AFOSR FY2011 MURI Topic #11
Nanofabrication of Tunable 3D Nanotube Architectures

AFOSR Grant # FA9550-12-1-0037 (PM: Dr. Joycelyn Harrison)

Vikas Prakash (co-PI)
Department of Mechanical and Aerospace Engineering
Case Western Reserve University

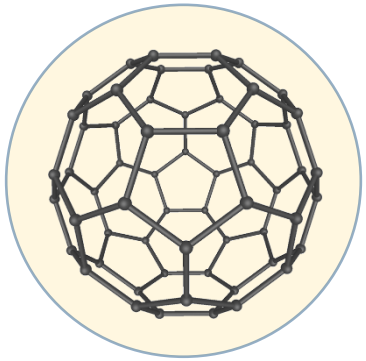
Project start date: Dec 2011

<u>MURI Team (8 faculty members)</u>
Case Western Reserve University (Lead)– L. Dai (PI), C.C. Liu & V. Prakash
Georgia Institute of Technology – Z.L. Wang
Purdue University – T. Fisher & X. Ruan
Kent State University – Q. Li
University of North Texas – Z. Xia

Motivation

Nanostructured Carbon -- What's Next?

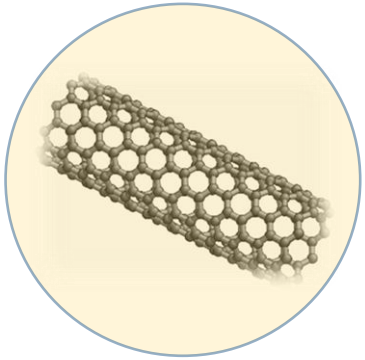
OD Fullerene



1985

1996 Nobel Prize in Chemistry

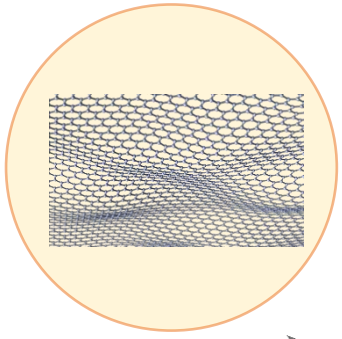
1D Carbon Nanotube



1991

High electrical conductivity; High thermal conductivity

2D Graphene

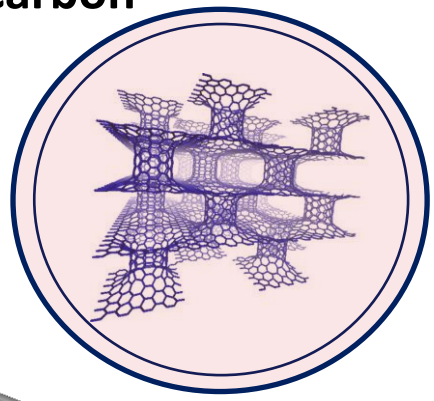


2004

2010 Nobel Prize in Physics

Ultra-high electron mobility; Ultra-high thermal conductivity; Ultra-high Surface Area (2675 m^2/gm)

3D Nanostructured Carbon



3D Tunable Nanoporous Networks

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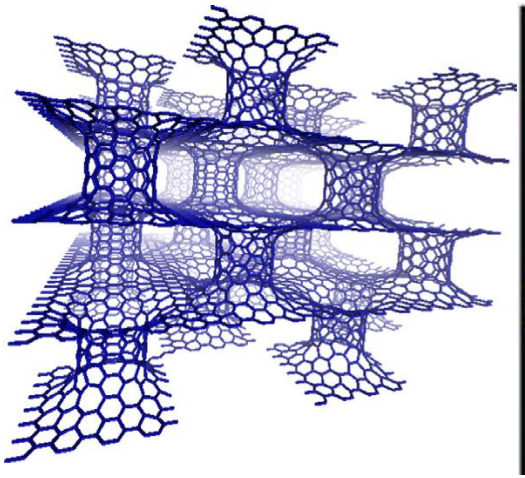
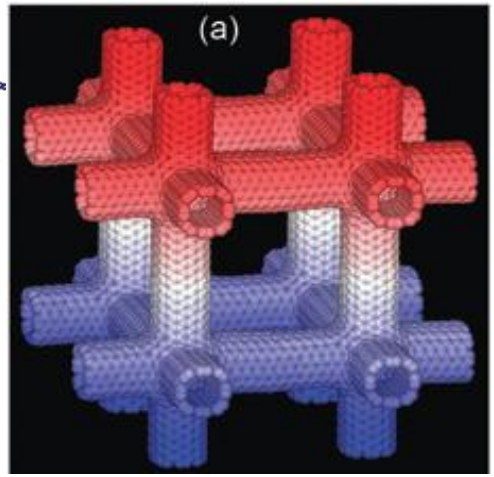
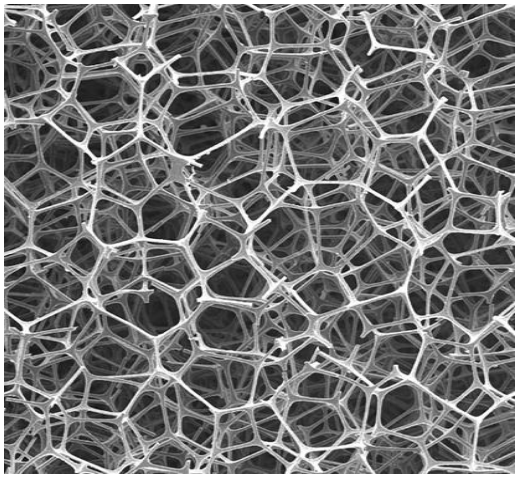
UNT University of North Texas

Scientific Challenges







Overarching Challenges

- Covalent junctions between building blocks leading to 3D networks
- Modeling/Characterization of the junctions and properties
- Scalable growth processes for 3D nanostructured solids
- Structure-property correlations of mechanical and transport properties

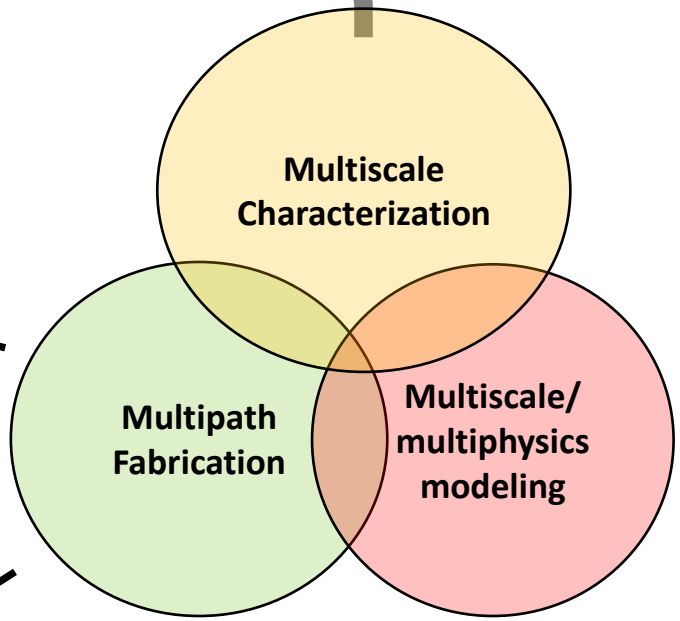
Potential Payoffs (Relevance to DoD)

- Translation of exceptional 1D and 2D properties of tubes and sheets to 3D
- High surface area for energy storage and conversion devices
- Orthogonal transport of phonons for thermal management
- Low density mechanical reinforcement

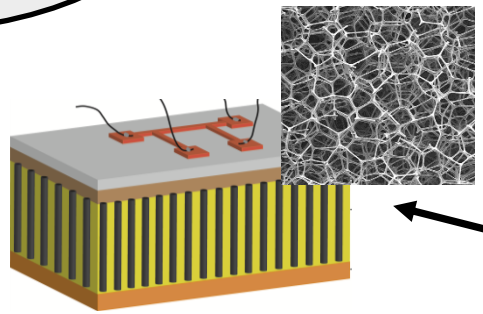
Technical Approach

Applications
- Thermal management
- Energy Systems
- Aerospace Systems

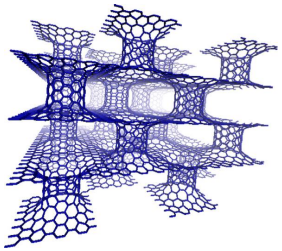
Device Integration

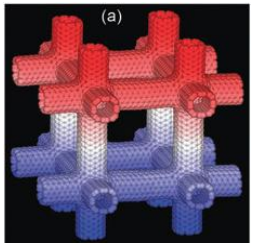


Macroscale
3D CNT-graphene hybrid materials and devices.
Hybridization & functionalization

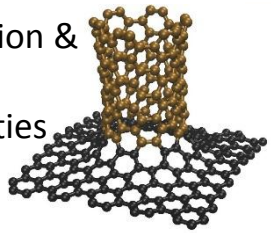


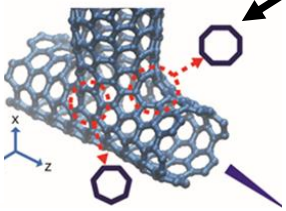
Microscale
CNT-CNT & CNT-graphene networks
- Inter pillar-distance
- Pillar height





Nanoscale
CNT-graphene junction & CNT-CNT junction
- Junction Properties





Major Tasks
- Multi-path synthesis and hybridization
- Multiscale structure-property characterization
- Multiscale multiphysics simulations
- Multifunctional applications

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THE MURI TEAM

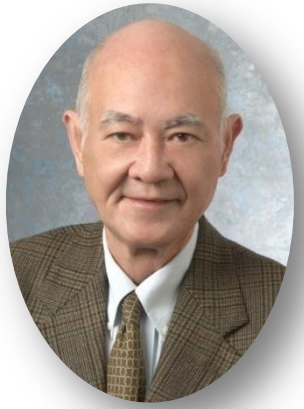
(8 faculty from 5 universities)

Tim Fisher
(Purdue)
"C-nanomaterial synthesis, thermal transport & nanotechnology"

Zhonglin Wang
(GaTech)
"nanoscale structure characterization & novel hybrids"

Zhenhai Xia
(NTU)
"multi-scale and process simulation"

Liming Dai **(PI)**
(CWRU)
"C-nanomaterials synthesis & devices"



Chung Chiun Liu
(CWRU)
"electrochemistry, sensors & energy devices"

Quan Li
(KSU)
"liquid crystal materials, chemistry & self-assembly"

Vikas Prakash
(CWRU)
"multi-scale structure-property characterization & thermal management"

Xiulin Ruan
(Purdue)
"thermal modeling of *e-p* & *p-p* coupling"

Graduate Students and Budget

Liming Dai:
Graduate students: Ryan Pierce, Xueliu Fan, Min Wang (L), Ishar Rosado Irizarry (L)
Post Docs: Shihao Hu (L), Yuhua Xue (L), Ming Xu
Vikas Prakash:
Graduate students: Jungkyu Park, Hao Jiang, Pankaj Kaul (L), Eric Mayhew (L)
C.C. Liu:
Graduate students: Chih-Chien Kung, Po-Yuan Lin (L), Xiong Yu (L)
Tim Fisher:
Graduate Students: Guoping Xiong, Arun S. Kousalya (L), Anurag Kumar (L)
Post docs: Rajib Paul
Xiulin Ruan:
Graduate students: Jingjing Li, Yan Wang
Zhong Lin Wang:
Graduate students: Ken Pradel (L)
Research Scientists: Yong Ding, Fang Zhang (L)
Quan Li:
Graduate students: Mengfei Wang (L)
Post docs: Hari Krishna Bisoyi, Hu He
Zhenhia Xia:
Graduate students: Jianbing Niu
Post docs: Mingtao Li

Graduate students: 9 + 10 (leveraged)
Post Docs/Research scientists: 6+ 3 (leveraged)

OVERALL BUDGET (planned)

Base Period					Option Period				
Period 1 6/1/11 to 9/30/11	Period 2 10/1/11 to 9/30/12	Period 3 10/1/12 to 9/30/13	Period 4 10/1/13 to 5/31/14	Base Period Cumulative	Period 5 6/1/14 to 9/30/14	Period 6 10/1/14 to 9/30/15	Period 7 10/15/15 to 5/31/16	Option Period Cumulative	All Periods Cumulative
892,616	1,370,871	1,399,999	870,984	4,534,470	560,635	1,462,715	905,349	2,928,699	7,463,170

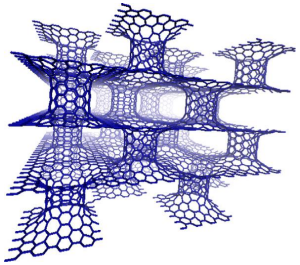
~ $1.5m/yr

Multi-path Synthesis of 3D Nanostructures

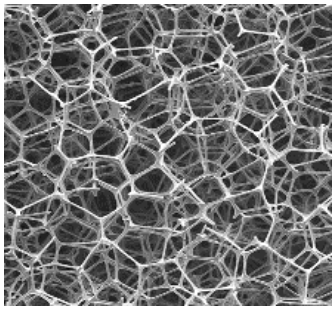
Accomplishments

Developed three different class of 3D Nanostructures

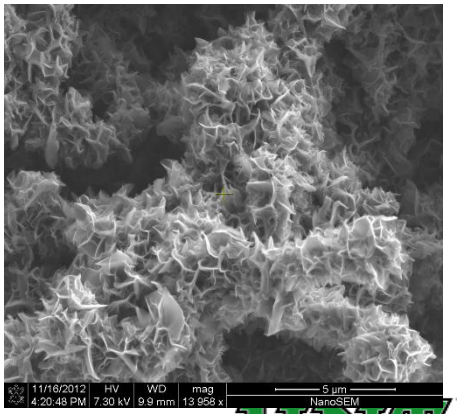
- 3D pillared graphene-carbon nanotube networks
  - Intercalation growth of CNTs into thermally-expanded graphite
  - Template-assisted sequential growth
  - Layer-by-layer transfer



- 3D graphene foams
  - Ni Foam template assisted growth
  - Freeze-drying process

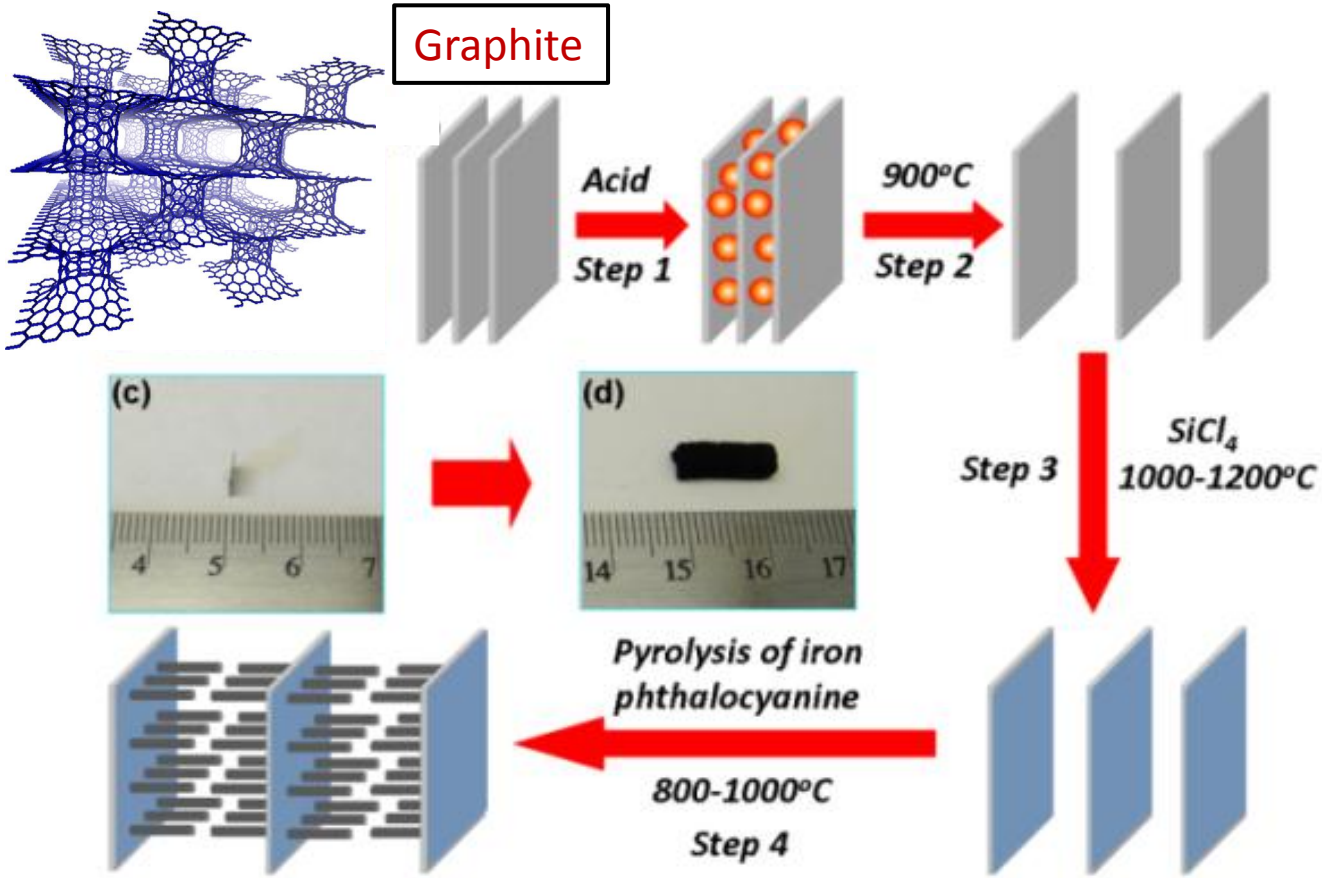


- 3D Graphene-petal based nanostructures



3D Nanostructure Fabrication

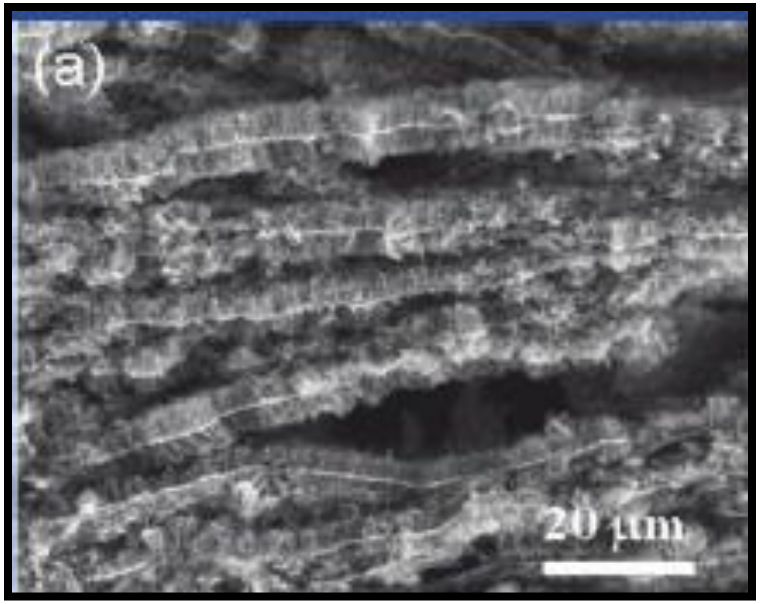
3D CNT-graphene Pillared Structures

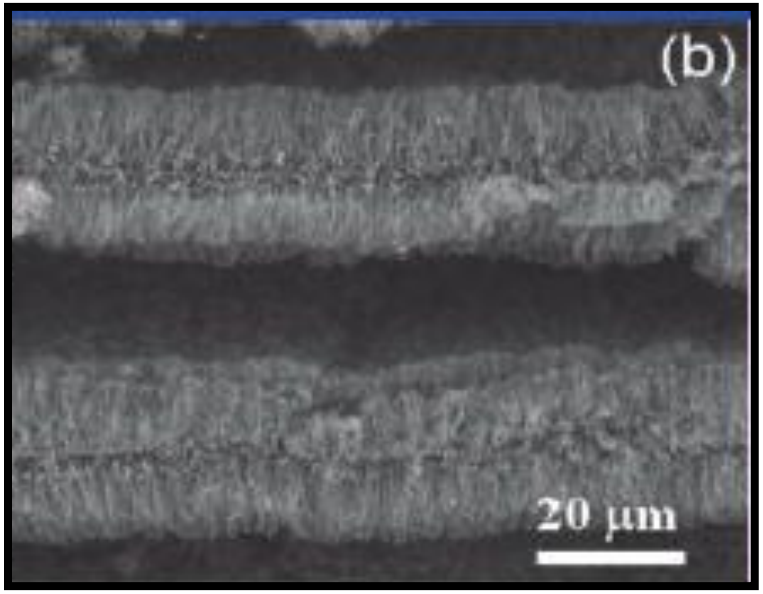


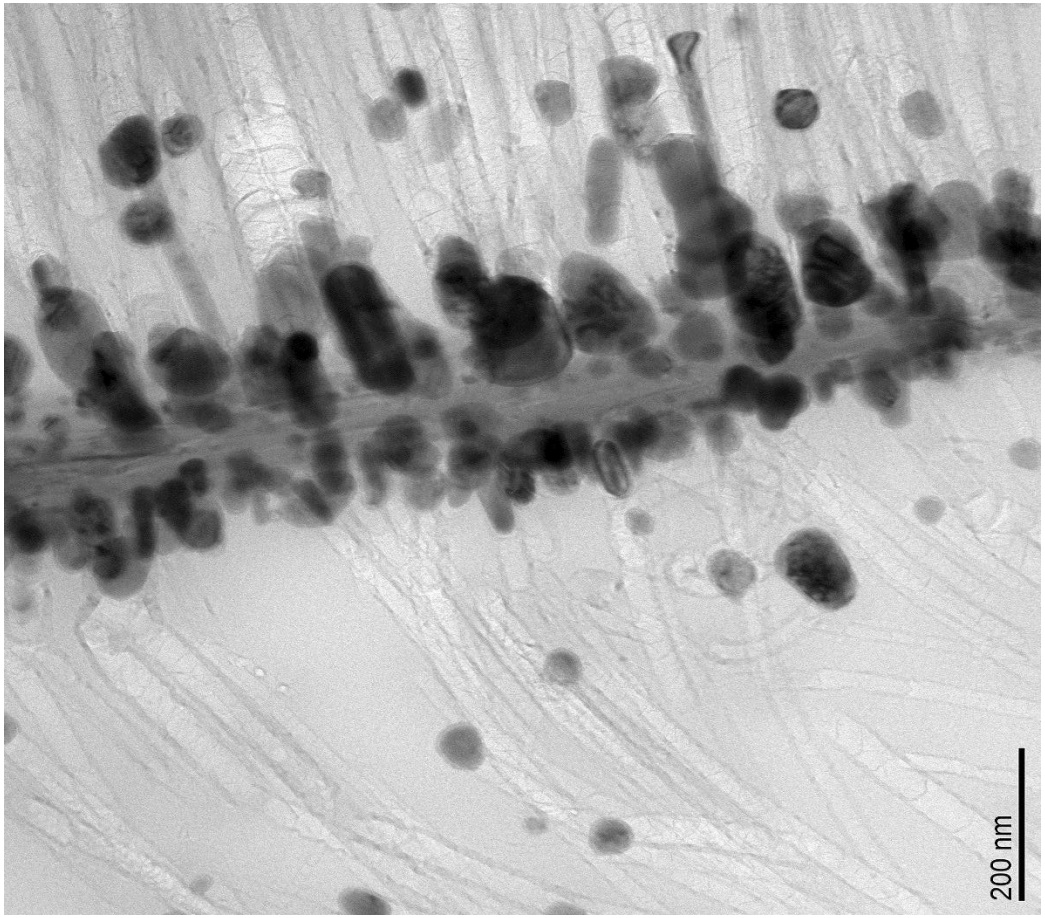
Thermally expand graphite

Use CVD for Intercalated growth of CNTs in expanded graphite

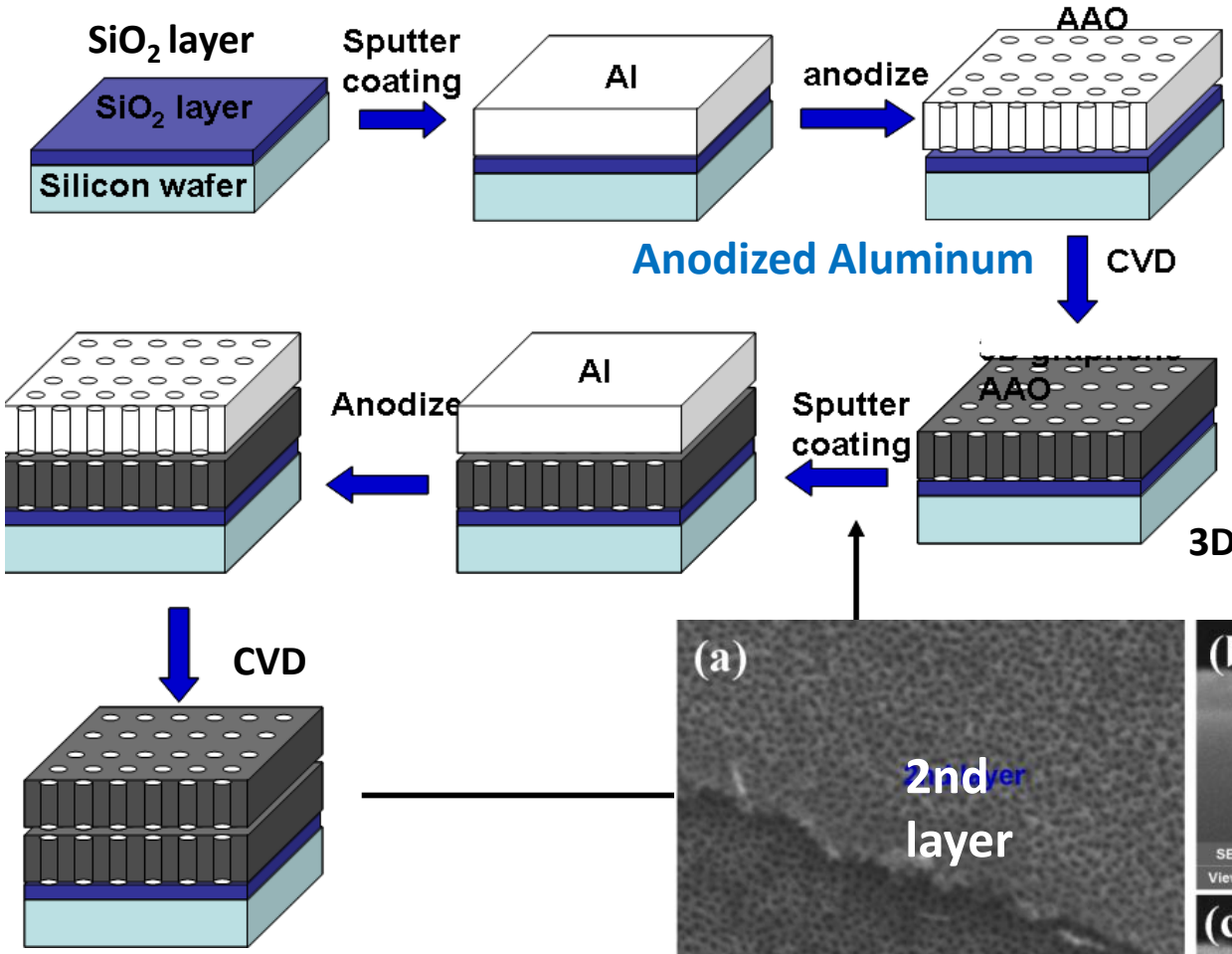
Intercalated Growth of 3D CNT-graphene



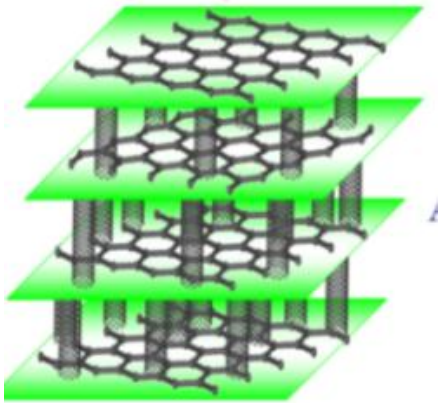




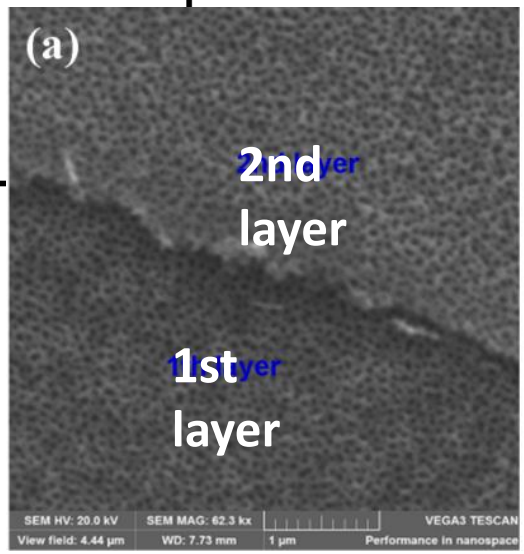
Template-assisted Sequential Growth

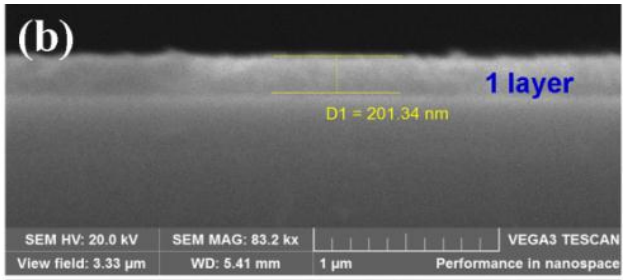


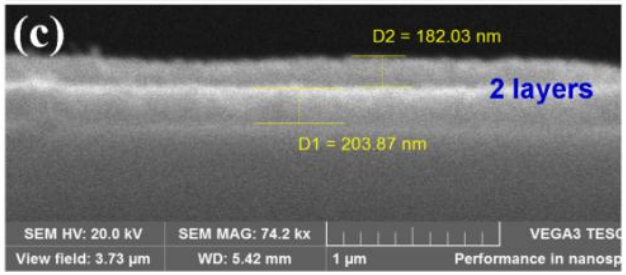
Multilayer 3D CNT graphene structures



3D Graphene

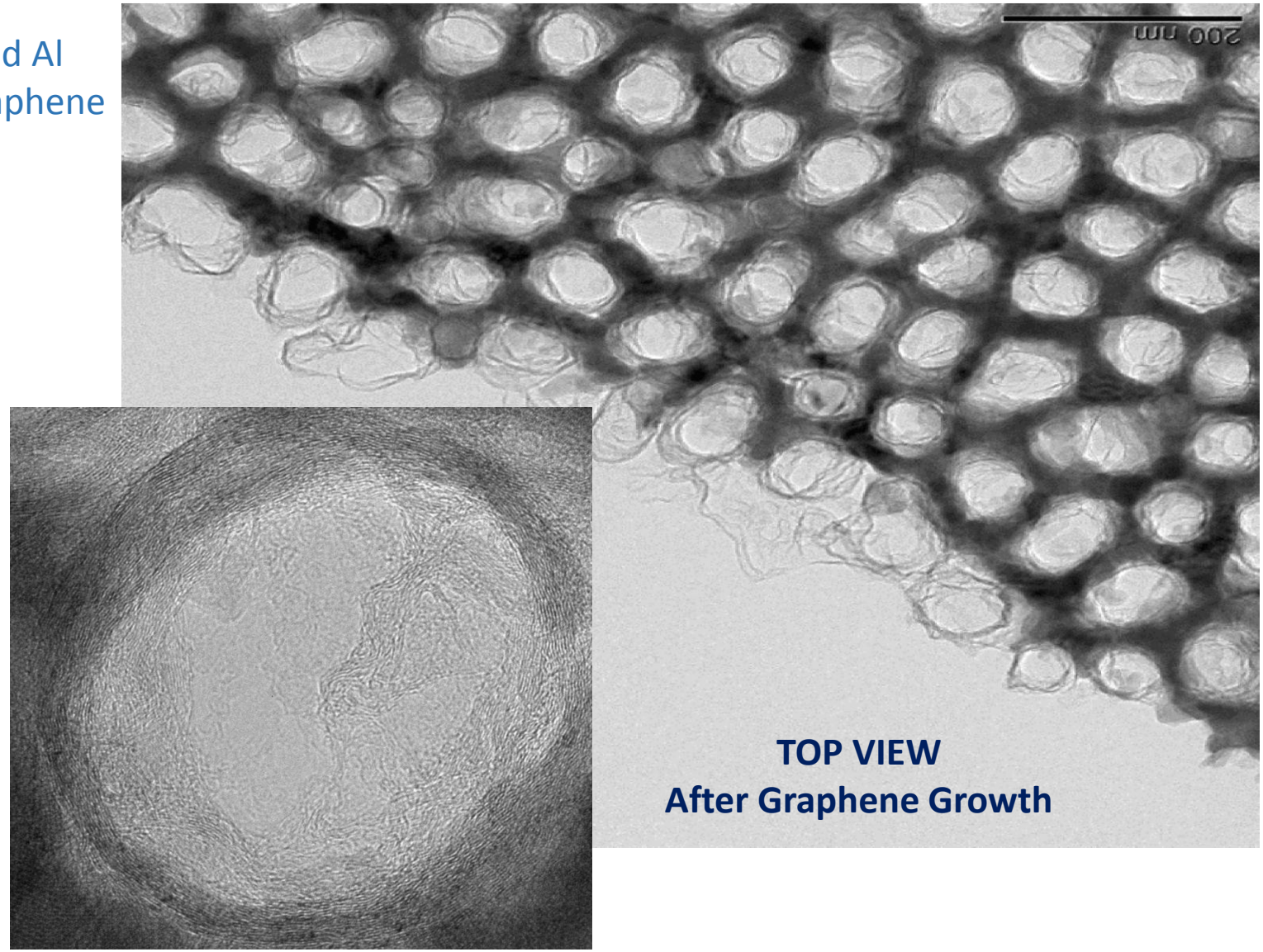




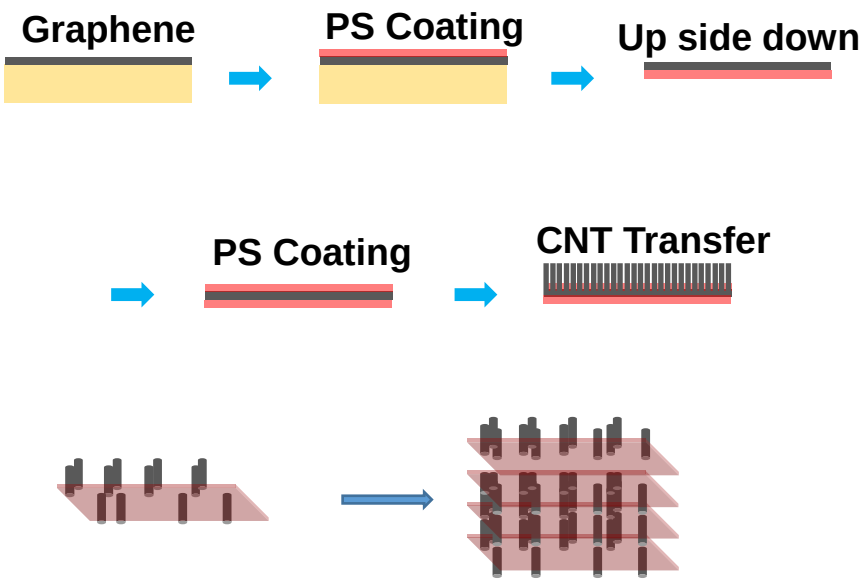


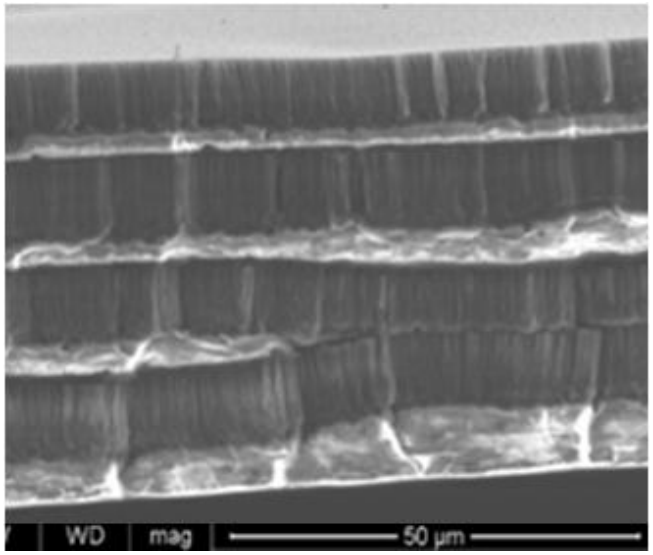
EELS Mapping in TEM mode

Anodized Al with graphene growth



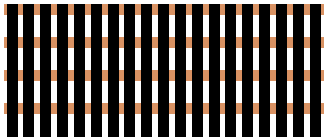
3D structures via Layer-by-Layer Transfer



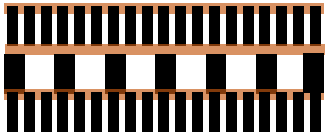


Tunable 3D Pillars

3D Pillars with homogenous CNTs



3D Pillars with Micro-patterned CNTs



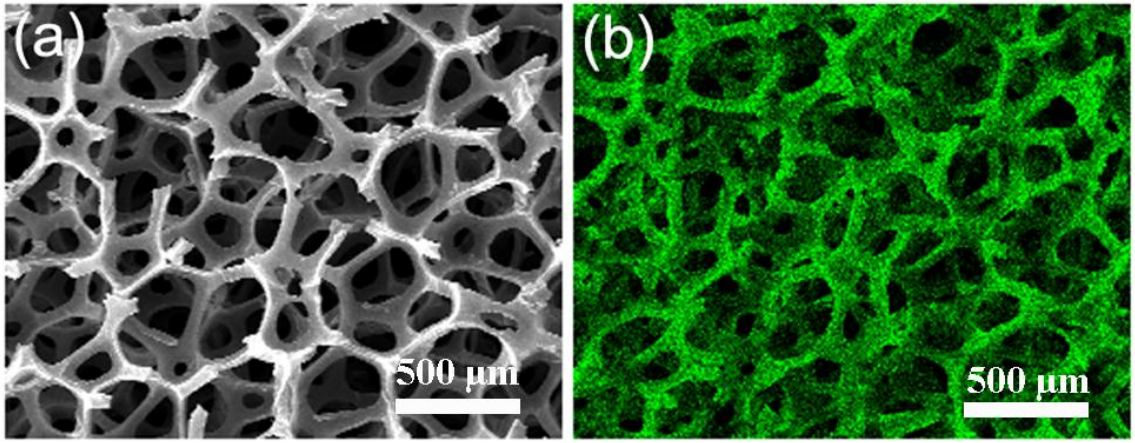
3D Pillars with titled CNTs

Layer by Layer Assembly of 3D CNT-graphene structure

Fabrication of 3D Graphene Foams

Template Synthesis of 3D Graphene Foams

Nickel Foam as template

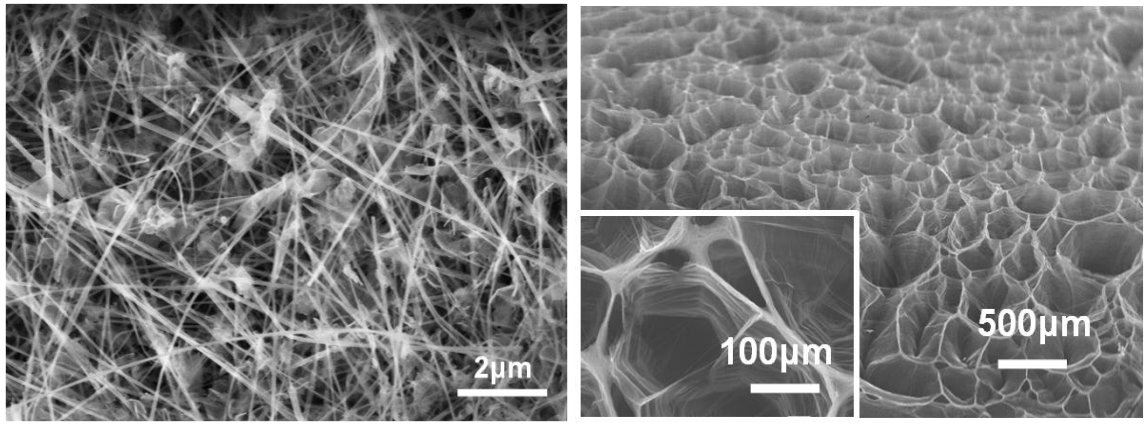


Dissolve Ni Template

Free standing graphene foam

Freeze-drying synthesis of 3D graphene Foams

Graphene Oxide
+
Thermal annealing in H_2/Ar
(Expose to NH_3 for N-doped foams)

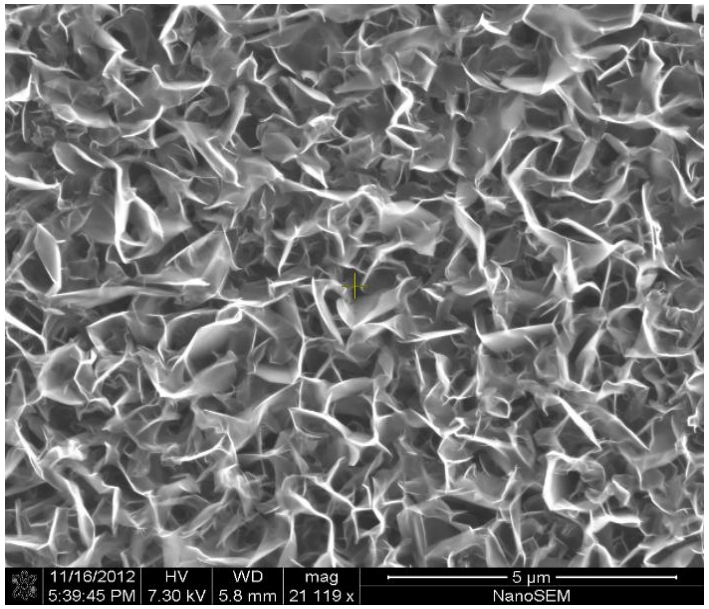


Unusually high thermal stability & elasticity

Graphene-petal-based 3D Structures

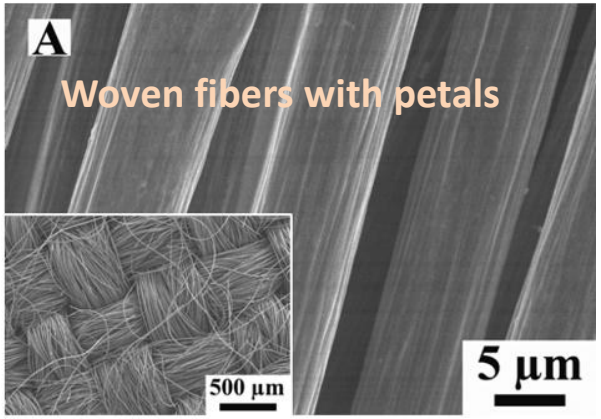
Basic structure

Graphene petals



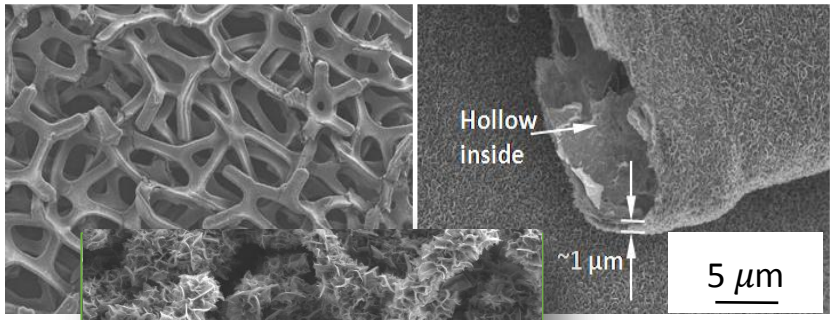
Microwave Plasma CVD

3rd Dimension

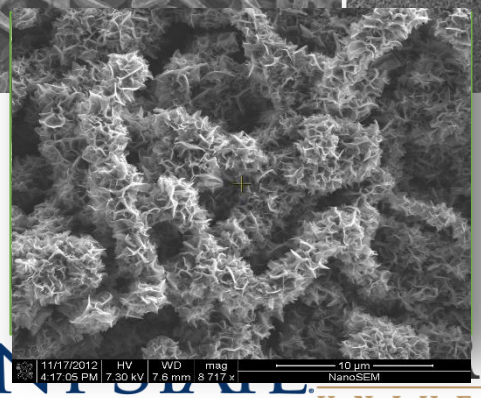


Petal-decorated Carbon cloth

Petal-decorated graphene foam



Petal-decorated CNT arrays



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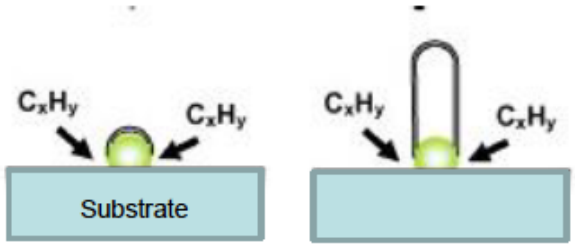
Process Modeling and Simulation

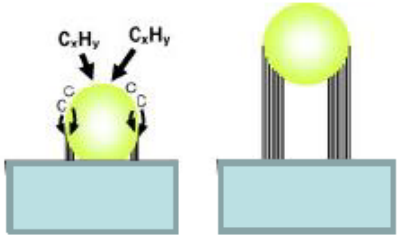
Density Functional Tight-Binding (DFTB)

Study CNT– graphene Junction Growth (Catalyst 1nm Fe particles)



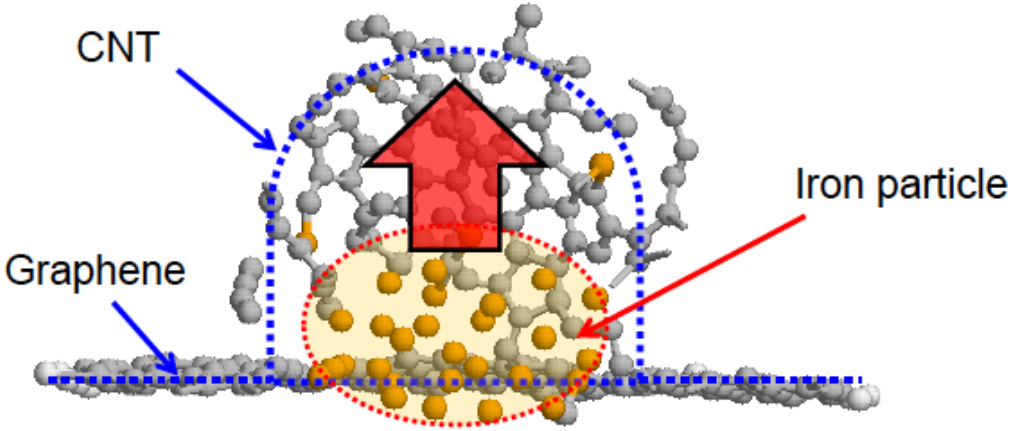
Base growth

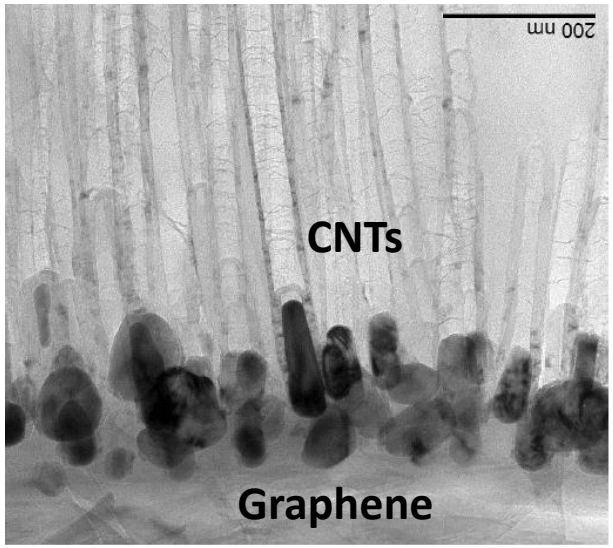
?



top growth

Gohier et al, Carbon 46, 2008, 1331–1338

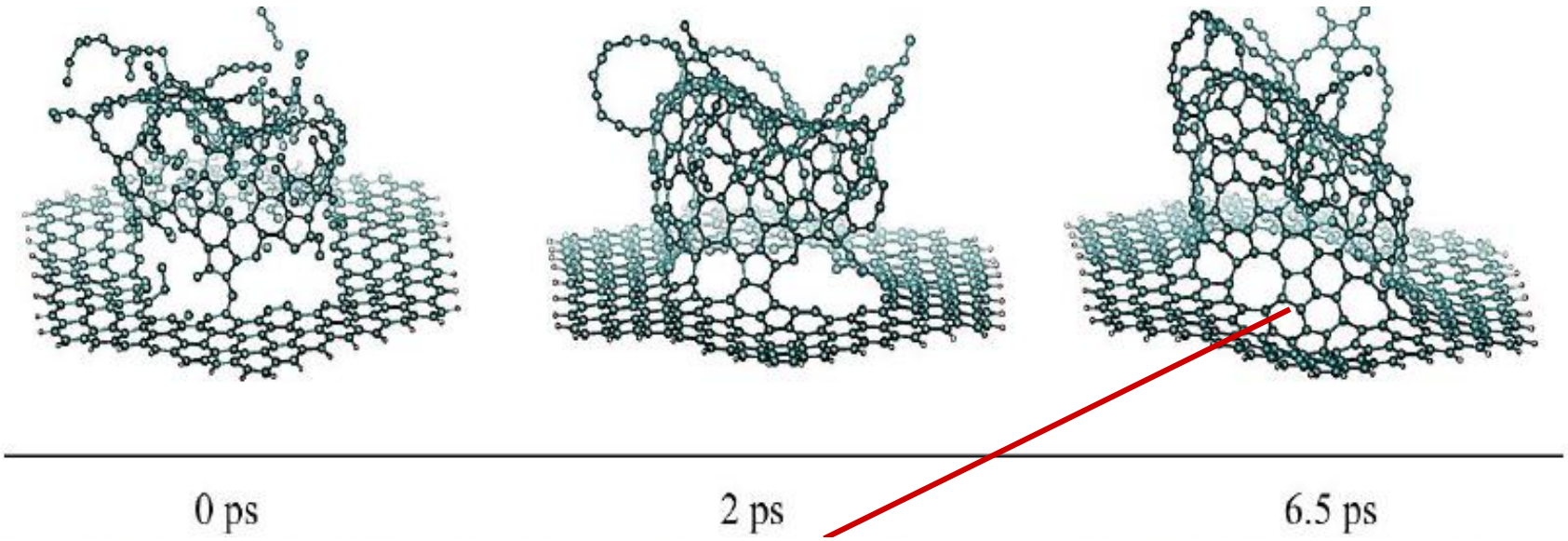




Base Growth Mechanism

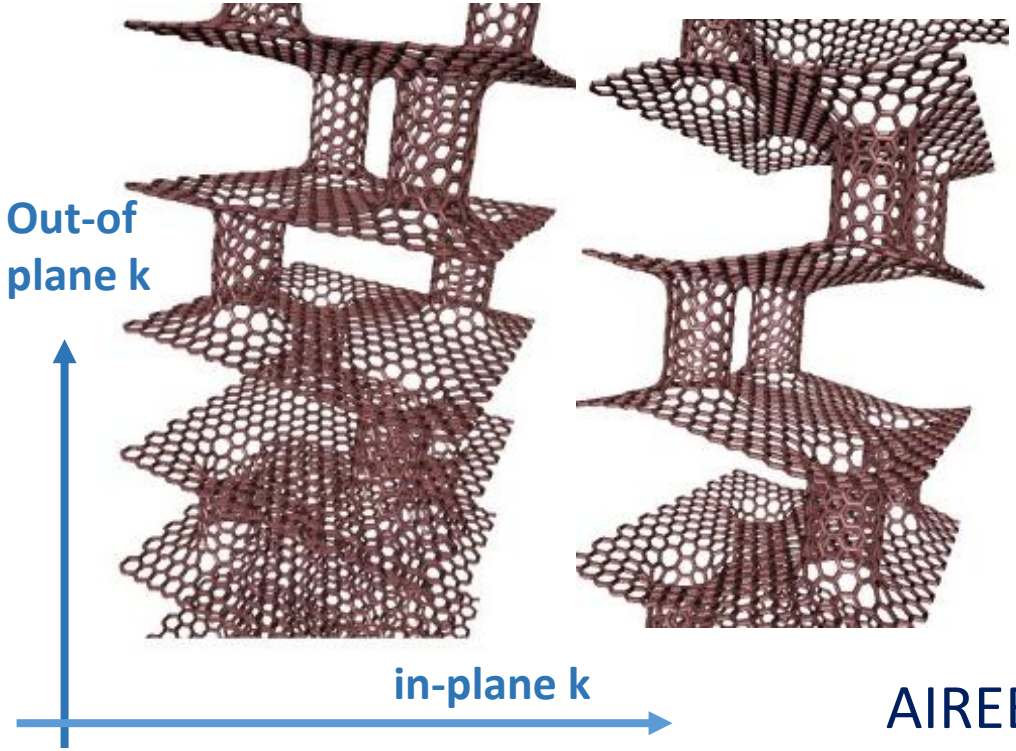
C-C Bonding at CNT-graphene Junction

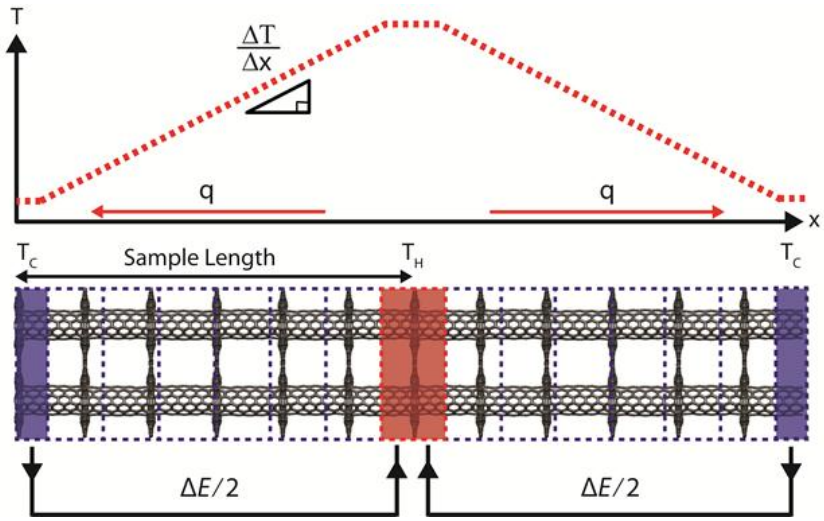
Density Functional Tight-Binding (DFTB) Calculations

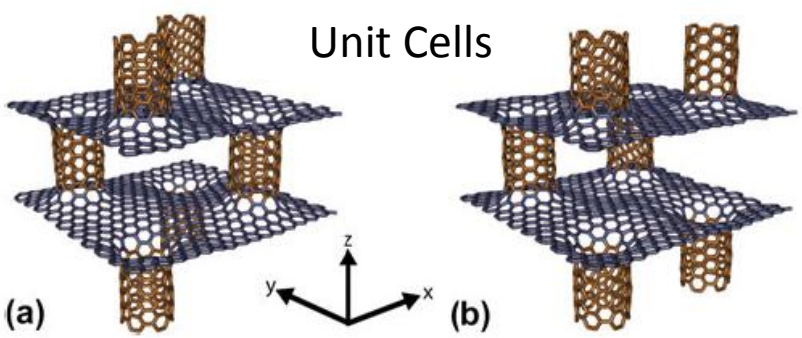


Catalyst removal and high temperature anneal
--- pure C-C bonds form at the Junction

Thermal Transport Modeling in 3D Superstructures (Reverse NEMD)





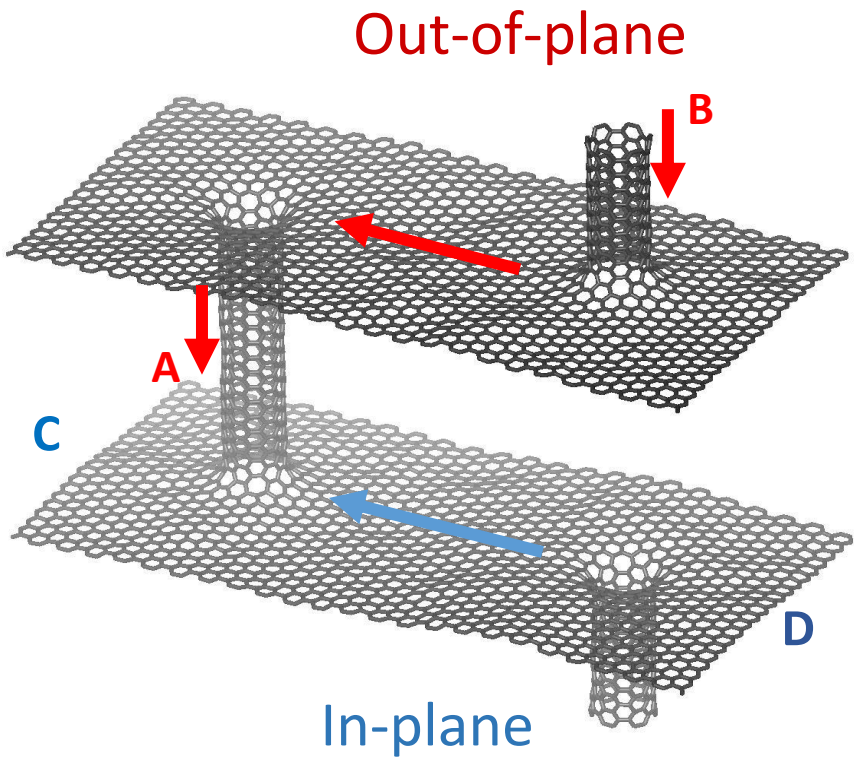


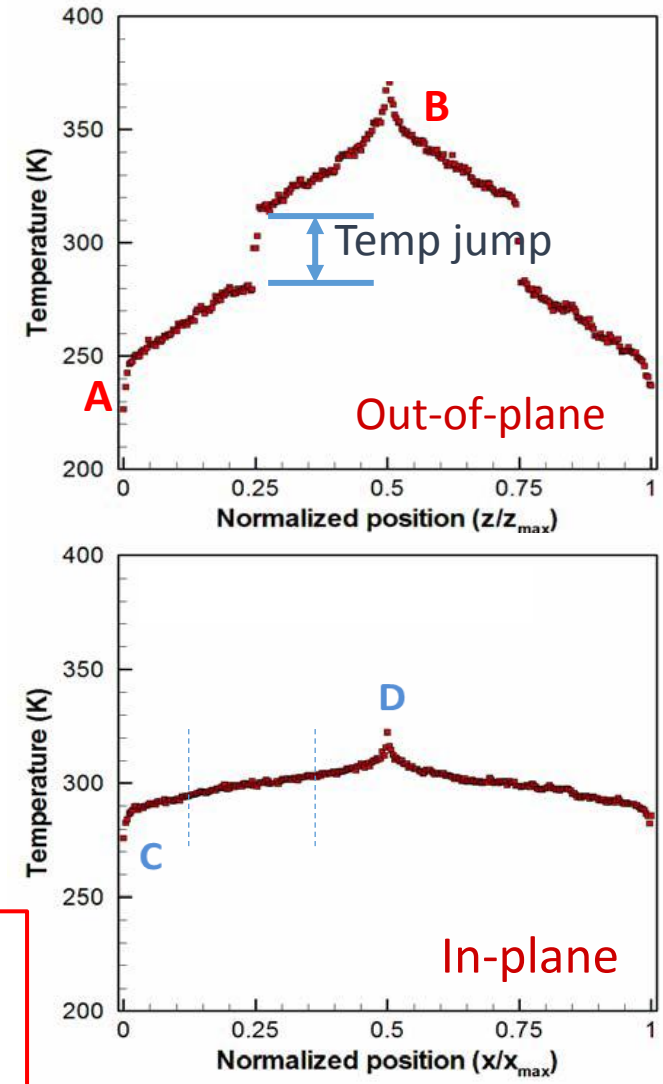
AIREBO potential

$$E^{AIREBO} = \frac{1}{2}\sum_{i}\sum_{j\neq i}\left[E_{ij}^{REBO} + E_{ij}^{LJ} + \sum_{k\neq i,j}\sum_{l\neq i,j,k} E_{kijl}^{tors}\right]$$

KENT STATE UNIVERSITY PURDUE UNIVERSITY UNT UNIVERSITY OF NORTH TEXAS

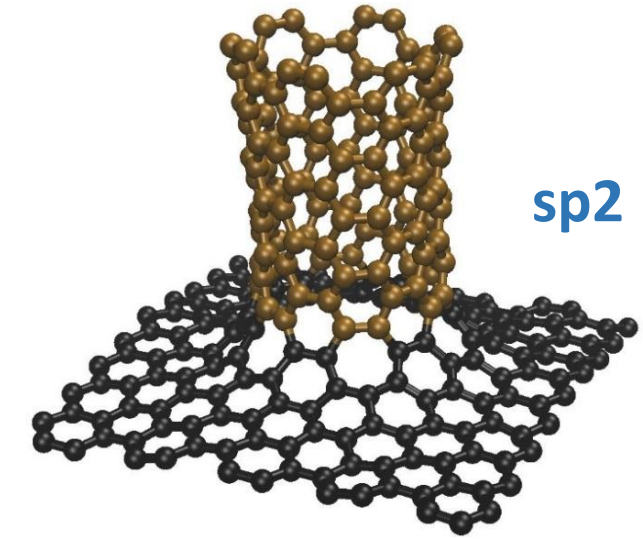
Thermal interfacial Resistance at CNT-graphene Junctions

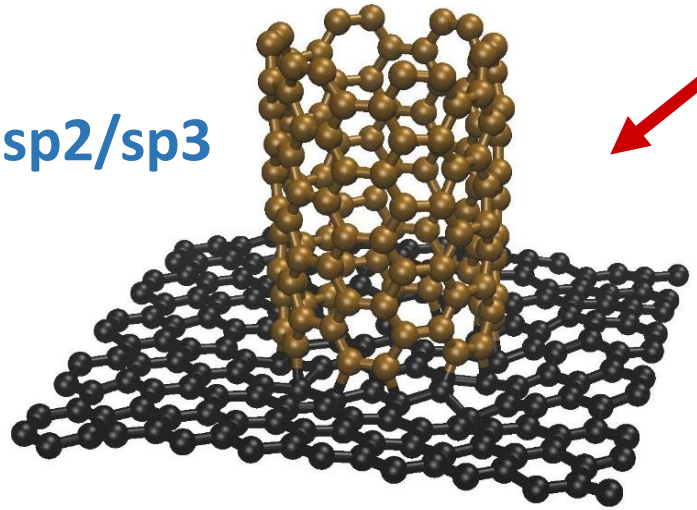


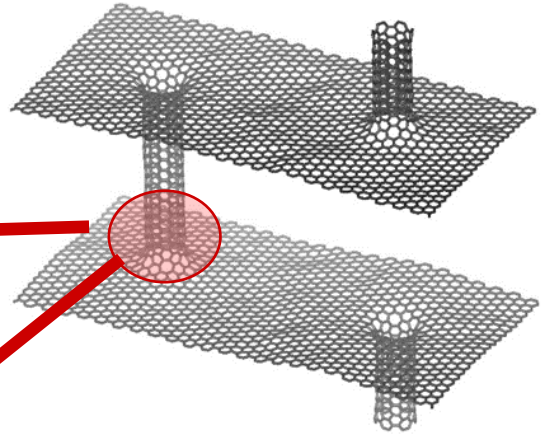


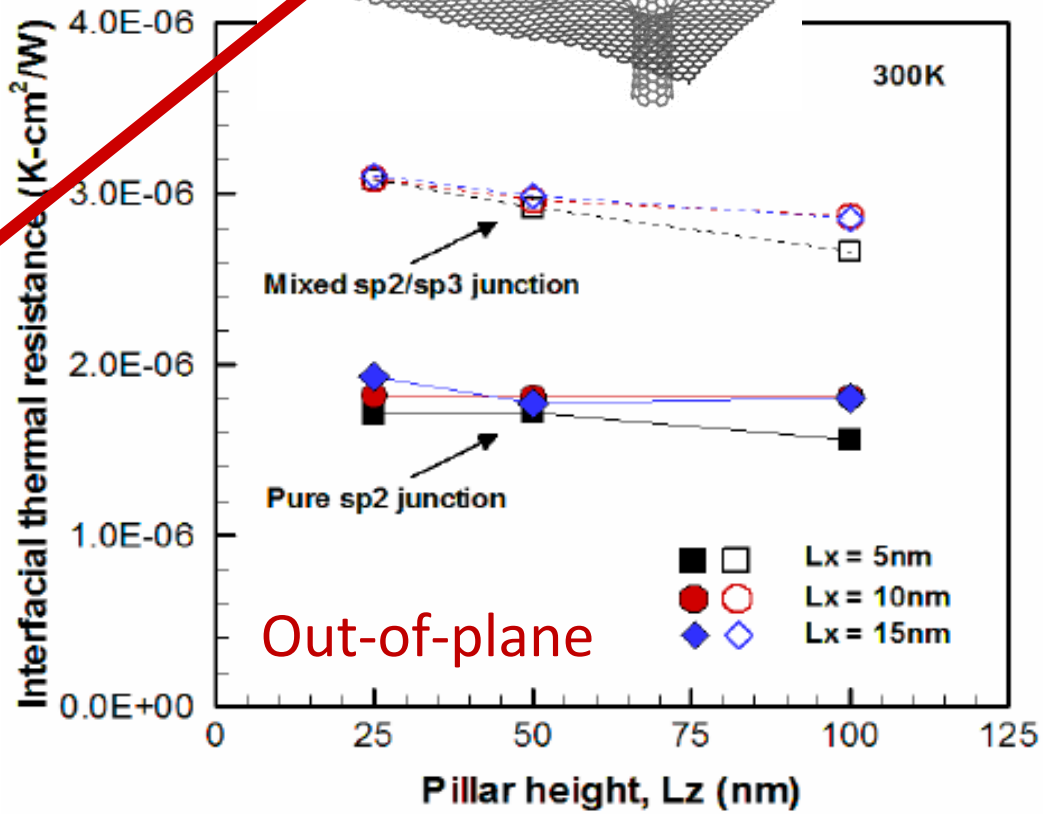
For out-of-plane thermal transport, CNT-graphene junctions show thermal resistance

Effect of Junction Bonding: Pure sp^2 vs. mixed sp^2/sp^3 bonding



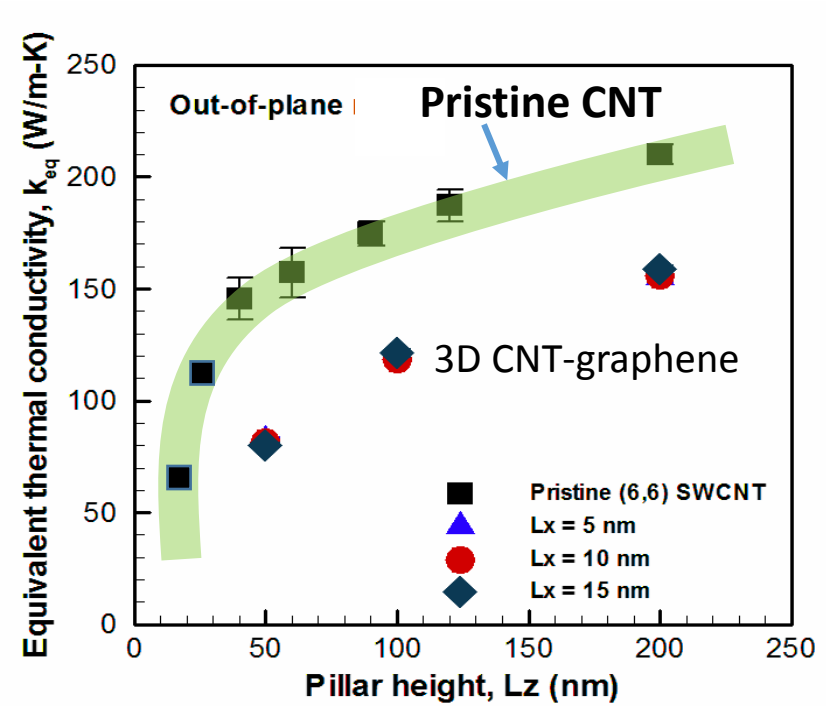


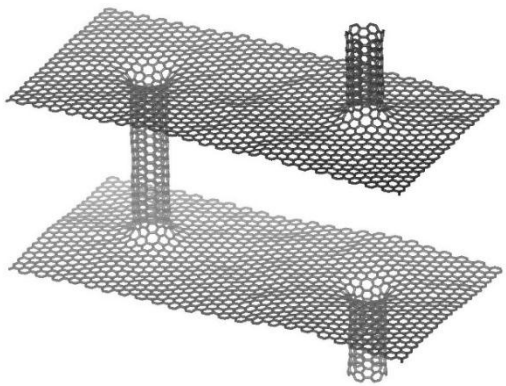


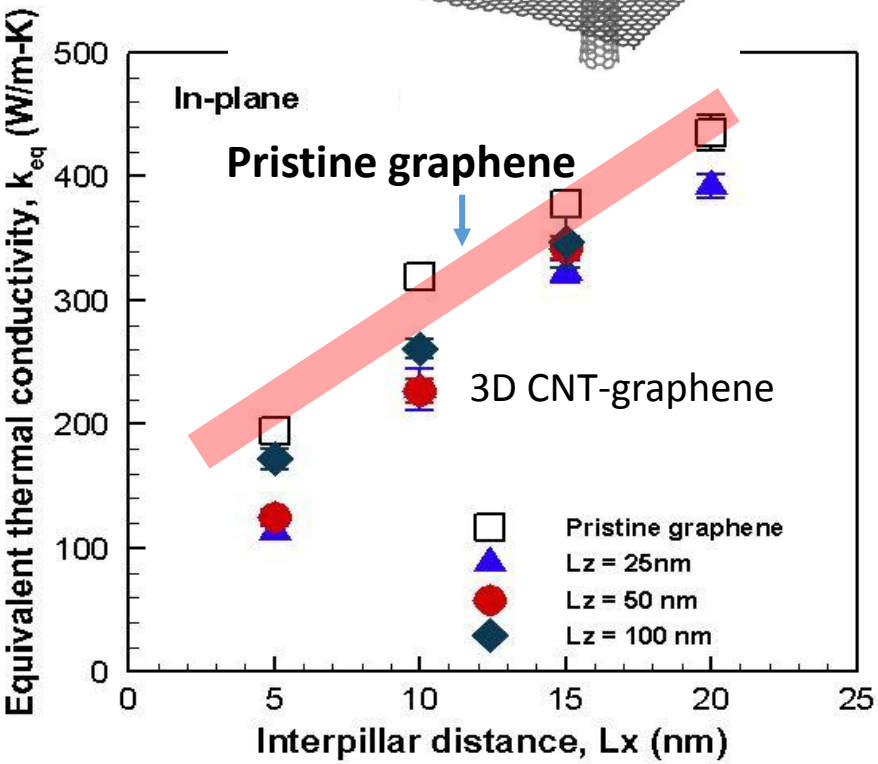


Size of the Unit Cell

Effect on Thermal Transport



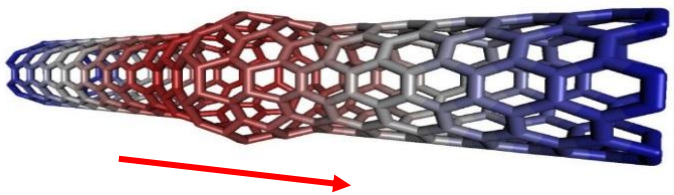




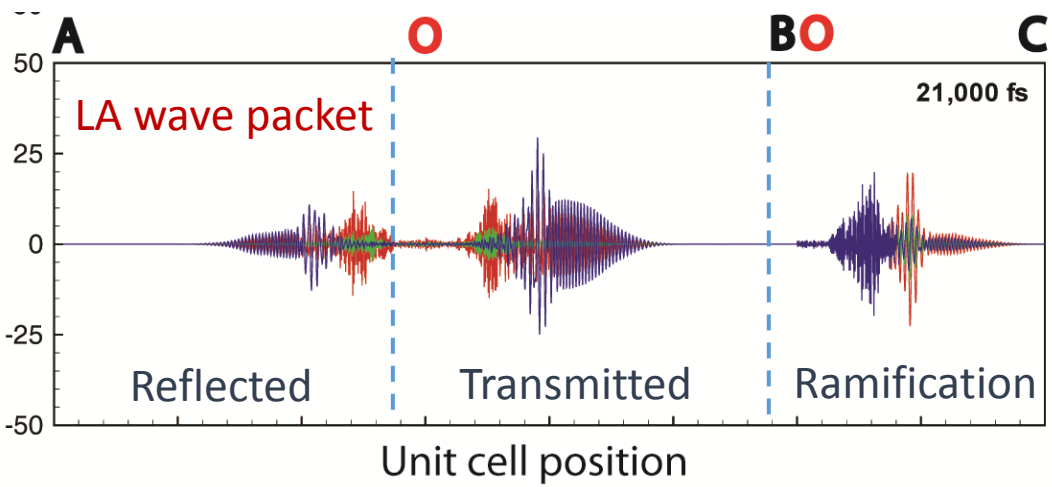
Ballistic transport lengths
(6,6) SWCNT ~ 25nm
SL Graphene ~ 65nm

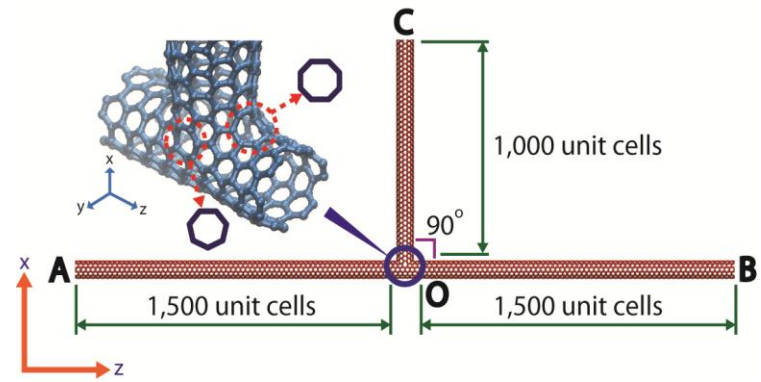
3D CNT-CNT Networks

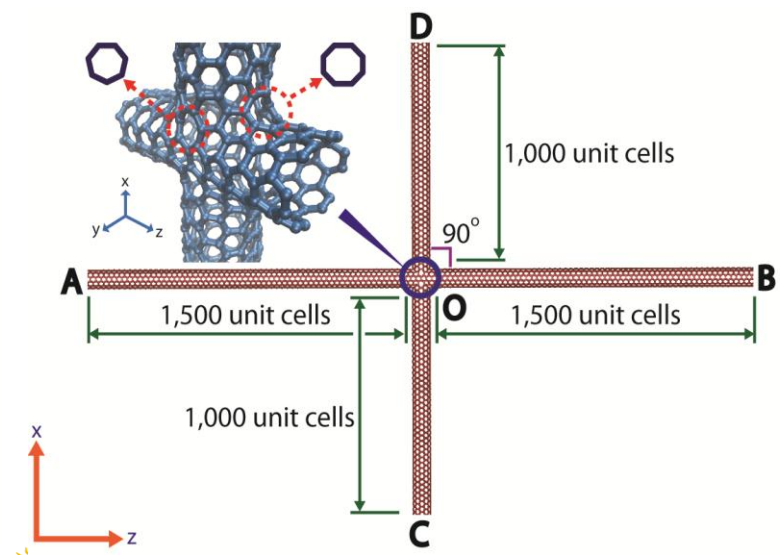
Phonon wave packet analysis-- *Transmission Function as a function of phonon frequency* – Develop models for thermal transport in 3D CNT-CNT Networks



$$u_{ni\alpha}^{\lambda} = \frac{A}{\sqrt{M}} \sum_{q} \exp\left[-\frac{(q-q_0)^2}{2\sigma^2}\right] \varepsilon_{i\alpha}^{\lambda}(q) \exp\left[iq(z_n - z_0)\right]$$







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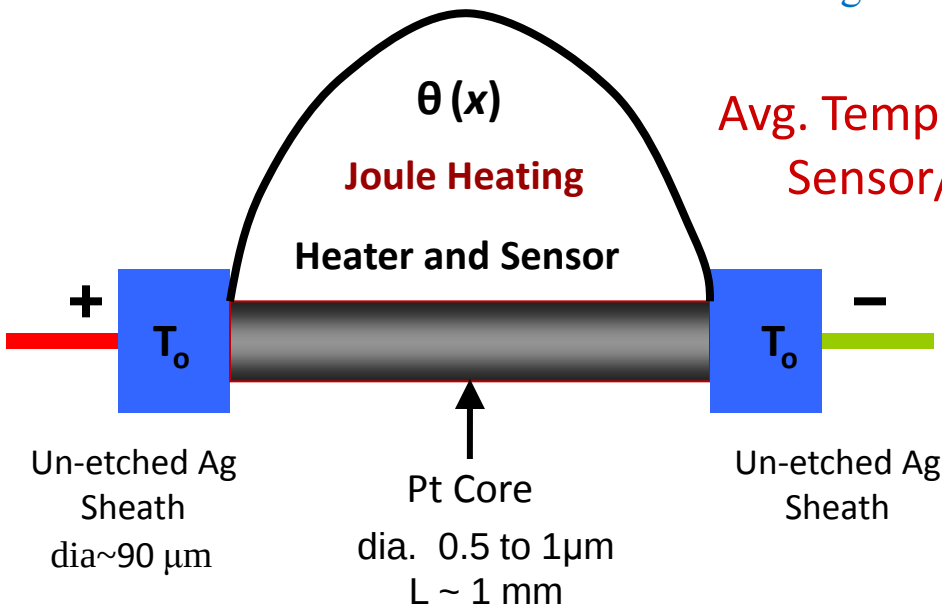
Experimental Characterization: Thermal Conductivity of Individual CNTs

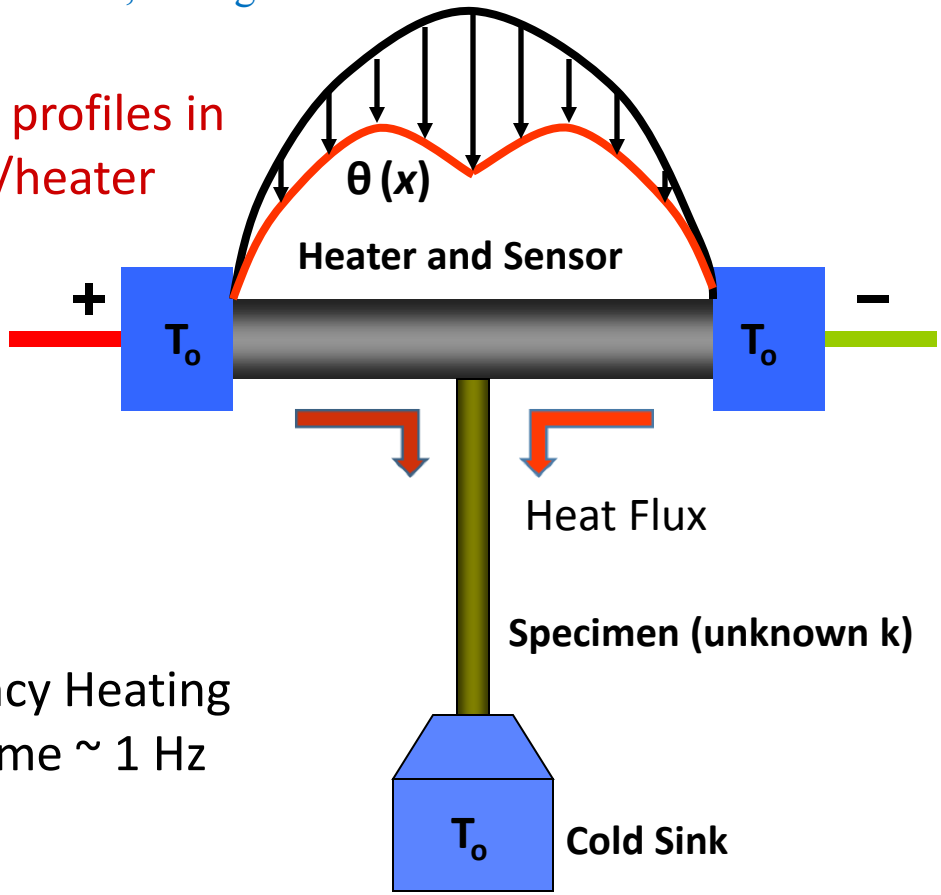
Wollaston wire (Ag/Pt)-- heater and sensing probe

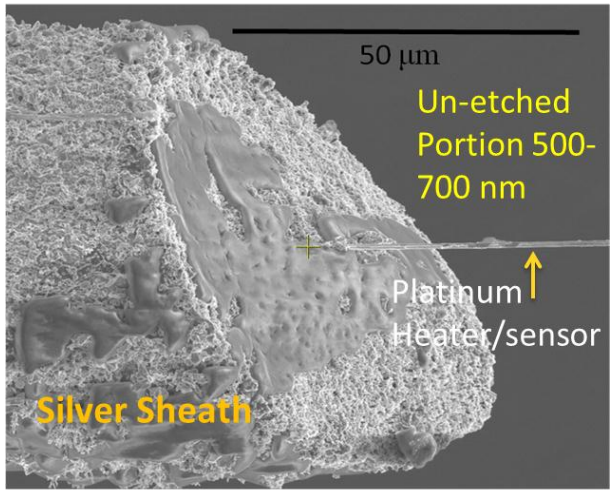
Hot Wire Probe Method

Sinusoidal current at ω leads to Joule heating in Pt. at 2ω; Voltage measurements at 3ω



Avg. Temp profiles in Sensor/heater

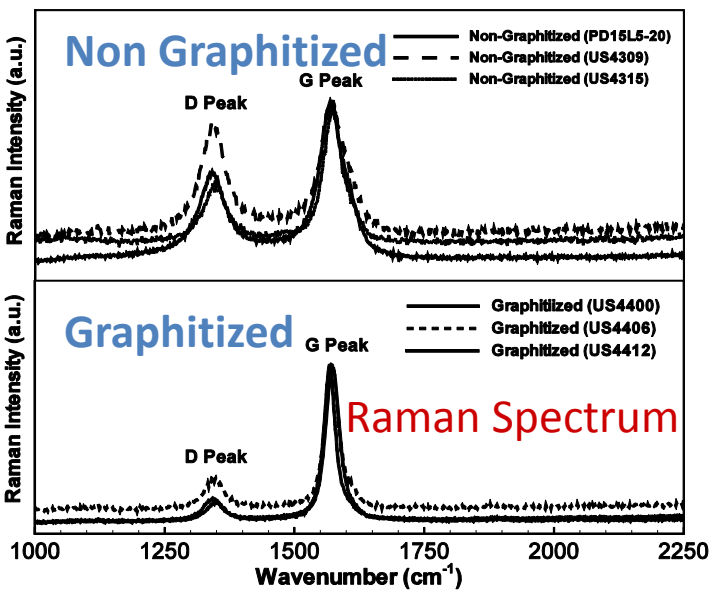




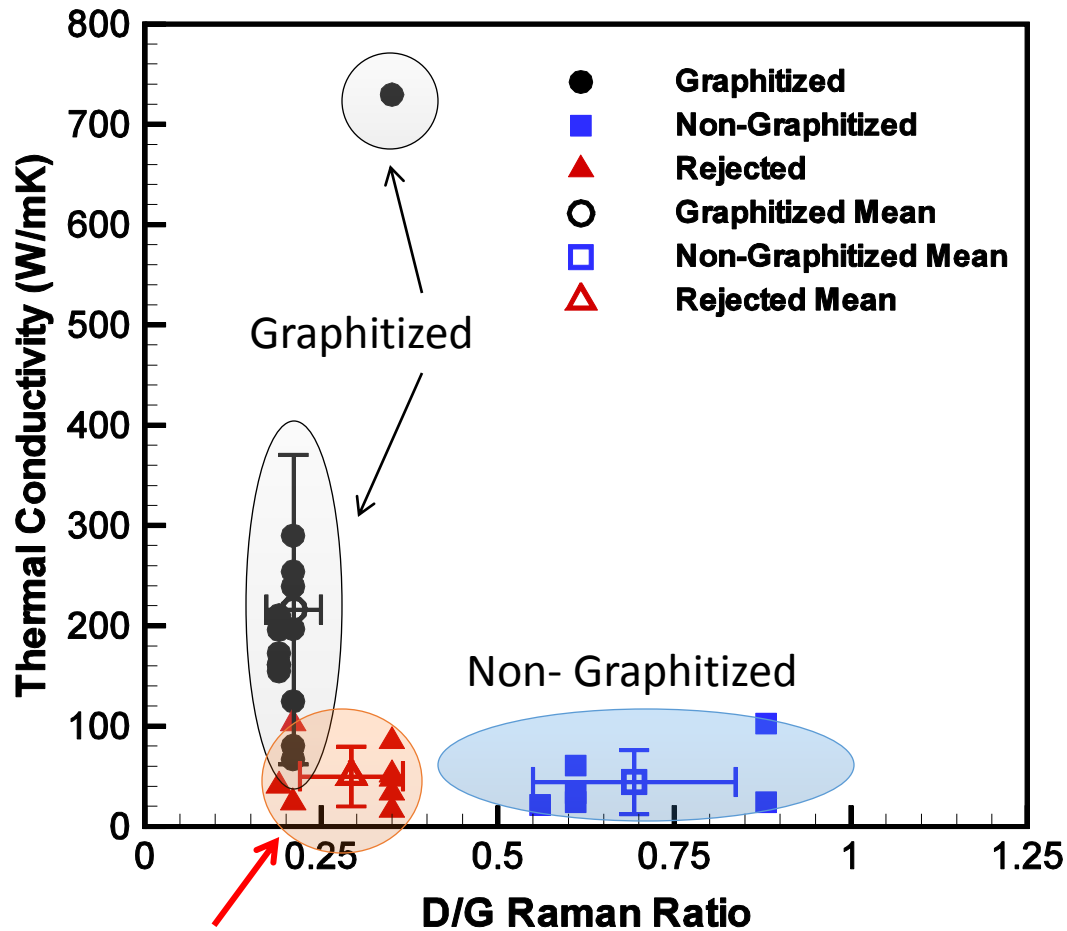
Low Frequency Heating Current Regime ~ 1 Hz

Change in average temperature -- Leads to a change in electrical resistance – leads to change in voltage at 3ω

3Ω Measurements on Individual MWCNTs



Smaller D/G ratio
Less number of defects

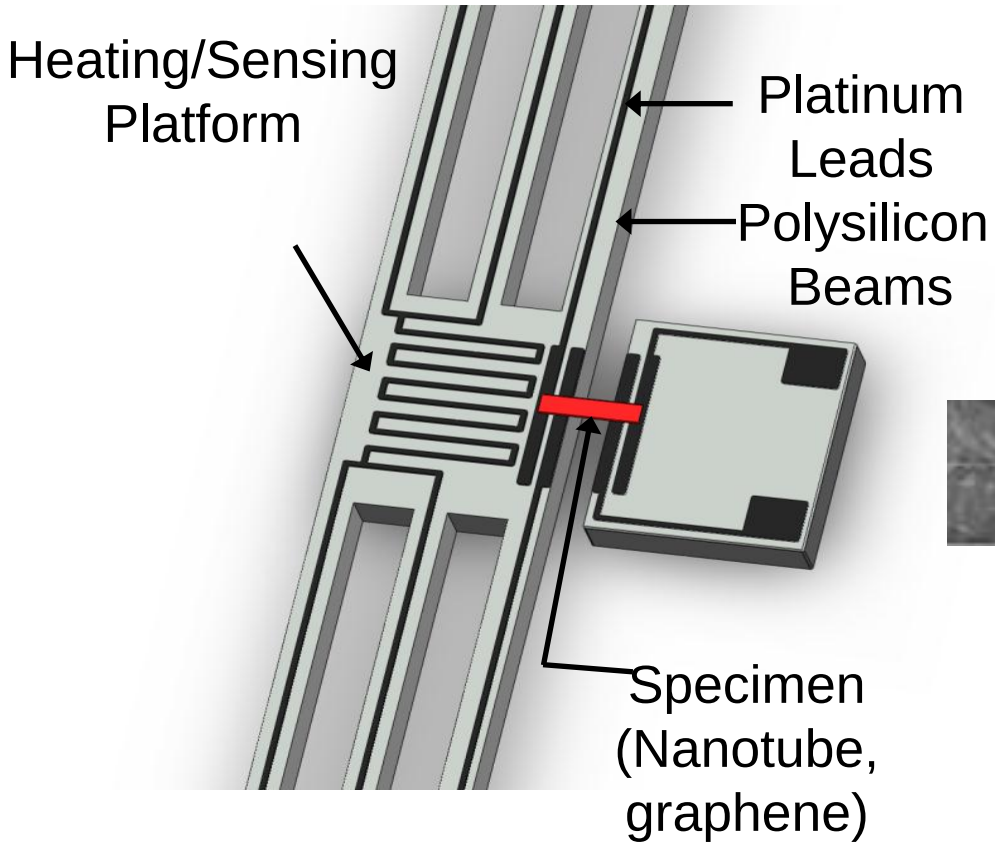


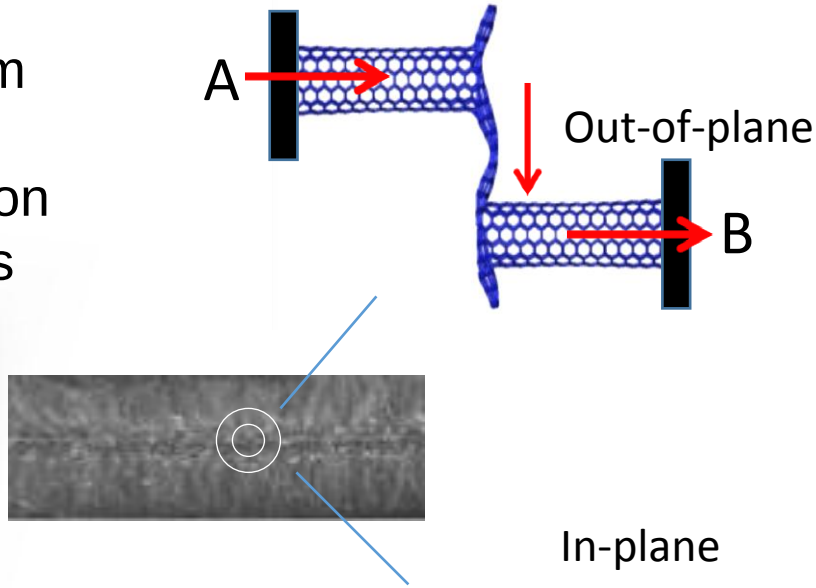
Graphitized MWCNT
20 hour, 3000°C Post-annealing heat treatment in argon

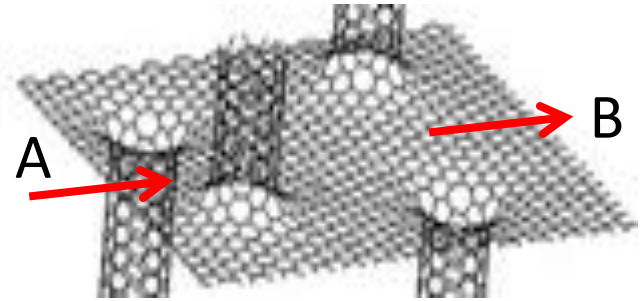
Graphitized but with morphological defects

CNT-Graphene Junction-level Characterization

Microfabricated Platform for Thermal Conductivity

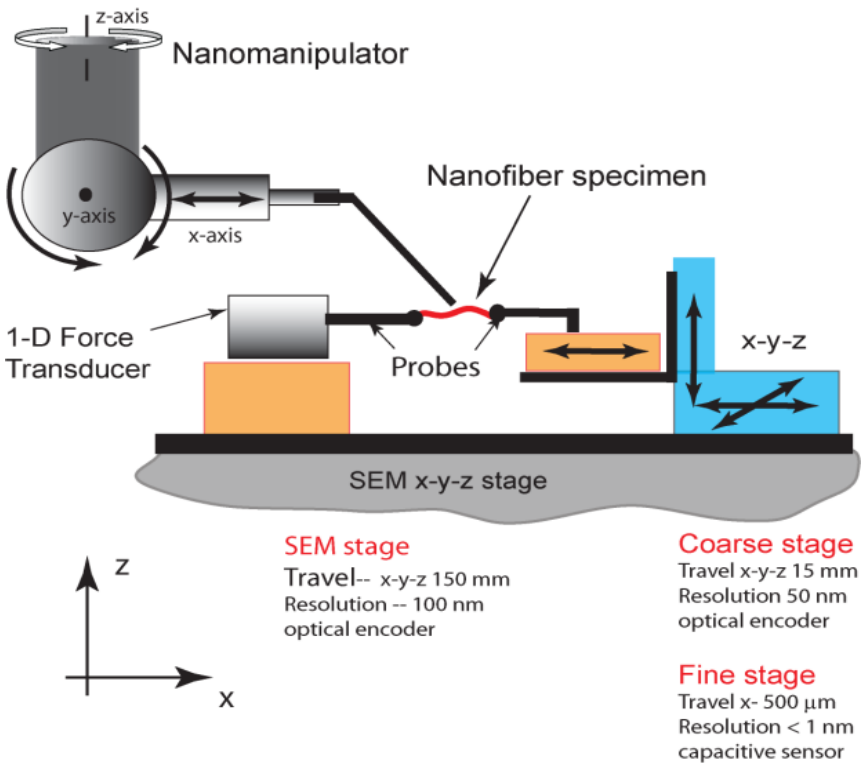


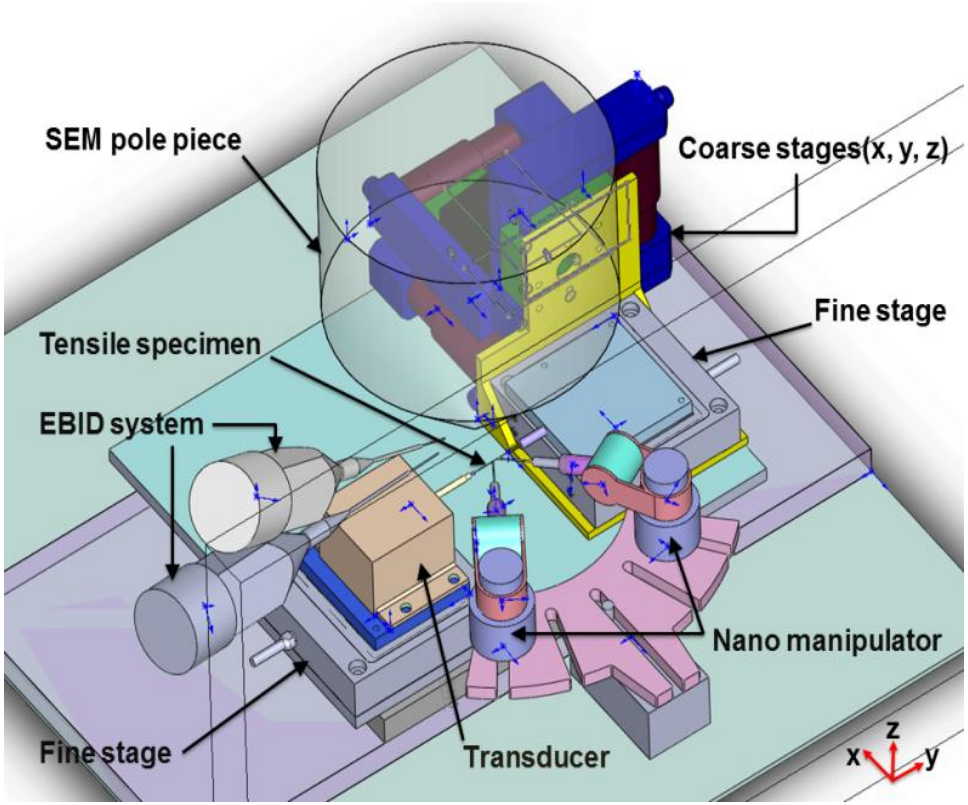




Nanomechanics of 3D Networks

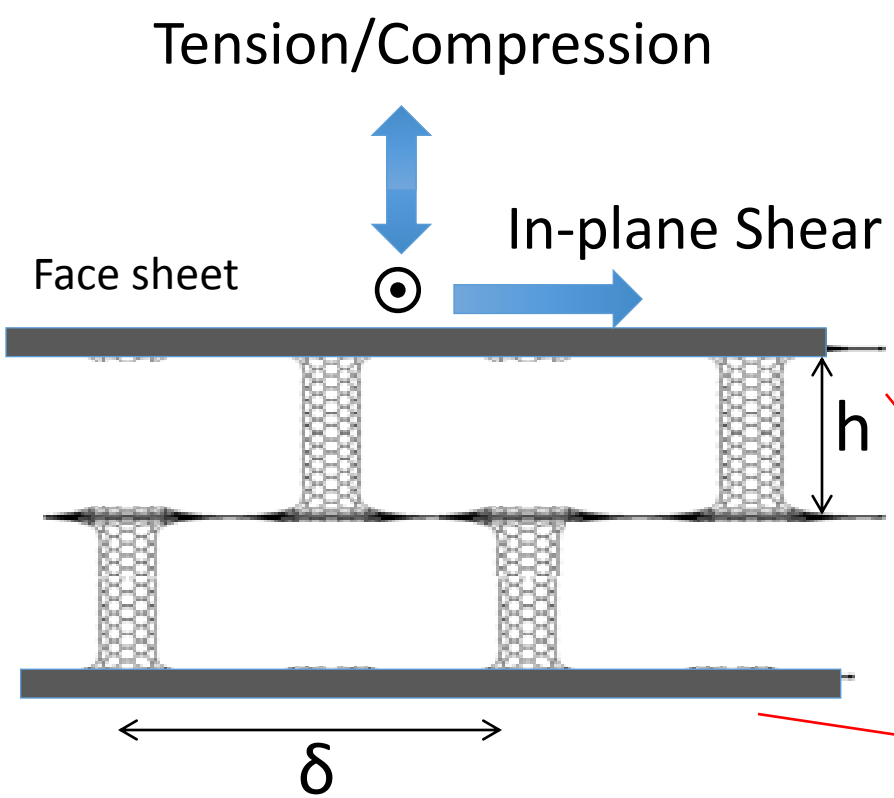
Nanotensilometer



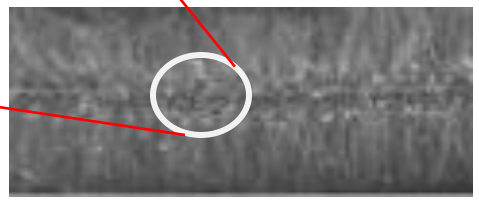


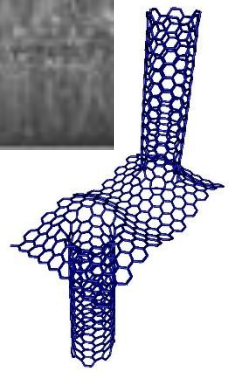
Force & Displacement Transducer: F_{max}= 10 mN with F_{res}=1nN
D_{max} = 500 µm with D_{res} = 0.2 nm

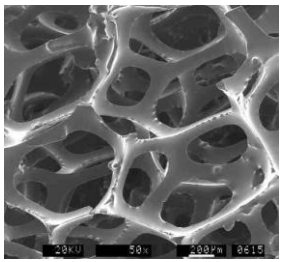
Nanomechanics of 3D Networks



- Tension/compression stiffness and strength
- Strength of CNT/graphene nodal points (junctions) in tension/shear
- Shear/buckling stability of the 3D super structure as a function of inter-pillar distance and pillar height.
- 3D Elastic moduli and Poisson's ratio







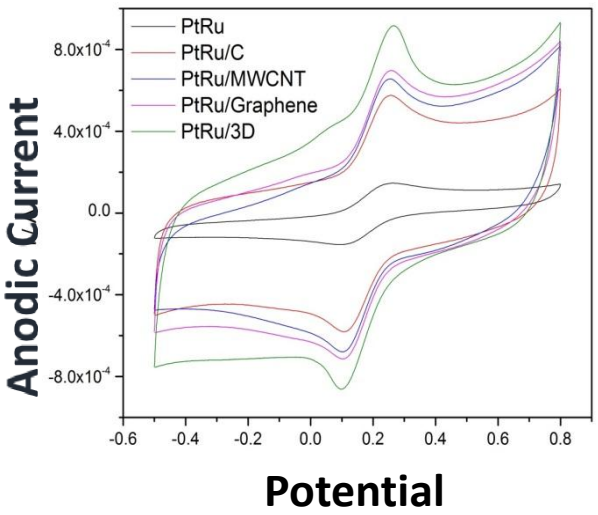
Use Structural Molecular Mechanics for interpretation of experimental results

Electrochemical Properties and Energy Storage

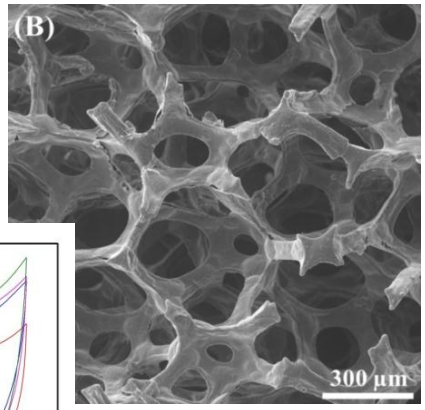
Accomplishments

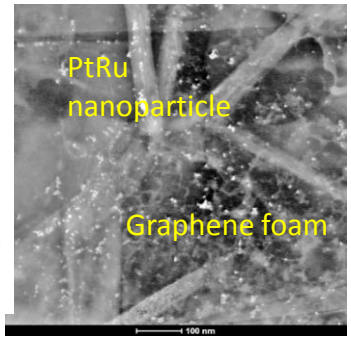
Direct methanol fuel cell (DMFC) & Direct ethanol fuel cell (DEFC)

Pt-Ru nanocatalyst on 3D graphene foam

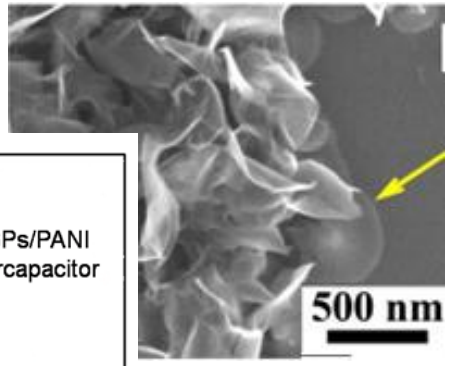


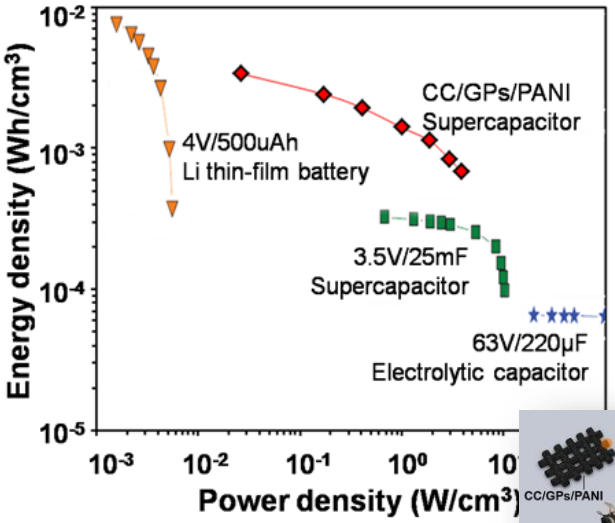
Cyclic Voltammogram

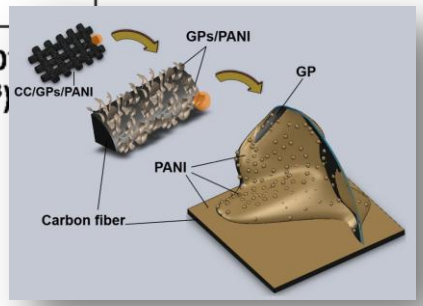




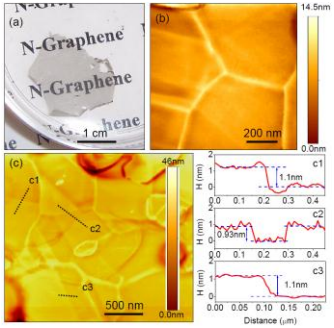
Carbon Cloth/Graphene-Petals/ PANI Supercapacitor







Electrochemical Properties of B & N-doped Nanotubes and Graphene as Metal-free Electrocatalysts



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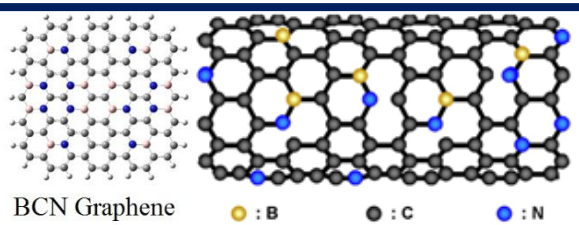
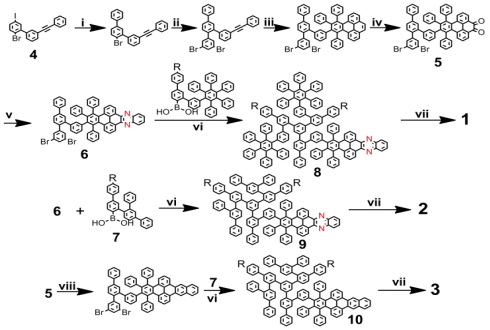
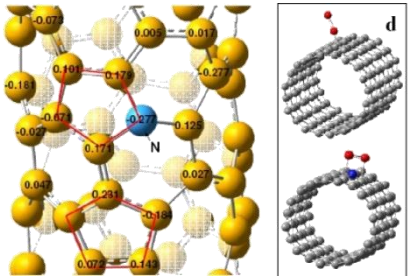


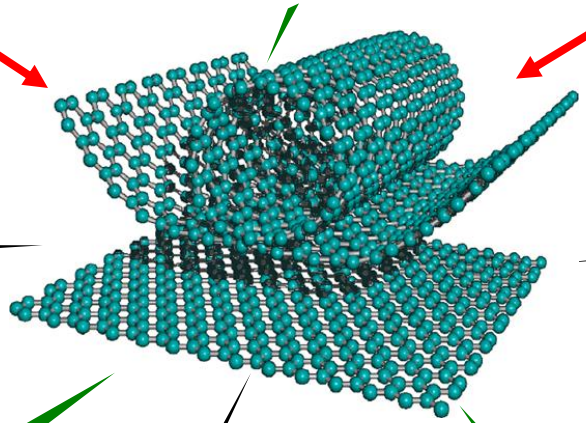
Wang, Dai, Roy *et al.*, *Angew. Chem.* **2011**, *50*, 11756.
Wang, Roy, Dai *et al.*, *Angew. Chem.* **2012**, *51*, 4209.

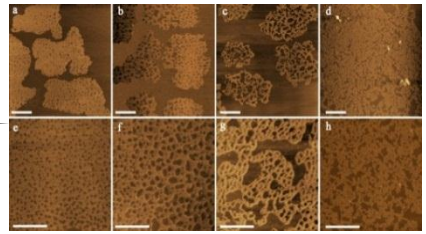


Li, Dai *et al.*, *JACS* **2012**, *134*, 18932.

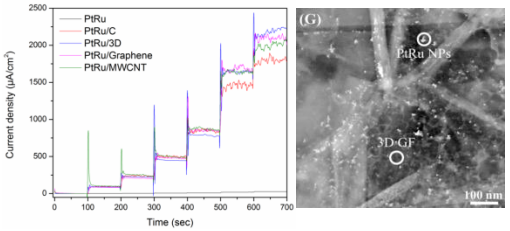


Gong; Du; Xia; Durstock; Dai
Science **2009**, *323*, 760.

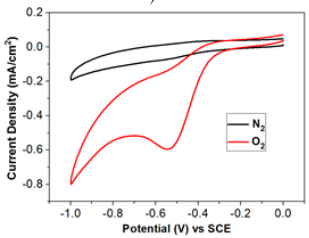




Wang, Dai, Shi, *et al.*, *Sci. Rep.* (in press).

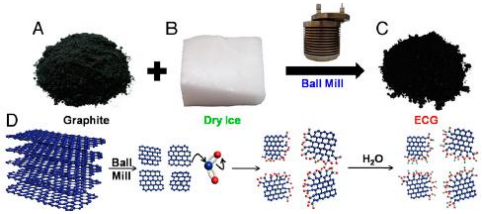


Courtesy of C.C. Liu



ORR for BCN Cloth

In collaboration with Fisher



(Edge-functionalized graphene by ball milling)
Jeon *et al.*, *JACS* **2013** , *135*, 1368; *PNAS* **2012** , *109*, 5588.
Chang *et al.*, *JACS* **2013** (in press).
Baek, Dai, Xia *et al.*, *Sci. Rep.* 5 Jun 2013.

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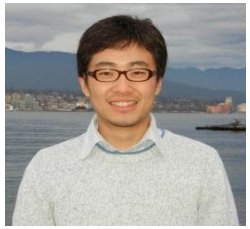
Collaborations/Networking and Team Meetings

- MURI Kick Off Meeting in Jan 2012 and MURI Review Meeting in DC in June 2013
- Three half-yearly meetings with all MURI team members and AFRL scientists
- Individual meetings of PI with team members from participating MURI universities
- Student/postdoc exchanges with AFRL
- Regular email/telephone exchanges among the team members and with AFRL
- Project website
- Quarterly & annual progress reports

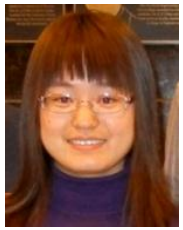
(Ryan Pierce)

(Kelly Rickey, intern at AFRL)



(Shihao Hu)

(Ishar Rosado Irizarry)



(Jianbing Niu)

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Publications in the First Year….

Journal publications during this Reporting Period

1. T. Chen, L. Dai *Materials Today* (in press).
2. D. W. Chang, E. K. Lee, E. Y. Park, H. Yu, H.-J. Choi, I.-Y. Jeon, G.-J. Sohn, D. Shin, N. Park, J. H. Oh, **L. Dai**, J.-B. Baek *J. Am. Chem. Soc.* (in press).
3. I.-Y. Jeon, H.-J. Choi, M. Choi, J.-M. Seo, S.-M. Jung, M.-J. Kim, S. Zhang, L. Zhang, Z. X *Report* (in press).
4. E. Nagelli, R. Naik, Y. X *Nanotechnology* (in pr
5. J. Xu, S. Dou, H. Liu, L.
6. Y. Xue, D. Yu, L. Dai, R. Liu, J. Qu *Phys. Chem.*
7. H. Cheng, Z. Dong, C. H *Nanoscale* 2013, 5, 34
8. C. Xue, O. Birel, Y. Xue *Physical Chemistry C* **2**
9. C. Xue, O. Birel, Y. Li, X *Journal of Colloid & Int*
10. Park, J., and Prakash, V Nanomaterials. 2013,
11. Park, J., Bifano, M. F. P Physics. 2013, vol. 113
12. Kaul, P. B., Bifano, M. Composite Materials.
13. T.-C. Hou, Y. Yang, Z.-H Chen, Z. L. Wang *Nano* http://dx.doi.org/ 10.1
14. Y. Yang, Z.-H. Lin, T. Ho 2012, published Online 012-0272-8.
15. Y. Yang, S. Wang, Y. Zh 6408–6413, 2012.
16. Z. L. Wang, W. Wu *Ang*
17. F. Zhang, Y. Ding, Y. Zh 9229–9236, 2012.
18. X. Yang, G. Zhu, S. Wa *Energy Environ. Sci.* 5,
19. Y. Yang, Y. Zhou, J. M. Wu, Z. L. Wang *ACS Nano* 6, 8456–8461, 2012.
20. L. Lin, Y. Hu, C. Xu, Y. Zhang, R. Zhang, X. Wen, Z. L. Wang *Nano Energy* 2012, published online: http://dx.doi.org/10.1016/j.nanoen.2012.07.019
21. Y. Xue, J. Liu, H. Chen, R. Wang, D. Li, J. Qu, L. Dai *Angew. Chem. Int. Ed.* 51, 12124-12127, 2012.
22. S. Wang, L. Zhang, Z. Xia, A. Roy, D. W. Chang, J. B. Baek, L. Dai *Angew. Chem. Int. Ed.* 51, 4209-4212, 2012.
23. D. Yu, Y. Xue, L. Dai *J. Phys. Chem. Lett.* 3, 2863-2870, 2012.
24. M. Zhang, L. Dai *Nano Engergy* 1, 514-517, 2012.

Roy, T.S. Fisher *Thin Solid Films* (in press, doi:10.1016/j.tsf.2012.08.059).

42. Y. Wang, X. L. Ruan, A. K. Roy *Phys. Rev. B* 85, 205311, 2012.
43. Y. Wang, Q. Li *Adv. Mater.* 24, 1926, 2012.
44. C. Xue, O. Birel, M. Gao, S. Zhang, L. Dai, A. Urbas, Q. Li *J. Phys. Chem. C* 116, 10396, 2012.
45. J. Park, V. Prakash MRS JMR Focus Issue on *De Nova* Carbon Nanomaterials vol. 28. DOI: 10.1557/jmr.2012.395.
46. E. Mayhew, V. Prakash *Carbon* (in press).
47. Kaul, P. B., Bifano, M. P., and Prakash, V. *J. Composite Mater.* (in press).
48. J. Park, M. F. P. Bifano, V. Prakash *J. Appl. Phys.* (in press).

B. Kaul, A. K. Roy, V. Prakash *J. Appl.*

S.H. Wang, C.C. Liu, B.J. Hwang
75-81, 2012.

Reporting Period

ifenberger, Graphitic petals
be arrays on carbon cloth.
rence #: 66126.
er, Reifenberger, R., Modified
ectrochemical energy storage
disclosure, Reference #: 2013-FISH-
51723757.
Fisher, Reifenberger, R., *et al.*
or the fabrication, and use of
t structures. Provisional patent
erial No. 61/523,646).

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- **Publications**

  51 refereed journal publications to date

  30% joint publications with team members and/or AFRL collaborators; About 1/2 impact factor > 5
- **Patent Applications 3**

  Book Chapters 8

  Conference Papers and Posters (numerous)
- **Panel Session and workshop with AFOSR/AFRL at ASME IMECE 2012 on related topics**
- **Special MRS Symposium planned on 3D Nanotube Networks at the 2014 MRS Conf in San Francisco.**
- **Collaboration plans are in the works between the two MURI teams on the topic.**

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