" and other techniques**

# Future Work (2)

- **Decrease the thermal conductivity**

✓ Control of density and porosity of the compacts through variations in the synthesis process

- **Extend theoretical calculations**

✓ Molecular analogues of graphene sheet functionalized with high Seebeck coefficient nano-crystallites

✓ Development of transport theory of nanoporous thermoelectric nano-ensembles

# Summary

- Bulk boron doped nanocarbon ensembles based on the concept of strongly enhanced electronic configurational entropy have been shown to exhibit promising TE properties.

- During the last year, power factors have been increased 20 to 40 fold over previous results primarily by high temperature annealing procedures which increases both the Seebeck coefficient and the electrical conductivity.

# Summary (2)

- The thermal conductivity of the nano-ensembles is in the $10^{-2}$ W/cmK range.

- The NCE TE's show a Seebeck coeff. that increases with T up to at least 1300K which has advantages for high T applications.

- Future work is aimed at the creation of transformational thermoelectric materials by increasing the Seebeck coefficient exploiting compositional changes and using new annealing/quench techniques.