Organic Molecule Functionalized Zn_3P_2 Nanowire Inorganic-Organic Hybrid Thermoelectrics

Sreeram Vaddiraju

Assistant Professor

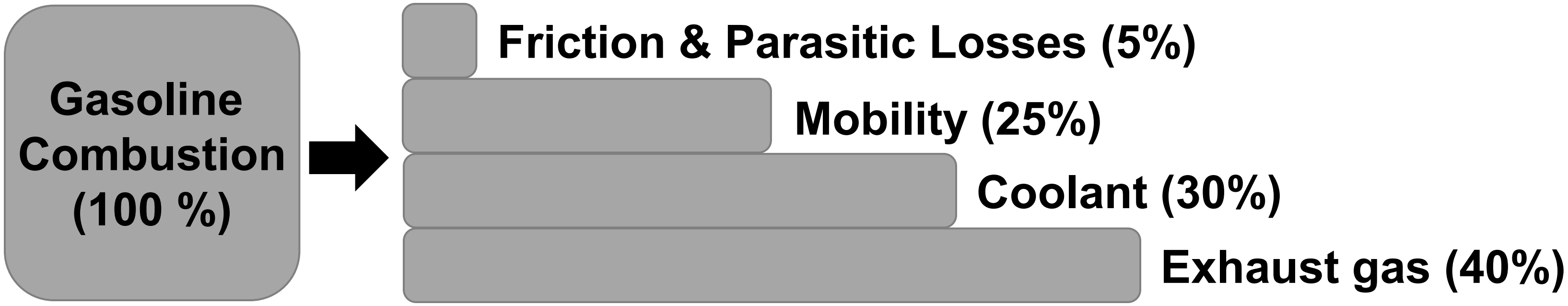
Department of Chemical Engineering

Texas A&M University

Email: Sreeram.vaddiraju@tamu.edu

Thermoelectrics for Automobiles

Energy path for vehicles running on gasoline-fueled internal combustion engine



Gasoline Combustion (100 %)

Friction & Parasitic Losses (5%)

Mobility (25%)

Coolant (30%)

Exhaust gas (40%)

Aim:

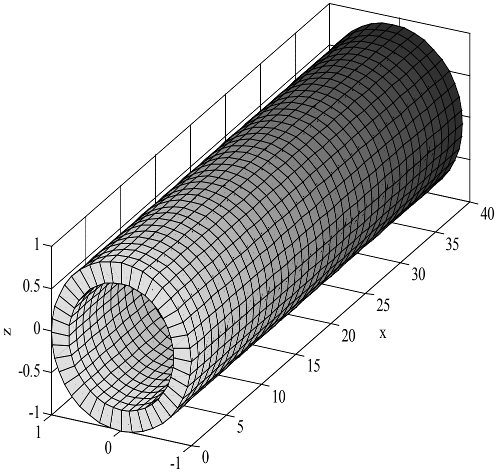
•Fabrication of highly efficient thermoelectric modules for recovering waste heat from automobile exhausts

Requirements:

- Materials that exhibit high thermoelectric performance
- Large-scale production of materials in the right format and dimensions
- Materials that exhibit high stabilities even at elevated temperatures

Yang *et.al*, Journal of Electronic Materials, 38, 1245, 2009.

Pictorial Representation of a thermoelectric module



Primary Requirements of Thermoelectrics for Automobiles

- Figure-of-merit for thermoelectrics, *ZT*, is

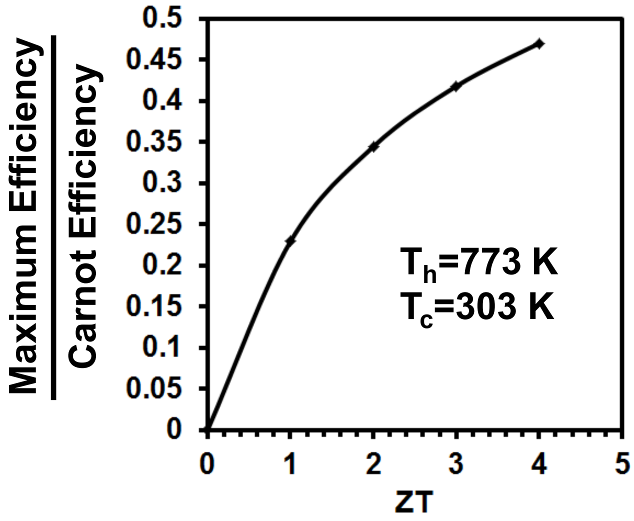
Seebeck coefficient

Electrical conductivity

$$ZT = \frac{S^2 \sigma T}{\kappa_e + \kappa_l}$$

Electronic thermal conductivity

Lattice thermal conductivity



- A large temperature difference, 800 ^{o}C, is available for power generation in vehicles.
- Both n-type and p-type materials with *ZT* ~3, with low contact resistances, are necessary for converting waste heat from the exhaust into electricity

- Matsubara and Matsuura, A Thermoelectric Application to Vehicles (Chapter 52), in Thermoelectrics Handbook: Macro to Nano, 2006.
- Tritt *et al*, MRS Bulletin, 33, 367, 2008
- Snyder and Toberer, Nature Materials, 7, 105, 2008

Strategy for Enhancing *ZT*: Tuning the Format of Materials

$$ZT = \frac{S^2 \sigma T}{\kappa_e + \kappa_l}$$

- **κ_e cannot be reduced without reducing σ (Wiedemann-Franz Law)**
- ***ZT* enhancement requires reduction in the κ_l of materials,**

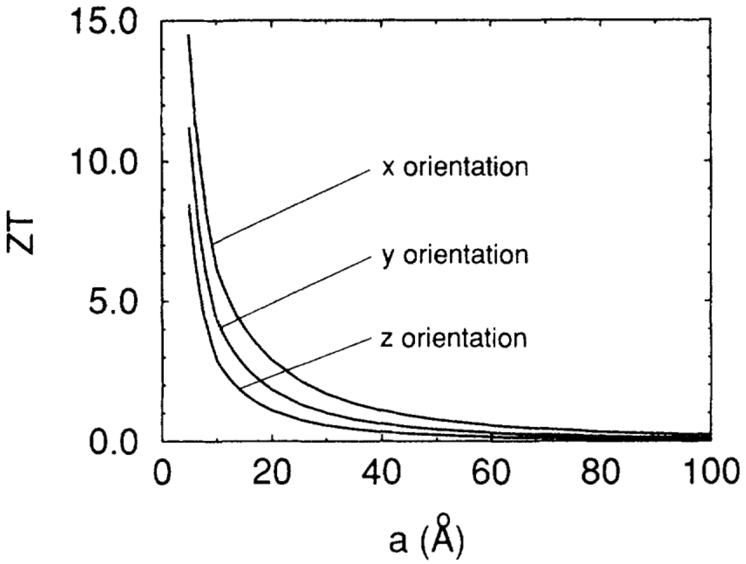
$$\kappa_l = \frac{1}{3}\int c_\lambda(\lambda, T)\, v(\lambda)\, L(\lambda, T)\, d\lambda$$

λ is the wavelength, c_λ is the spectral specific heat per unit wavelength, v is the group velocity, L is the spectral mean-free path.

- **Theoretical predictions indicate that κ_l of materials could be reduced**
  - **either by a reduction in $c_\lambda(\lambda,T)\ v(\lambda)$ through phonon confinement in nanowires and superlattices with extremely small dimensions, or**
  - **by a reduction in $L(\lambda,T)$ through enhanced phonon scattering in boundaries and interfaces in nanowires and composites.**

Strategy for Enhancing *ZT*: Tuning the Format of Materials

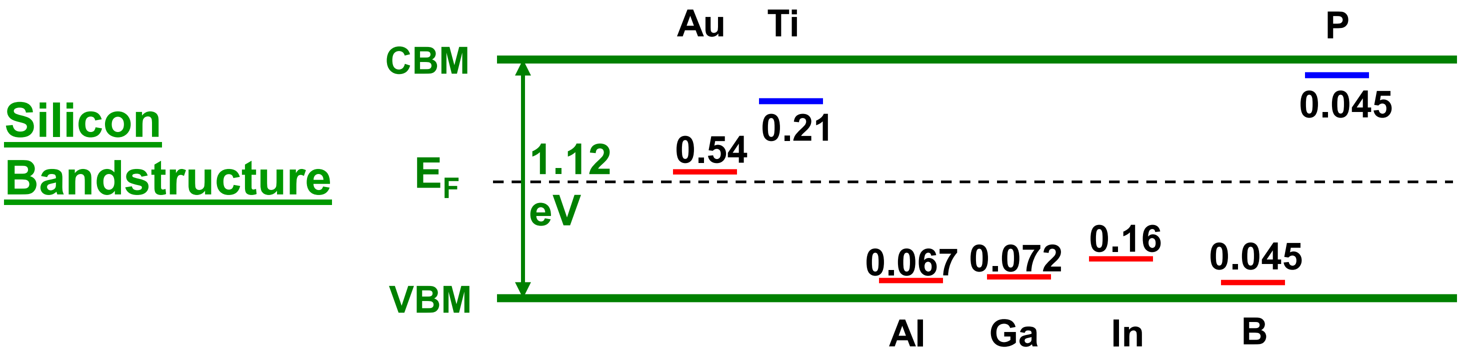
- **Single-crystalline nanowires exhibit good electrical conductivity (*σ*) along their lengths.**
- **Lattice thermal conductivity in nanowires can be scaled to (diameter/roughness)^2, and hence can be reduced through**
  - **a reduction in their diameters (to sub-10 nm length scales)**
  - **enhancing surface roughnesses**



- **How can the synthesis of nanowire powders with <u>sub-10 nm diameters</u> be accomplished in a pristine and <u>contaminant-free</u> manner?**

•Chen and Dames, Thermal Conductivity of Nanostructured Thermoelectric Materials. In Thermoelectrics Handbook, CRC Press, 2005.
•Martin *et al*, Phys. Rev. Lett., 102, 2009.
•Hicks and Dresselhaus, Physical Review B, 47, 16631, 1993.

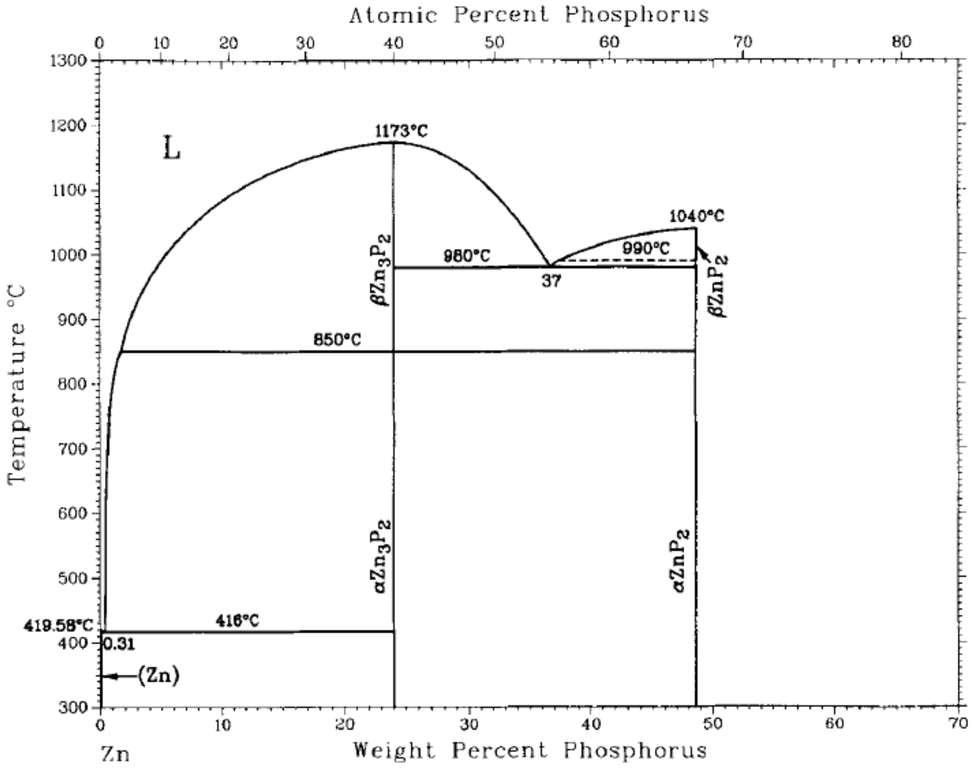
Catalyst-Assisted Synthesis of Nanowires



- Only 8 atoms per nanowire, 10 nm-thick and 1 micron long, are required to achieve doping density of $10^{17}/cm^3$
- Typical heavy metals employed as catalysts for nanowire synthesis also serve as dopants for many well-known compound semiconductor thermoelectric materials
  - Dopants for *p*-type $CoSb_3$: Ni, Pt, Pd
  - Dopants for n-type $CoSb_3$: Cr, Sn, Fe

•Sze, S. and Ng, K. K. (2006) Physics and Properties of Semiconductors—A Review, in Physics of Semiconductor Devices, John Wiley & Sons, Inc., Hoboken, NJ, USA.
•Park *et al.*, Physica Scripta, T139, 014009, 2010.
•Caillat et al., J. Appl. Phys., 80 (8), 4442, 1996.

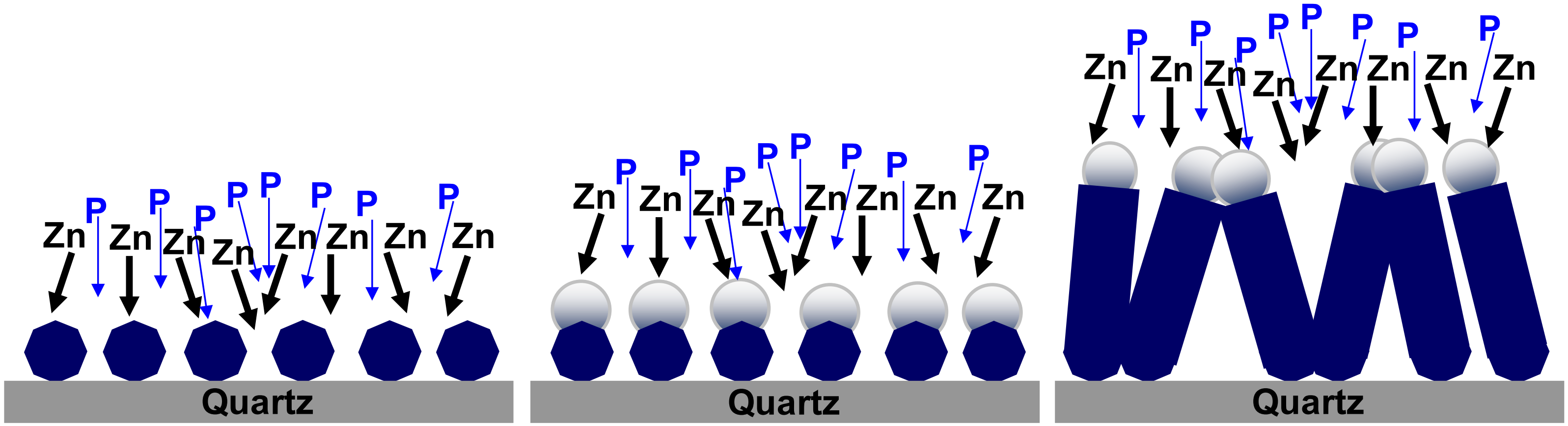
Self-Catalysis: Contaminant-Free Synthesis of Zn_3P_2 Nanowires in a Controlled Manner



- Vapor transport of zinc and phosphorus onto substrates leads to the formation of nanowires under certain experimental conditions (under excess zinc conditions).
- Zinc droplets at the tips of the nanowires self-catalyze their growth

•Dutkiewicz, J., The P-Zn (Phosphorus-Zinc) system, Journal of Phase Equilibria, 12(4), 435-436, 1991
•ASM Alloy Phase Diagrams Center, P. Villars, editor-in-chief; H. Okamoto and K. Cenzual, section editors; http://www.asminternational.org/AsmEnterprise/APD, ASM International, Materials Park, OH, USA, 2006.

Self-Catalysis: Contaminant-Free Synthesis of Zn_3P_2 Nanowires in a Controlled Manner



STEP 1: Formation of Zn_3P_2 nuclei

STEP 2: Selective wetting and zinc droplet formation on top of the Zn_3P_2 nuclei

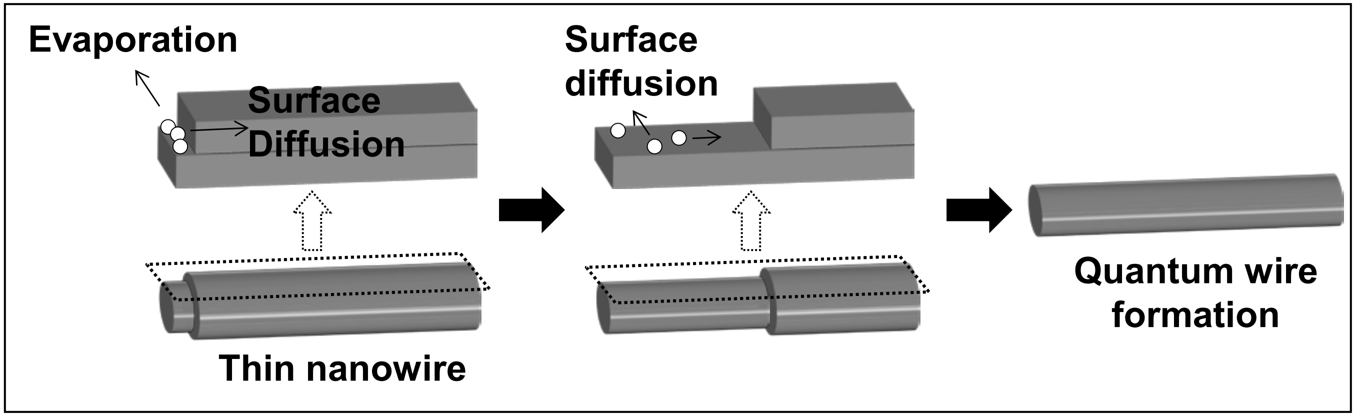
STEP 3: Liquid phase epitaxy through the zinc droplet for Zn_3P_2 nanowire formation

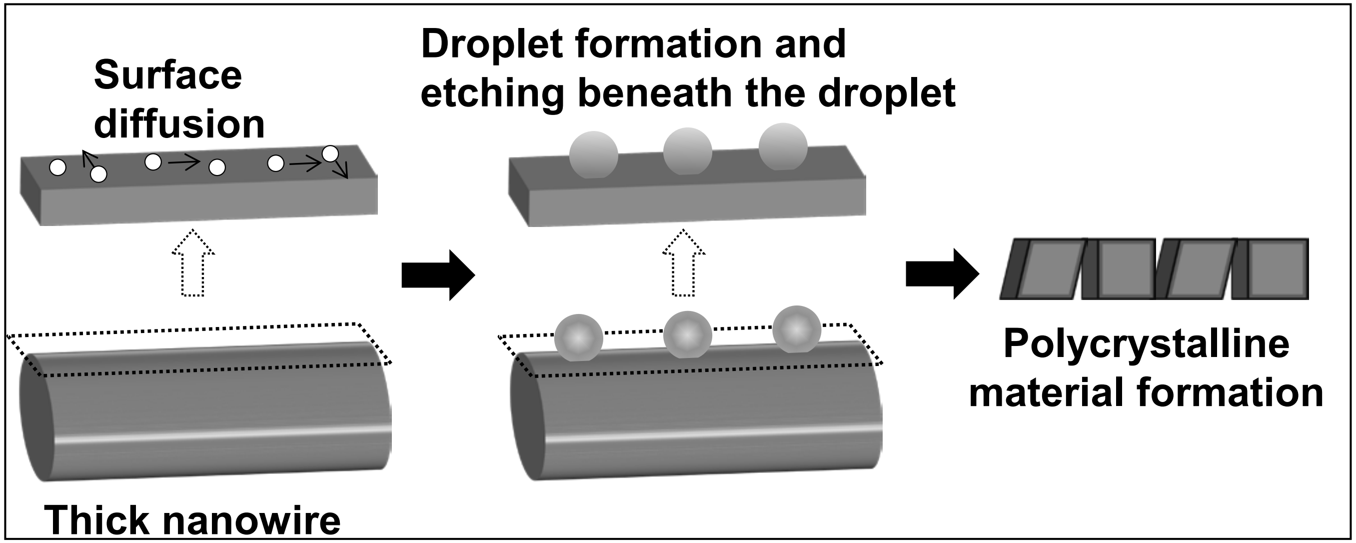
- Similar procedure yields InSb or $CoSb_3$ nanowires
- Allows for comparing the effect of nanowire composition (Zn_3P_2 vs. InSb) on their *ZT* values

•How can the diameters of the obtained nanowires be reduced below 10 nm?

Vaddiraju *et al.*, Nano letters, 5, 1625, 2005

Post-Synthesis Decomposition for Reducing Diameters of Zn_3P_2 Nanowires



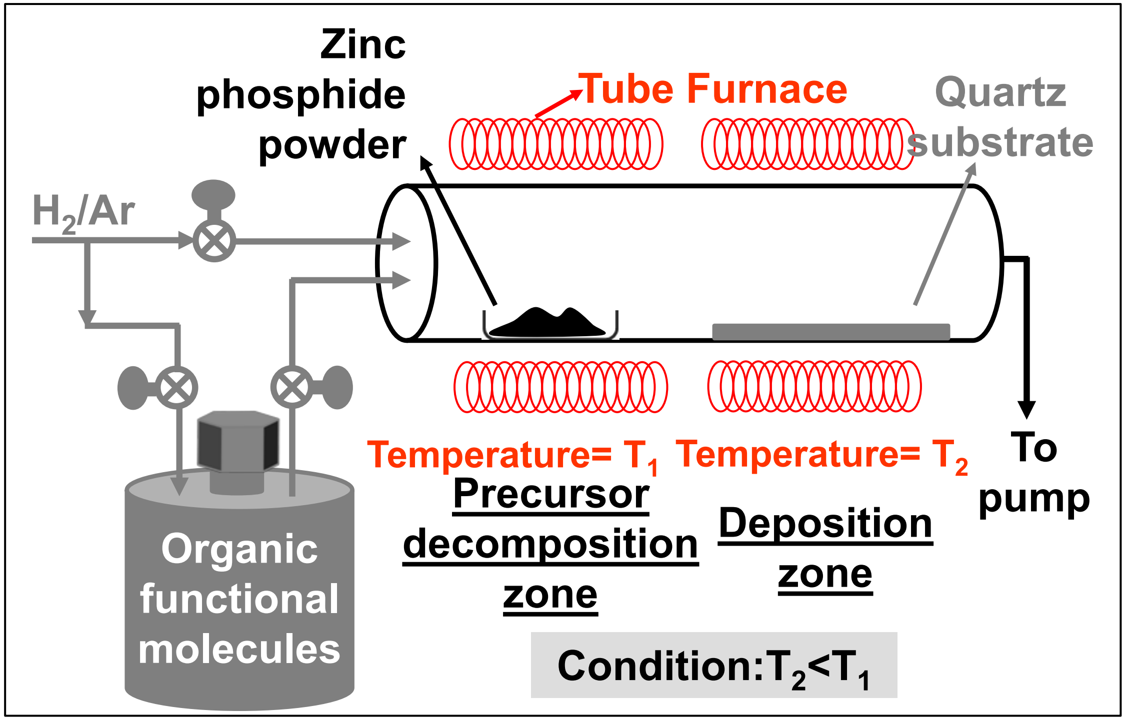


- Decomposition at nanoscale, unlike bulk decomposition, occurs in a layer-by-layer fashion

L. Brockway, C. Pendyala, J. Jasinski, M. K. Sunkara, S. Vaddiraju, Crystal Growth & Design, 11(10), 4559-4564, 2011

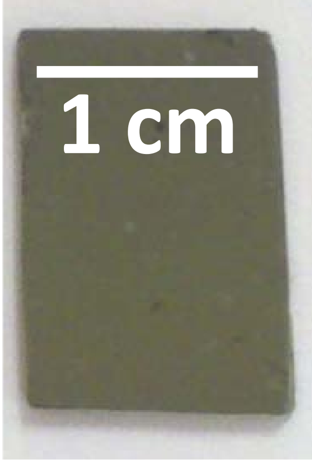
Experimental Approach: Small-Scale Synthesis of Zn_3P_2 Nanowires

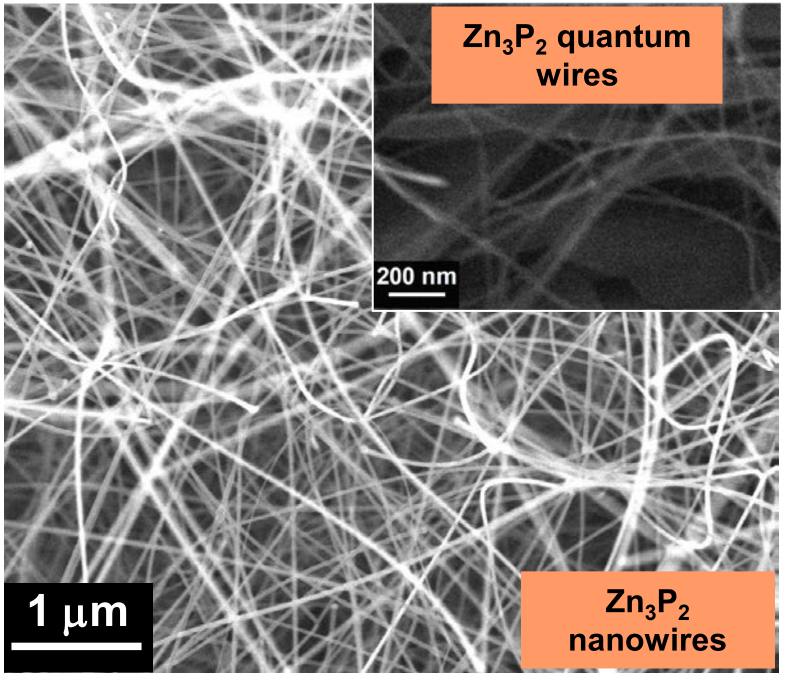
- Small-scale synthesis of Zn_3P_2 nanowires was accomplished using zinc and phosphorus onto quartz substrates.
- Both unfunctionalized and functionalized nanowires were synthesized
- Postsynthesis decomposition was also performed to obtain Zn_3P_2 quantum wires

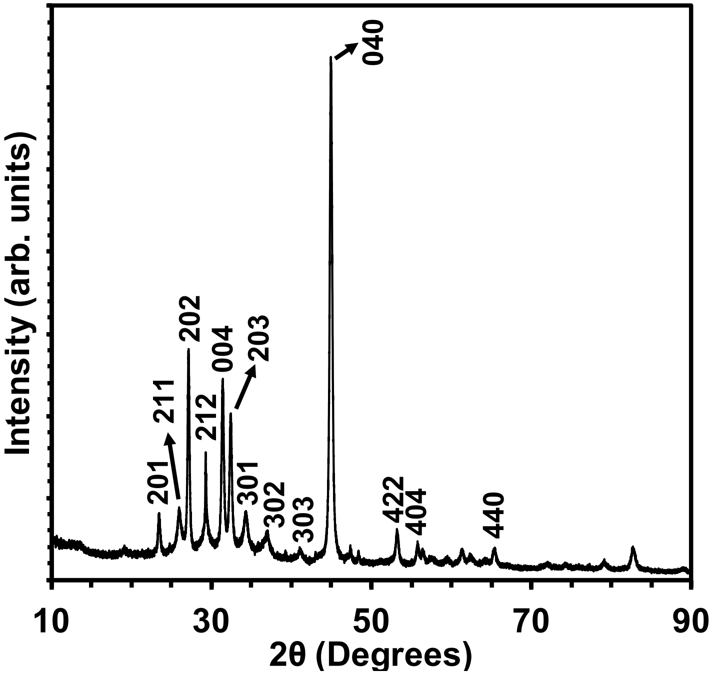


Experimental Approach: Small-Scale Synthesis of Zn_3P_2 Nanowires

Quartz substrate covered with Zn_3P_2 nanowires

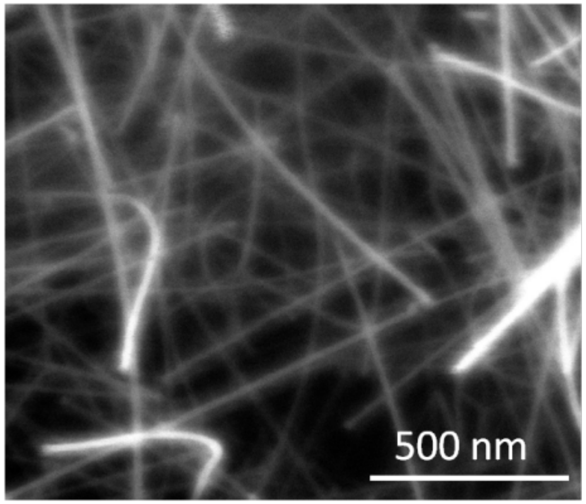




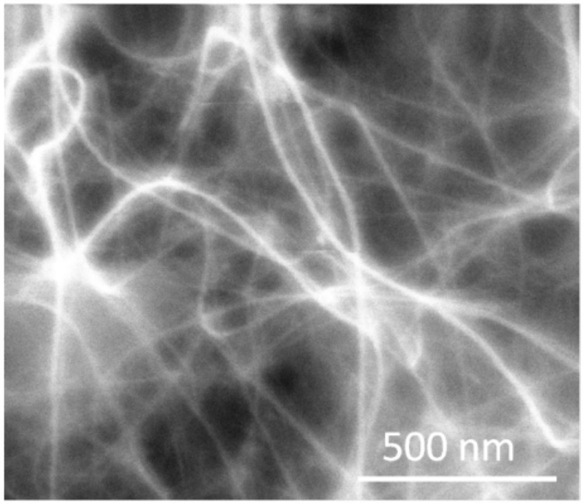


- •Average diameter of nanowires=25 nm
- •Length of nanowires>10 µm
- •Diameter of quantum wires=8-10 nm
- •Weight of nanowires obtained=2-3 mg/cm^2

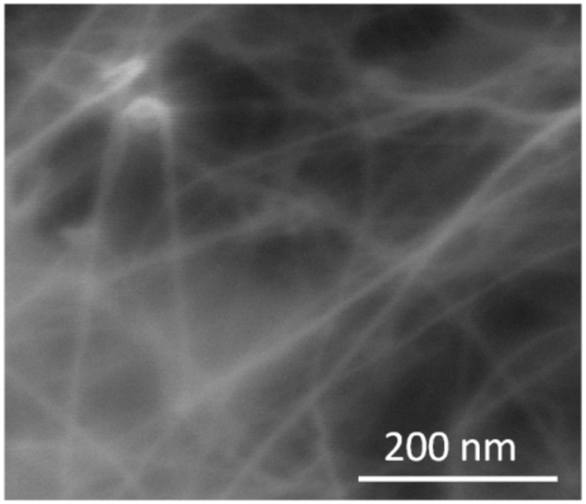
Post-Synthesis Decomposition for Reducing Diameters of Zn_3P_2 Nanowires



- As-obtained nanowires
- Average diameter = 25 nm



- After 5 minute decomposition at 650 ^{o}C
- Average diameter = 15 nm

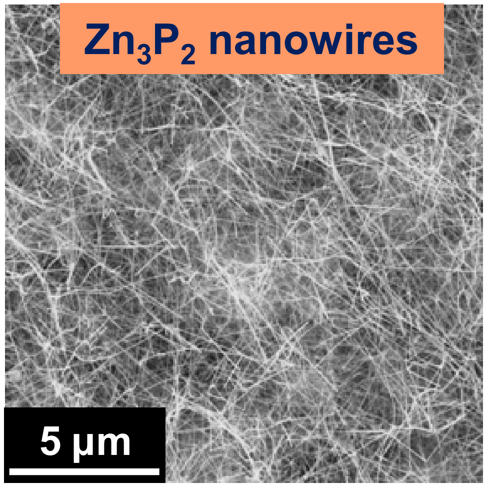


- After 10 minute decomposition at 650 ^{o}C
- Average diameter = 8 nm

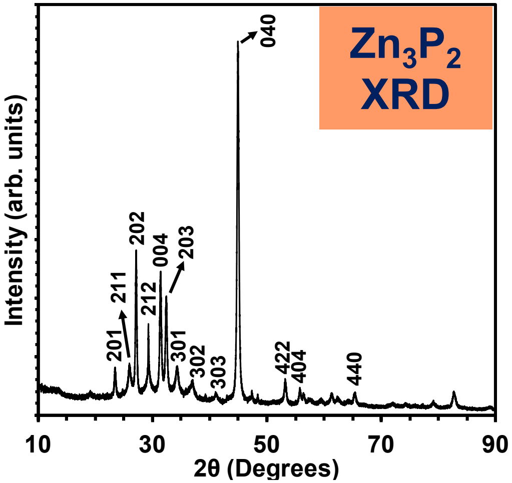
- How can large-scale synthesis of nanowires be accomplished?
- How can the large-scale assembly of nanowires with engineered interface be performed in a simple, reliable and reproducible manner ?

Experimental Approach: Large-Scale Synthesis of Zn_3P_2 Nanowire Powders

Zn_3P_2 nanowires on top of zinc foil



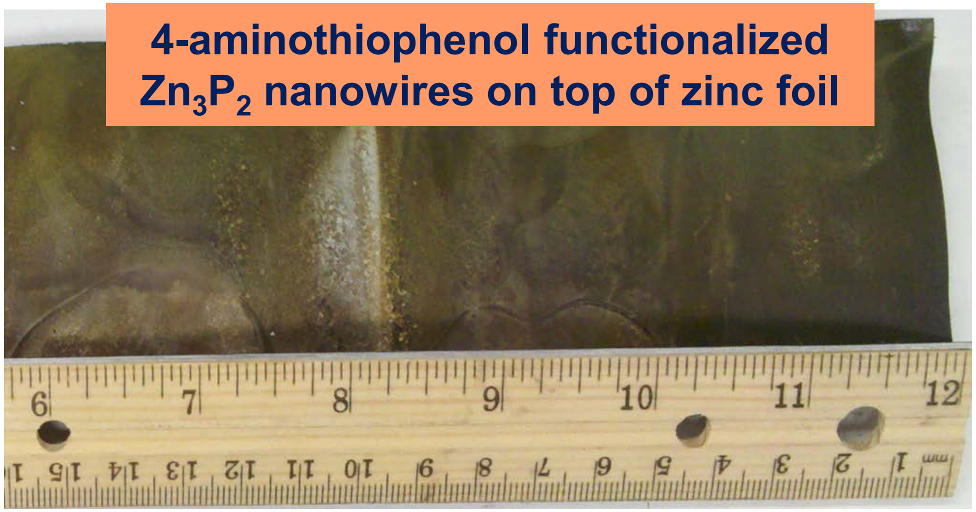
Zn_3P_2 nanowires



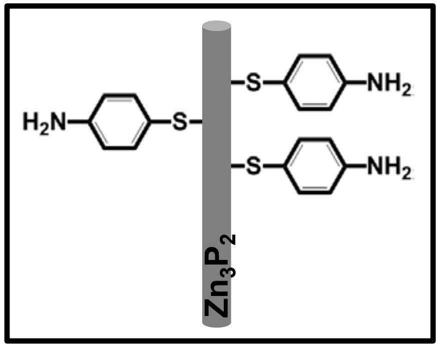
Zn_3P_2 XRD

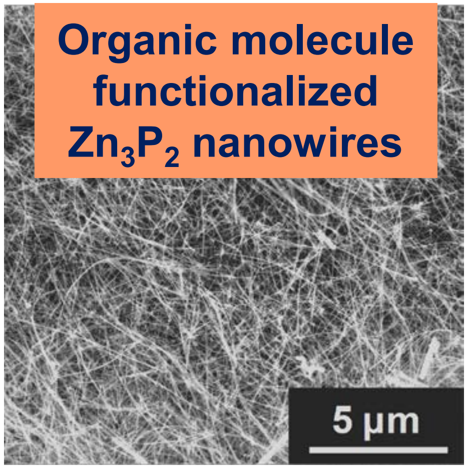
- Vapor transport of phosphorus onto zinc foils was employed for the self-catalytic synthesis of Zn_3P_2 nanowires
- Surfaces of foils with areas as large as 240-480 cm^2 were completely converted into Zn_3P_2 nanowires
- 0.5-1 gram of nanowire powder produced in an experimental run lasting 2 hours

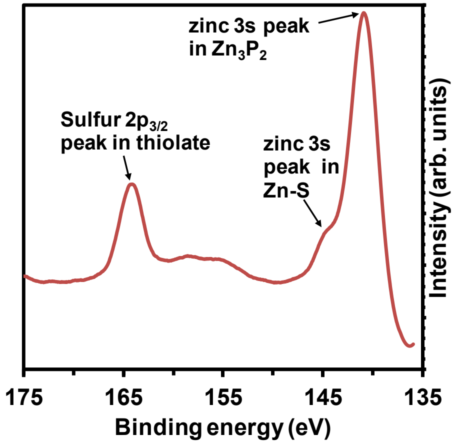
Experimental Approach: Large-Scale Synthesis of *In-situ* Functionalized Zn_3P_2 Nanowire Powders

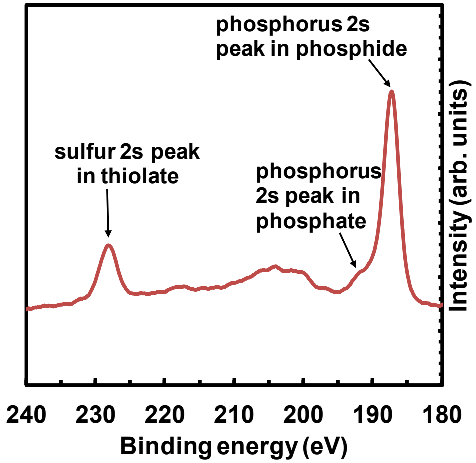

4-aminothiophenol functionalized Zn_3P_2 nanowires on top of zinc foil

- Vapor transport of phosphorus onto zinc foils was employed for the self-catalytic synthesis of Zn_3P_2 nanowires
- *In-situ* vapor phase functionalization of the nanowires with 4-aminothiophenol was performed immediately after their synthesis
- *In-situ* functionalization led to the formation of strong thiolate bonds between the nanowire surfaces and 4-aminothiophenol molecules, without impacting nanowire morphologies or their dimensions




Organic molecule functionalized Zn_3P_2 nanowires



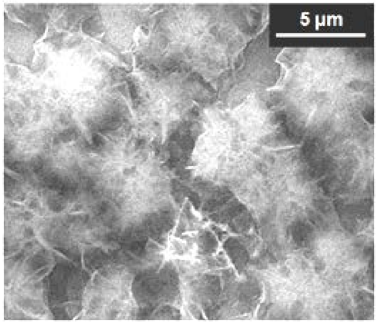


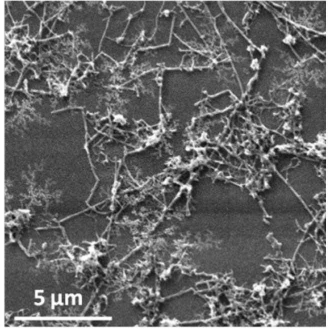
Experimental Approach: Large-Scale Synthesis and *In-situ* Functionalization of Nanowires

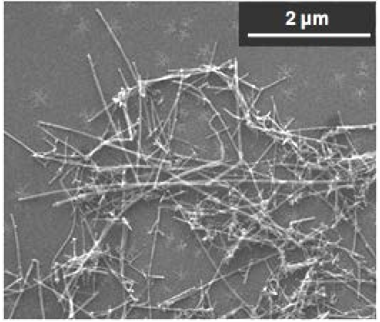
Unfunctionalized Zn_3P_2 nanowires

***Ex-situ* functionalized Zn_3P_2 nanowires**

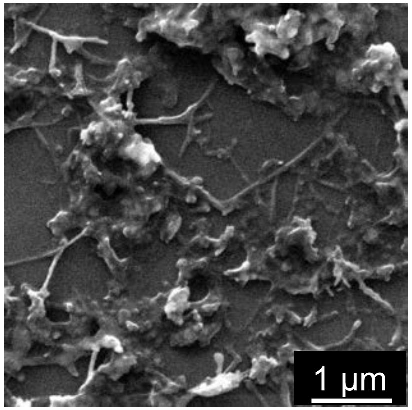
***In-Situ* functionalized Zn_3P_2 nanowires**

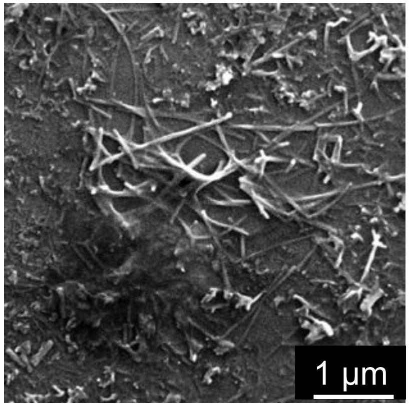


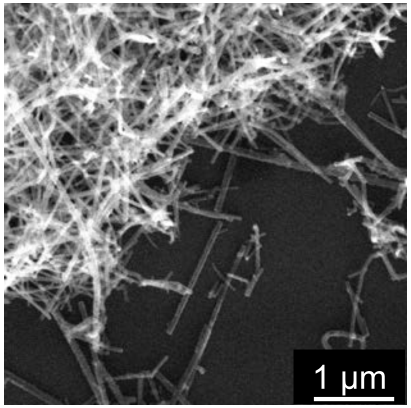




Zn_3P_2-4-aminothiophenol system





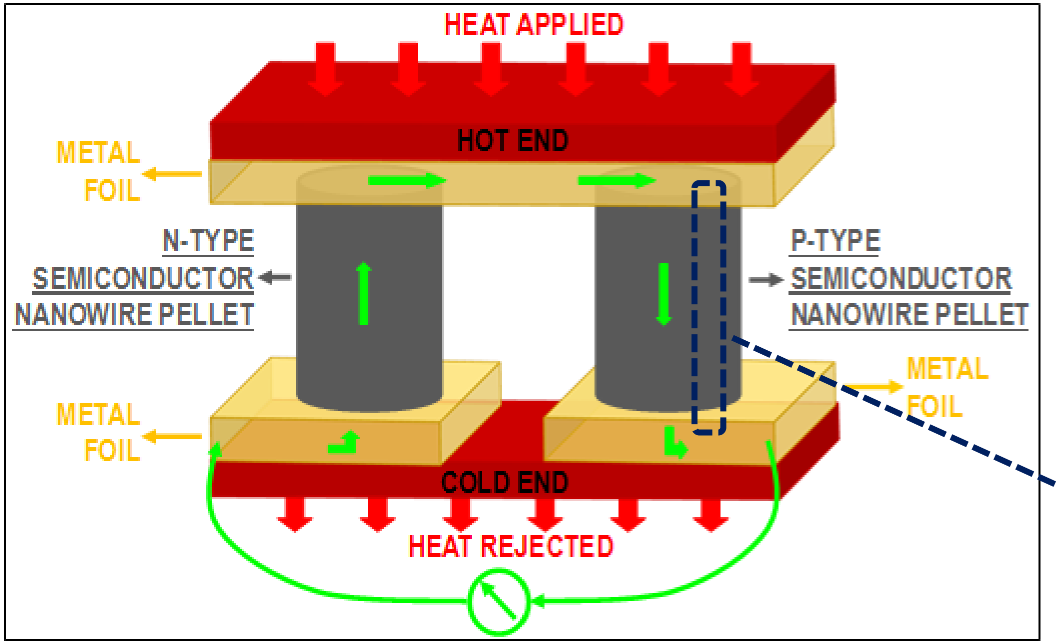


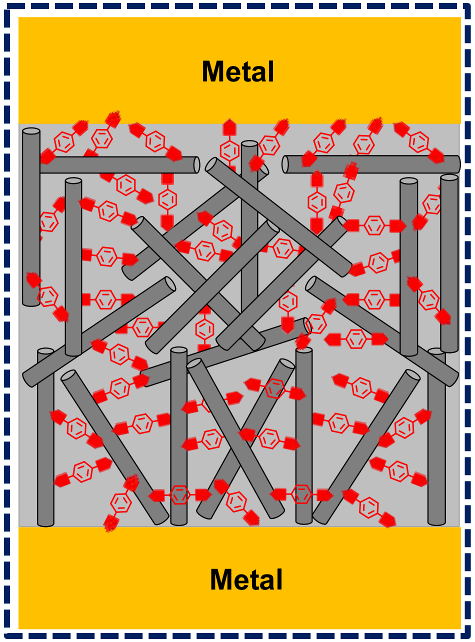
Zn_3P_2-1,3-propanedithiol system

- Typically, Zn_3P_2 reacts with moisture and decomposes into $Zn(OH)_2$ and PH_3
- *In-Situ* functionalized Zn_3P_2 nanowires remain stable for weeks and months

Large-scale Assembly of Nanowires

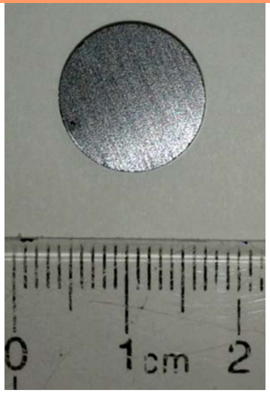
- Molecular wiring of nanowires to each other
  - Leads to the formation of robust nanowire pellets by covalently binding nanowires together
  - Interfacial electrical and thermal transport tunable through variations in the linker molecule chemistry (e.g., 1,4-benzenedithiol, 1,3-propanedithiol)

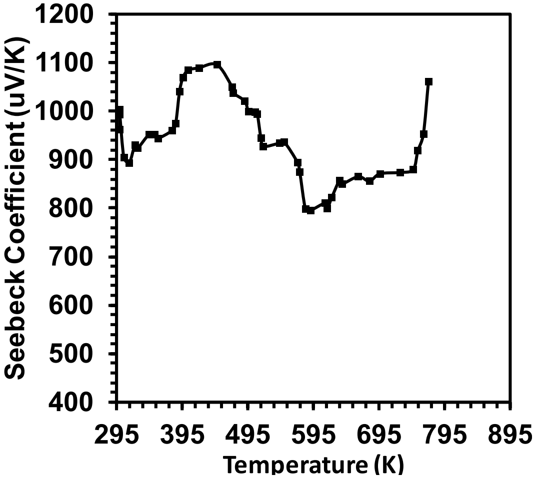


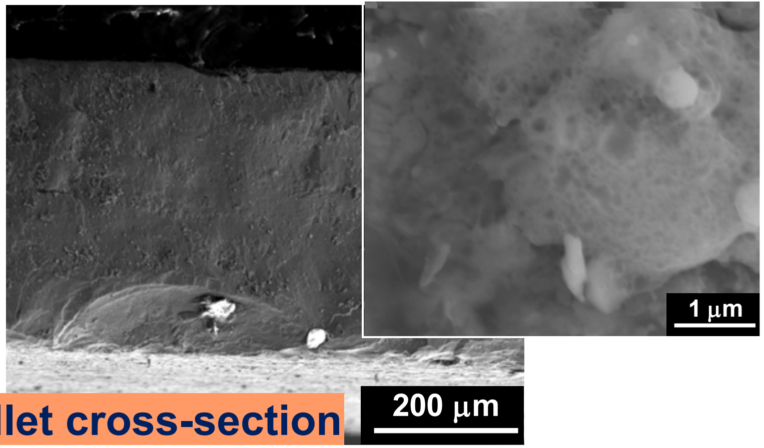


Thermoelectric Performance of Zn_3P_2 Nanowire Pellets

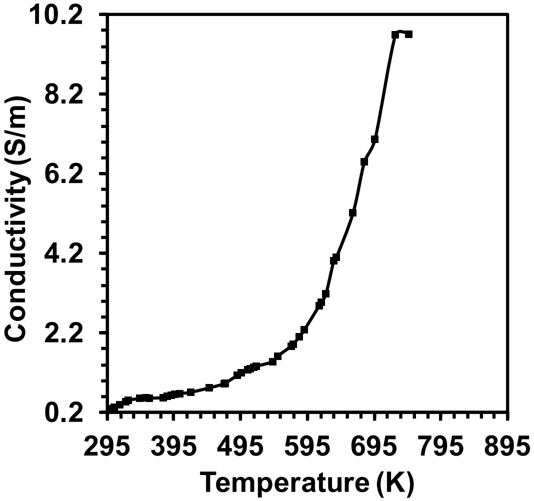
Zn_3P_2 nanowire pellet (12 mm diameter, 2 mm thick)

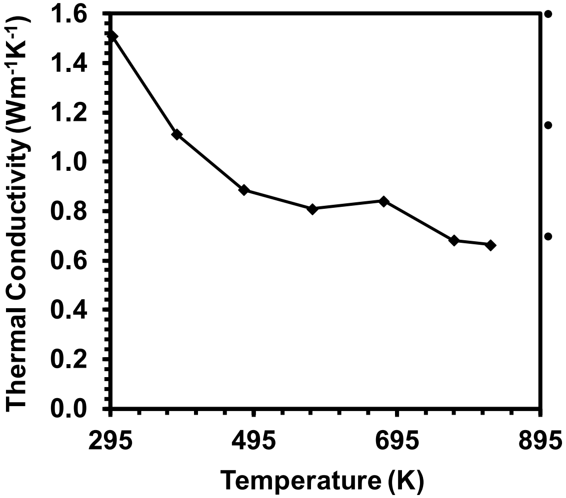






pellet cross-section

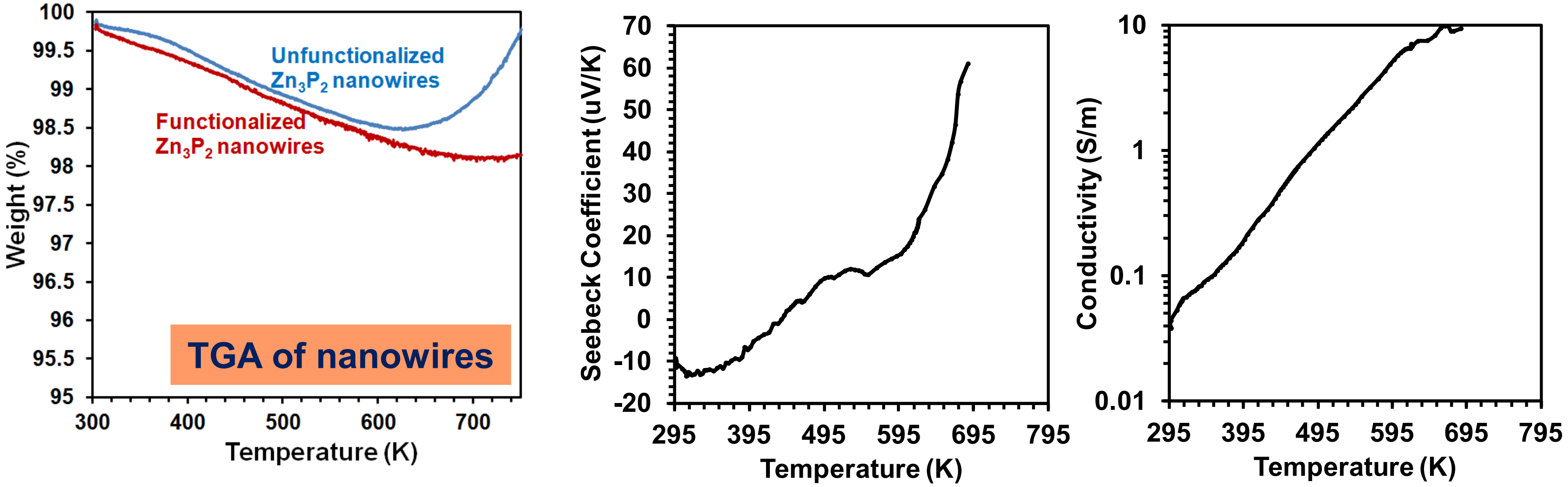




- The densities of hot-pressed nanowire pellets (4.48 gm/cm^3) were close to that of single-crystalline Zn_3P_2 (4.55 gm/cm^3)
- Electron microscopy of the pellets indicated that nanowire morphology is preserved on pelletization of nanowire powders into pellets
- Thermoelectric performance (*ZT* value) of Zn_3P_2 nanowire pellets was observed to be 5 times that observed in spark plasma sintered Zn_3P_2 nanoparticle pellets

•Nagamoto, Y., Hino, K., Yoshitake, H., Koyanagi, T., *Thermoelectric properties of α-Zn_3P_2*, Proceedings of the XVII International Conference on Thermoelectrics, 24-28 May 1998, pp 354-357.

Thermoelectric Performance of Zn_3P_2 Nanowire-1,4-Benzendithiol Inorganic-Organic Hybrid Pellets



- Functionalized nanowires were observed to be more stable than unfunctionalized nanowires even at elevated temperatures
- Preliminary experiments indicated that Zn_3P_2 nanowires wired together using 1,4-benzenedithiol molecules exhibit *n*-type behavior at low temperatures and *p*-type behavior at high temperatures
- Preliminary measurements indicated that the thermal conductivity of inorganic-organic hybrids is 0.3 $Wm^{-1}K^{-1}$ at 300 K (1/5th of that observed in unfuntionalized Zn_3P_2 nanowire pellets)

Concluding Remarks

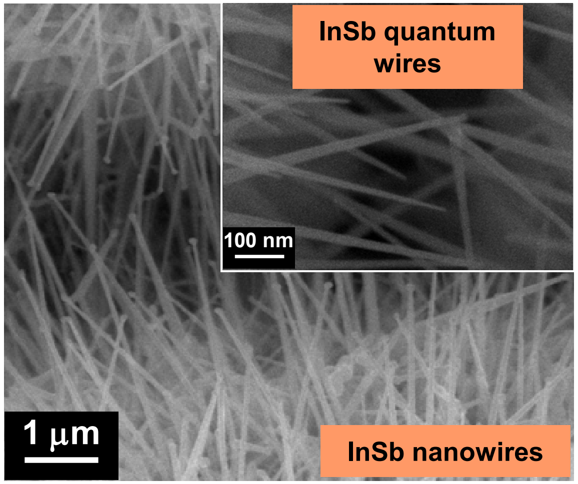
- Accomplished the large-scale synthesis of both unfunctionalized and functionalized Zn_3P_2 nanowire powders using vapor transport of phosphorus onto heated zinc foils and *in-situ* vapor phase functionalization

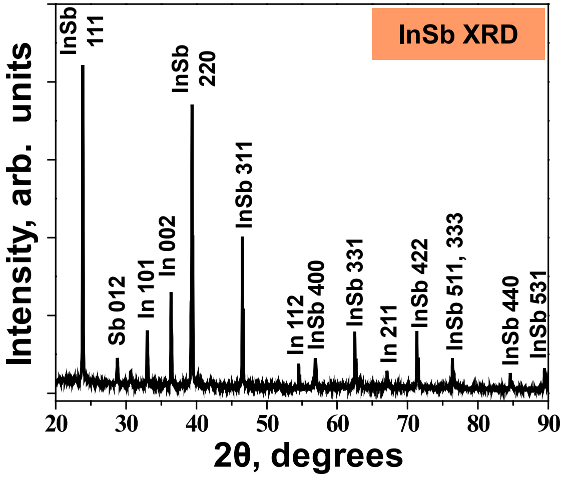
- Evaluated the thermoelectric performance of pellets obtained by hot pressing Zn_3P_2 nanowire powders. Thermoelectric performance of Zn_3P_2 pellets was observed to be better than that reported for spark plasma sintered Zn_3P_2 nanoparticle powders

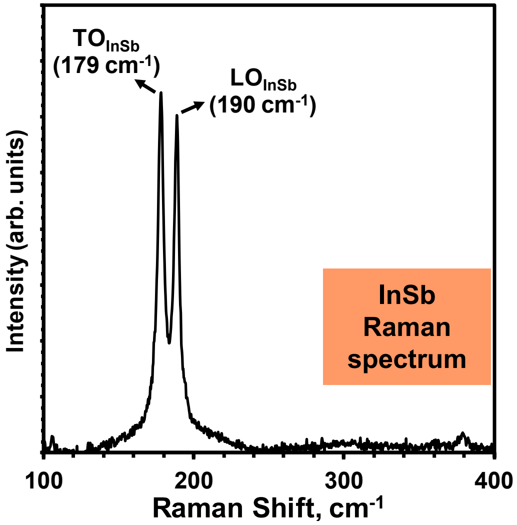
- Thermal conductivity of Zn_3P_2 nanowire-benzendithiol inorganic-organic hybrid pellets was observed to be lower than that of Zn_3P_2 nanowire pellets

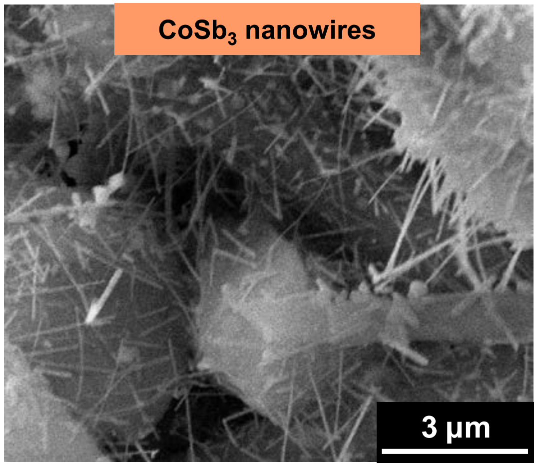
- In the immediate future, effect of nanowire diameter on the thermoelectric performance of Zn_3P_2 will be evaluated

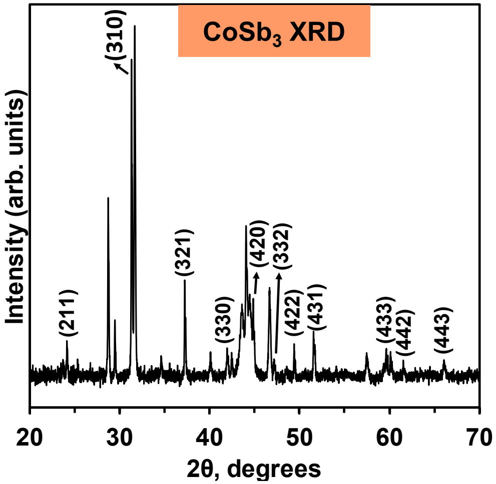
Future Work











- **Determination of the effect of nanowire morphologies and their dimensions on the thermoelectric properties of phase-pure $CoSb_3$ and InSb nanowire and quantum wire powders**

Acknowledgements

- NSF/DOE Thermoelectric Partnership for financial support

- Dr. J. P. Fleurial and Dr. Sabah Bux for thermoelectric performance measurement of nanowire pellets

Additional Information

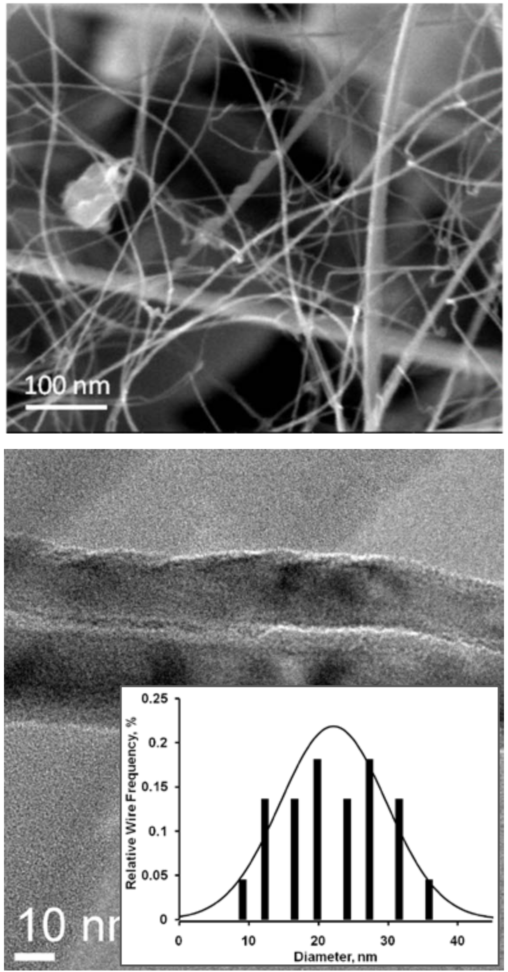
Sreeram Vaddiraju

Email: *Sreeram.vaddiraju@tamu.edu*

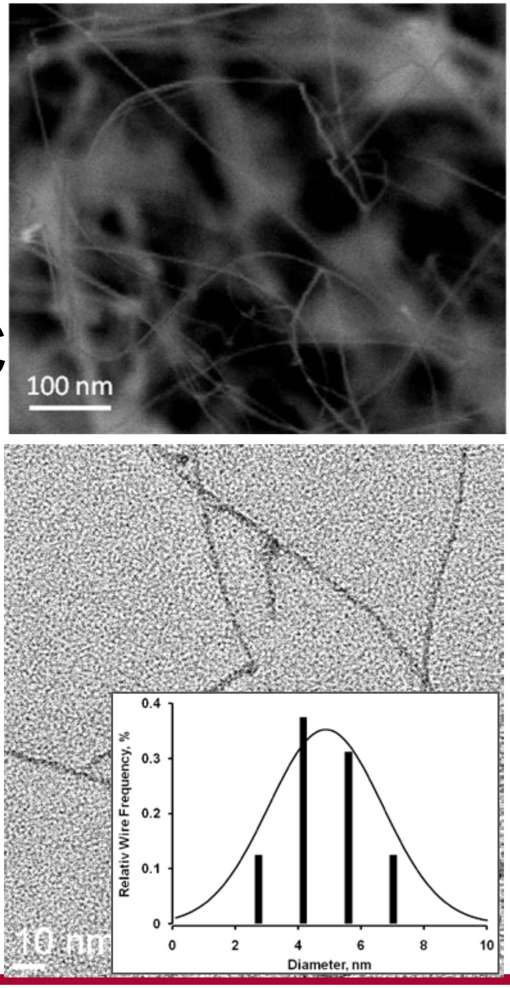
Why $CoSb_3$ and InSb?

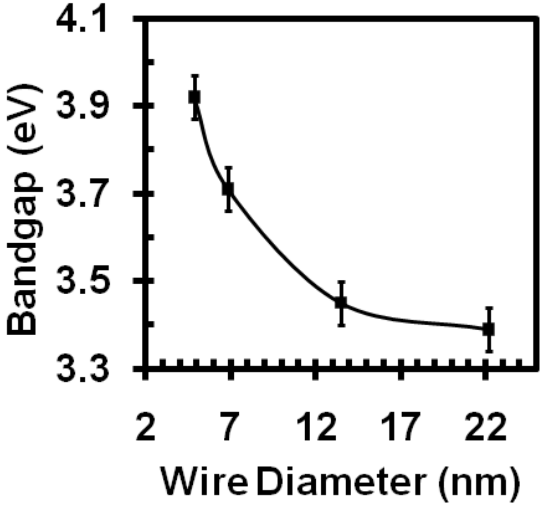
- InSb has a zincblende crystal structure with very large Bohr exciton radius of 54 nm and high mobility of $7.8x10^4$ $cm^2V^{-1}S^{-1}$. The large Bohr exciton radius of InSb (54 nm) makes it an ideal candidate for understanding its thermoelectric behavior under quantum confined conditions.
- $CoSb_3$ has a skutterudite structure with empty cages in the lattice. Phonon scattering could also be enhanced and hence the lattice thermal conductivity could be reduced in skutterudites by either employing quantum wires with diameters less than the mean free path of the phonons or by filling the cages with foreign atoms.

GaN Quantum Wire Synthesis



$$\xrightarrow[\text{NH}_3]{900\ \text{C}}$$





L. Brockway, C. Pendyala, J. Jasinski, M. K. Sunkara, S. Vaddiraju, Crystal Growth & Design, 11(10), 4559-4564, 2011