Practice Your Scales!
Thermal and Energy Nanomaterials for Fast Processes

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School of Mechanical Engineering, and
Birck Nanotechnology Center
Purdue University

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Acknowledgements

- Special thanks to my students and collaborators (highlighted throughout the talk)
- BNC staff (all of them)
- Financial support:
  - Office of Naval Research under the thermal transport program (PM: Dr. Mark Spector)
  - Air Force Office of Scientific Research (AFOSR) under the MURI program on Nanofabrication of Tunable 3D Nanotube Architectures (PM: Dr. Joycelyn Harrison)
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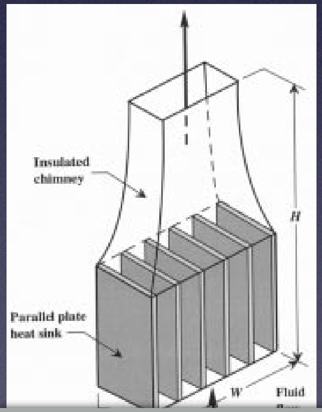
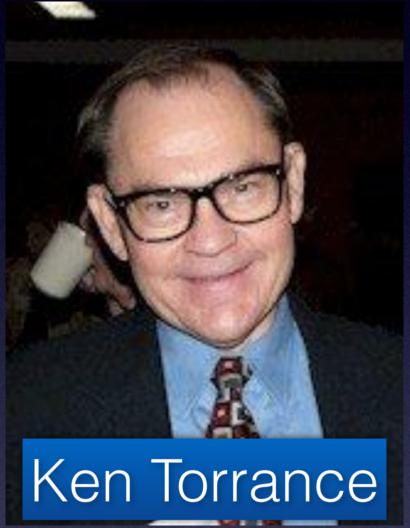
Cornell

(1987-1991, 1993-1998)

- Pre-college: “I’ll only pay for college if you study engineering.”
  - my dad (Purdue BS Mgmt ’66)
- Undergraduate research (NSF/SRC funded) led directly to interest in graduate school
- 2 years at Motorola between undergrad and grad
- Grad school
  - PhD on **chimney flow**
  - Also, Asst. Varsity Baseball Coach
  - Also, House Dad at KKΓ sorority



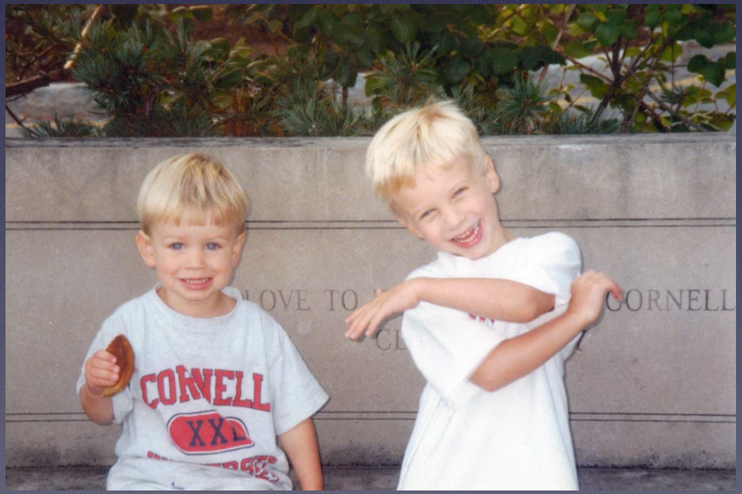
T.S. Fisher et al., IEEE CPMT, 20, 111, 1997.



Ken Torrance

Subrata

Al Sievers



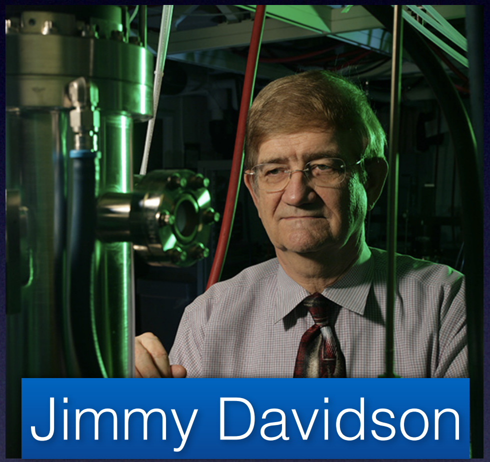
Vanderbilt

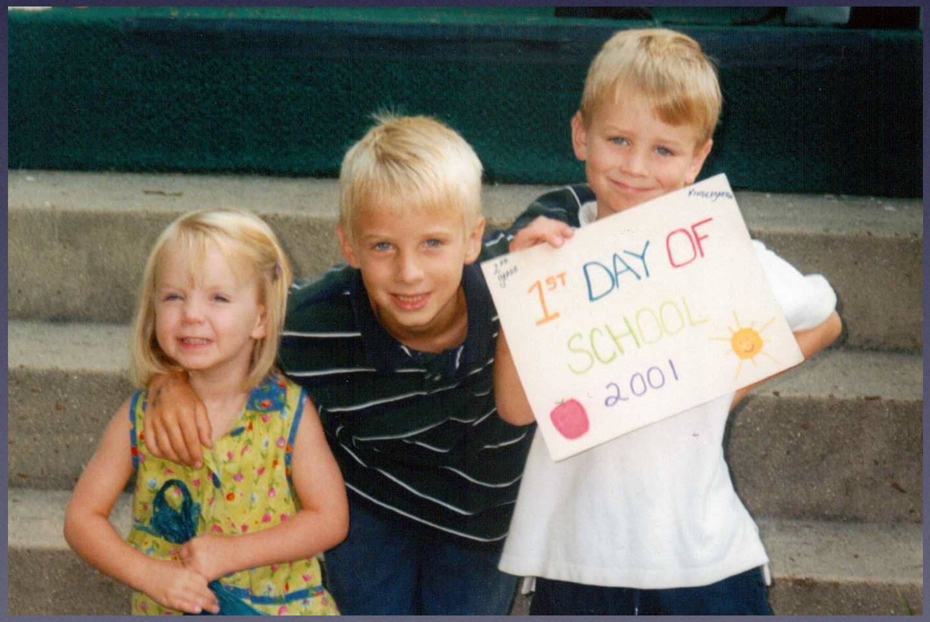
(1998-2002)

- "I know about your graduate research, and if you try to keep doing it here,
  <u>you will fail.</u>"
  - Dean Ken Galloway
  (my 2nd week at Vanderbilt)

- What to do?

  - Micro/nano with 'Diamond Jimmy'





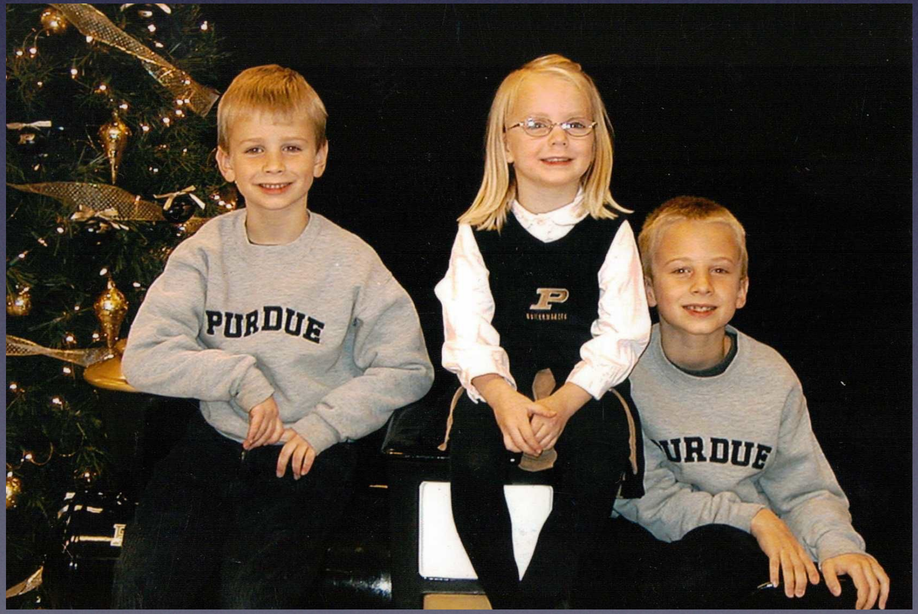
Purdue

(2002 to present)

- Recruited to help build up experimental nano (pre Birck donation)
    - Extended family unhappy with decision not to move
- 2nd recruitment worked (post Birck donation)
    - Immediate family unhappy with decision to move
- Granted some lab space in ECE Bldg (thanks to Kent Fuchs)

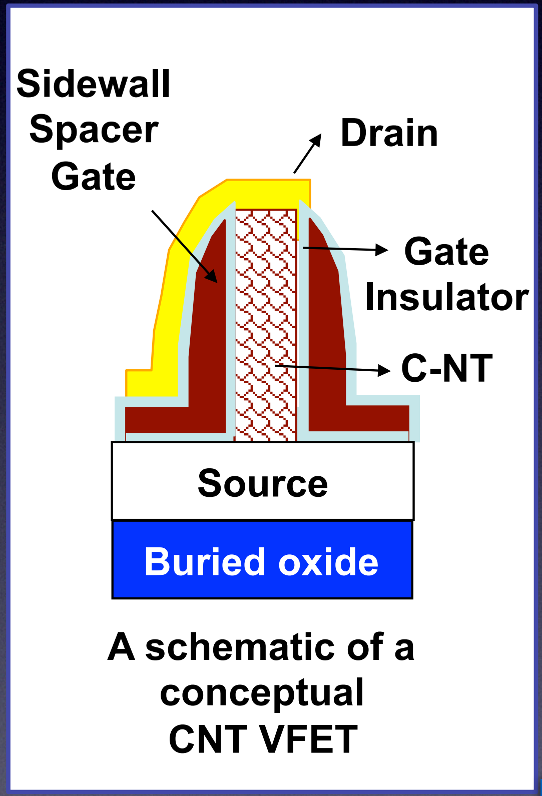

Dan Hirleman

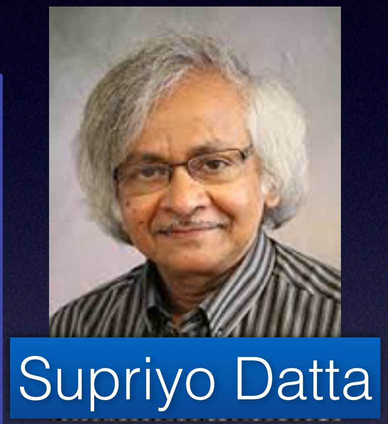

Jay Gore

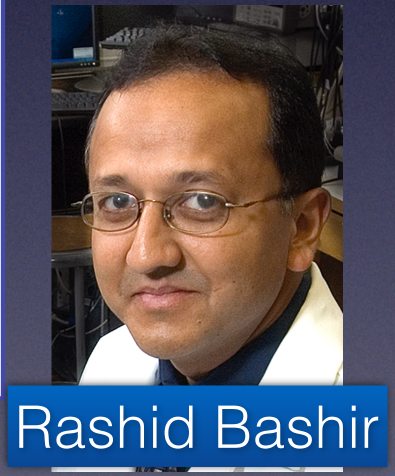


Nanotechnology

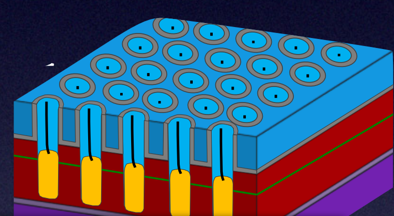
- First project based on a cartoon in the INAC proposal
    - No idea how to make it
    - Very patient mentors (thank you)
- Planning of the Birck Center



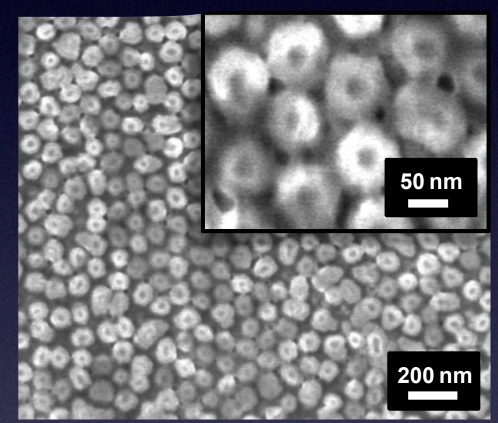




CNTs in PAA



A. D. Franklin et al. J Vac Sci Technol B, 25, 343–347, 2007.



Tim Sands

Matt Maschmann

Dave Lubelski

Aaron Franklin

David Janes

- Significant unresolved issues:
  - chirality control
  - uniform hole filling
  - gate optimization

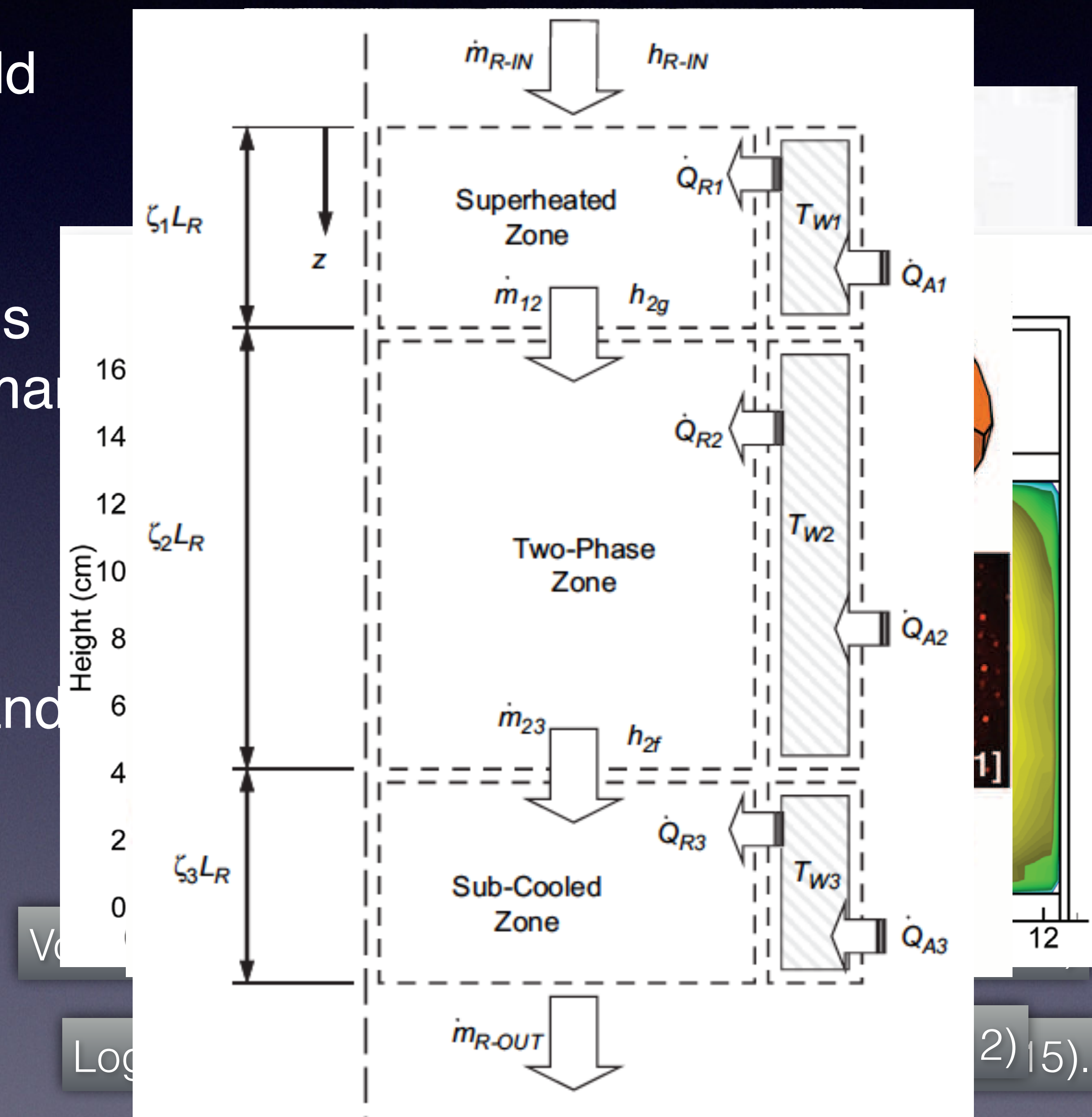
Practicing scales is an age-old method to achieve excellence

- "It dawned on me that scales aren't just about putting in the time. They are a testing ground. An ideal laboratory or controlled environment for developing the fundamental building blocks of our technique…. It's an opportunity to strip away the dozens of other variables we would otherwise encounter … so that we can tweak and experiment with the little tiny details and truly master the fundamentals."
    - Noa Kageyama, Ph.D., *Why I'd Spend a Lot More Time Practicing Scales If I Could Do It All Over Again* (http://www.bulletproofmusician.com)
- "10,000 hours is the magic number of greatness."
    - Malcolm Gladwell, *Outliers*
    - For a deeper and more nuanced analysis, see Hambrick et al., *Intelligence* **45** 112 (2014)

HowCast: Guitar Lessons
(https://www.youtube.com/watch?v=BExdsIJRDtc)

Multi-scale X seems to be everywhere. What does it mean here?

- System scale - how do we incorporate real-world dynamics into thermal/energy system design?
- Micro-to-macro scale - how do we assemble collections of nano/micro objects into ensembles that are lightweight, fast, and reliable at the human scale?
- Nanoscale III - how do we make nanoscale synthesis go faster?
- Nanoscale II - how do we control composition and morphology in scalable processes?
- Nanoscale I - how do we incorporate atomistic knowledge into nanoscale device design?
- Atomistic - how does energy flow in heterogeneous atomic-scale structures?



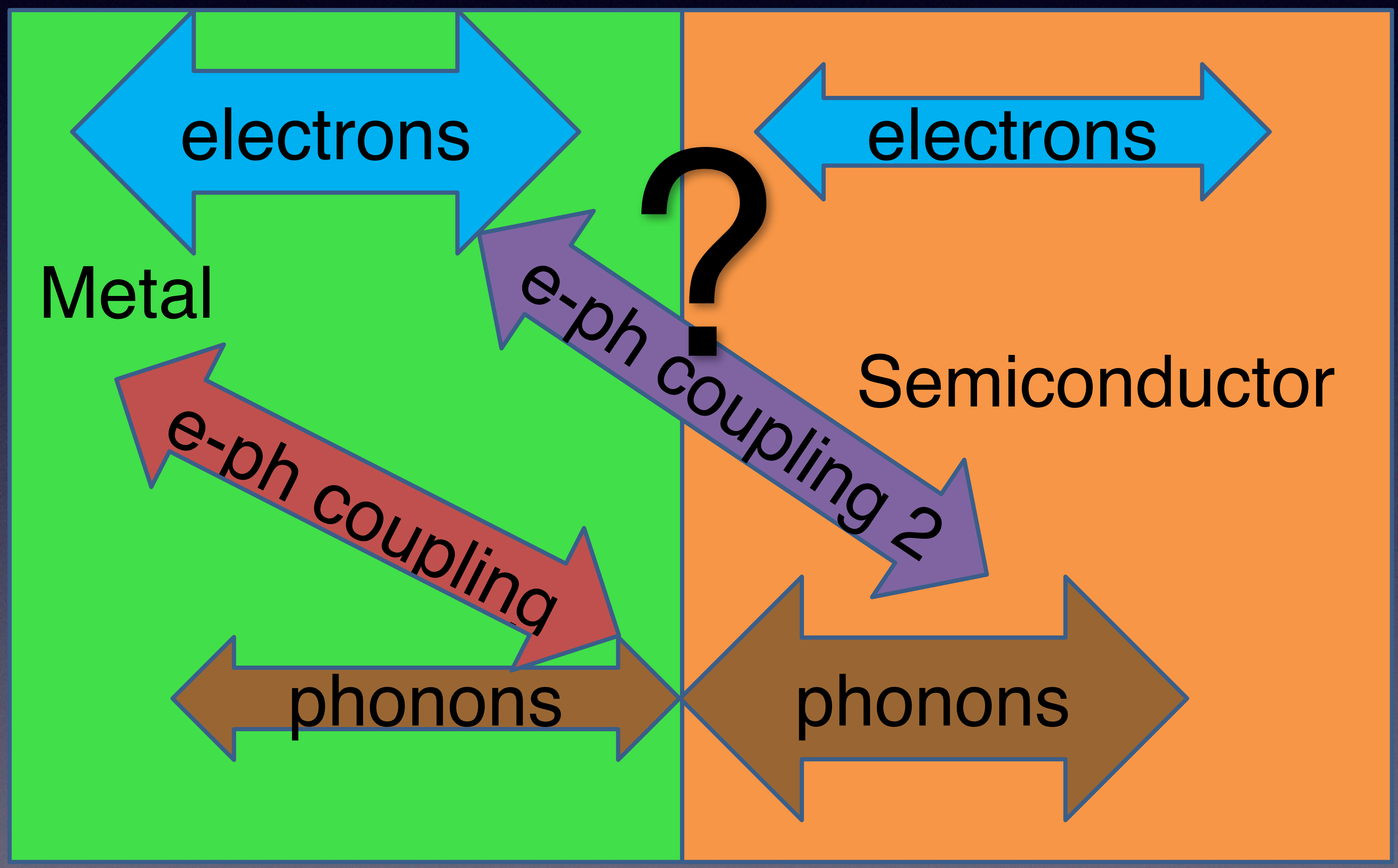
McKinley & Alleyne, Int. J. Refrig. **31** 1253 (2008)

Atomistic scale: Electron-phonon coupling across heterogeneous interfaces

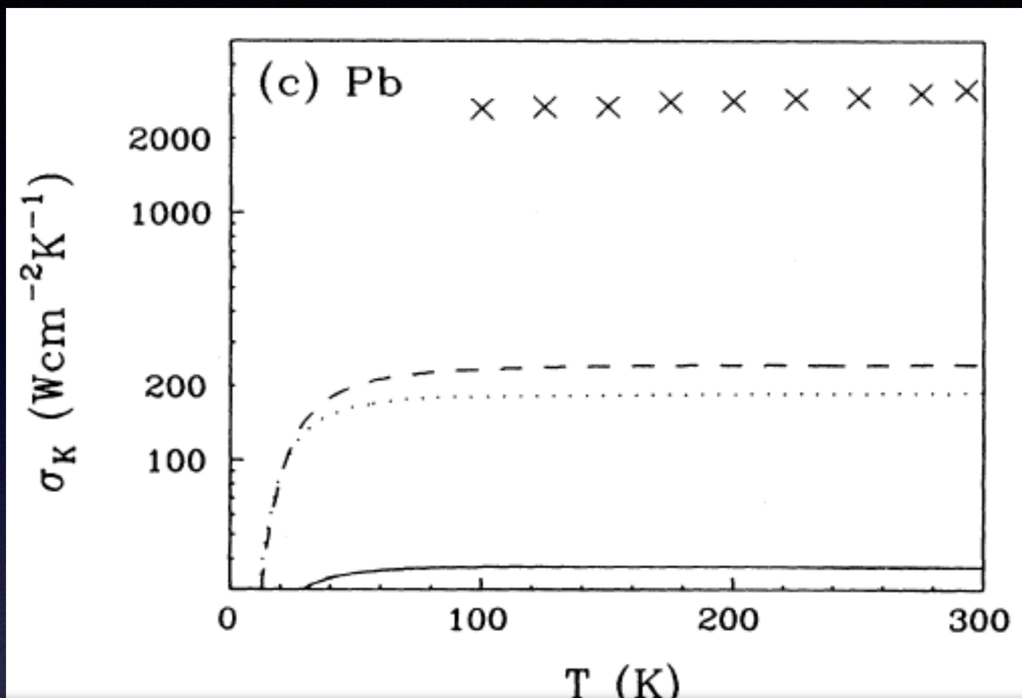
Sridhar Sadasivam (PhD student)

Umesh Waghmare (JNCASR, Bangalore)

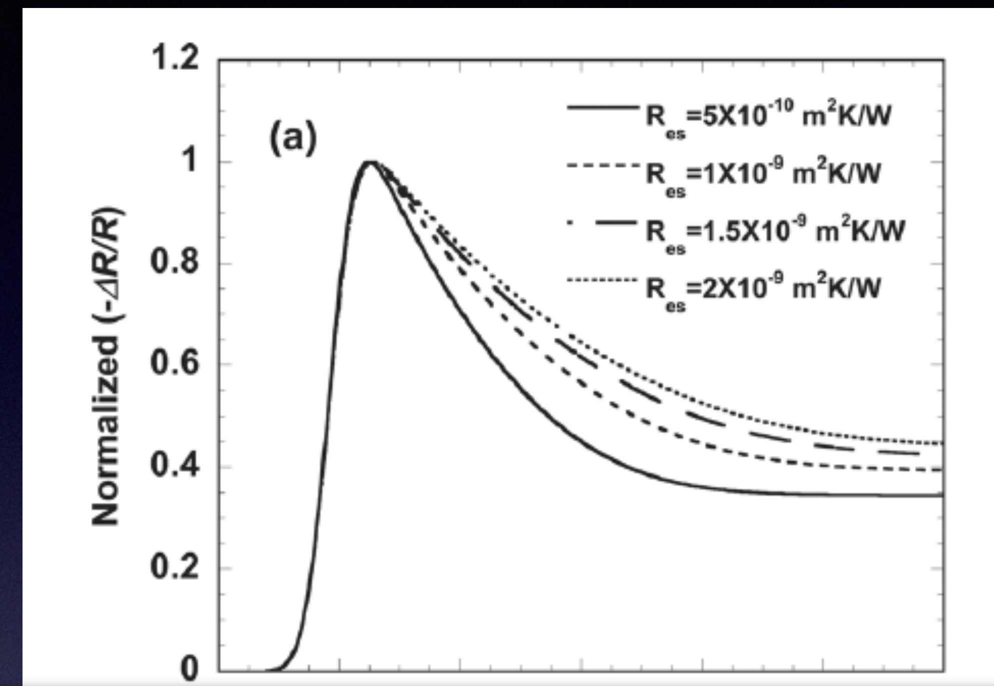
Electrons are primary thermal carriers in metals. Phonons are primary in semiconductors. The mechanism of coupling is not clearly understood.



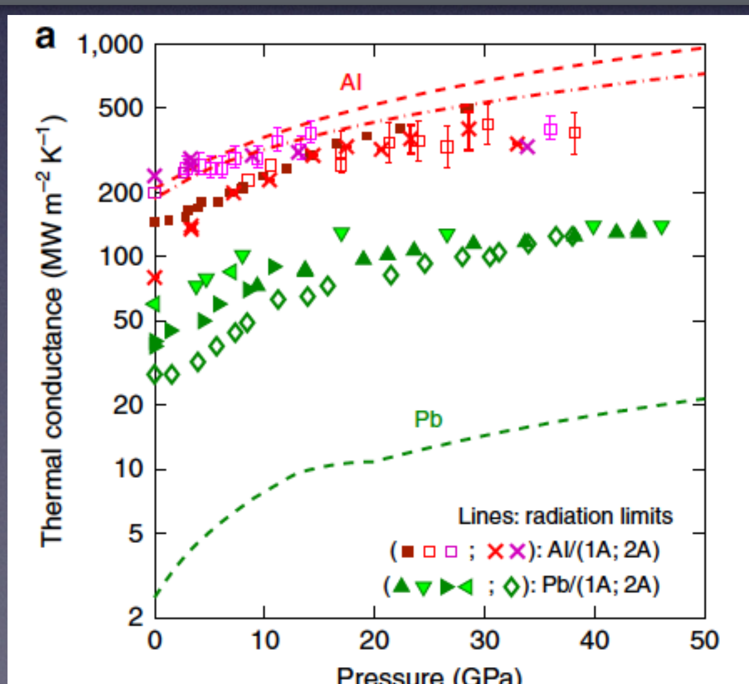
Experimental measurements suggest that direct coupling from metal electrons to semiconductor phonons may be a significant heat transfer pathway



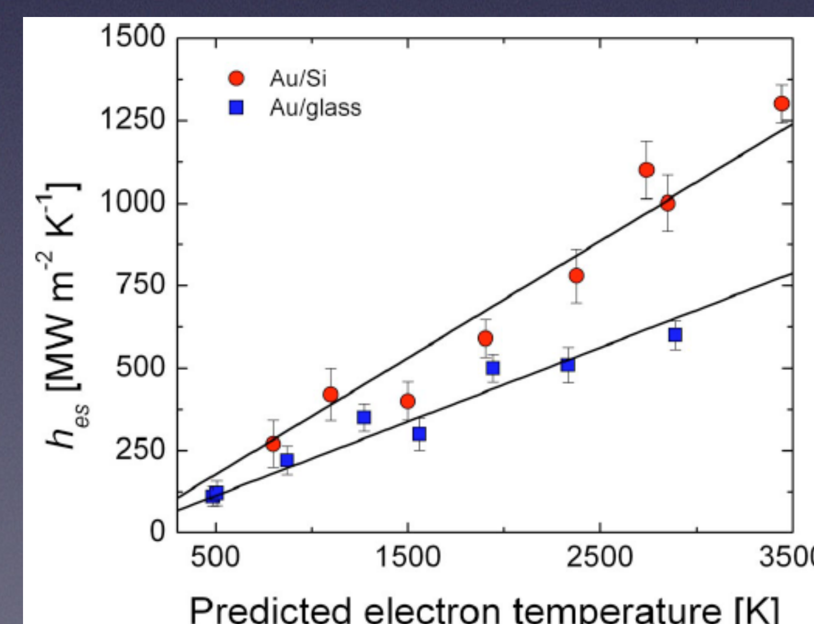
Stoner and Maris, Phys. Rev. B, **48** 16373 (1993)



Liang et al., J. Heat Transfer, **134** 042402 (2012)



Hohensee et al. Nat. Comm. **6** 6578 (2015)

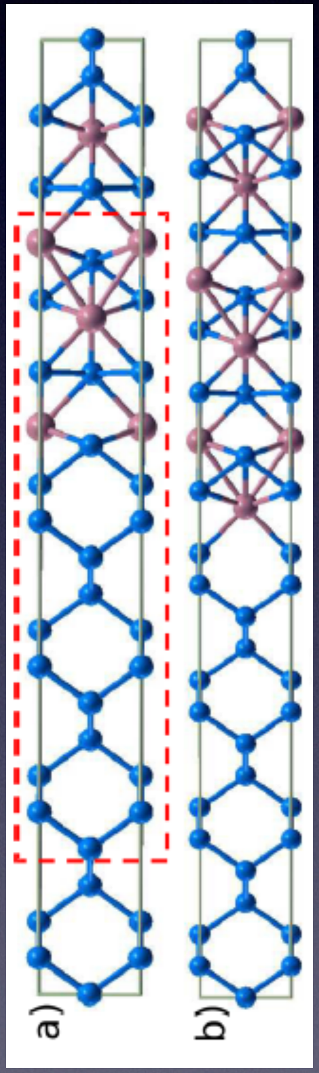


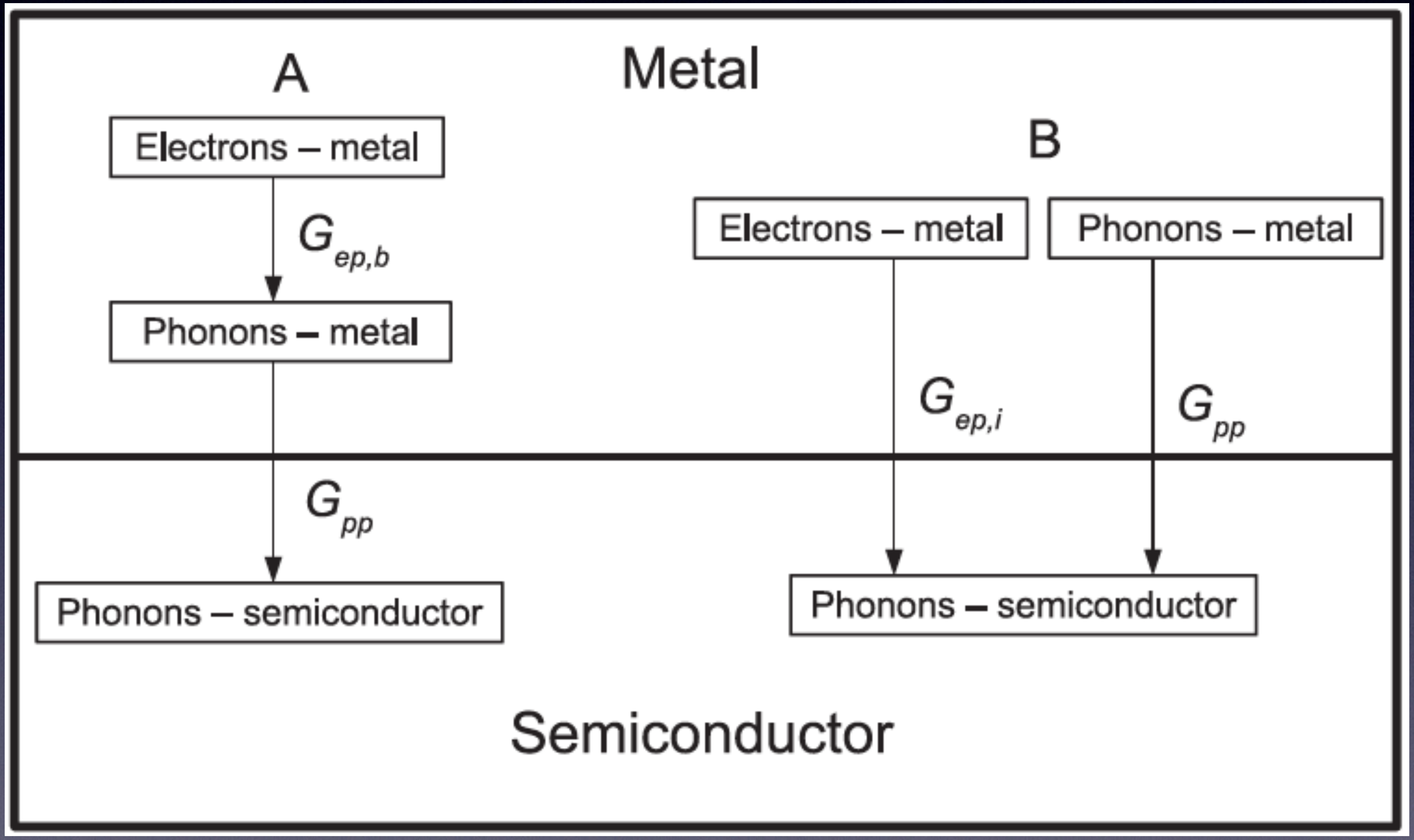
Hopkins et al., J. Appl. Phys., **105** 023710 (2009)

Understanding of cross-interface thermal transport remains elusive (in general)

$TiSi_2$

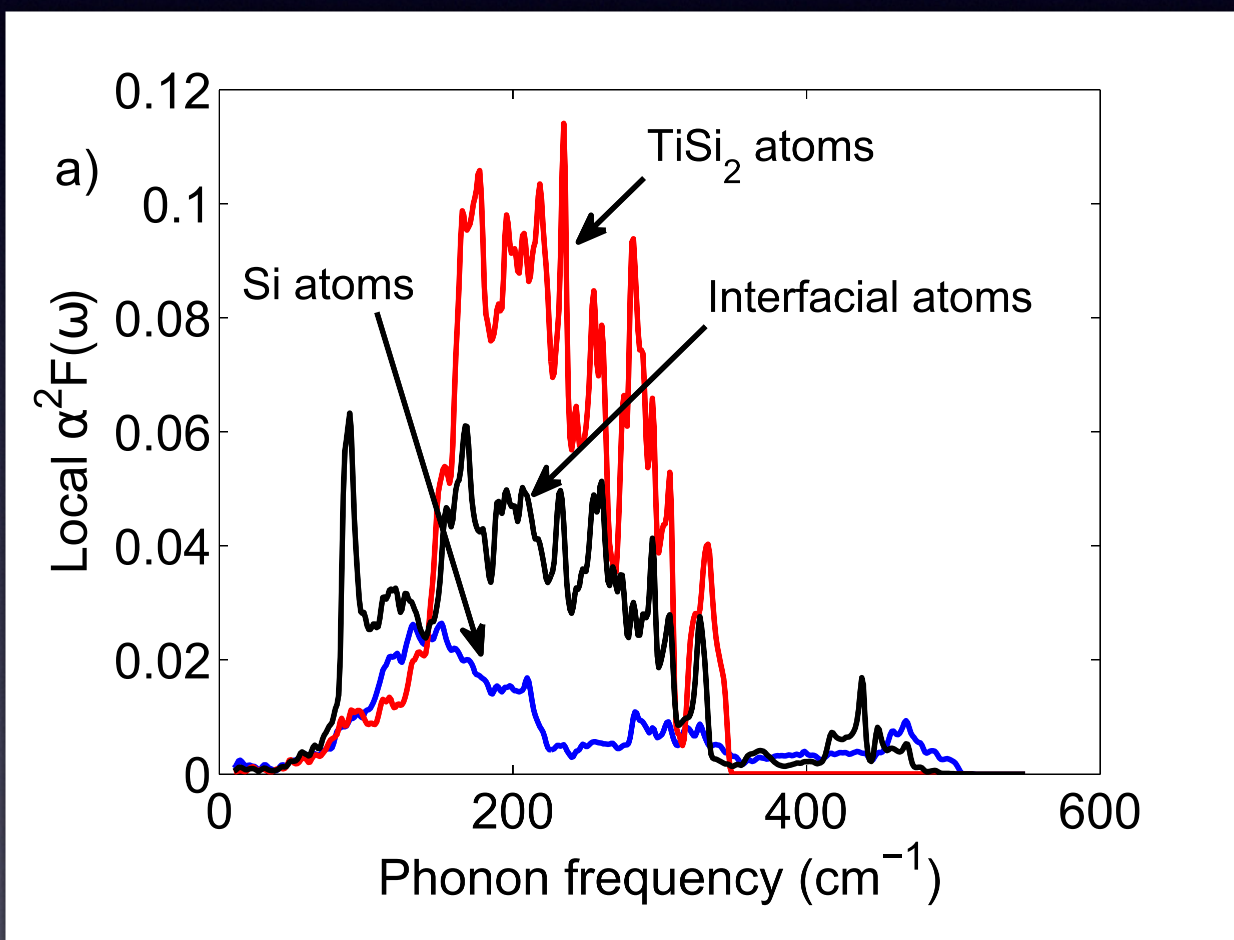
Si

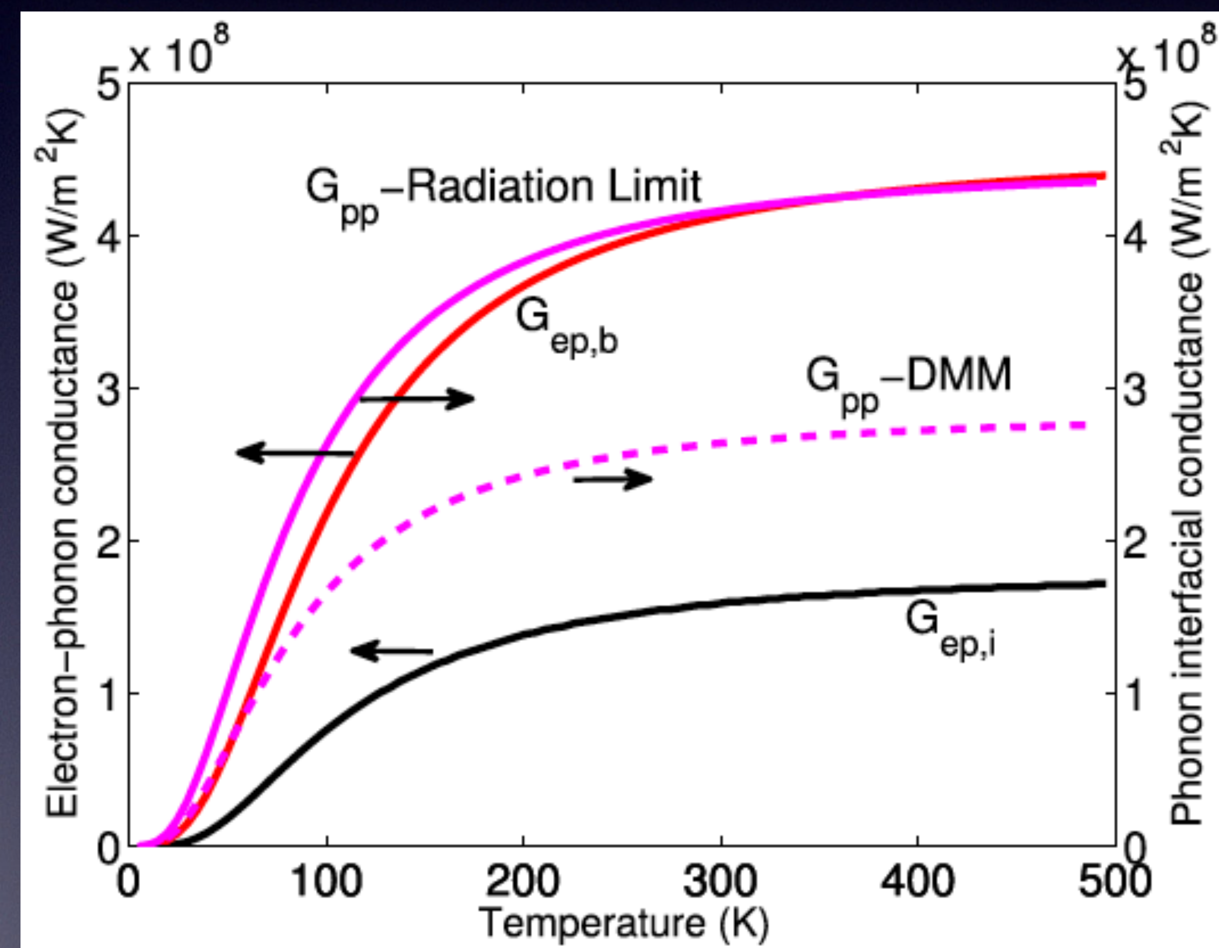




Sadasivam, Waghmare, Fisher, J Appl Phys, **117** 134502 (2015)

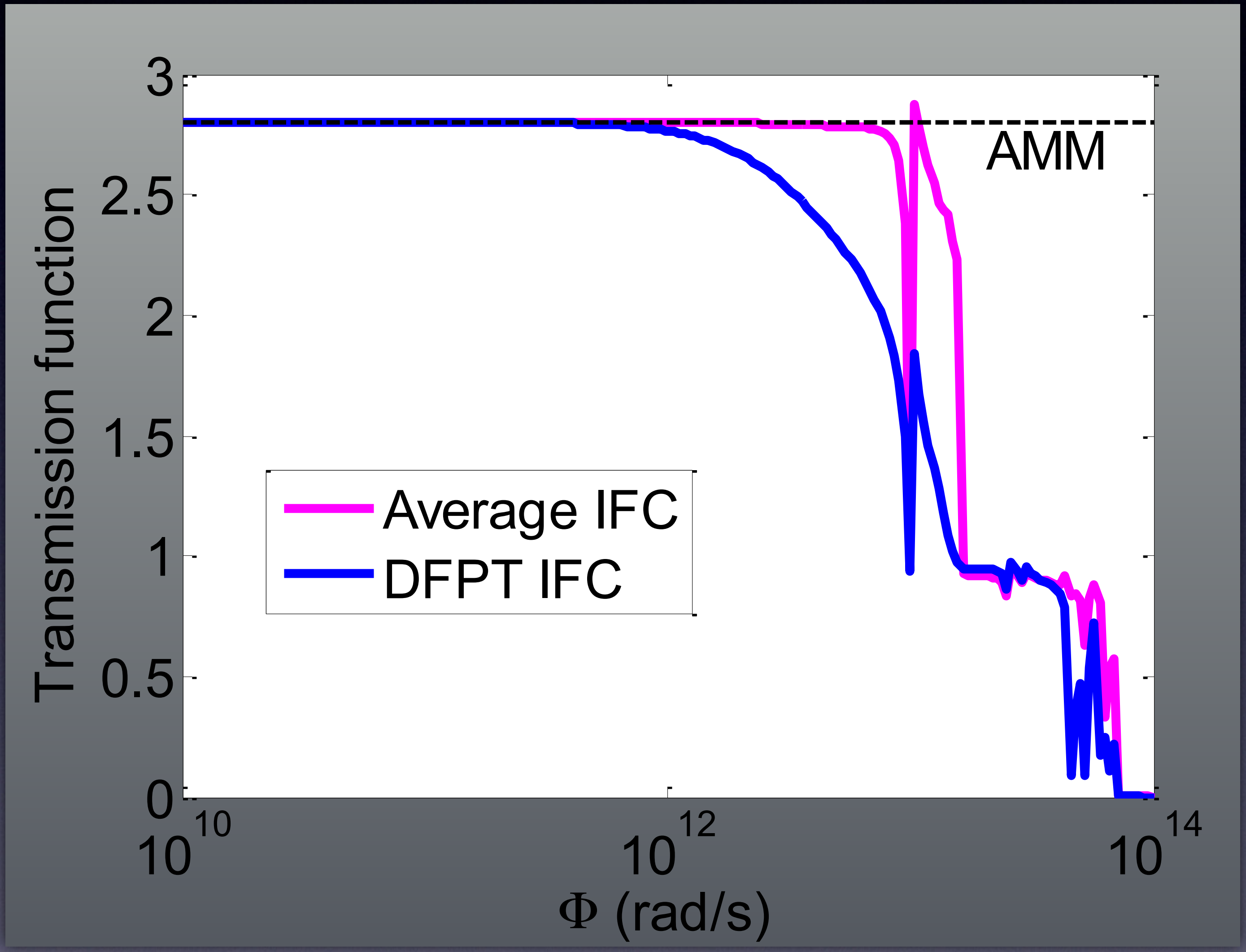
Electron-phonon coupling across the interface is significant

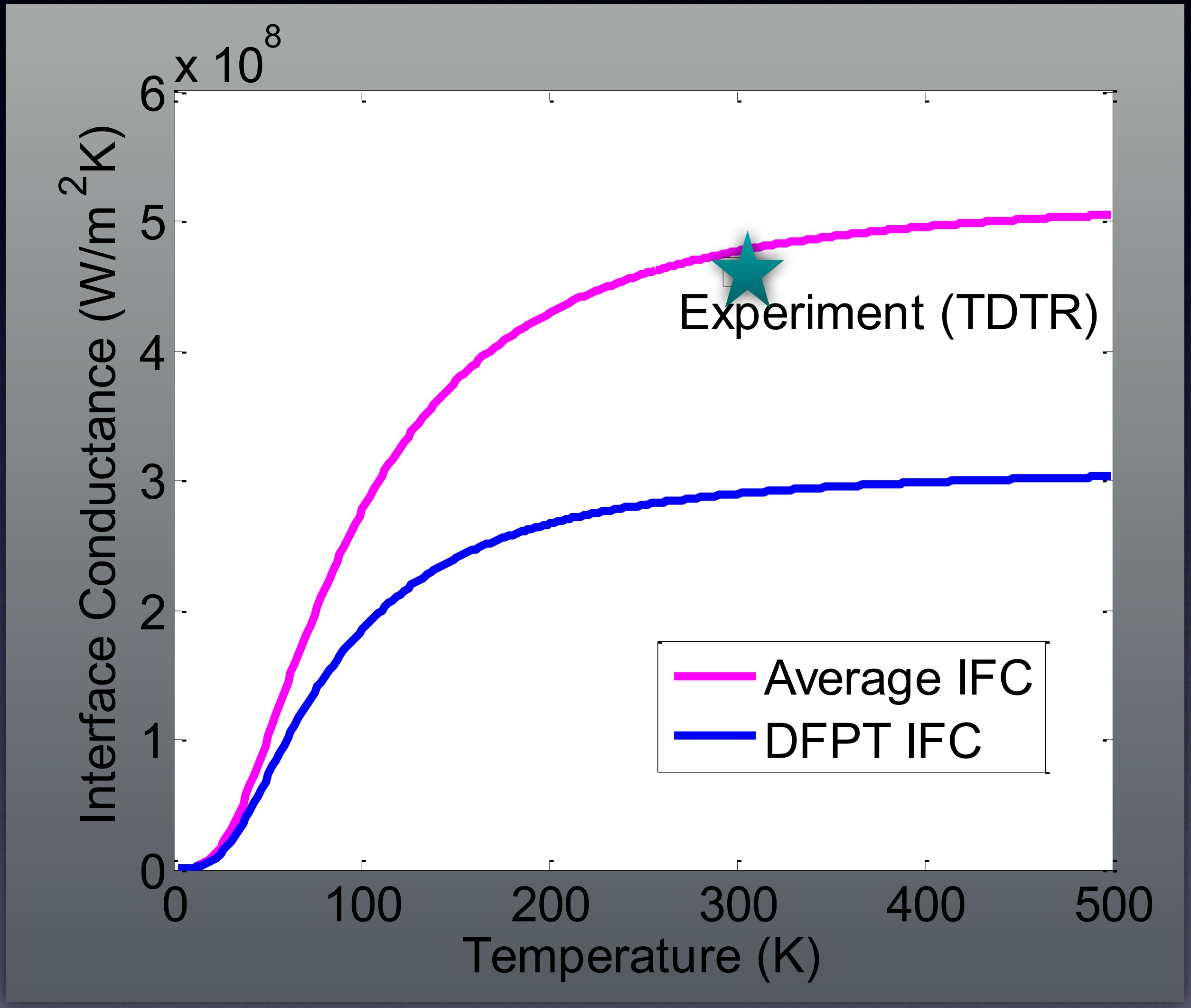




$$J_{ep} = 2\pi D(E_f)\int_0^\infty (\hbar\omega)^2 \alpha^2 F(\omega)(f_{BE}^o(\omega,T_e) - f_{BE}^o(\omega,T_l))d\omega$$

New modeling with validating experiments on $CoSi_2$ support e-ph coupling





Experiments (preliminary) by Feser group, U. Delaware

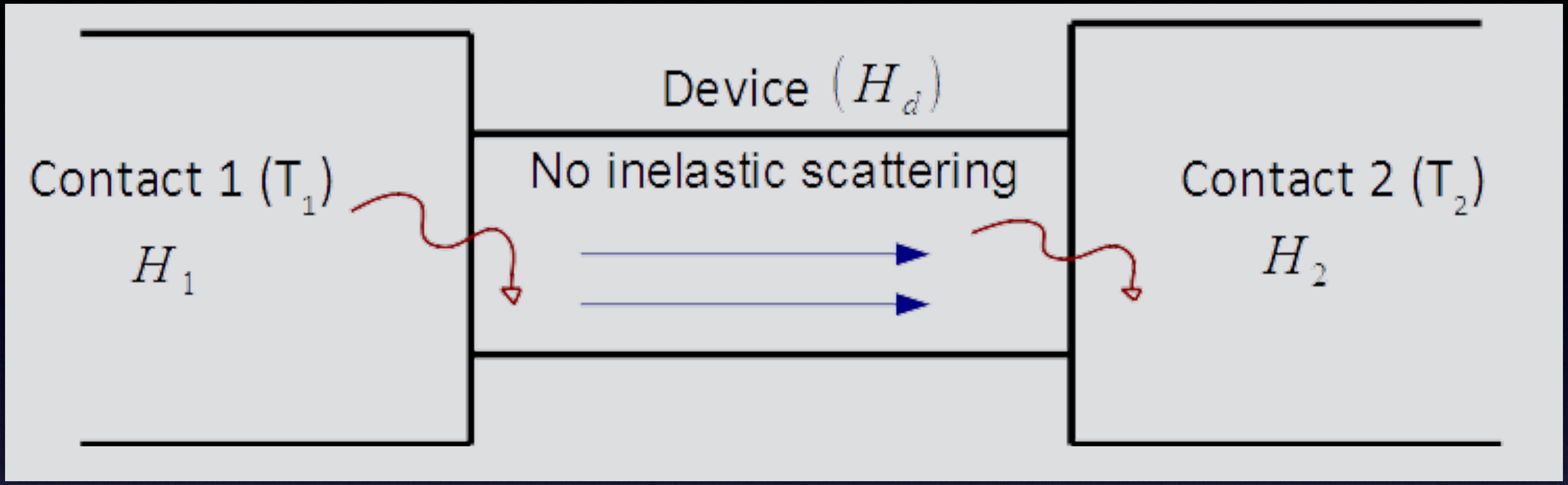
Nanoscale I: Using atomistic knowledge in devices (brief)

Kai Miao (PhD student, ECE)

Sridhar Sadasivam (PhD student)

Tillmann Kubis (Res. Faculty, ECE)

General atomistic Green's function method



$$G_d = [\omega^2 I - H_d - \Sigma_1 - \Sigma_2]^{-1}$$ Device Green's function

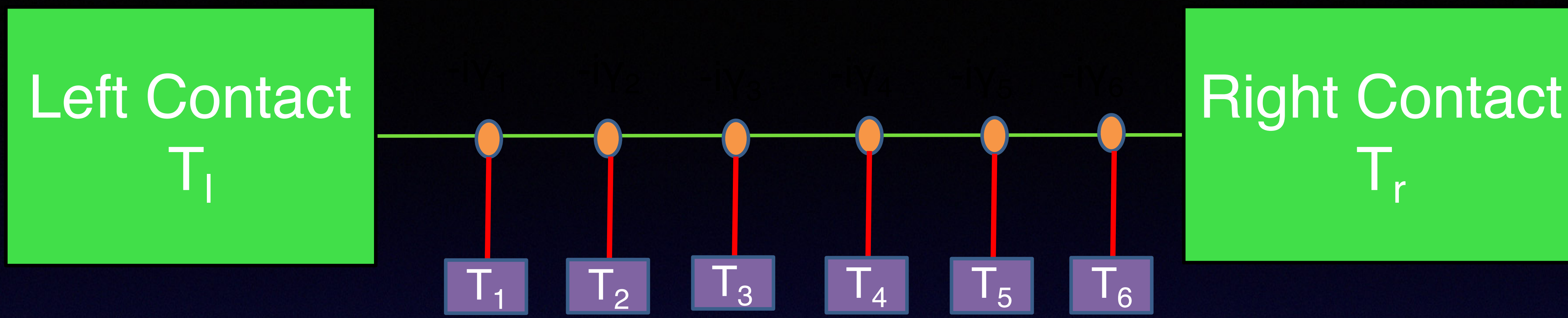
$$\Sigma_1 = \tau_1 g_1 \tau_1^{\dagger} \qquad \Sigma_2 = \tau_2 g_2 \tau_2^{\dagger}$$ Contact self-energies

$$\Gamma_1 = i(\Sigma_1 - \Sigma_1^{\dagger}) \qquad \Gamma_2 = i(\Sigma_2 - \Sigma_2^{\dagger})$$ 'Escape rate' matrices

$$\mathrm{T}(\omega) = Tr[\Gamma_1 G_d \Gamma_2 G_d^{\dagger}]$$ Transmission function

Matrices $\boldsymbol{H_d}$, $\boldsymbol{\tau}_1$ and $\boldsymbol{\tau}_2$ are readily obtained from bulk and cross-interface inter-atomic force constants obtained from density functional perturbation theory (DFPT)

Büttiker probes add inelastic scattering to the AGF

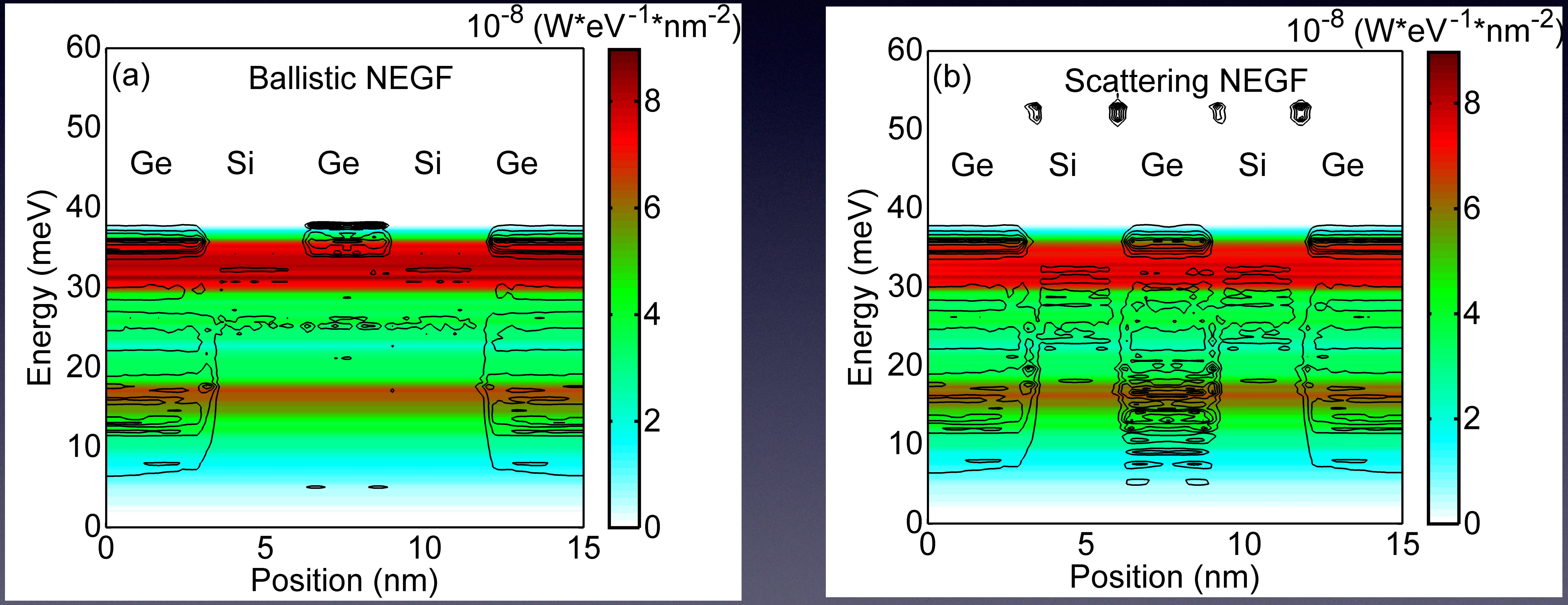


$$G_d = (\omega^2 I - H - \Sigma_l - \Sigma_r - \Sigma_{BP})^{-1}$$

$$\Sigma_{BP}(\omega) = \begin{pmatrix} -i\gamma_1(\omega) & 0 & 0 & 0 & 0 \\ 0 & -i\gamma_2(\omega) & 0 & 0 & 0 \\ 0 & 0 & -i\gamma_3(\omega) & 0 & 0 \\ 0 & 0 & 0 & -i\gamma_4(\omega) & 0 \\ 0 & 0 & 0 & 0 & -i\gamma_5(\omega) \end{pmatrix} \qquad \gamma(\omega) = \frac{\omega}{\tau_{ep}(\omega)}$$

Imaginary part of self-energy is proportional to scattering or escape rate.

Büttiker phonon probes for Si-Ge devices



Miao et al., in review

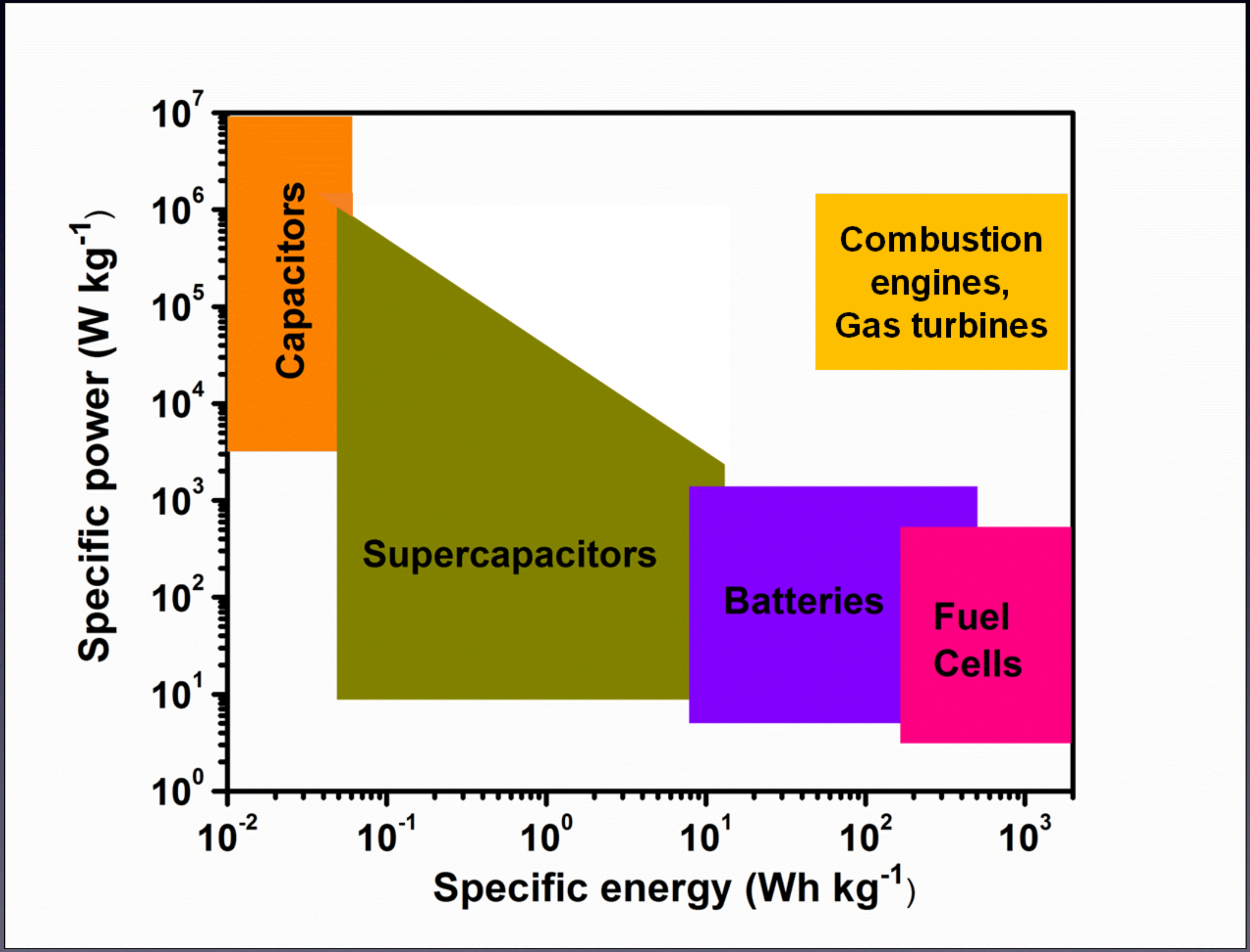
Nanoscale II: Controlling nanomaterial morphology and composition

Guoping Xiong (Posdoc)

Pingge He (Visiting PhD student)

Everyone* wants a faster, more durable battery

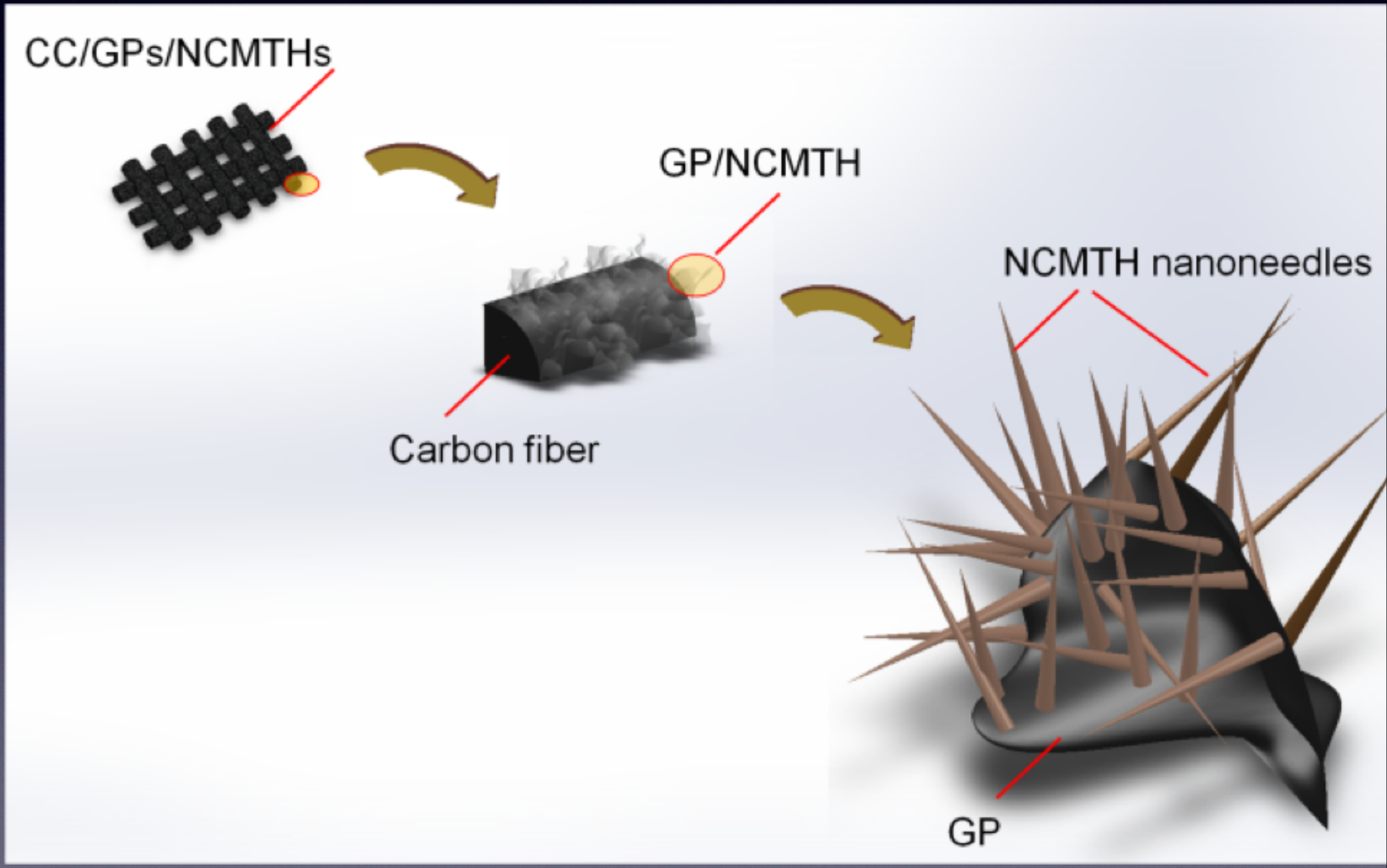
- High energy density (volume and weight)
- High power density for charging (less so for discharging)
- Infinite cycle life (*except the battery companies)
- Non-toxic and safe



Xiong, Kundu, Fisher, *Thermal Effects in Supercapacitors* (2015)

NiCoMn-based nanoneedles

- CC = carbon cloth
- GP = graphitic petal
- NCMTH = NiCoMn triple hydroxide

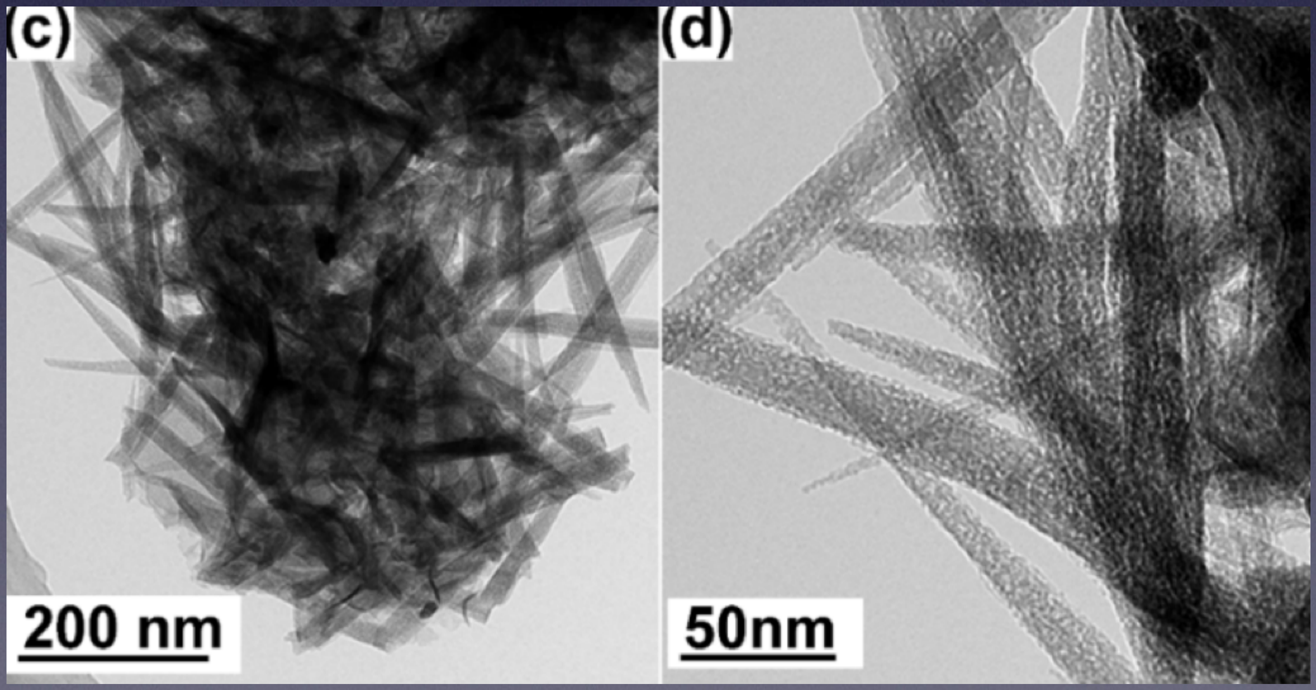


Xiong et al. J. Mat. Chem. A, **3** 22940 (2015)

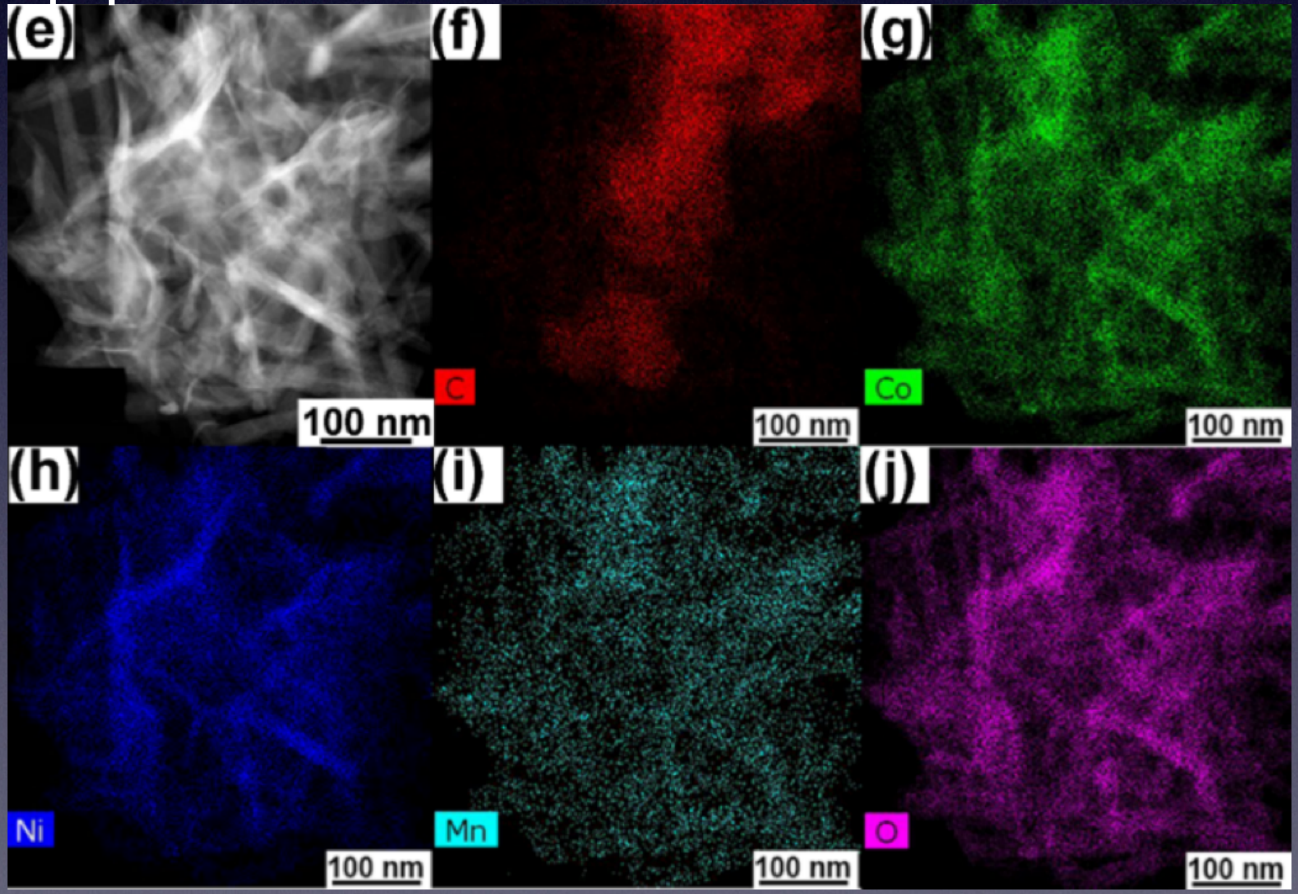
Consistent nanoneedle morphology & composition

Hydrothermal synthesis

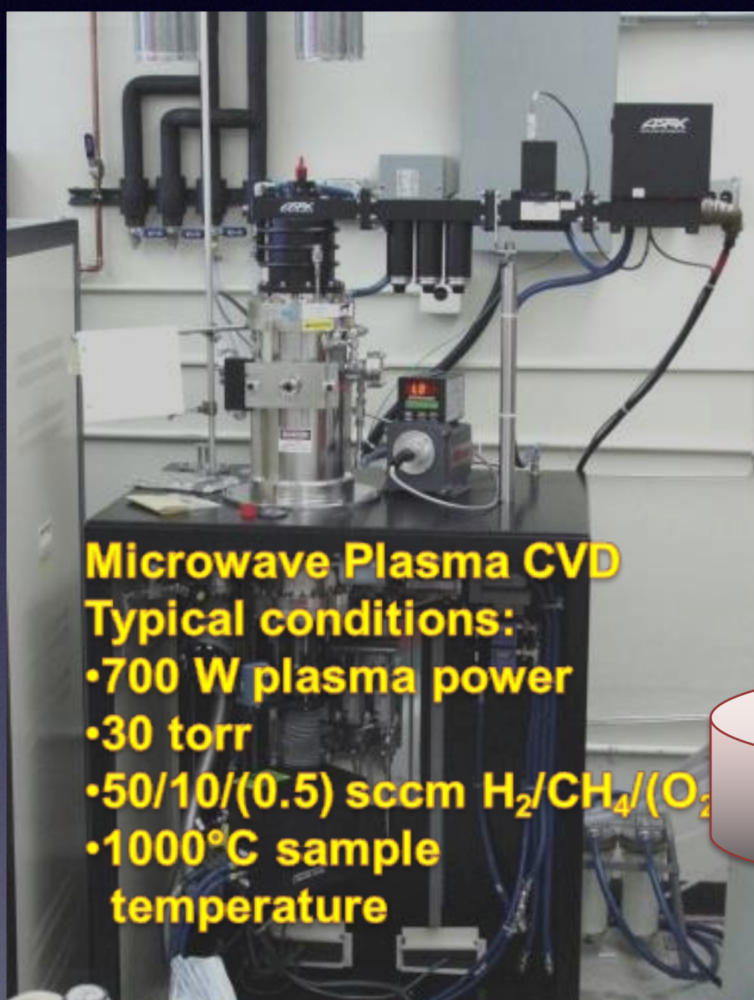
- 1.455 g Co(NO3)2•6H2O, 1.45 g Ni(NO3)2•6H2O, 1.255 g Mn(NO3)2•4H2O and 0.9 g urea 70 mL water
- Autoclave at 135C for 90 min
- Dried at 80C in air for 3 hr
- Resulting BET area of 55 m^2/g

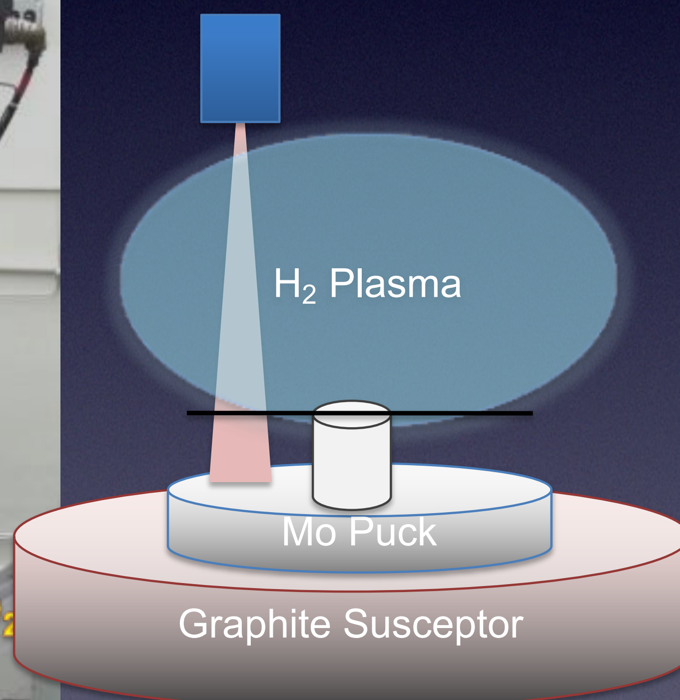


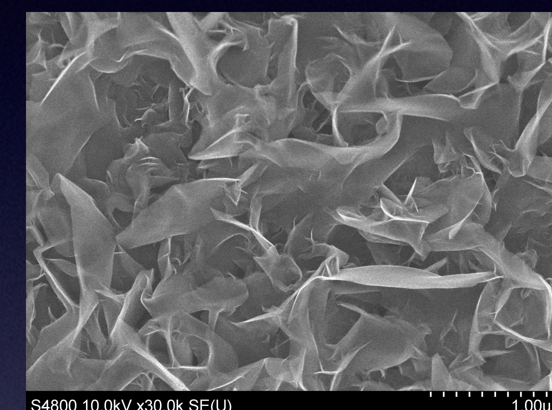
EDX elemental mapping
(approx. Ni:Co:Mn:O = 5:5:1:20)

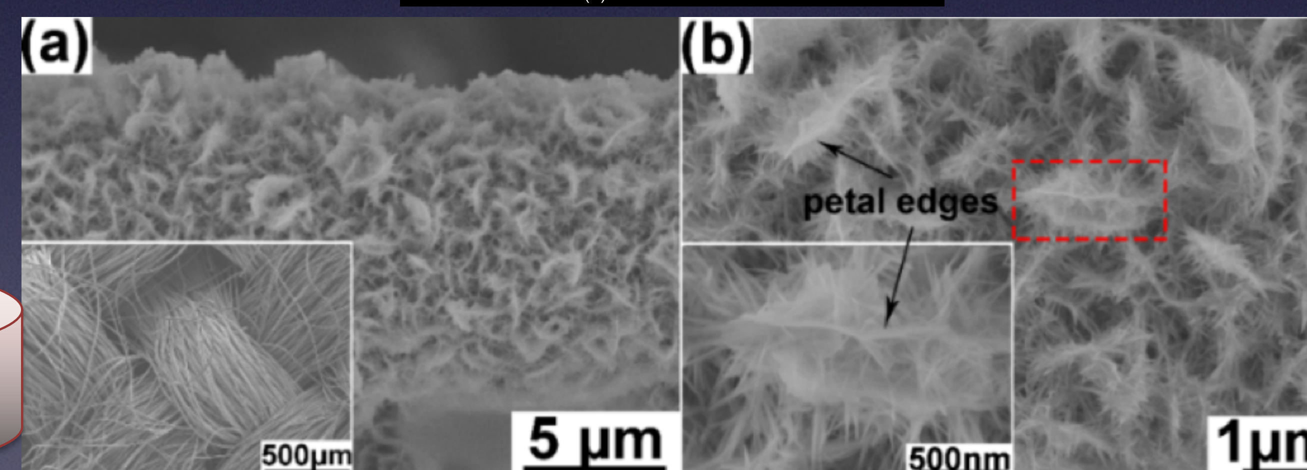


Graphitic petal substrates





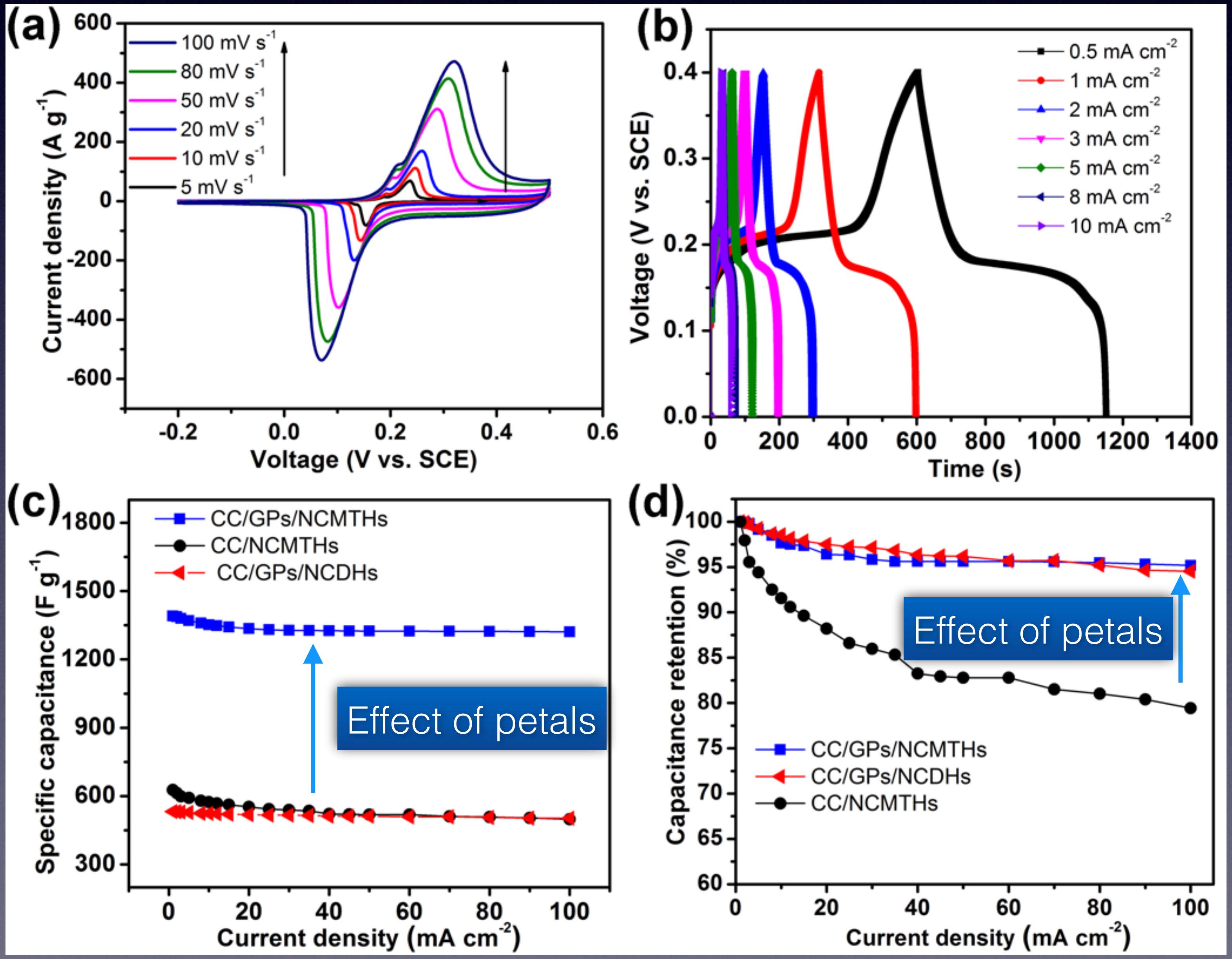




Bhuvana et al., ACS Appl. Mat. Interfaces, **2** 644 (2010)

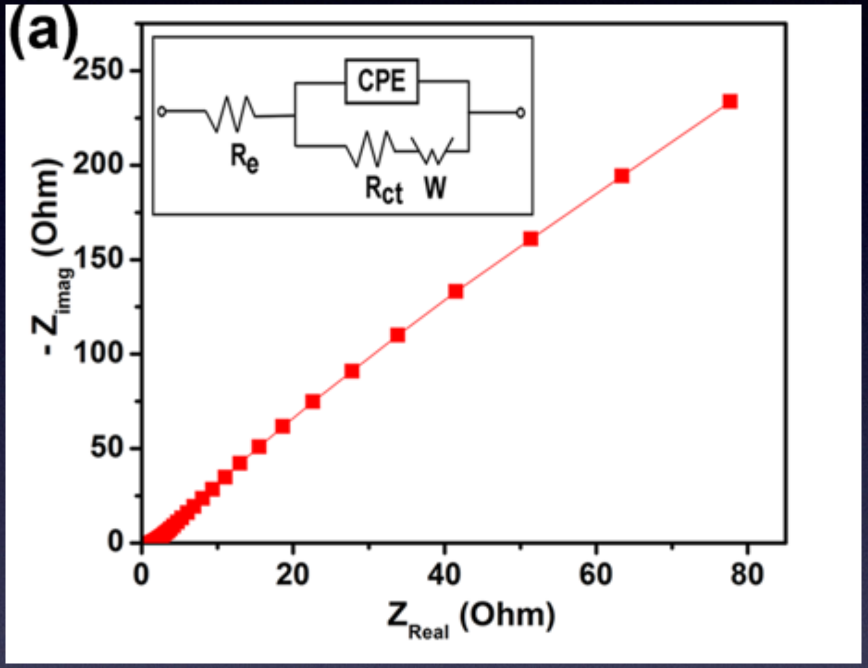
Good overall electrochemical performance

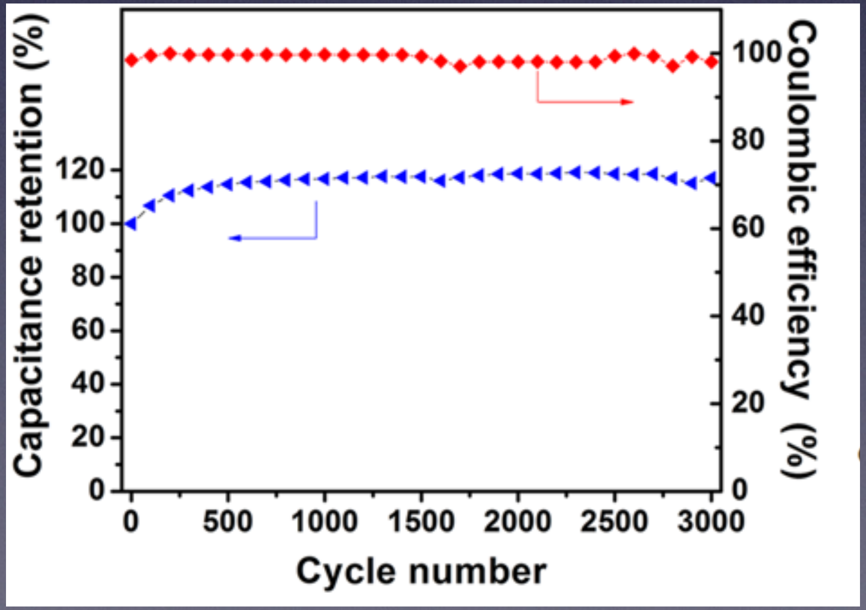
- Single electrodes in 2M KOH
- Clearly dominated by pseudocapitance
- Effect of graphitic petals is strong
- Double hydroxide shows much lower capacitance (vs. triple)

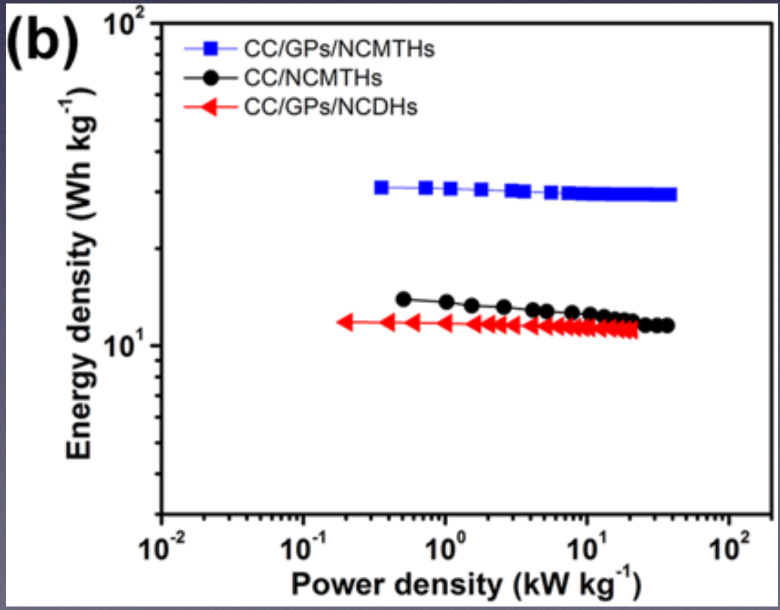


Other electrochemical characteristics, also quite good

- Charge transfer resistance of only 0.3 Ω from Nyquist plot
- Triple hydroxide has much higher energy density than double
- Good cycle life (compared to batteries)



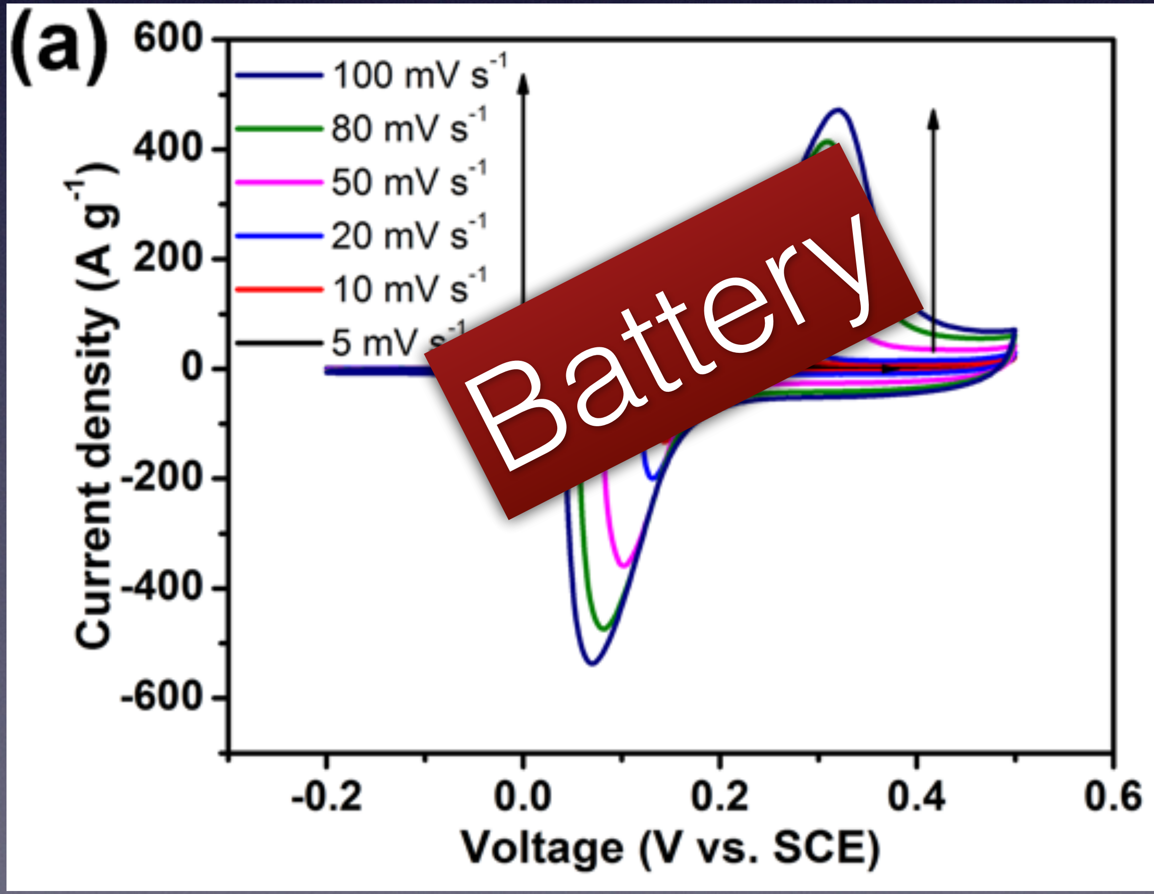




Is it a battery?
Or a supercapacitor?

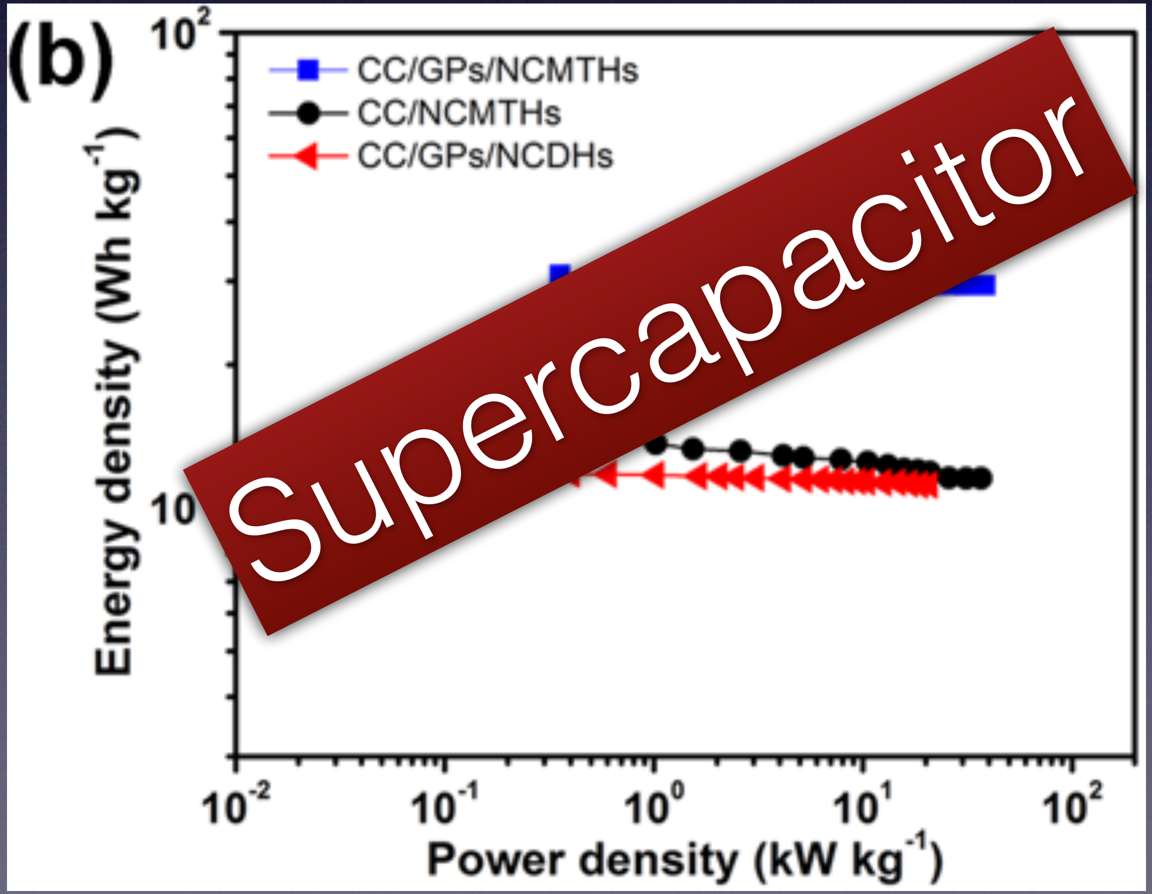
The ACS position

(based on P. Simon et al, Perspective: Where do batteries end and supercapacitors begin? Science, 343, 1210-1211, 2014)



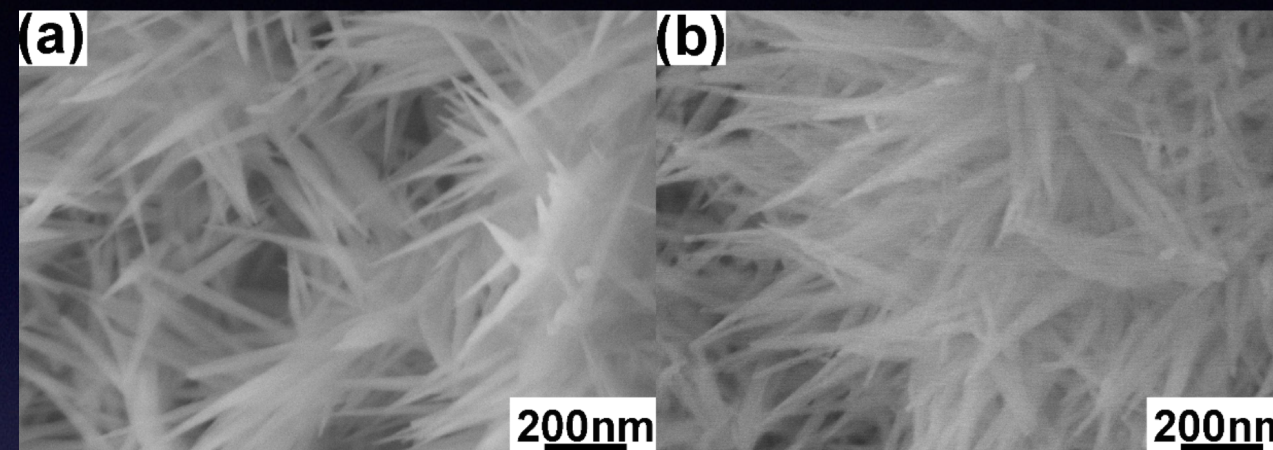
The RSC position

(based on Augustyn et al. Pseudocapacitive oxide materials for high-rate electrochemical energy storage. Energy Environ. Sci., 7, 1597, 2014)



Surprising durability

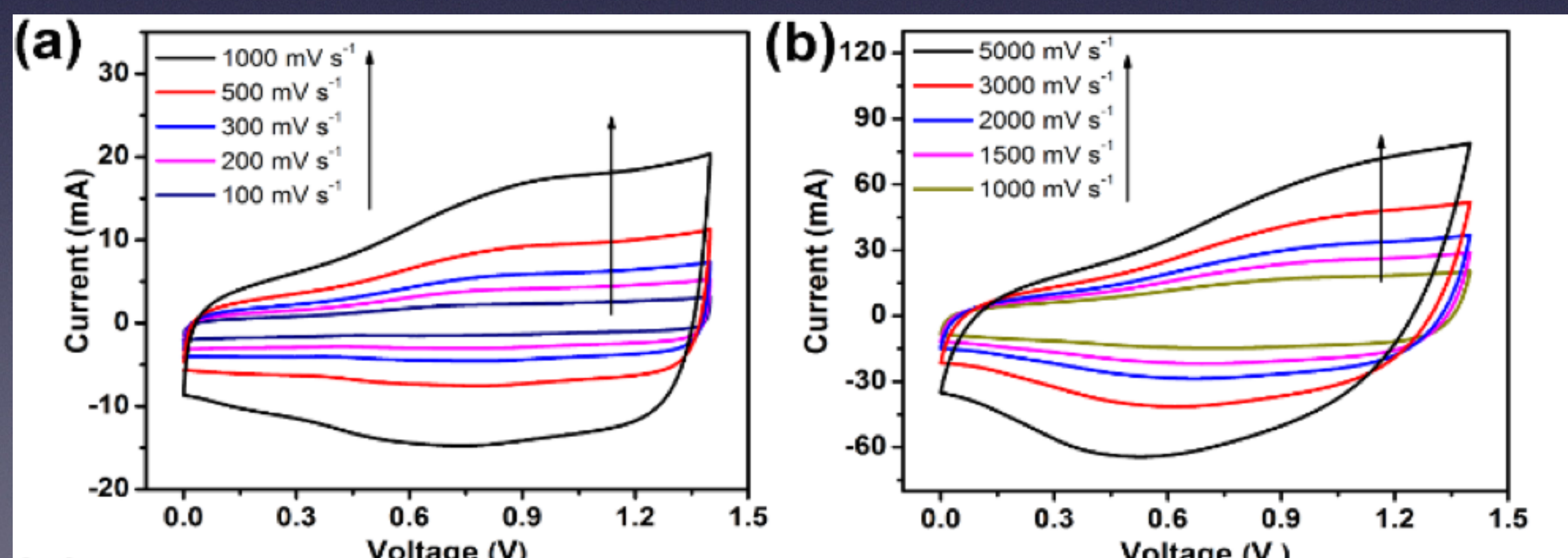
Retains nanoneedle morphology after cycling



As-grown

After 3000 cycles

Extremely high rates in a full two-terminal asymmetric device




Alfredo Tuesta (PhD, now at NRL)


Kim Saviers (PhD student)


Majed Alrefae (PhD student)


Nick Glavin (PhD student)

Nanoscale III: Making nanomaterials faster


Anurag Kumar (Postdoc)

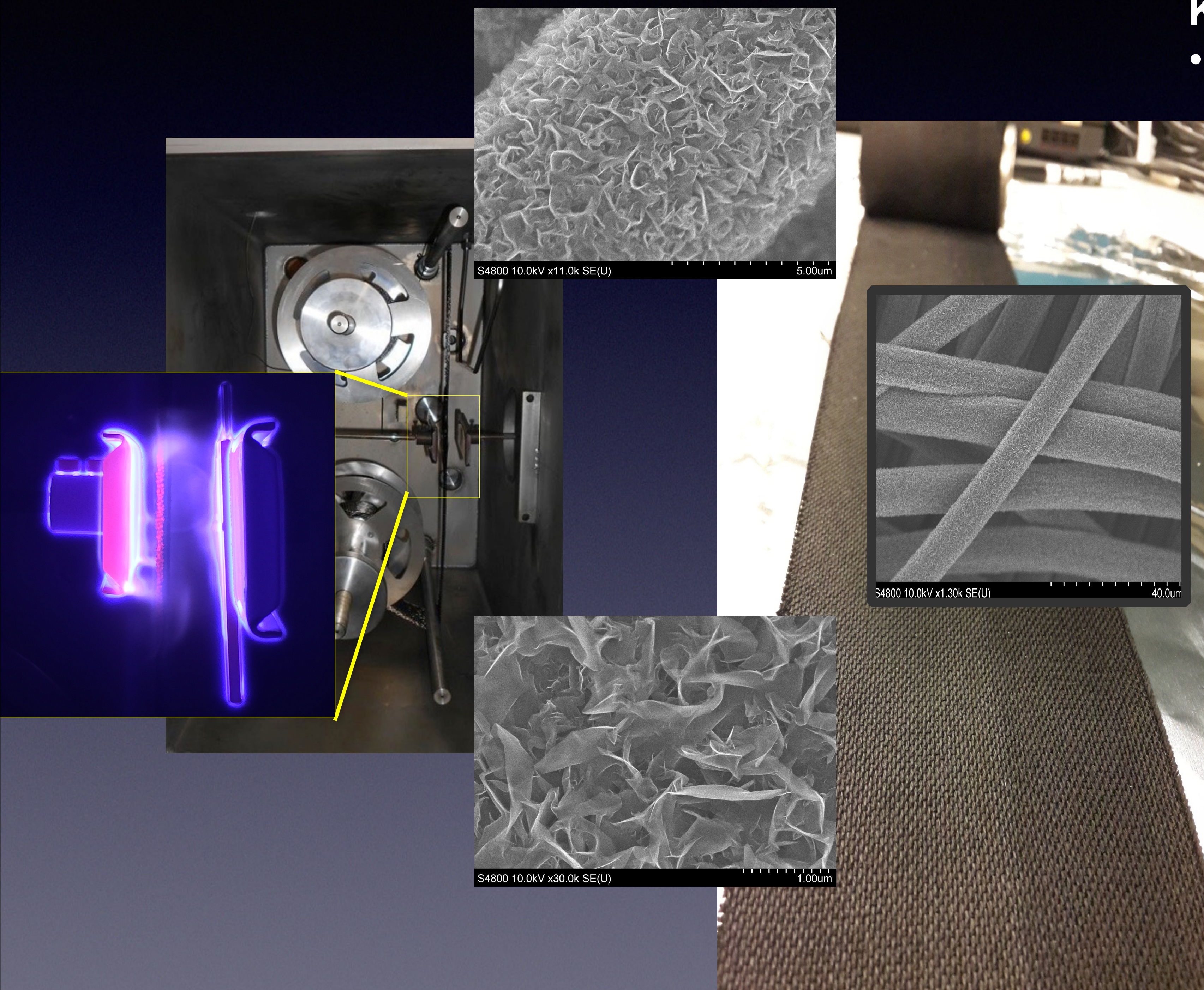

Ritu Gupta (Postdoc, now Faculty at IIT-J)


Andrey Voevodin (Formerly AFRL/RX, Faculty N. Texas)


Alina Alexeenko (AAE Faculty)


Bob Lucht (ME Faculty)

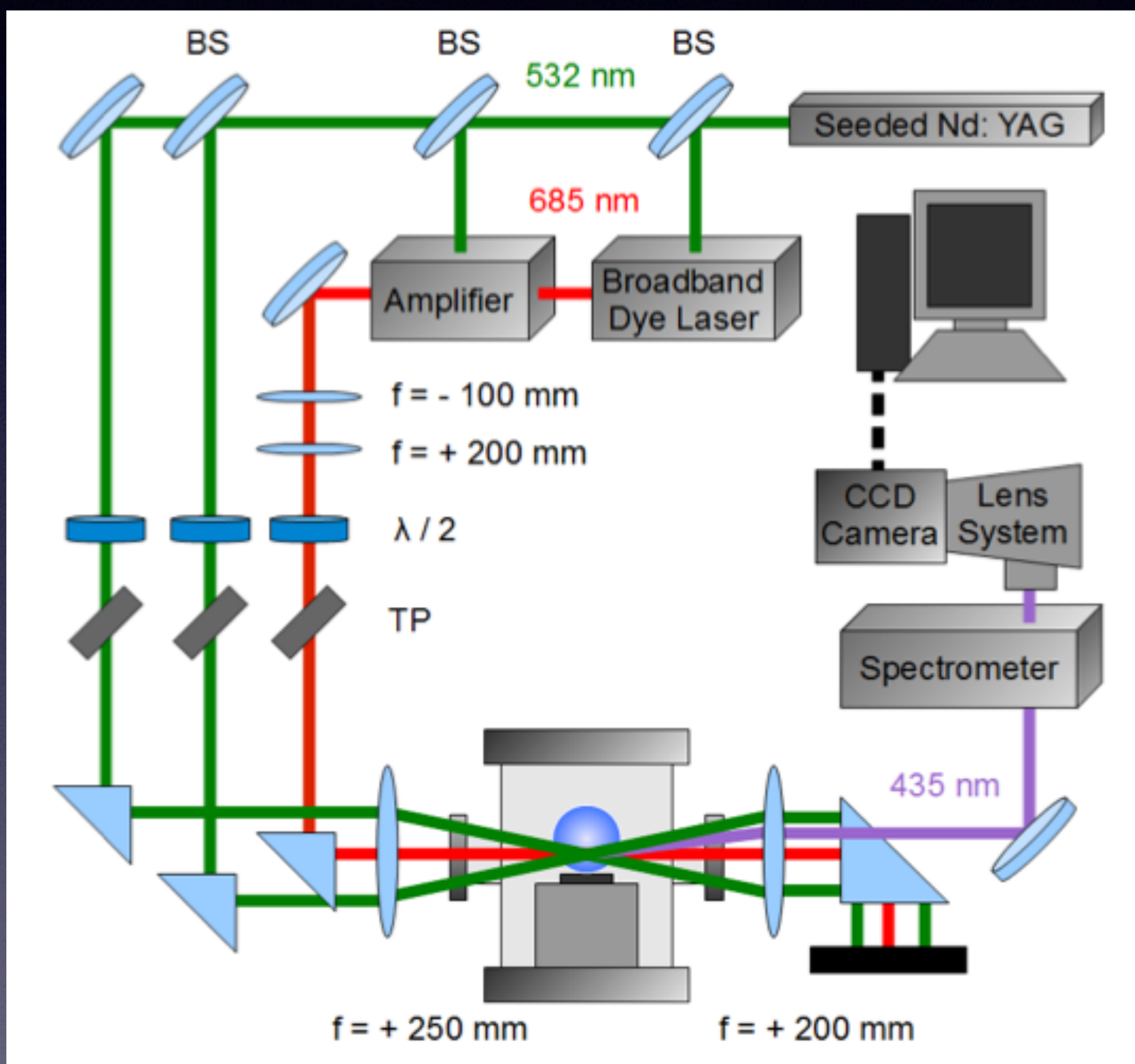
Scaling up: Roll-to-roll plasma deposition of graphitic nanopetals

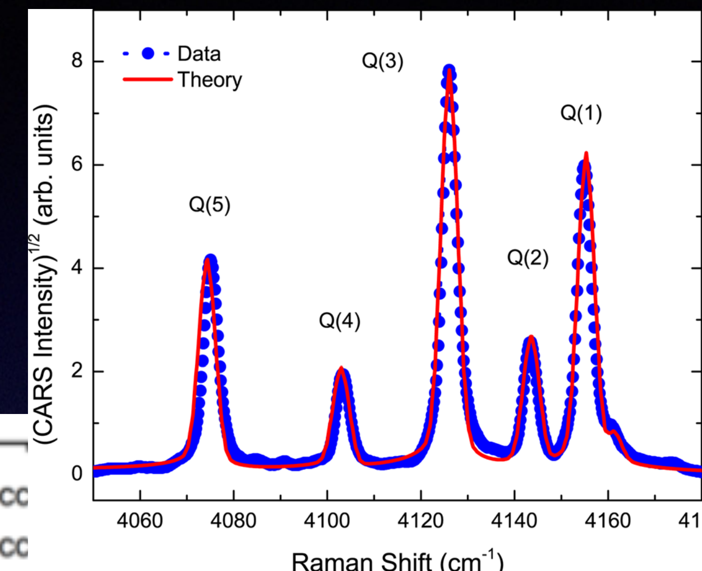


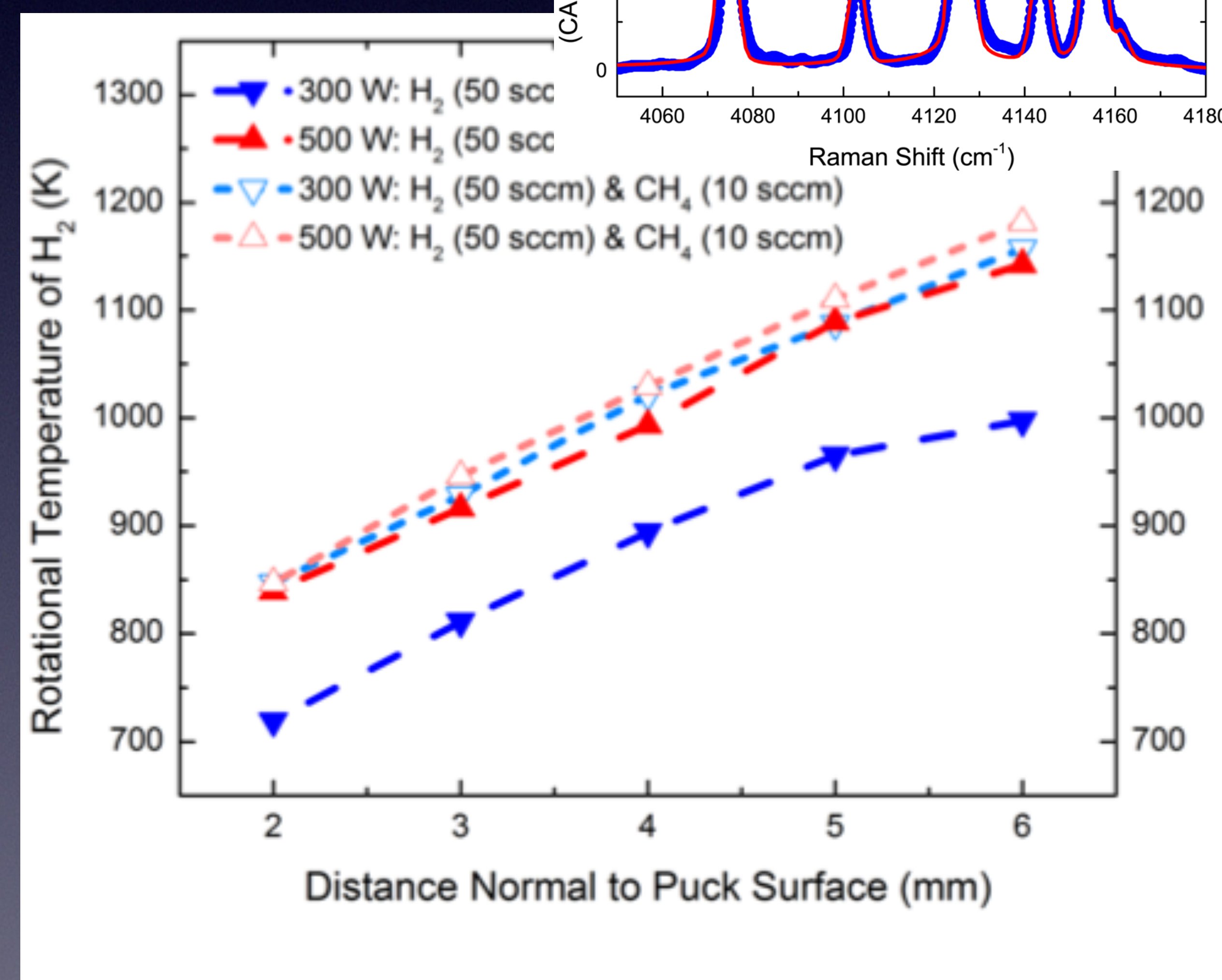
Key Features

- Custom-designed plasma deposition system with reel system inside vacuum chamber
  Low-frequency RF plasma couples to moving web
  Web width up to 10 cm, with web speed up to 500 cm/min (usually much slower)
  Through-chamber viewports for optical diagnostics of the growth region
  Pyrometer temperature measurement
  Pressure control from 1 to 100 Torr
  Gases
    - Hydrogen, 1000 sccm
    - Methane 1000 sccm
    - Nitrogen, 1000 sccm
    - Oxygen, 50 sccm
    - Argon, 5000 sccm
- Plasma power up to 5000 W

Laser diagnostics of graphene plasmas gives a wealth of information



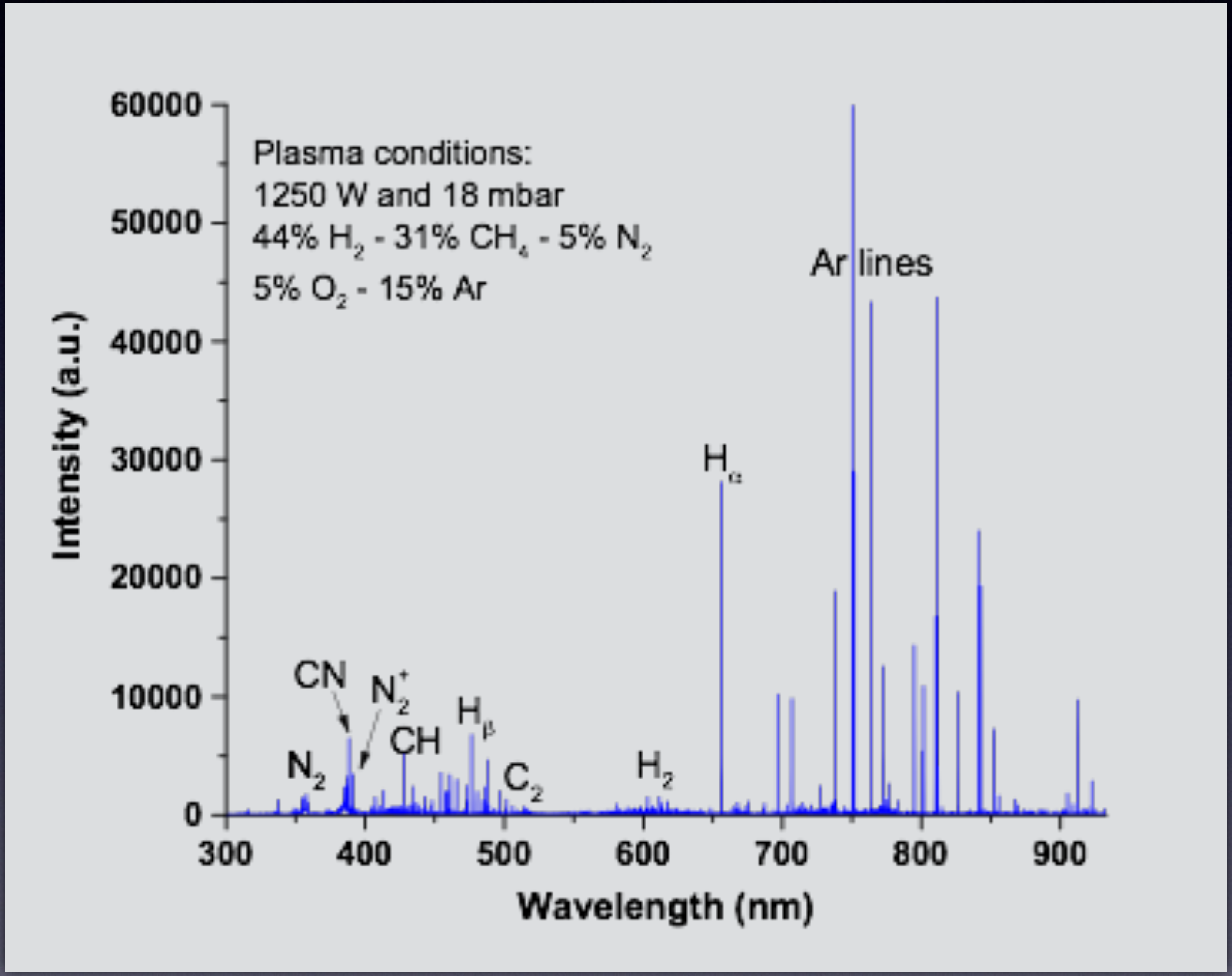




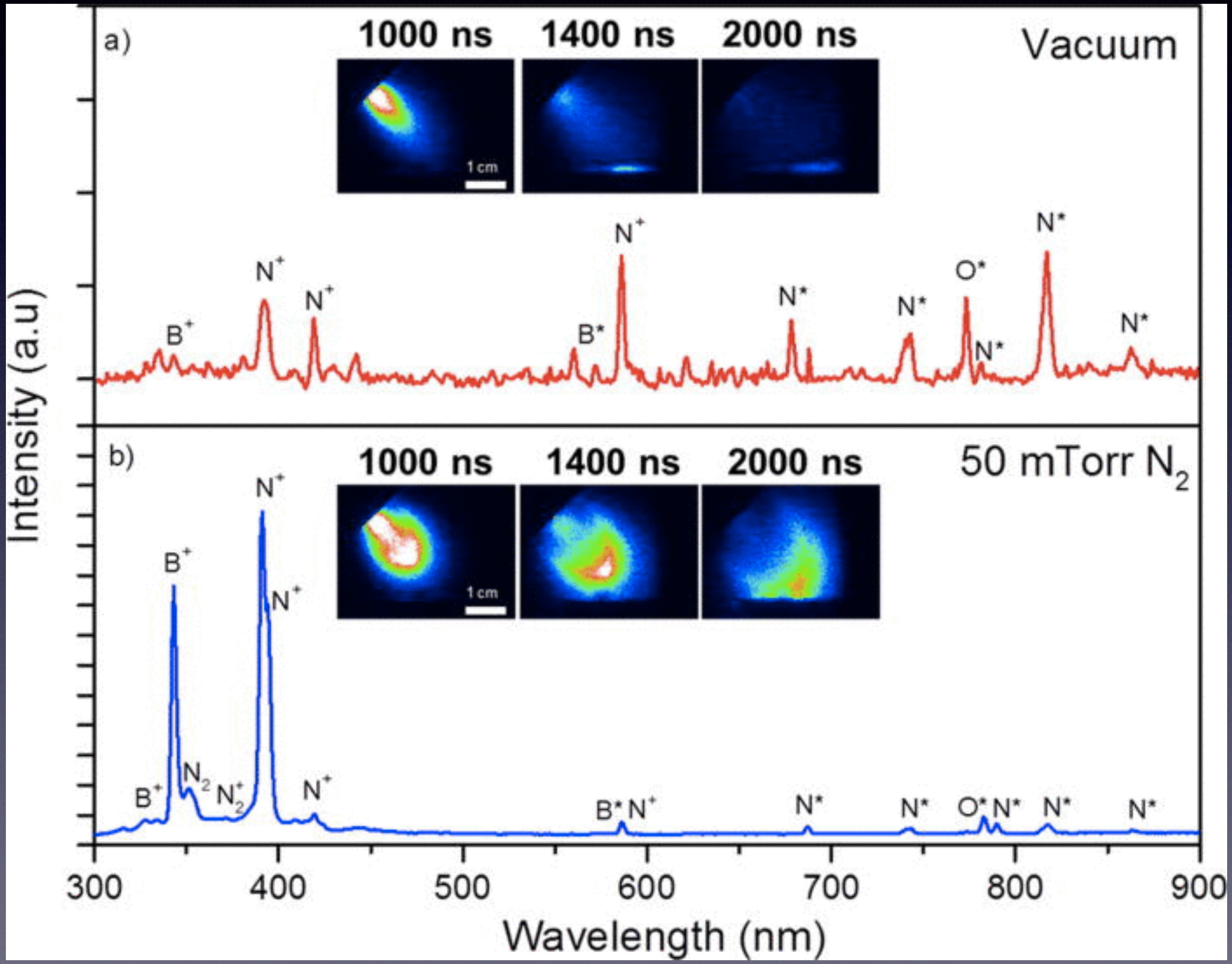
A.D. Tuesta et al., J. Micro and Nano-Manufacturing, 4 011005 (2016)

R2R diagnostics: Simple optical emission spectroscopy gives rich and rapid output

- Emission from excited states of molecules or atoms used as an indication of abundance of these species in the mixture
- For example, a 60-sec survey spectrum can be used to monitor the important species in the plasma such as: N2, CN, CH, H and Ar

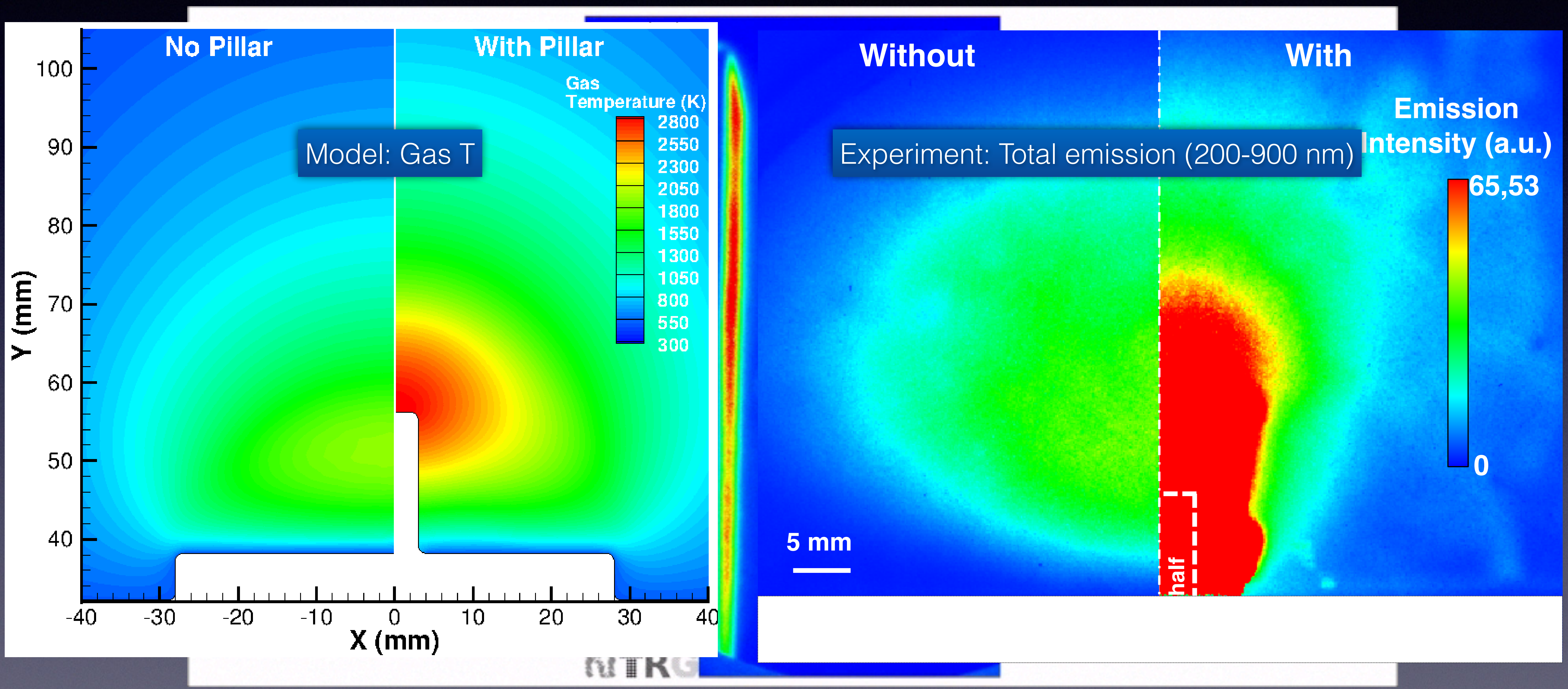


Time-resolved spectral-spatial imaging provides unique insights into PLD of BN films



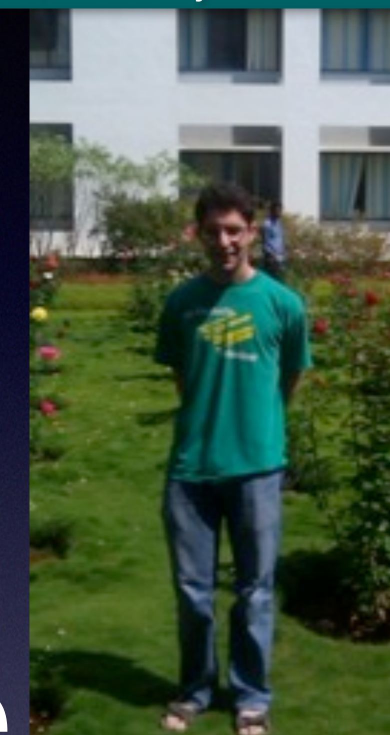
Glavin et al., J Appl Phys **117**, 165305 (2015)

Early results from imaging of graphene-producing plasmas



G. Shivkumar, et al., J. Appl. Phys. 119 113301-13 (2016)

Kyle Smith
(PhD graduate, Faculty at UIUC)



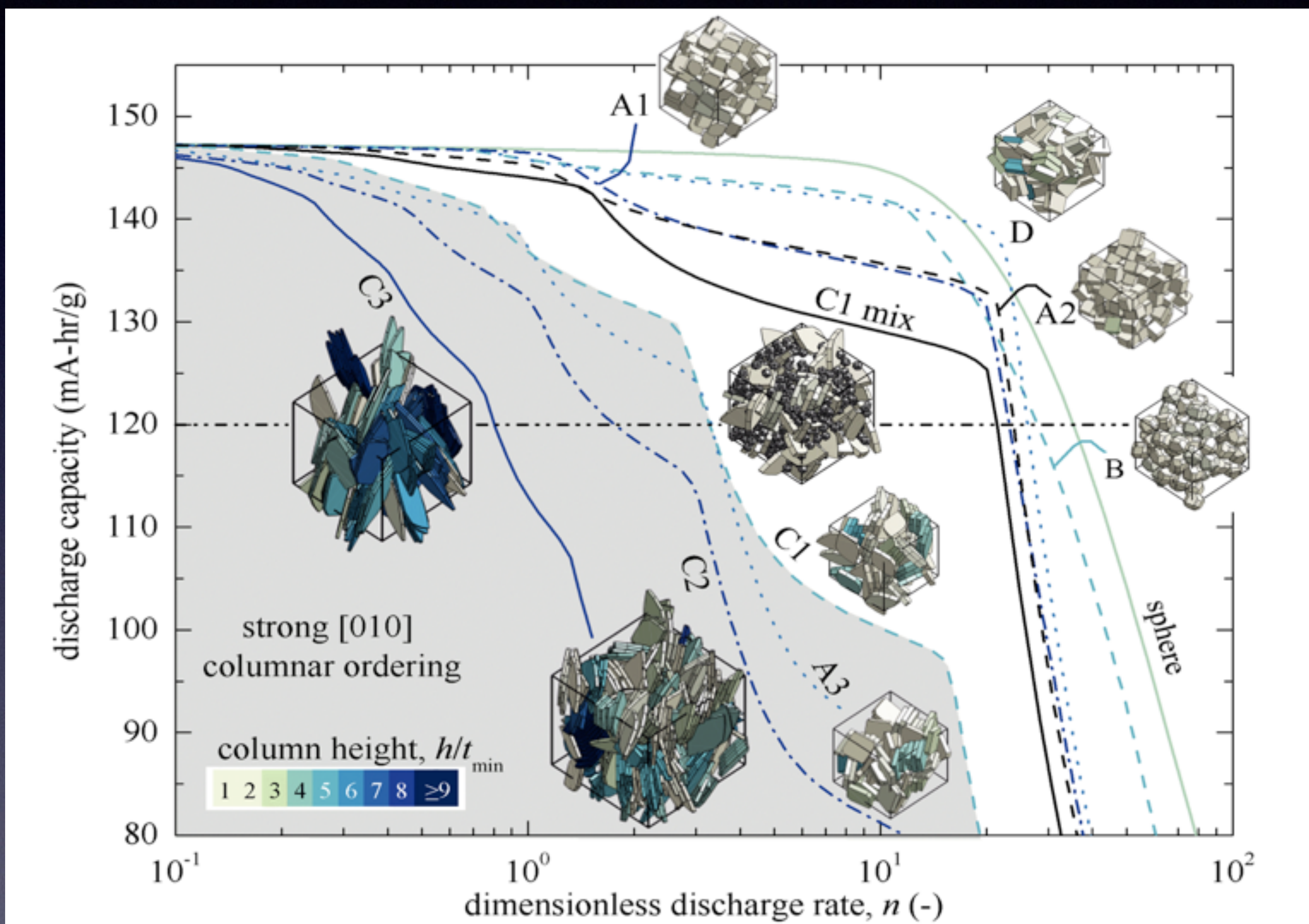
Micro-to-macro scale: Assemblies of nano/micro materials for the human scale

Ishan Srivastava (PhD student)

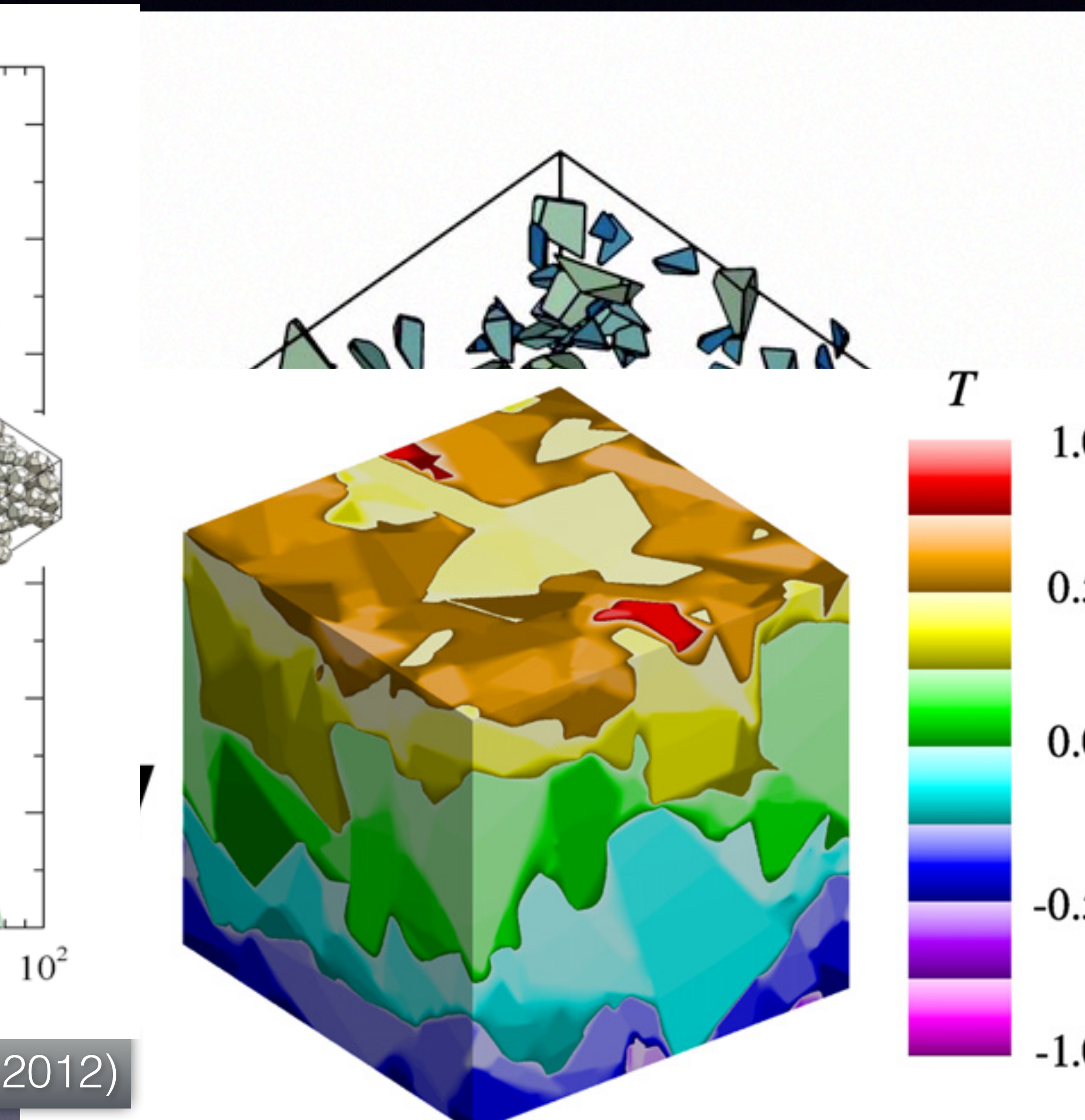
Sridhar Sadasivam (PhD student)

Meheboob Alam (Faculty, JNCASR)

Granular mechanics are important to an amazingly broad array of technologies

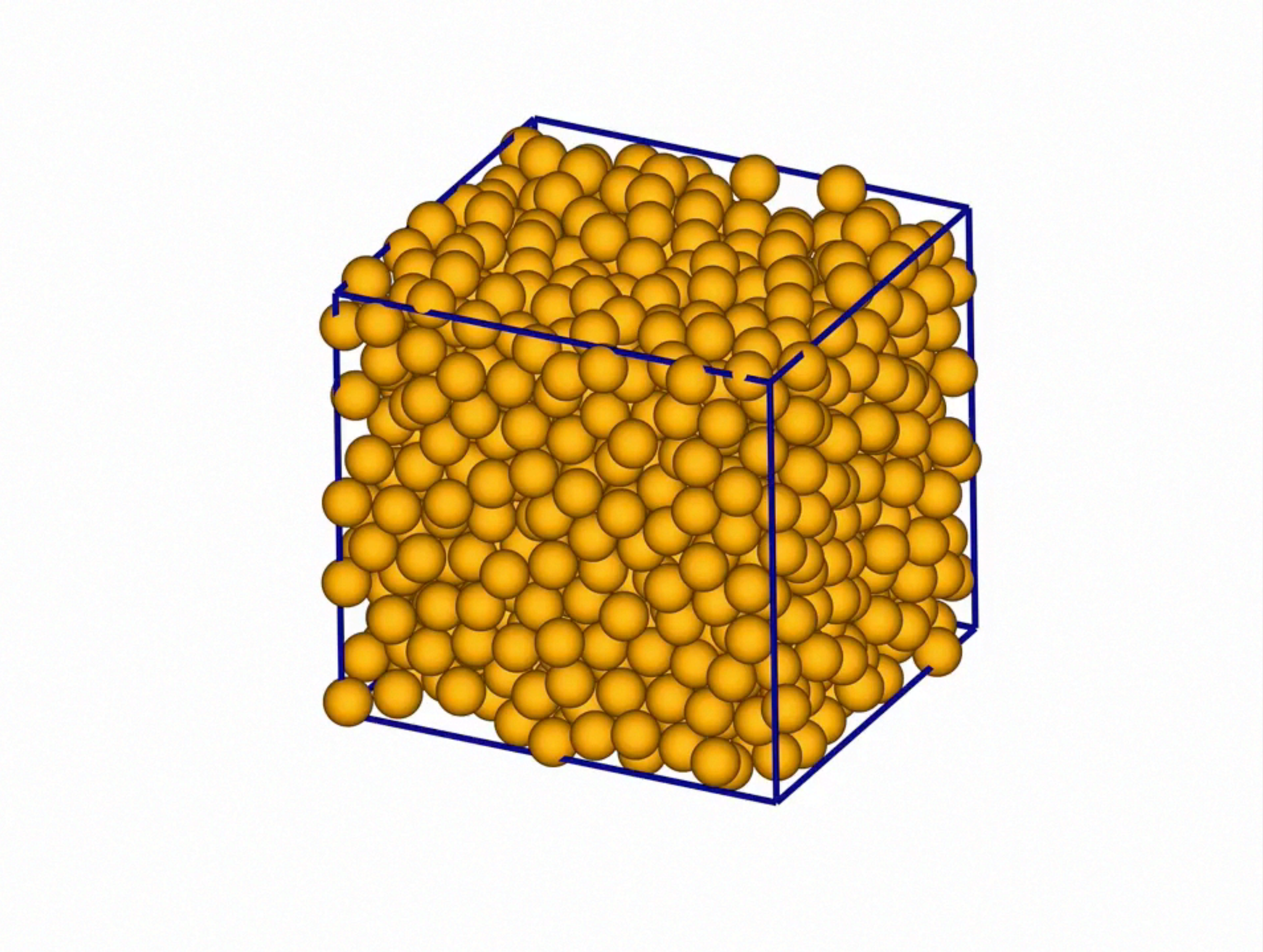


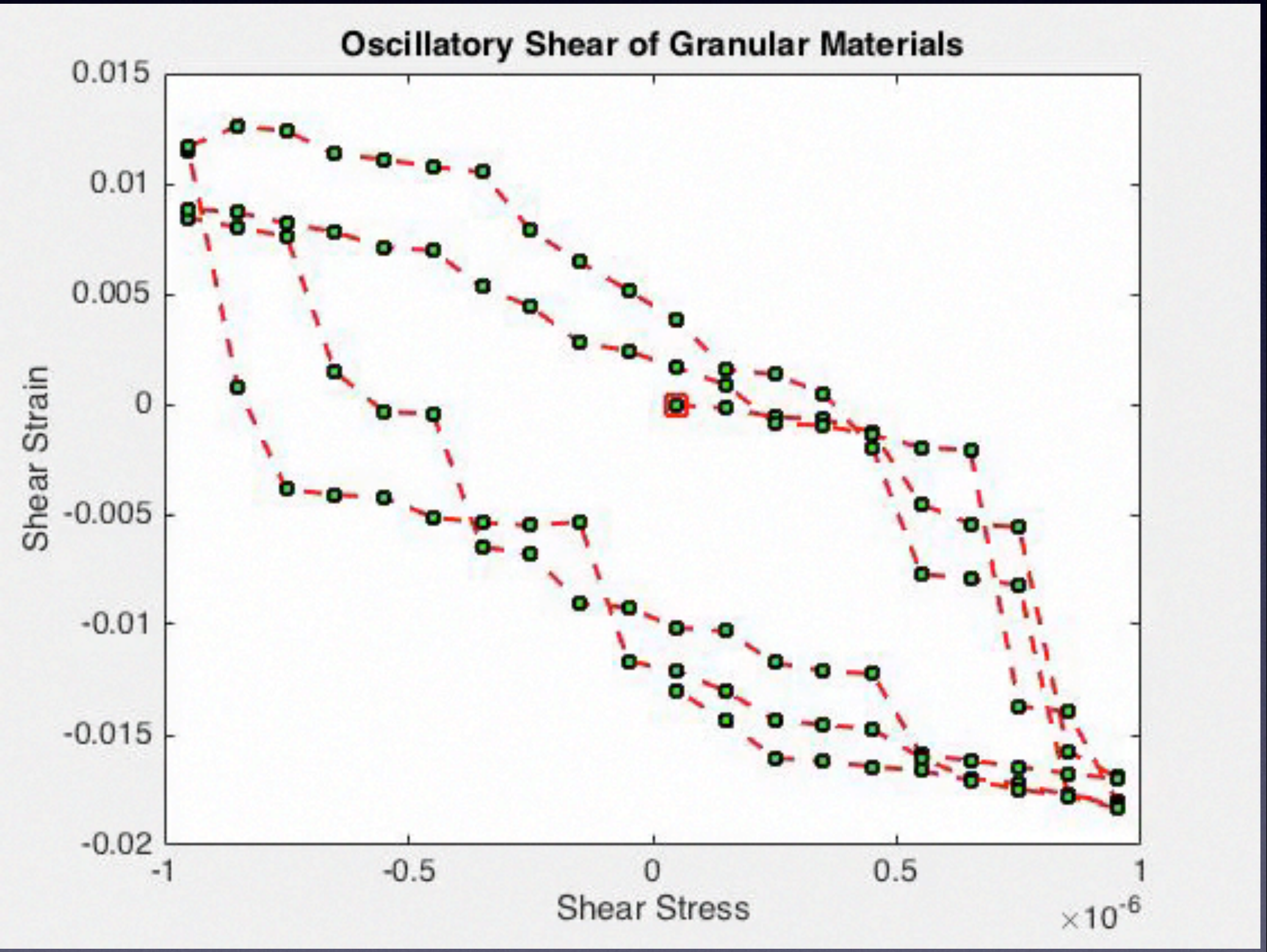
Smith, Mukherjee & Fisher, Phys. Chem. Chem. Phys. **14** 7040 (2012)



Smith & Fisher, Int. J. Hyd. Energy **37** 13417 (2012)

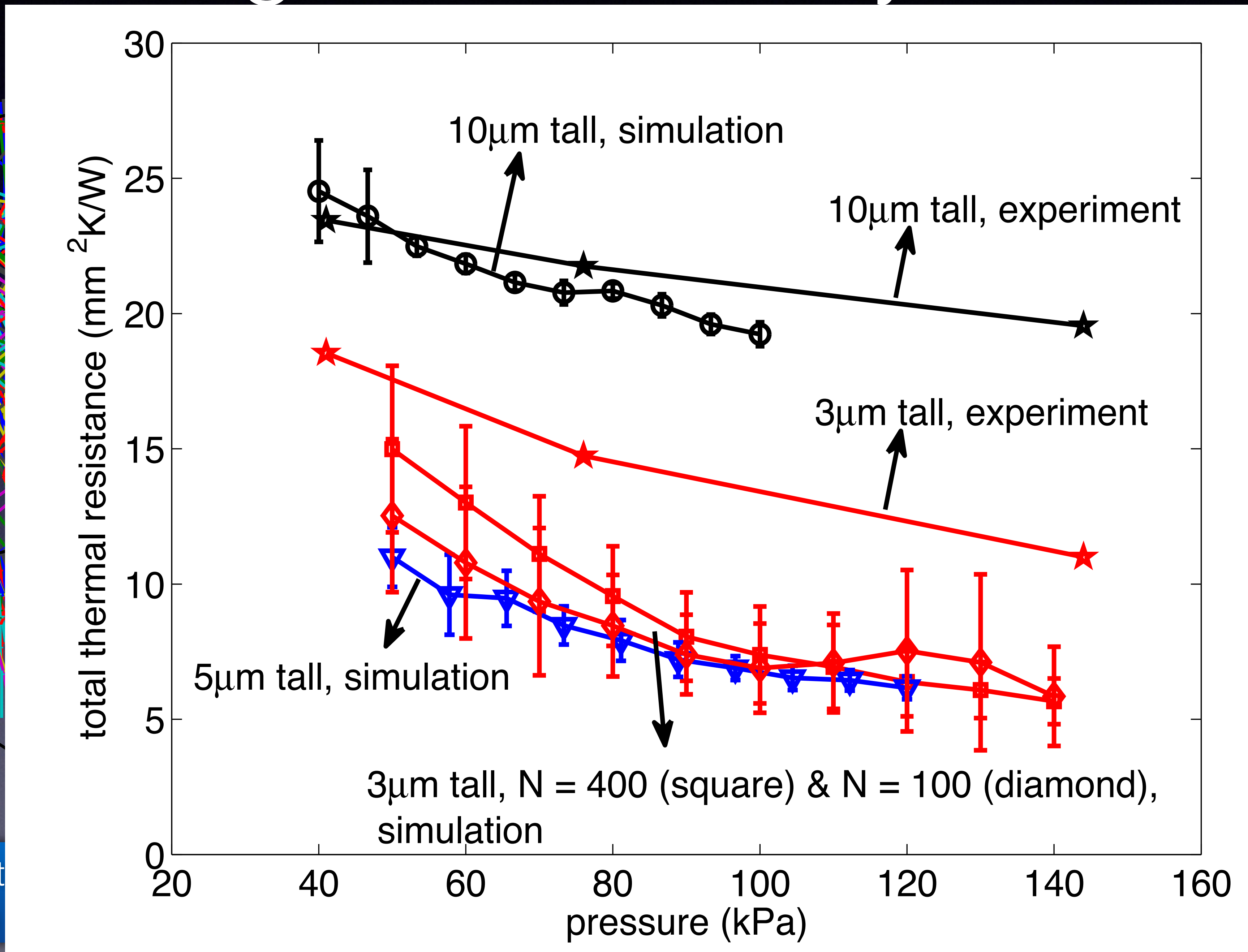
Variable cell approach: Enabling realistic boundary conditions, showing hysteresis and stick-slip





New results enabled by the methods in Smith et al. Physical Review E, **89** 042203 (2014)

Granular mechanics principles applied to coarse-grain CNT array deformation



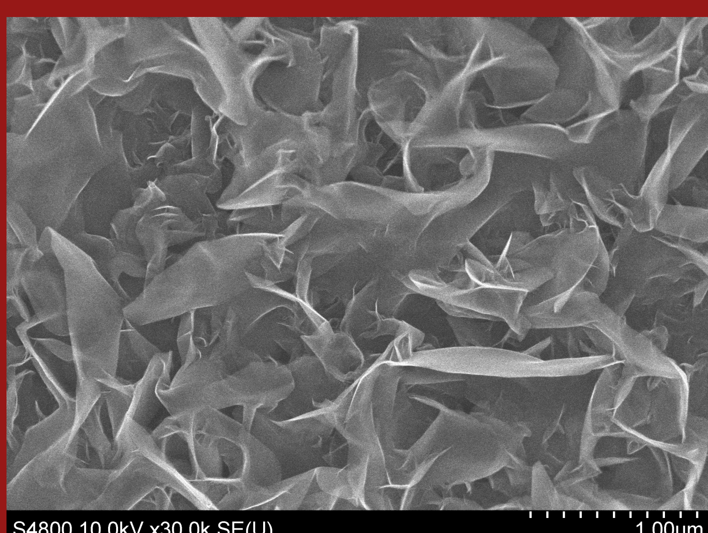
Equilibrium struct
400 CNTs with

CNTs under
sion

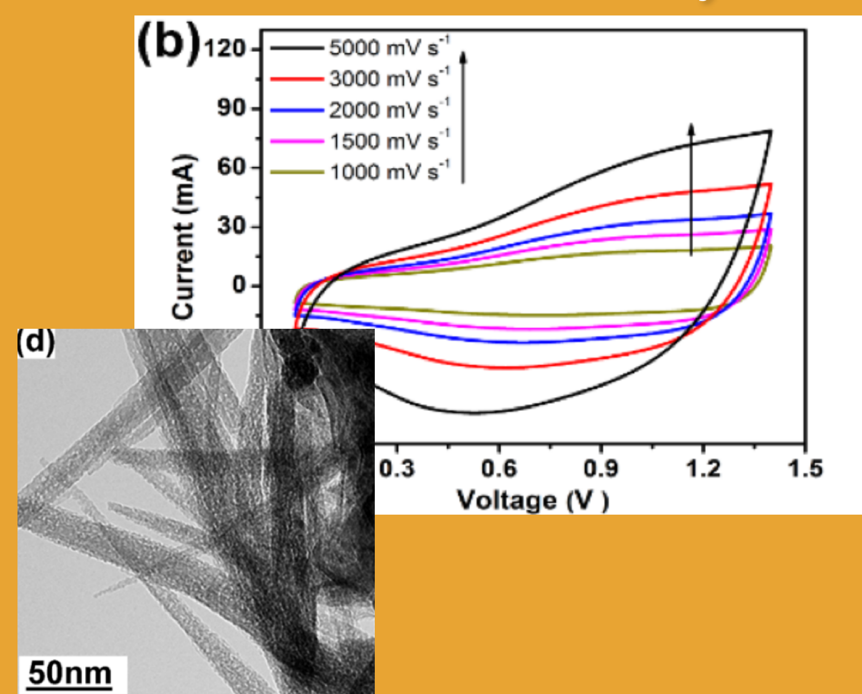
Sadasivam et al. *J. Heat Transfer,* **38** 042402 (2016)

Closing

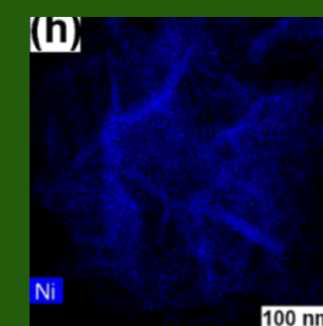
Graphene and other nano materials have the potential to dramatically improve energy technologies

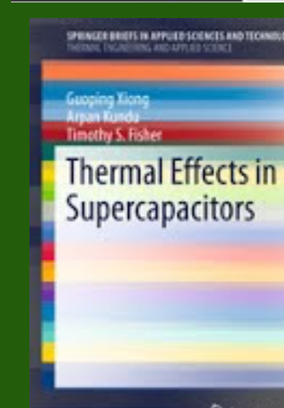


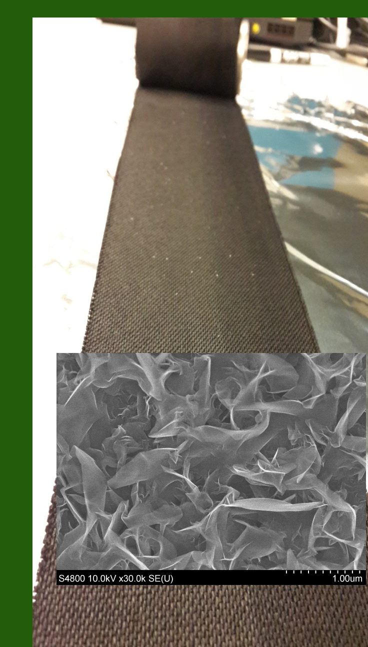
Even traditional materials (e.g., metal oxides) can show surprising attributes when structured differently



Practicing all the way to human scales is crucial to achieve high impact







Some general benefits to practicing scales

- Versatility in teaching
- Broad engagement with professional societies
- The larger the scale, the more collaborators needed and available (did you notice?)
- Valued by industry (especially)
- Clearer pathways to entrepreneurship and/or general technology translation

Thank You