Vertically Aligned Carbon Nanotubes Embedded in Ceramic Matrices for Hot Electrode Applications

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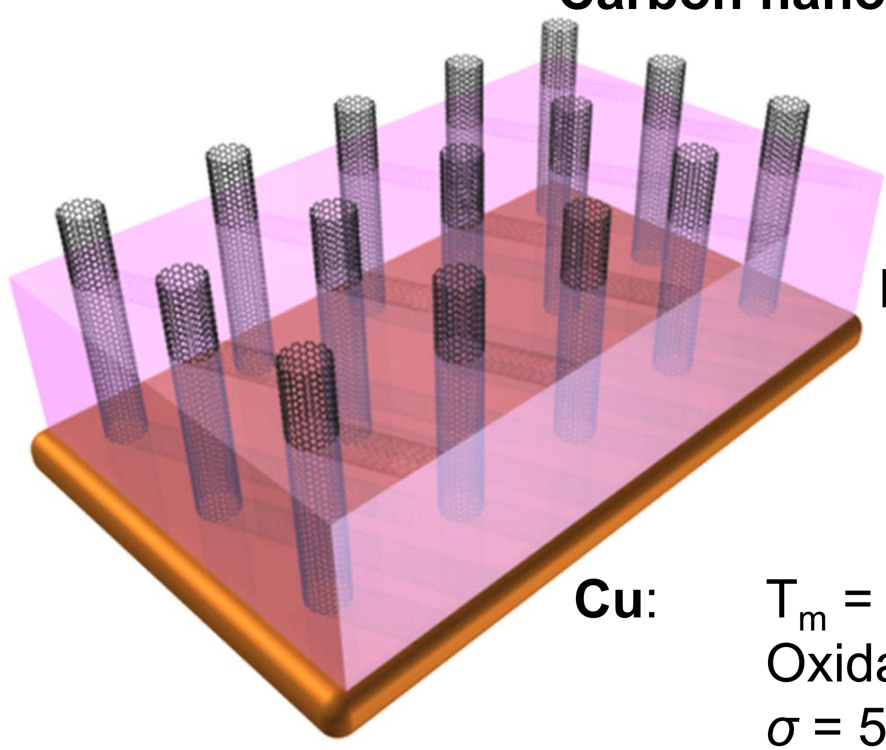
Outline

1. Goal and Objectives
2. Background and Motivations
3. Accomplishments
    1) Building a water-vapor-assisted chemical vapor deposition (WVA-CVD) system
    2) Growing ultralong vertically aligned carbon nanotubes (VACNTs)
    3) Fabricating VACNT-Cu structures
    4) Building a laser-assisted chemical vapor deposition (LCVD) system for growing BN
4. Deliverables
5. Planned Activities in the Next-Phase
6. Student Training

1. Goal and Objectives

Primary goal: Develop CNT-BN composite structures in which VACNTs are embedded in BN matrices for hot electrode applications in magnetohydrodynamics (MHD) power systems.



Carbon nanotubes:

T_m > 1726 ˚C
Oxidation resistance ~ 750 ˚C
$\sigma = 10^6 – 10^7$ S/m
K = 200 – 30,000 W/(m·K)

BN:

T_m > 2900 ˚C
Oxidation resistance ~ 1500 ˚C
Insulator
K = 600 - 740 W/(m·K)

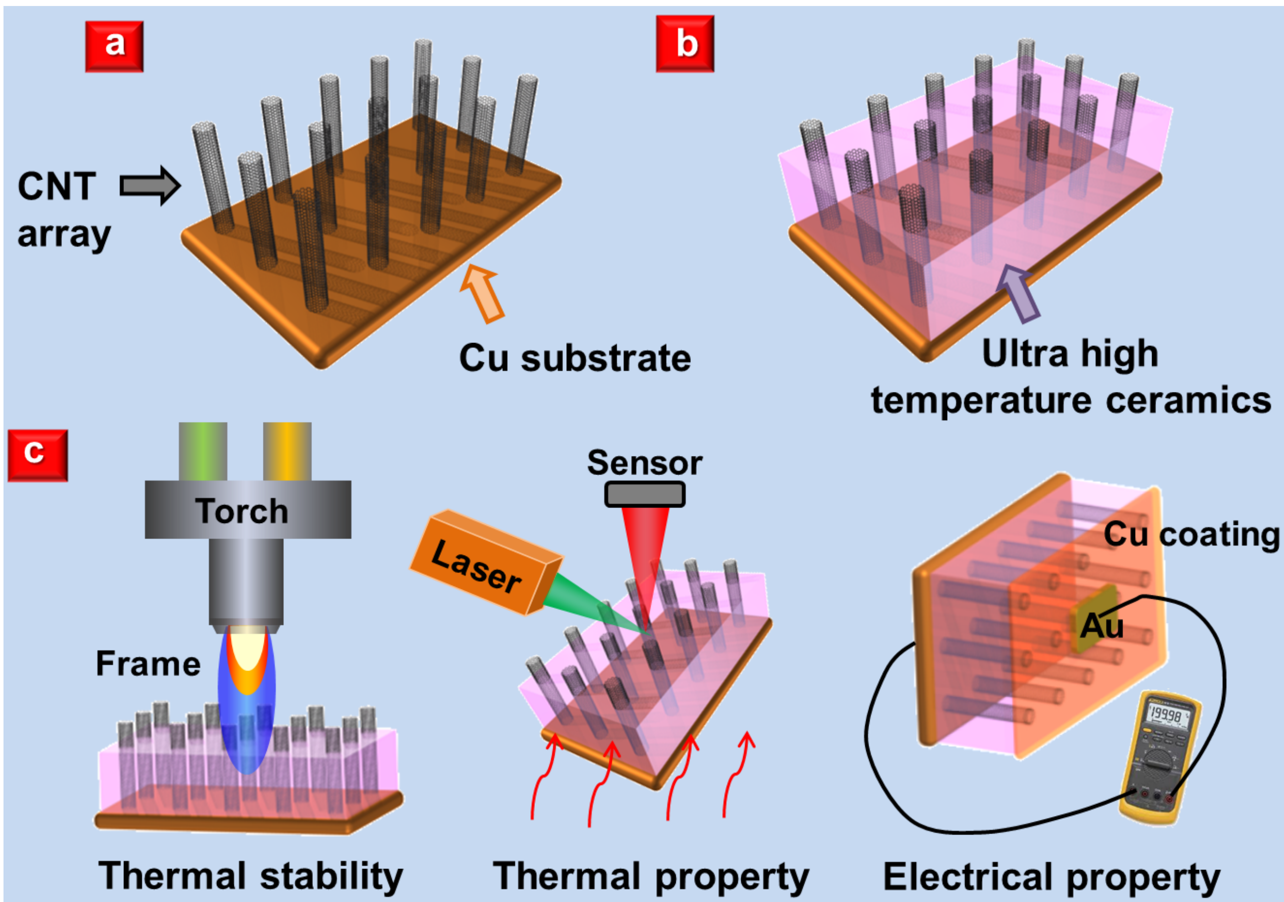
Cu:

T_m = 1084 ˚C
Oxidation resistance < 200 ˚C
$\sigma = 59.6 \times 10^6$ S/m
K = 401 W/(m·K)

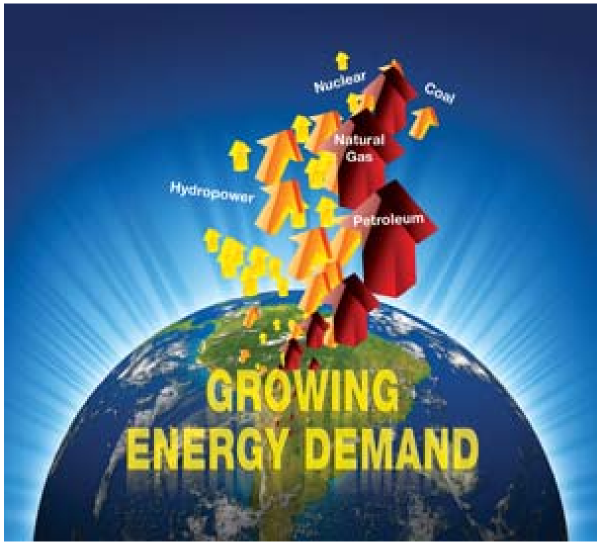
1. Goal and Objectives

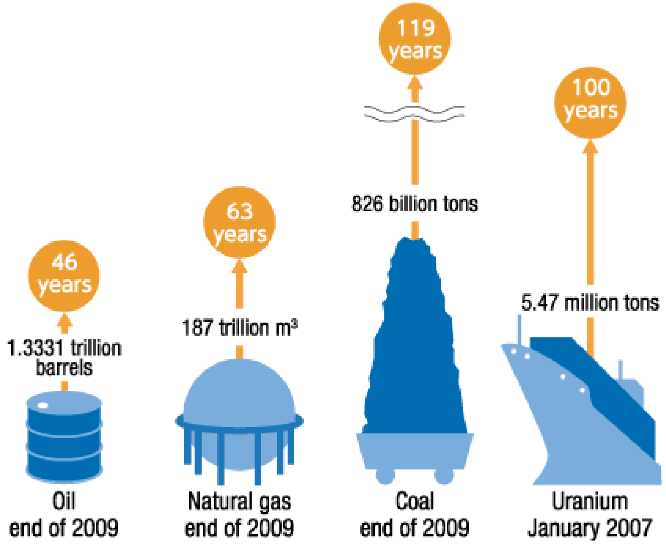
Objectives:

1. Super growth of VACNT carpets
2. Fabrication of CNT-BN composite structures
3. Stability and resistance studies of the CNT-BN composite structures
4. Thermionic emissions from the CNT-BN composite structures



2. Background and Motivations





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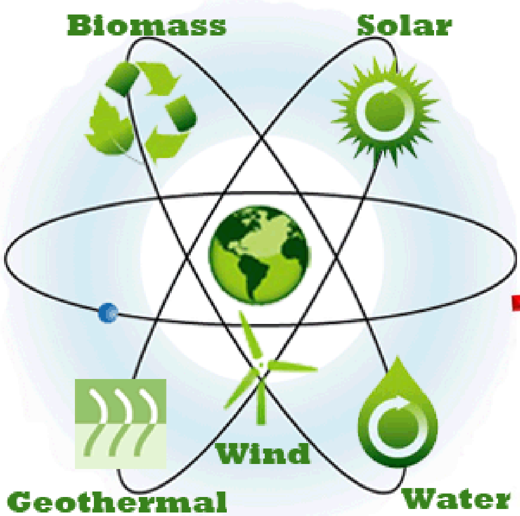


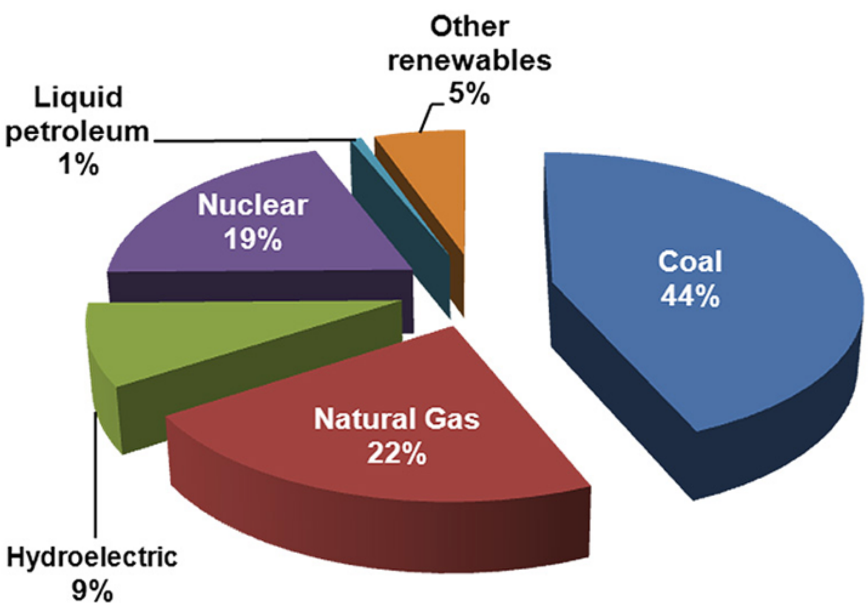
New Energy Sources

Search for solutions

High Energy Efficiency

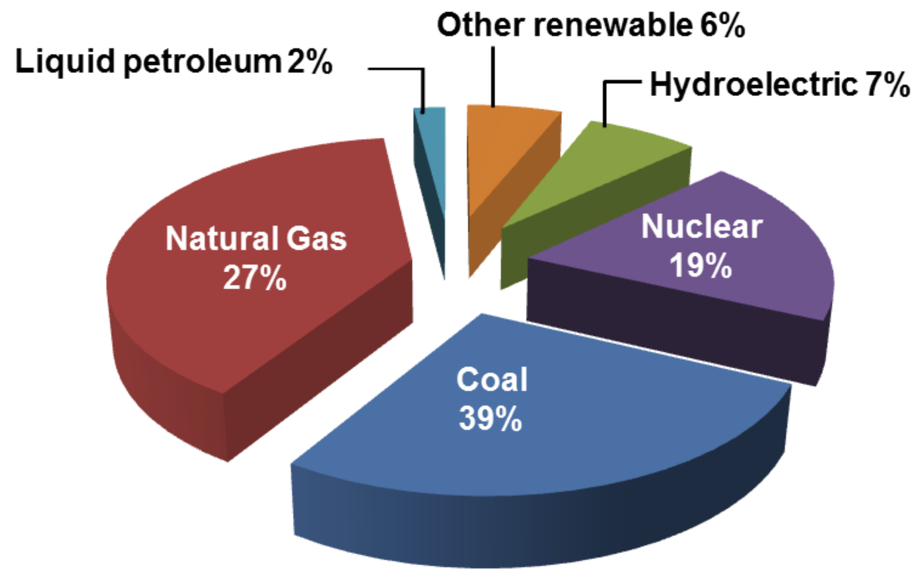
2. Background and Motivations

U.S. Electricity Generation (2010)



http://crf.sandia.gov/index.php/coal-use-and-carbon-capture-technologies/#.VBaDbvldV8E

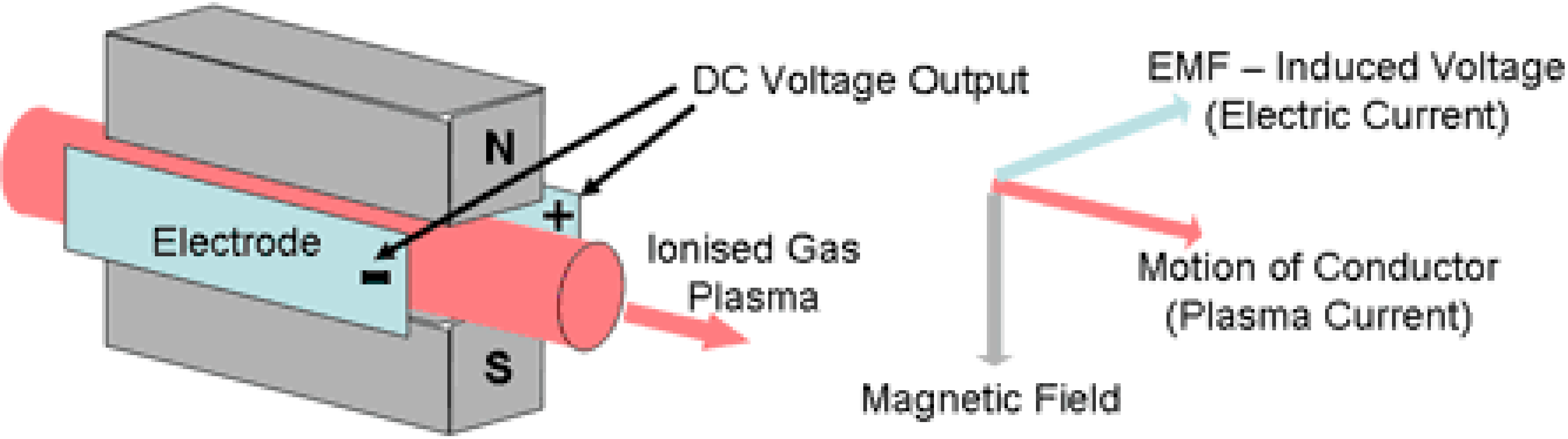
U.S. Electricity Generation (2013)



http://www.eia.gov/tools/faqs/faq.cfm?id=427&t=3

Method	Efficiency (%)	Ref.
Nuclear	33 – 36	Efficiency in Electricity Generation, EURELECTRIC "Preservation of Resources" Working Group's "Upstream" Sub-Group in collaboration with VGB, 2003
Coal	39 - 47	
Natural gas	< 39	
MHD	~ 65%	http://www.mpoweruk.com/mhd_generator.htm

2. Background and Motivations



Magnetohydrodynamic Power Generation (Principle)

1) Only working fluid is circulated without moving mechanical parts;
2) The ability to reach full power level almost directly.
3) Lower infrastructure cost than conventional generators.
4) A very high efficiency (60% for a closed cycle MHD).

http://en.wikipedia.org/wiki/Magnetohydrodynamic_generator#Generator_efficiency

2. Background and Motivations

Material Challenges for a MHD Generator

Requirement	Remarks
Electrical conductivity (σ)	$\sigma > 1$ S/m, flux ≈ 1 amp/cm^2
Thermal conductivity (k)	High heat flux from the combustion fluids at 2400 K
Thermal stability	Melting point (T_m) above 2400 K
Oxidation resistance	Resistant to an oxygen partial pressure about 10^{-2} atm at 2400 K
Corrosion resistance	Potassium seeds and aluminosilicate slags
Erosion resistance	High velocity hot gases and particulates
Thermionic emission	The anode and cathode should be good acceptor and emitters, respectively.

2. Background and Motivations

	CNTs
Electrical conductivity (σ)	$10^6 – 10^7$
Thermal conductivity (K)	200 – 3000
Thermal stability	$T_m > 1726$ ˚C
Oxidation resistance	~ 750 ˚C
Corrosion resistance	Yes
Erosion resistance	Yes
Thermionic emission	Yes

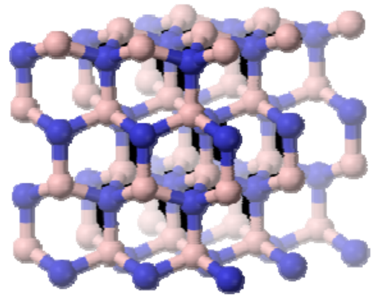
Y. Won, Y. Gao et al., PNAS, 2013, 110(51), 20426-20430.

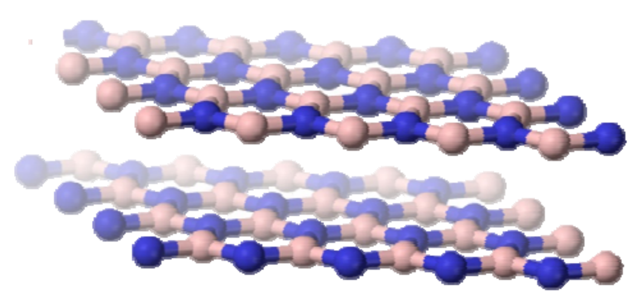
1000 X current density of copper
5 X electrical conductivity of copper
15 X thermal conductivity of copper
1/7 density of copper and ½ or Al

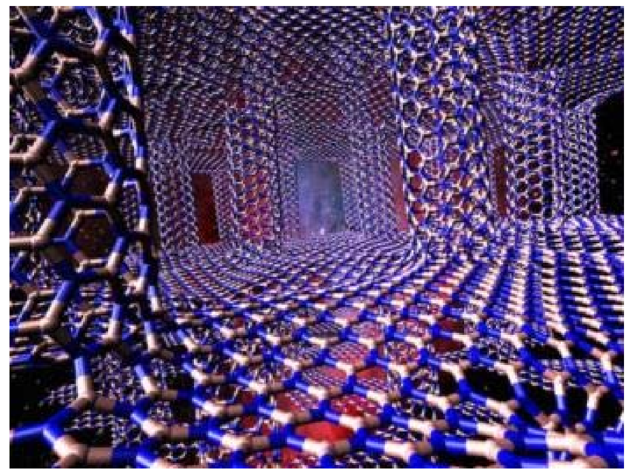
3,500 pounds of Cu and 147,000 pounds of Al in a Boeing 747

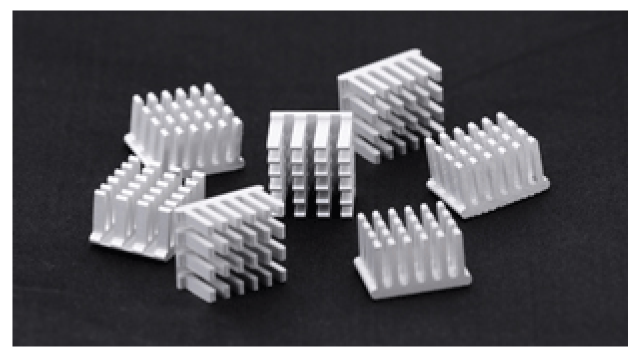
2. Background and Motivations

	BN
Electrical conductivity (σ)	Insulating
Thermal conductivity (K)	600 - 740
Thermal stability	T_m = 2973
Oxidation resistance	~ 1500 ˚C
Corrosion resistance	Yes
Erosion resistance	Yes
Thermionic emission	N.A.



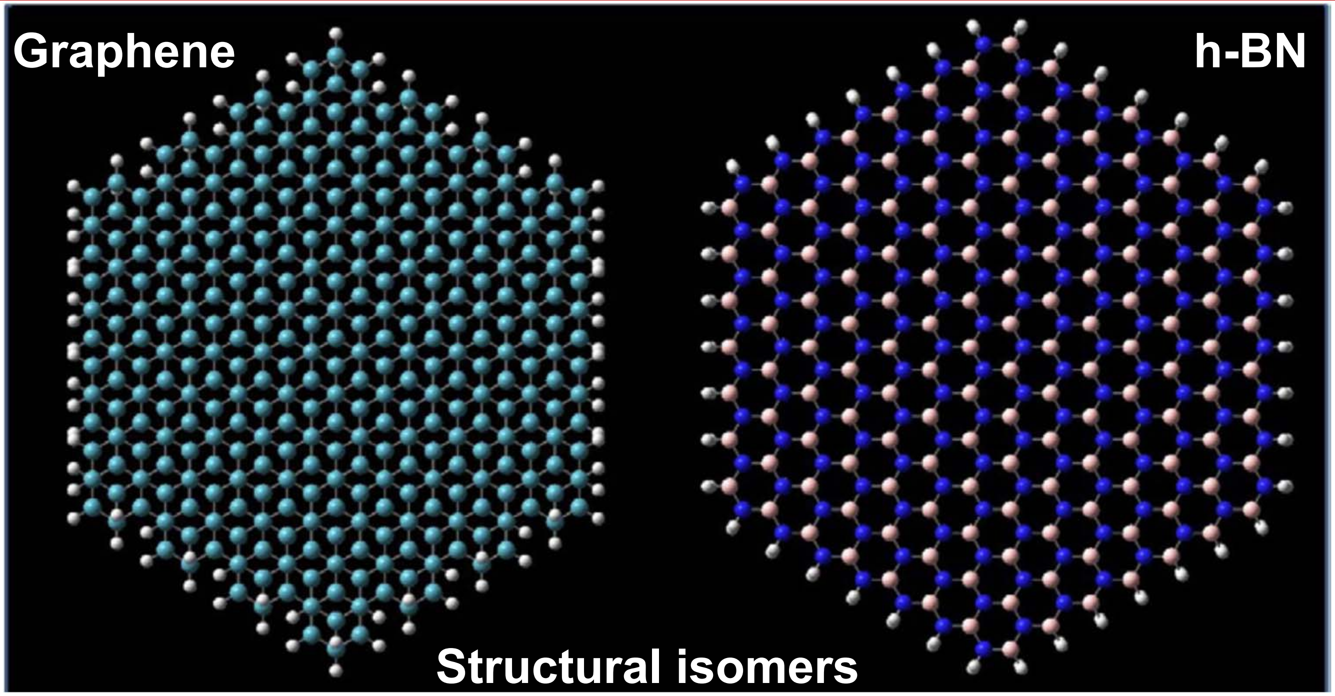






http://www.graphene-info.com/3d-white-graphene-could-cool-electronics

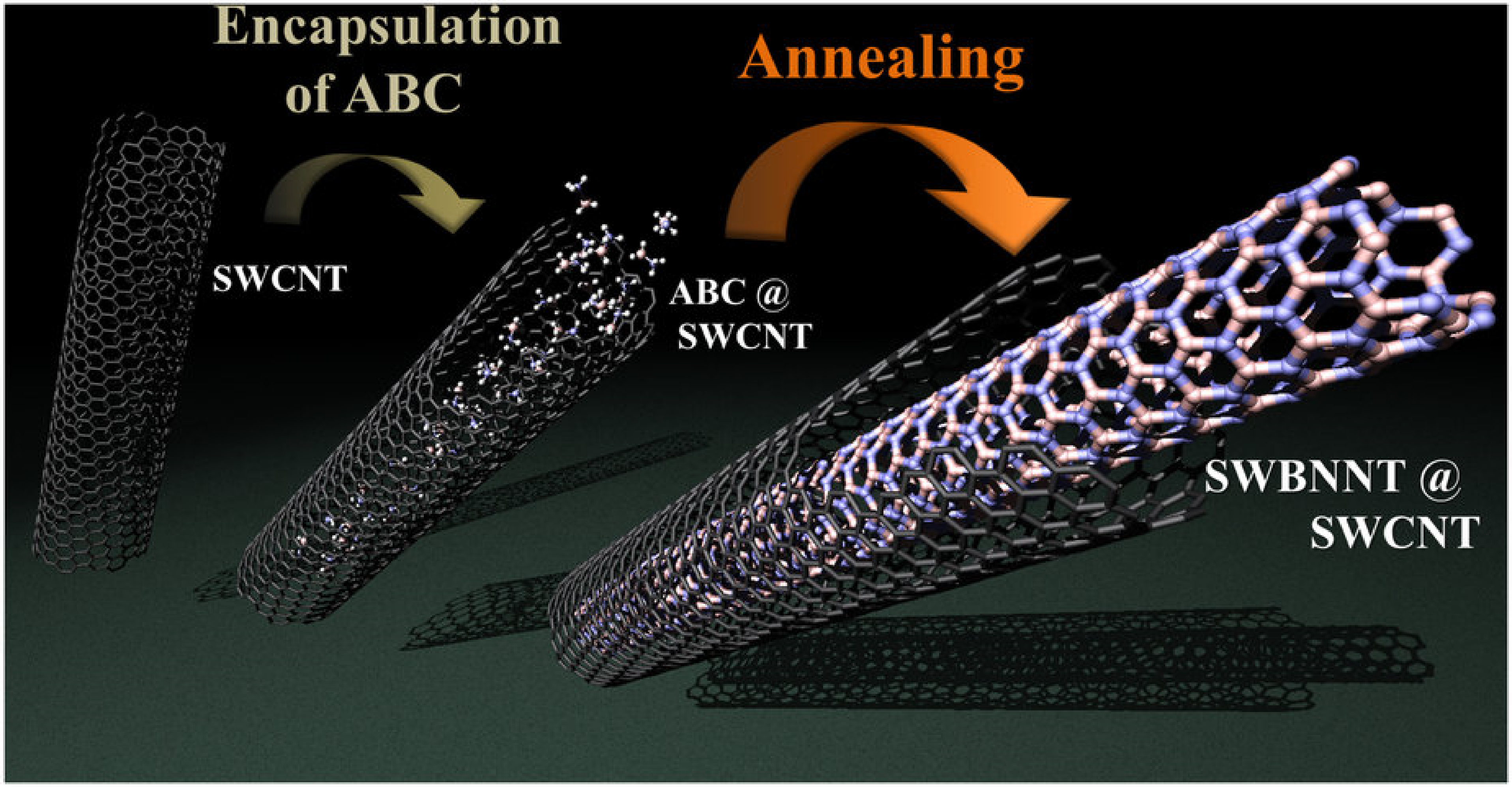
2. Background and Motivations



	Graphene	h-BN
Space group	P_{63}	P_{63}
Lattice constant, *a* (Å)	2.46	2.50
Lattice constant, *c* (Å)	6.70	6.66
Thermal expansion coefficient (10^{-6} ˚C^{-1})	-1.5 ǁ, 25 ⊥	-2.7 ǁ, 38 ⊥

Within the basal planes (ǁ) and perpendicular to them (⊥)

2. Background and Motivations

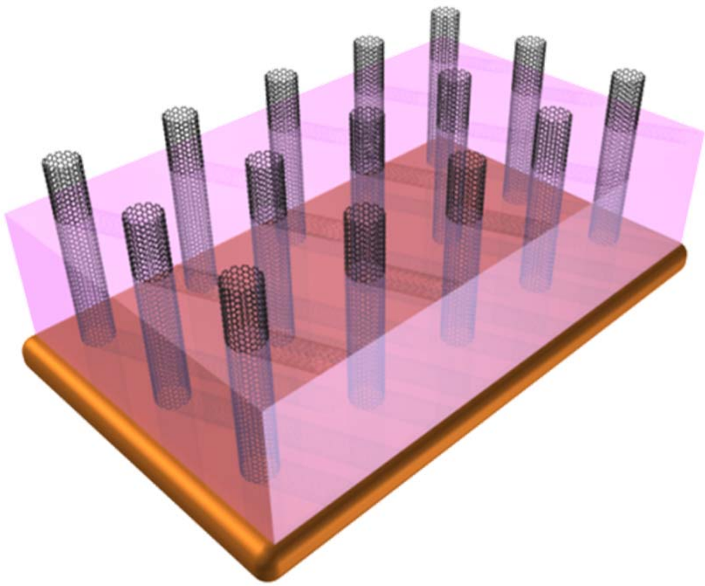


It is feasible to insert BNNTs in CNTs, and vice verse.

http://www.nature.com/articles/srep01385

2. Background and Motivations

Proposed Solution: CNT-BN Composite Structures



VACNTs: **Electrical and thermal conductive channels.**

BN: **Protective layer shielding CNTs from erosive and corrosive environments.**

Property	BN	CNT
Melting point (˚C / K)	2973 / 3246	> 1726 / 2000
Chemical inertness	Inert to acids but soluble in alkaline molten salts and nitrides	Yes
Oxidation resistance in open air (˚C / K)	1500 / 1773	< 750 / 1023
Electrochemical passiveness	Yes. Used as electrode.	Yes.
Electrical conductivity (S/m)	Insulating	10^6 - 10^7
Thermal conductivity [W/(m·K)]	600 - 740	Up to 3000

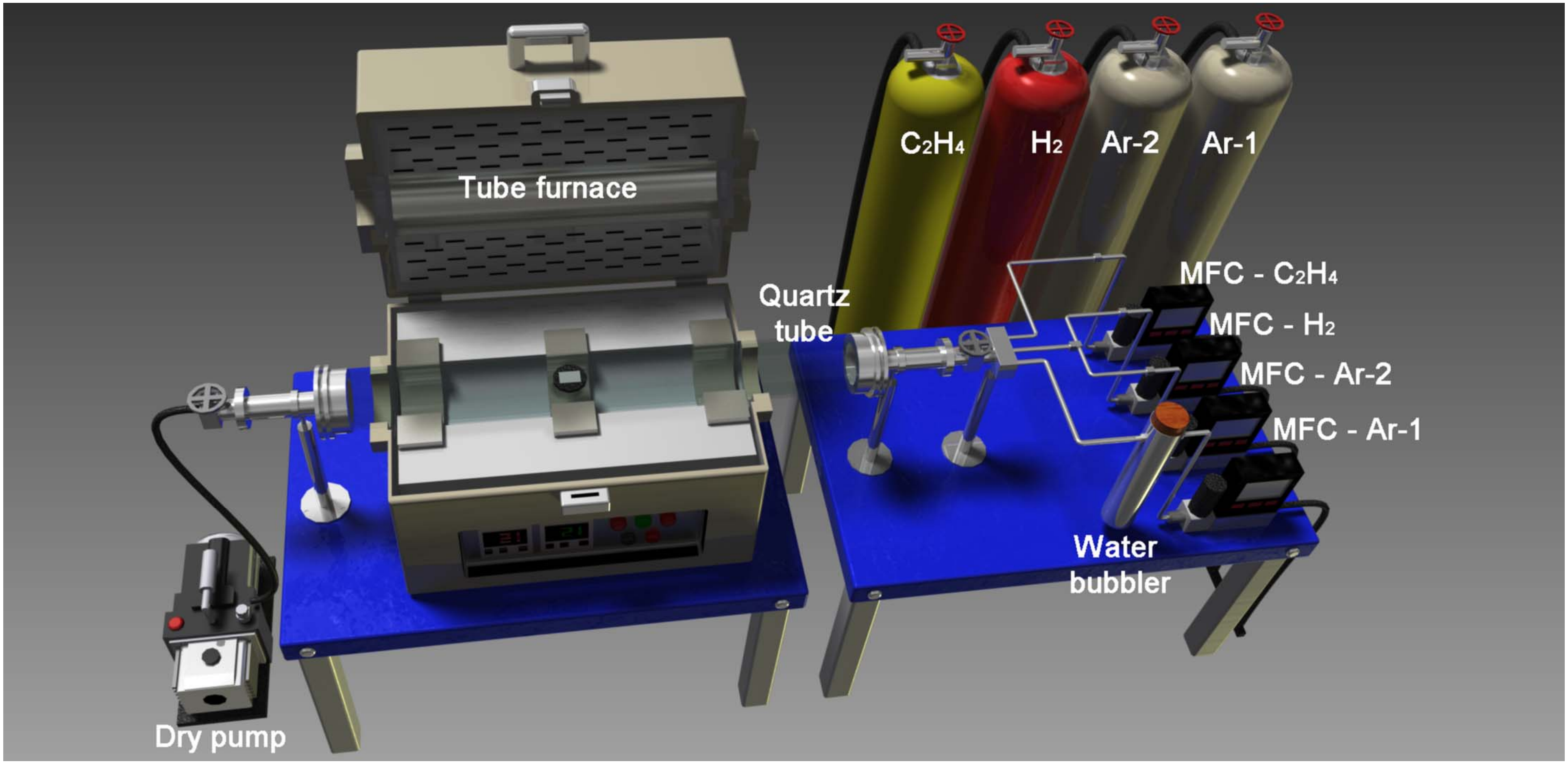
3. Accomplishments

1) Building a water-vapor-assisted chemical vapor deposition (WVA-CVD) system
2) Growing ultralong vertically aligned carbon nanotubes (VACNTs)
3) Fabricating VACNT-Cu structures
4) Building a laser-assisted chemical vapor deposition (LCVD) system for growing BN

3. Accomplishments

- Building a WVA-CVD system

Dry Rotary Pump	Two-Zone Tube Furnace	Gas Cylinders and Four-Way MFC Station

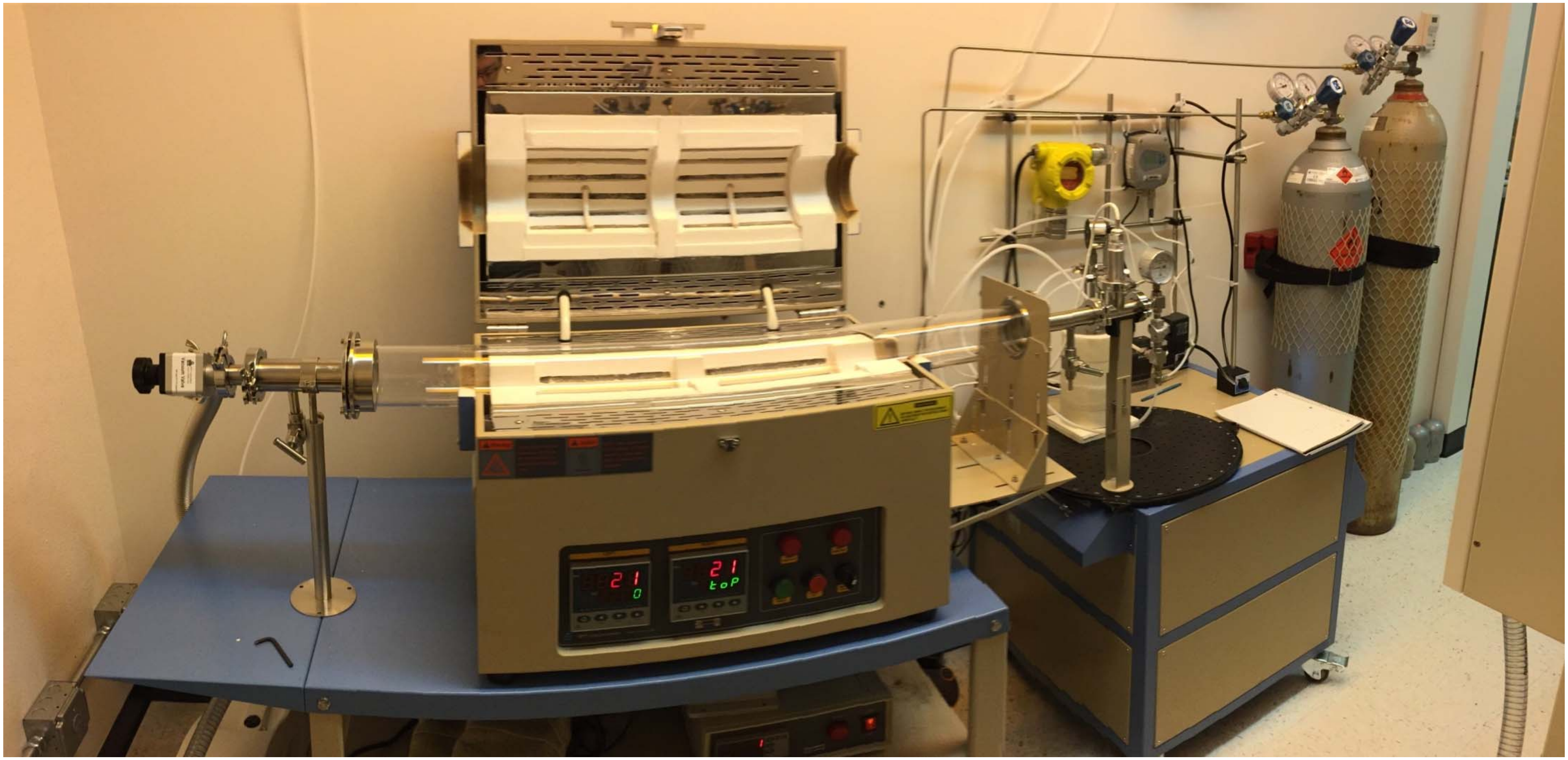


3. Accomplishments
- Building a WVA-CVD system

Dry Rotary Pump

Two-Zone Tube Furnace

Gas Cylinders and Four-Way MFC Station



3. Accomplishments
- Building a WVA-CVD system

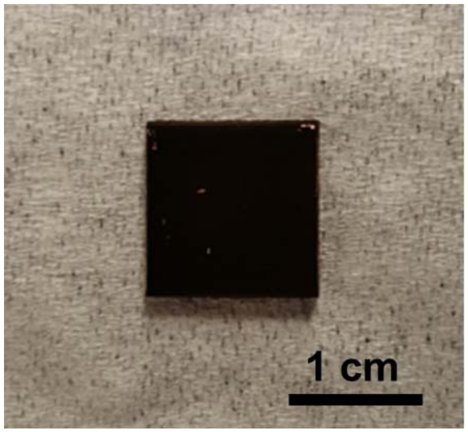
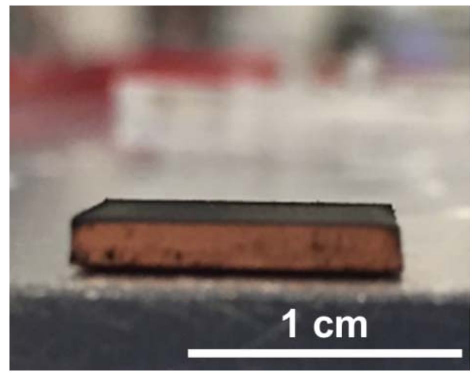
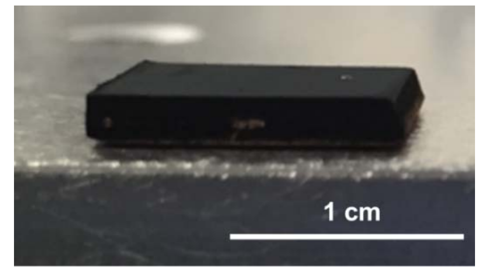
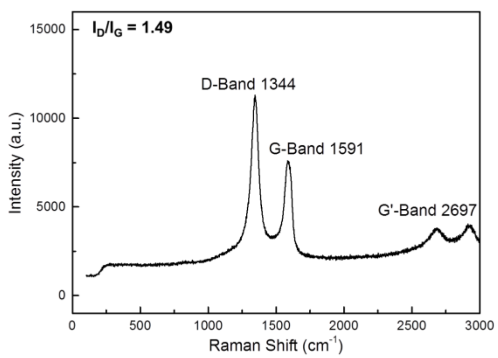
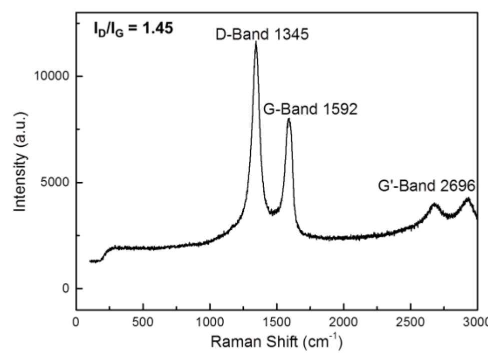
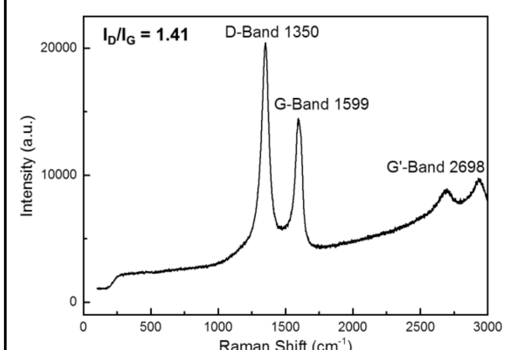
A water-vapor-assisted (WVA)-CVD system was established.

3. Accomplishments
- Growing ultralong VACNTs

VACNTs on Cu using WVA-CVD
Single-temperature-zone

	Catalyst pretreatment	Feeding H_2O	CNT growth	Flushing	Cooling
T (˚C)	RT → 750	750	750	750	750 → RT
Time (min)	20	0	15	1	> 60
Ar (sccm)	1000	1000	400	1000	1000
H_2 (sccm)			400		
C_2H_4 (sccm)			Variable		
Ar for carrying H_2O vapor (sccm)		60	60	60	
Catalyst	Fe / Al (nm / nm) : 3 / 20				

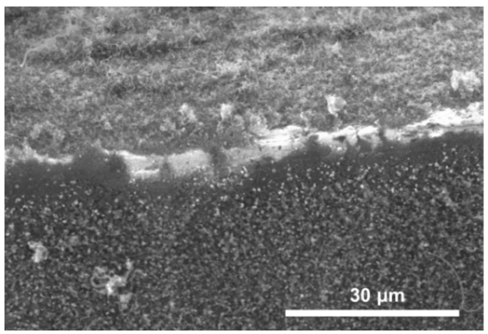
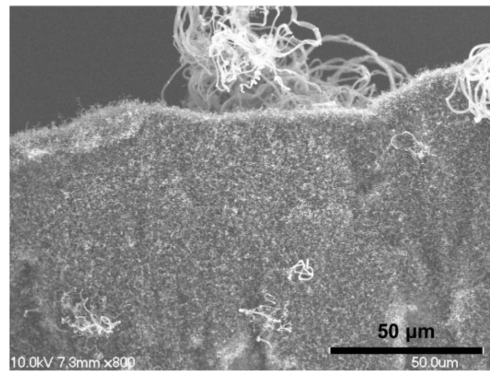
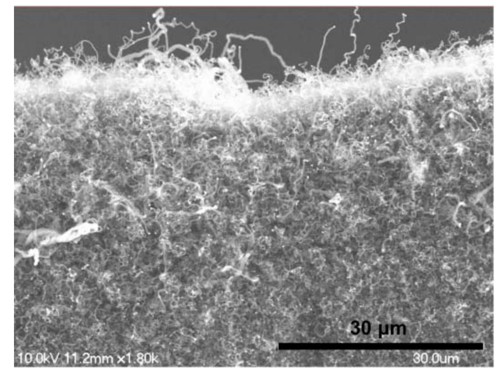
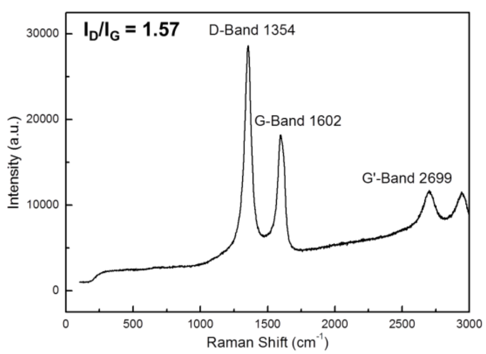
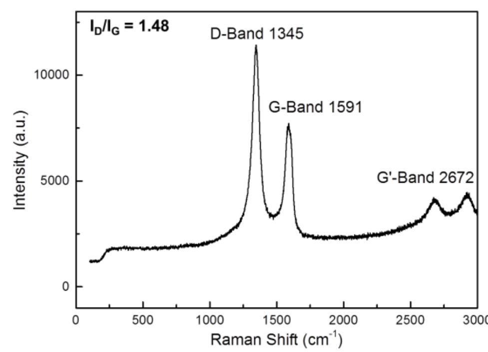
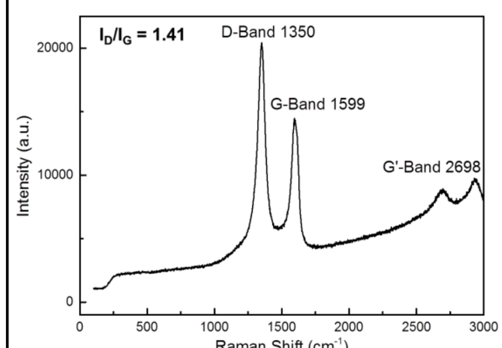
3. Accomplishments
- Growing ultralong VACNTs

C_2H_4 flow rate (sccm)	100	150	200
Optical image			
Raman spectrum			

3. Accomplishments
- Growing ultralong VACNTs

	Catalyst pretreatment	Feeding H_2O	CNT growth	Flushing	Cooling
T (˚C)	RT 750	750	750	750	750 RT
Time (min)	20	0	Variable	1	> 60
Ar (sccm)	1000	1000	400	1000	1000
H_2 (sccm)			400		
C_2H_4 (sccm)			200		
Ar for carrying H_2O vapor (sccm)		60	60	60	
Catalyst	Fe / Al (nm / nm) : 3 / 20				

3. Accomplishments
- Growing ultralong VACNTs

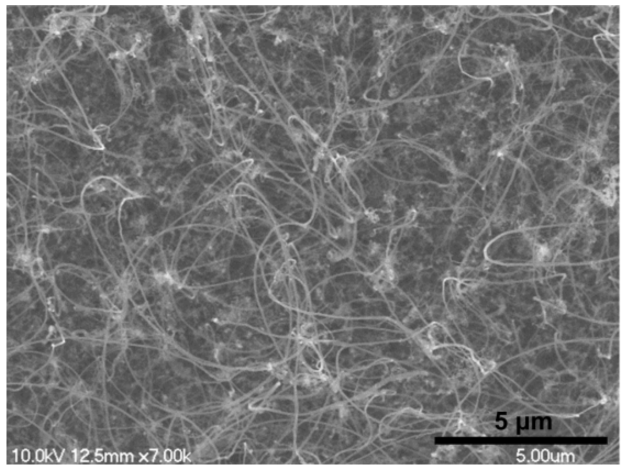
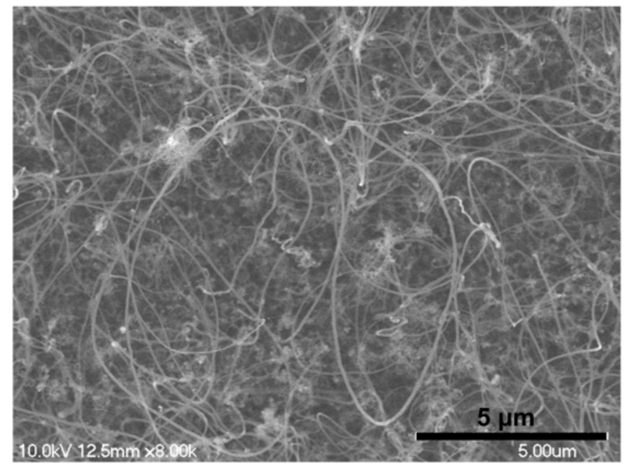
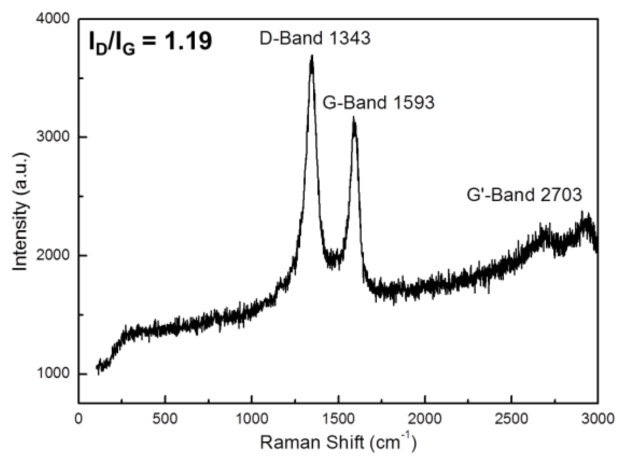
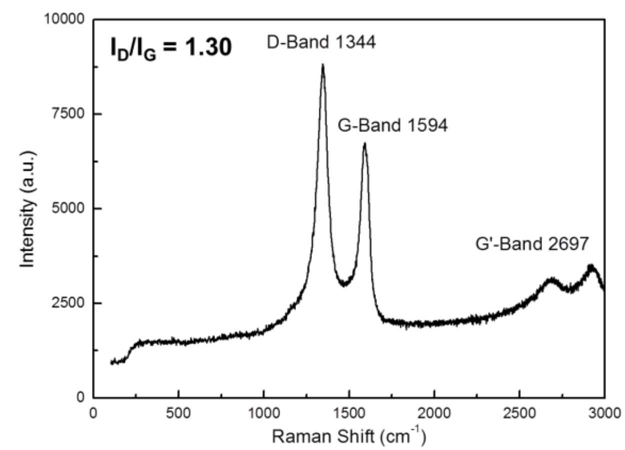
Growth time (min)	20	25	30
SEM micrograph			
Raman spectrum			

3. Accomplishments
- Growing ultralong VACNTs

Variable humidity investigated

	Catalyst pretreatment	Feeding H_2O	CNT growth	Flushing	Cooling
T (˚C)	RT 750	750	750	750	750 RT
Time (min)	20	0	40	1	> 60
Ar (sccm)	1000	1000	400	1000	1000
H_2 (sccm)			400		
C_2H_4 (sccm)			200		
Ar for carrying H_2O vapor (sccm)		Variable	Variable	Variable	
Catalyst	Fe / Al (nm / nm) : 3 / 20				

3. Accomplishments
- Growing ultralong VACNTs

Relative humidity (%)	0.4	0.5
SEM micrograph		
Raman spectrum		

3. Accomplishments
- Growing ultralong VACNTs

Only random CNTs were obtained on Cu.

X

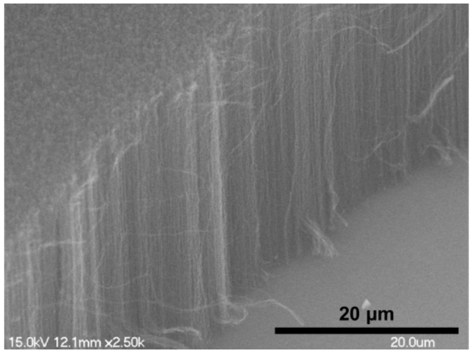
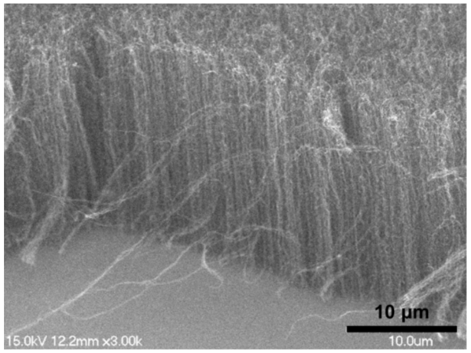
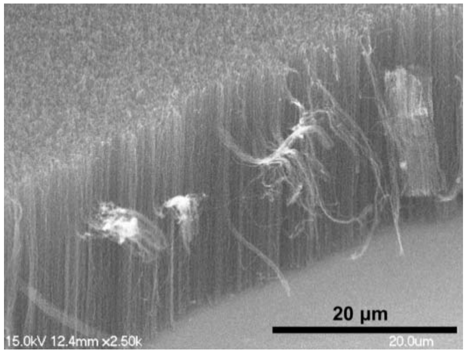
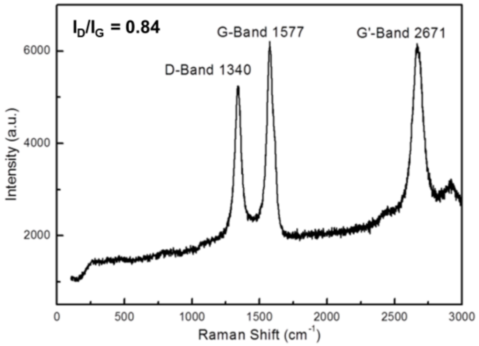
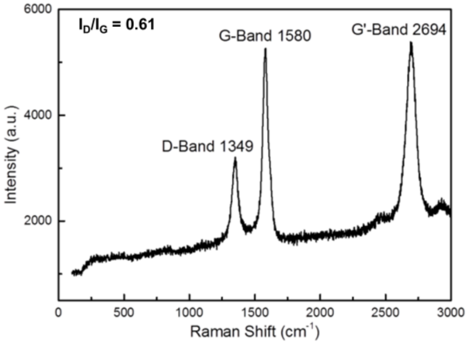
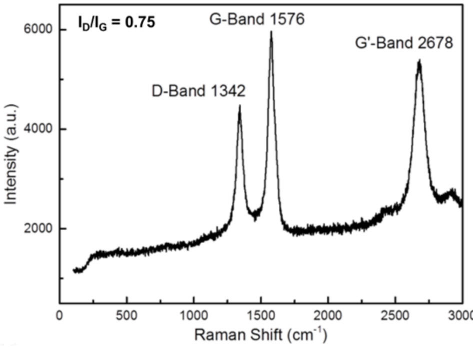
Direct growth of well aligned ultralong VACNTs on Cu turns out to be a very challenging task.

3. Accomplishments
- Growing ultralong VACNTs

VACNTs on SiO_2/Si using WVA-CVD
Single-temperature-zone reactor

	Catalyst pretreatment	Feeding H_2O	CNT growth	Flushing	Cooling
T (˚C)	RT → 750	750	750	750	750 → RT
Time (min)	20	5	10	1	> 60
Ar (sccm)	600	600	540	600	1000
H_2 (sccm)	400	400	360	400	
C_2H_4 (sccm)			100		
Ar for carrying H_2O vapor (sccm)		50	50	50	
Catalyst	Fe/Al_2O_3 (top to bottom)		Variable		

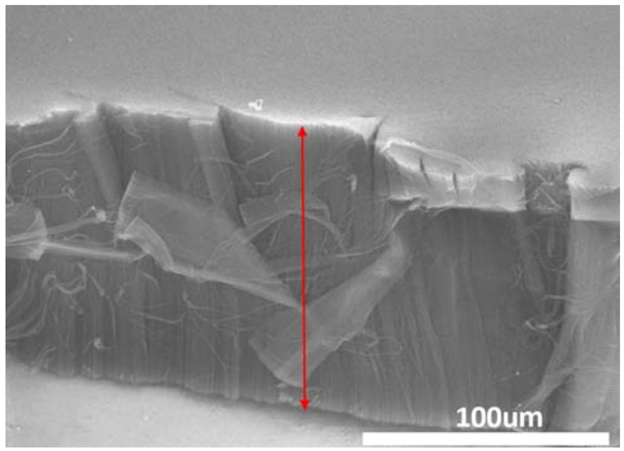
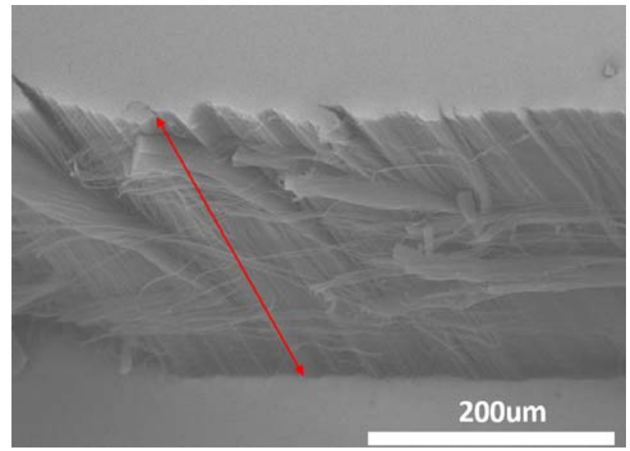
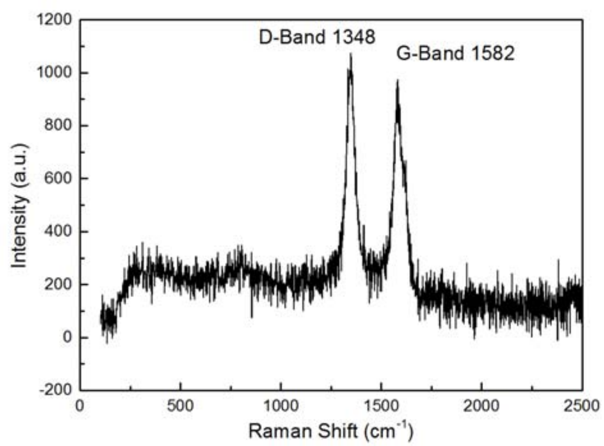
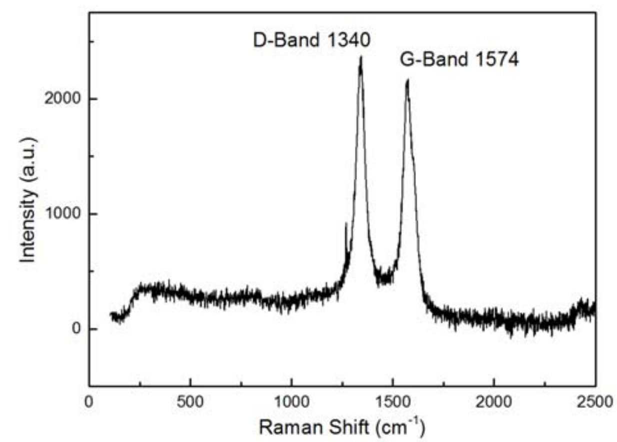
3. Accomplishments
- Growing ultralong VACNTs

Fe/Al_2O_3 (nm/nm)	1/20	2/20	4/20
SEM micrograph			
Raman spectrum			

3. Accomplishments
- Growing ultralong VACNTs

	Catalyst Pretreatment	Feeding H_2O	CNT Growth	Flushing	Cooling
T(°C)	RT 750	750	750	750	RT
Time(min)	20	5	40	1	>60
Ar(sccm)	200	200		200	500
H_2(sccm)	300	300	300	300	
C_2H_4(sccm)			Variable		
H_2O carrier gas Ar(sccm)		25	25	25	
Catalyst	Fe/Al_2O_3(nm/nm): 2/20				

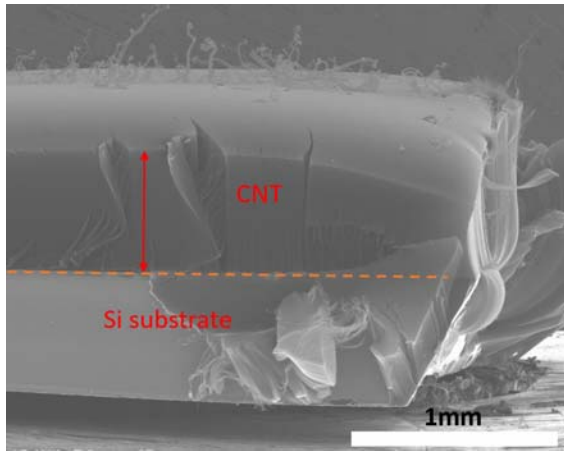
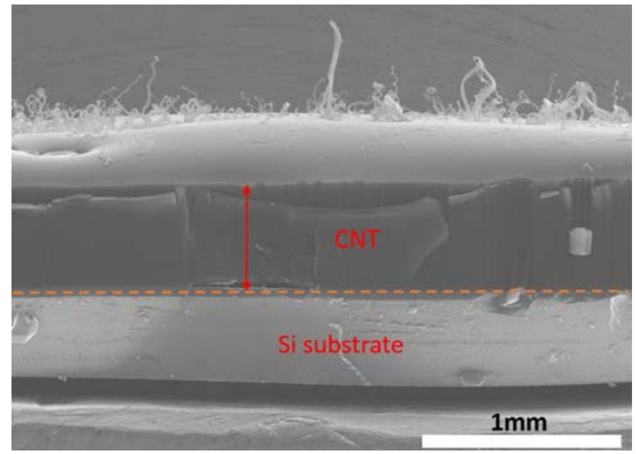
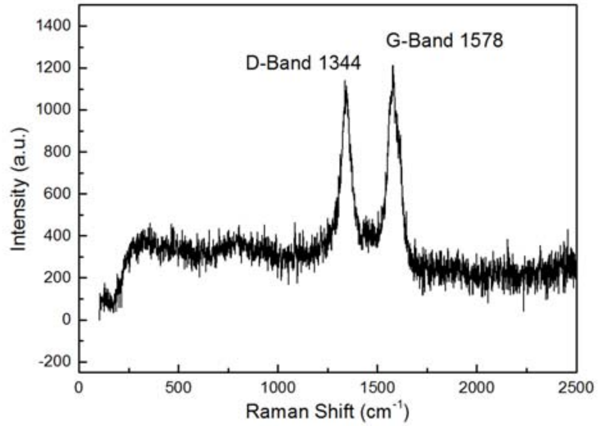
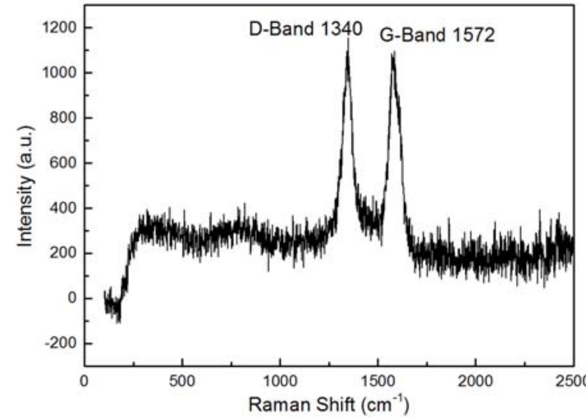
3. Accomplishments
- Growing ultralong VACNTs

C_2H_4 flow rate (sccm)	100	200
SEM micrograph		
Raman spectrum		

3. Accomplishments
- Growing ultralong VACNTs

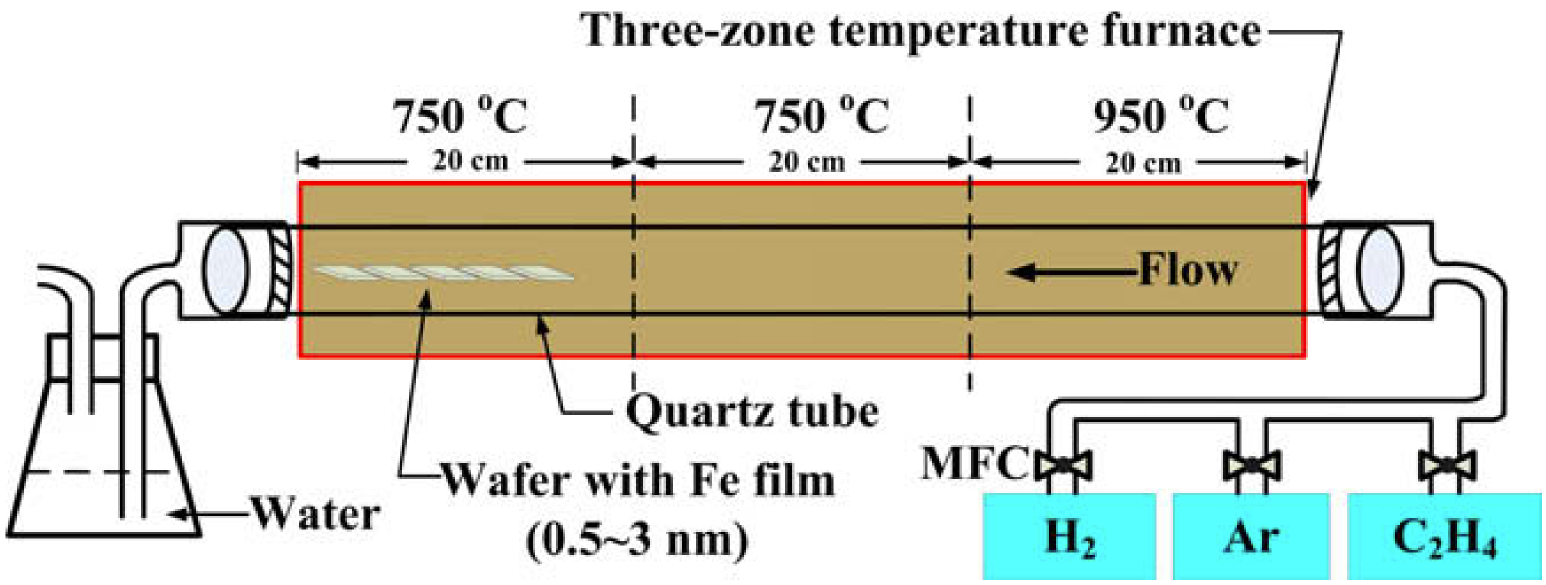
	Catalyst Pretreatment	Feeding H_2O	CNT Growth	Flushing	Cooling
T(°C)	RT – 750	750	750	750	RT
Time(min)	20	5	variable	1	>60
Ar(sccm)	200	200		200	500
H_2(sccm)	300	300	300	300	
C_2H_4(sccm)			200		
H_2O carrier gas Ar(sccm)		25	25	25	
Catalyst	Fe/Al_2O_3(nm/nm): 3/20				

3. Accomplishments
- Growing ultralong VACNTs

Growth time (min)	40	60
SEM micrograph		
Raman spectrum		

3. Accomplishments
- Growing ultralong VACNTs

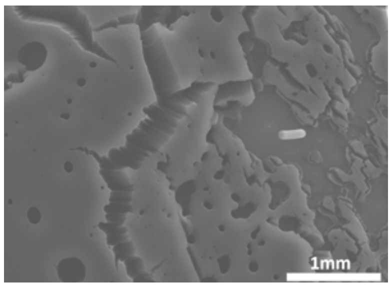
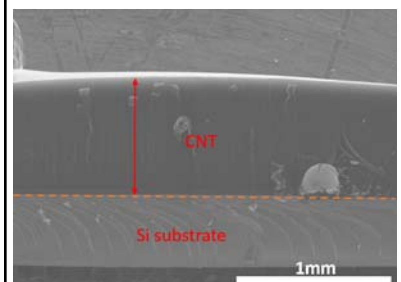
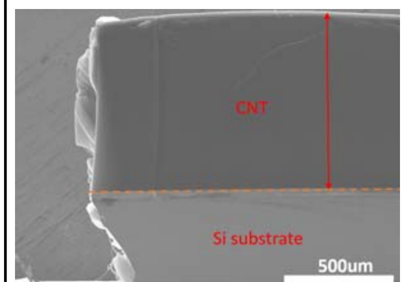
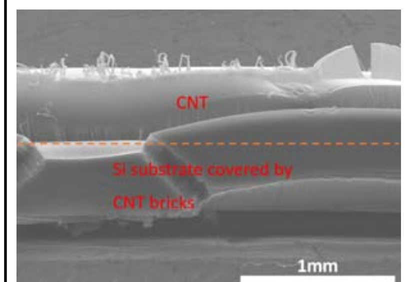
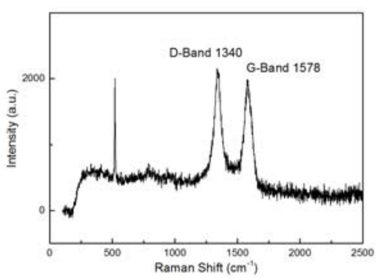
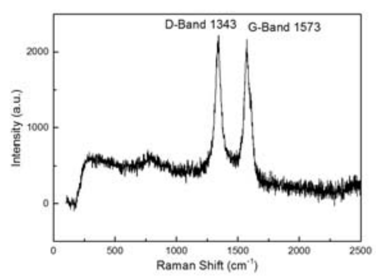
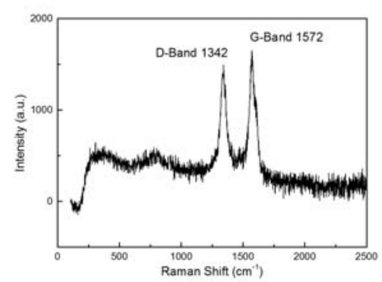
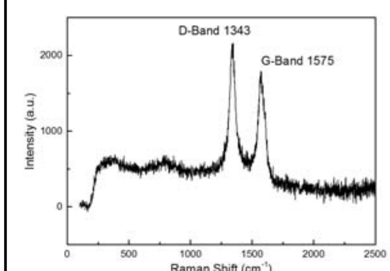
VACNTs on SiO_2/Si using CVD
Dual-temperature-zone reactor
Without water vapor



3. Accomplishments
- Growing ultralong VACNTs

	Catalyst Pretreatment	CNT Growth	Flushing	Cooling
T(°C)	RT 750	750	750	RT
Time(min)	20	60	1	>60
Ar（sccm）	600	600	600	1000
H_2(sccm)	400	400	400	
C_2H_4(sccm)		200		
Catalyst	Fe/Al_2O_3 (nm/nm) - Variable			

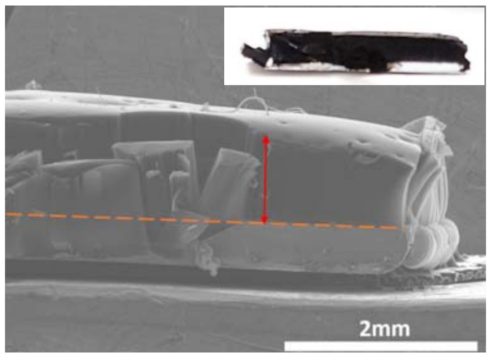
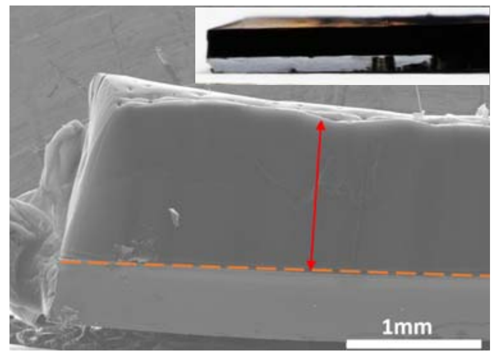
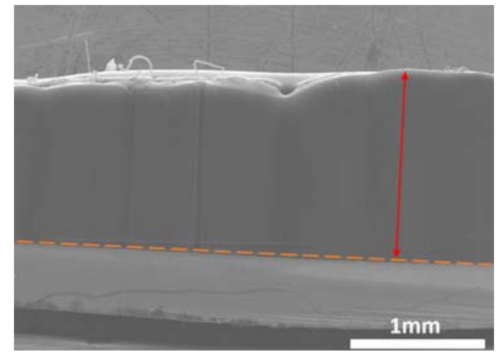
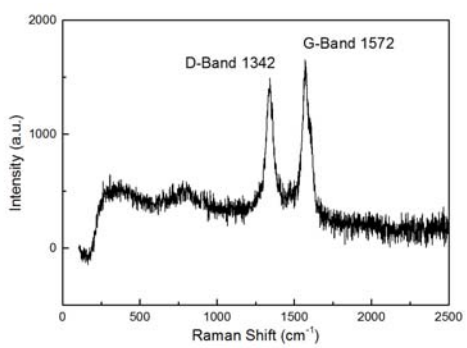
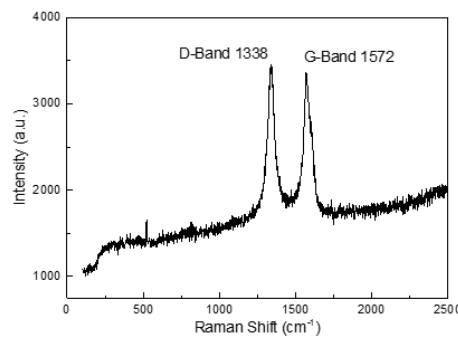
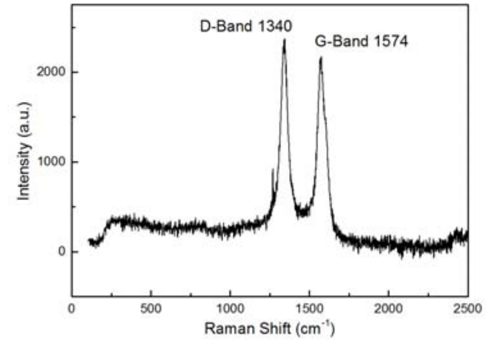
3. Accomplishments
- Growing ultralong VACNTs

Fe/Al_2O_3 (nm/nm)	4/20	3/20	2/20	3/40
SEM micrograph				
Raman spectrum				

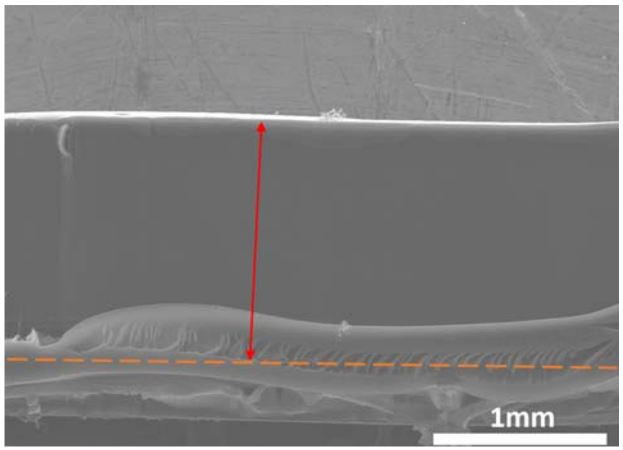
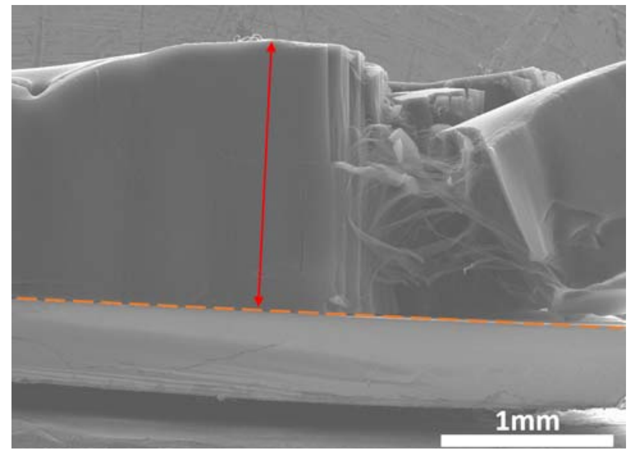
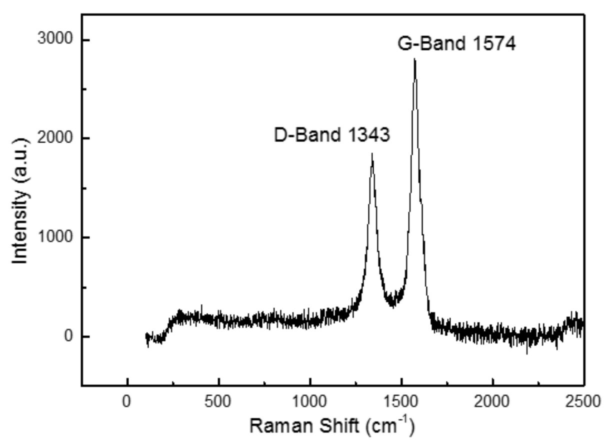
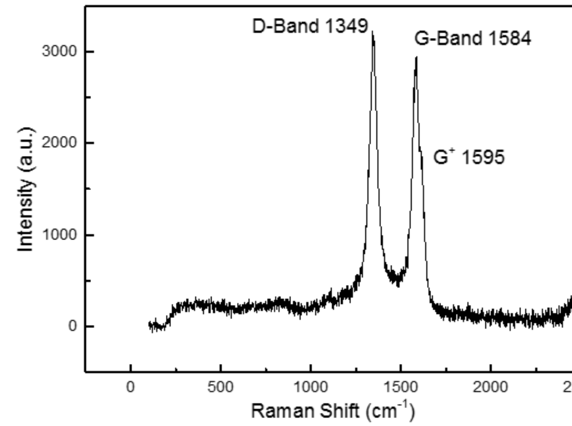
3. Accomplishments
- Growing ultralong VACNTs

	Catalyst Pretreatment	CNT Growth	Flushing	Cooling
T(°C)	RT 750	750	750	RT
Time(min)	20	60	1	>60
Ar(sccm)	600	600	600	1000
H_2(sccm)	400	400	400	
C_2H_4(sccm)		variable		
Catalyst	Fe/Al_2O_3(nm/nm): 2/20			

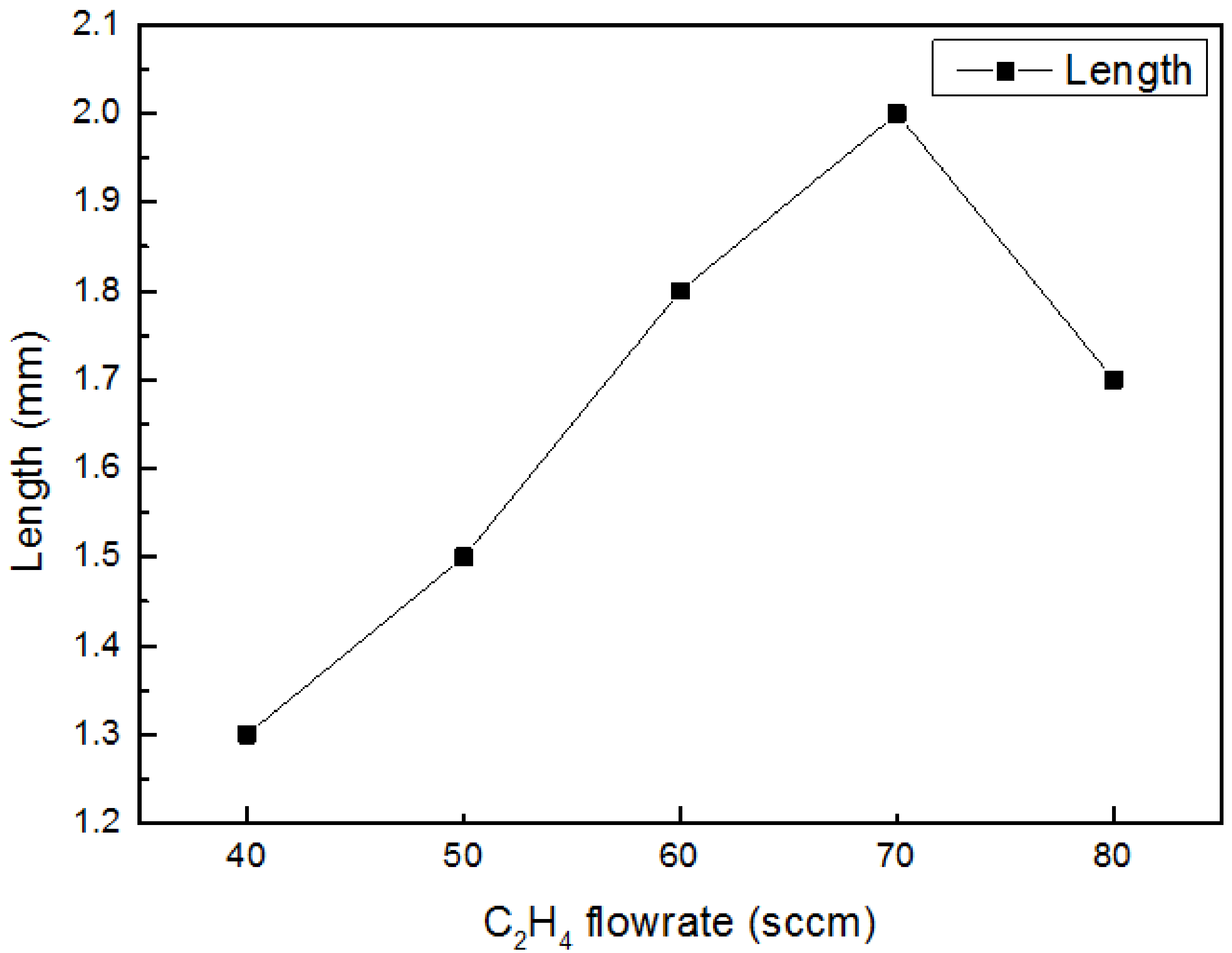
3. Accomplishments
- Growing ultralong VACNTs

C_2H_4 flow rate (sccm)	40	50	60
SEM micrograph			
Raman spectrum			

3. Accomplishments
- Growing ultralong VACNTs

C_2H_4 flow rate (sccm)	70	80
SEM micrograph		
Raman spectrum		

3. Accomplishments
- Growing ultralong VACNTs



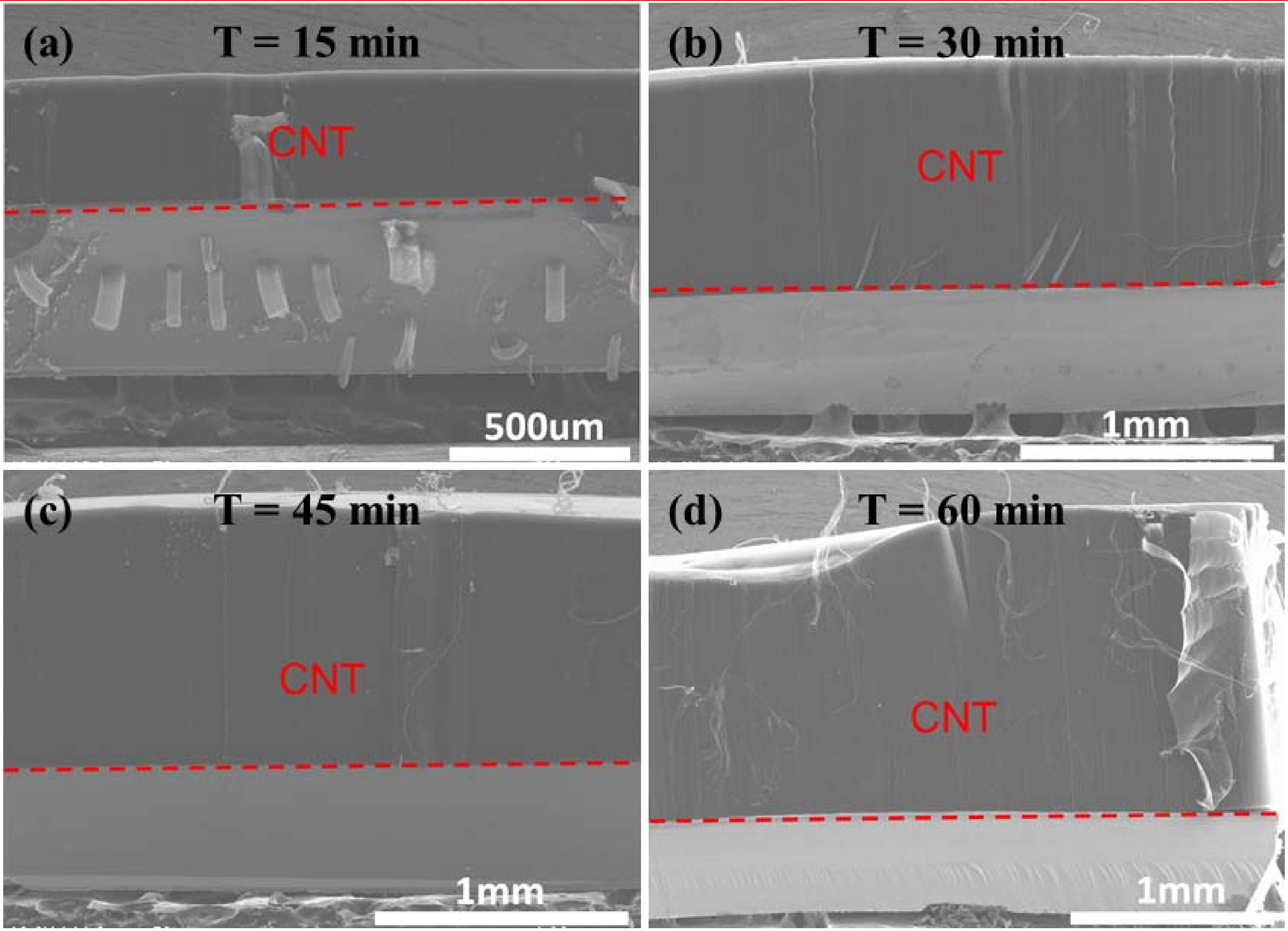
VACNT length vs C_2H_4 flow rate, while all other parameters were fixed

3. Accomplishments

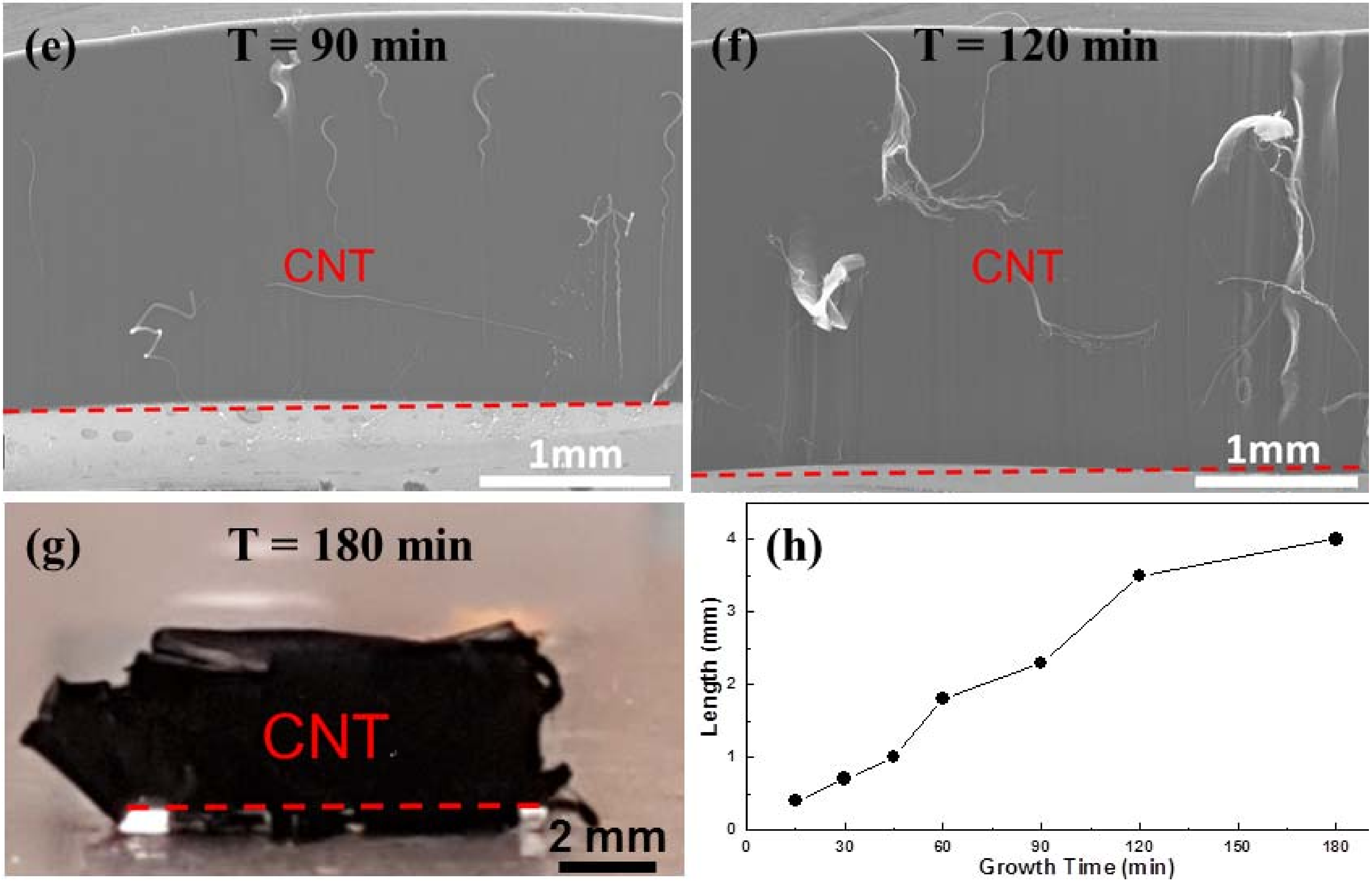
- Growing ultralong VACNTs

	Catalyst Pretreatment	CNT Growth	Flushing	Cooling
T(°C)	RT → 750	750	750	750 → RT
Time(min)	20	variable	1	>60
Ar(sccm)	600	600	600	1000
H_2(sccm)	400	400	400	
C_2H_4(sccm)		70		
Catalyst	Fe/Al_2O_3(nm/nm): 2/20			

3. Accomplishments
- Growing ultralong VACNTs



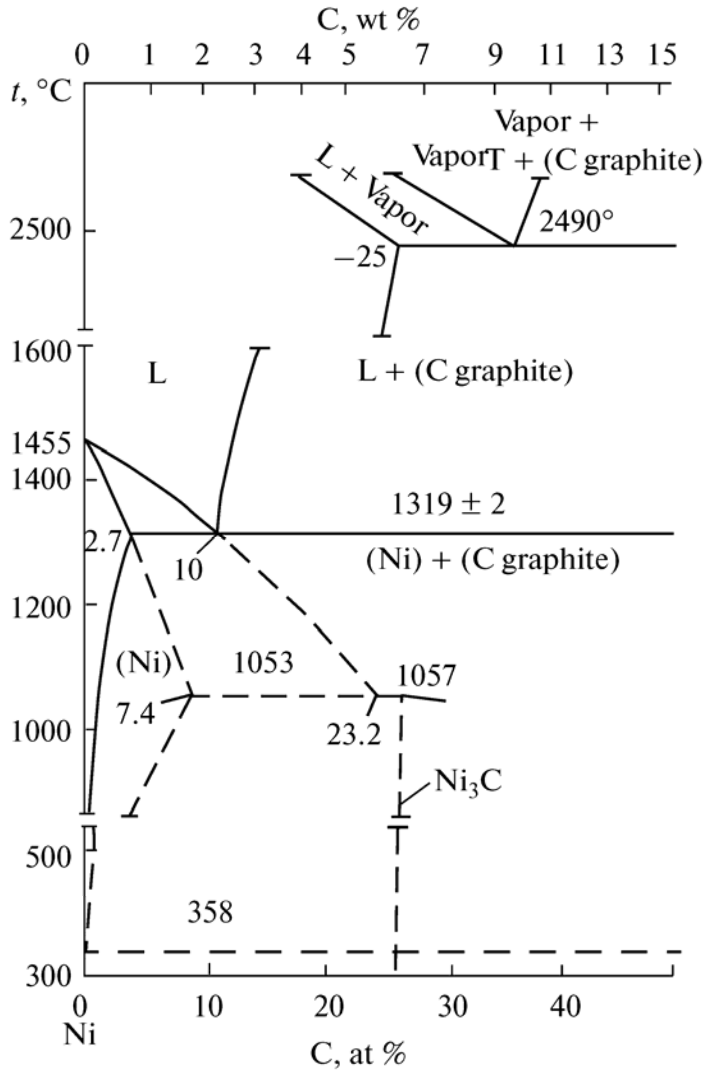
3. Accomplishments
- Growing ultralong VACNTs



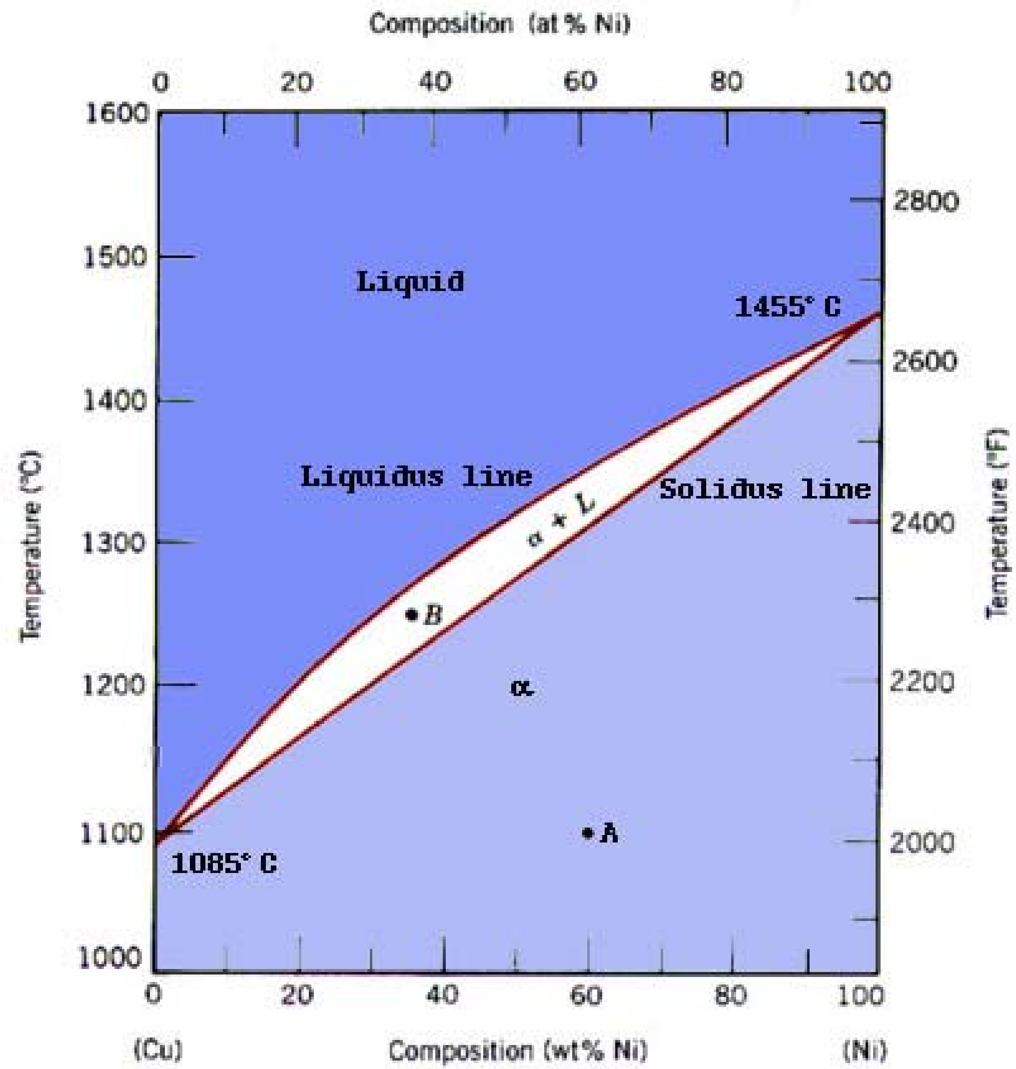
3. Accomplishments
- Growing ultralong VACNTs

VACNTs up to 4 mm long were obtained via a thermal CVD method using a dual-temperature-zone reactor without using water vapor.

3. Accomplishments
- Fabricating VACNT-Cu structures

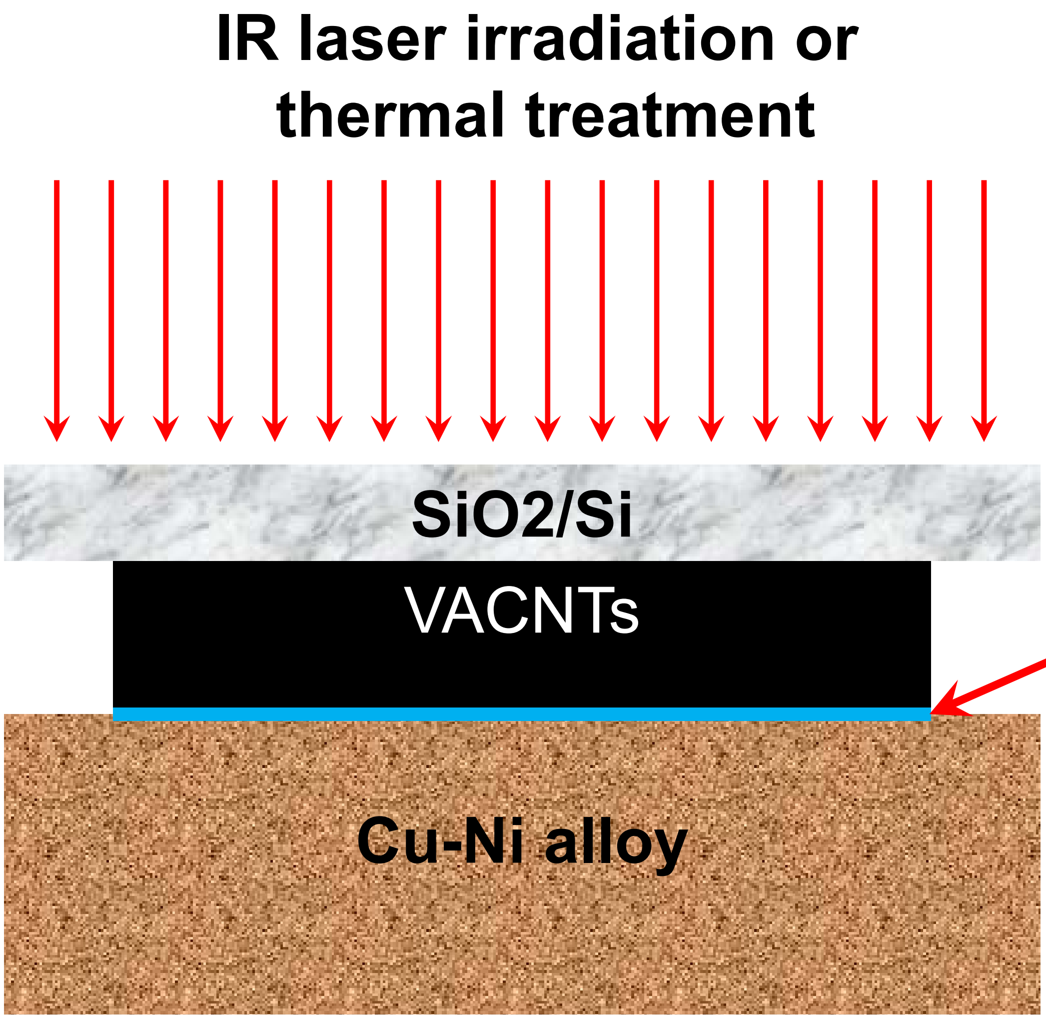


Ref.: Physics of Metals and Metallography 2010, 109, (2), 153-161



http://www.copper.org/publications/newsletters/innovations/2006/03/neptunes_daughters.html

3. Accomplishments
- Fabricating VACNT-Cu structures

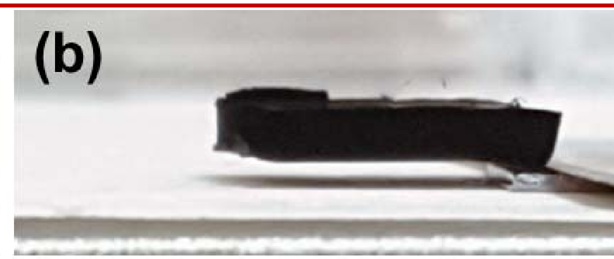


Formation of a carbide interfacial layer to ensure stable contact with metallic thermal and electrical conductivity

3. Accomplishments
- Fabricating VACNT-Cu structures

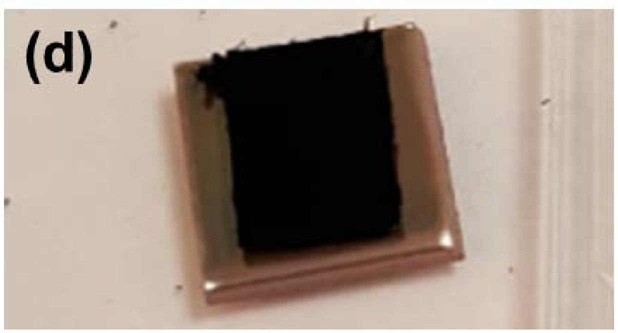
(a)

(b)

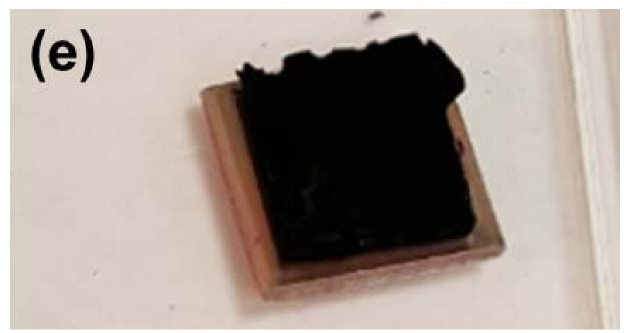


(c)	Heating	Annealing	Cooling
T(°C)	RT → 550	550	RT
Time(min)	15	30	air cooled to RT
Ar(sccm)	500	500	500

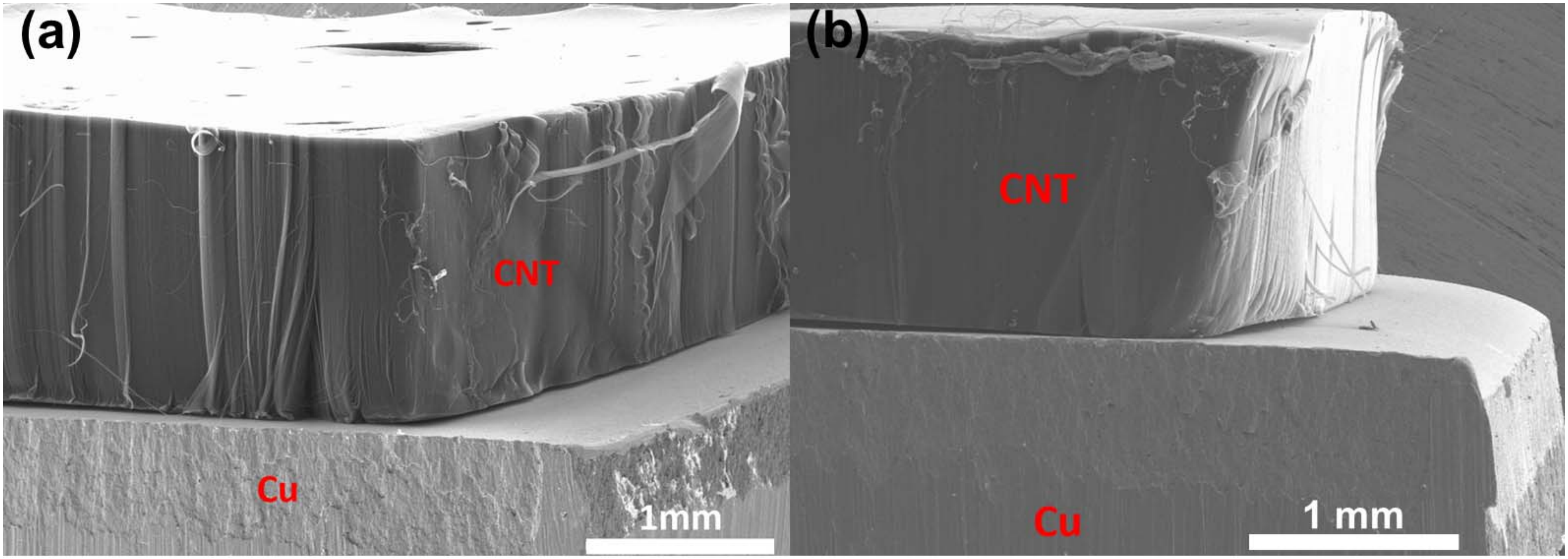
(d)



(e)

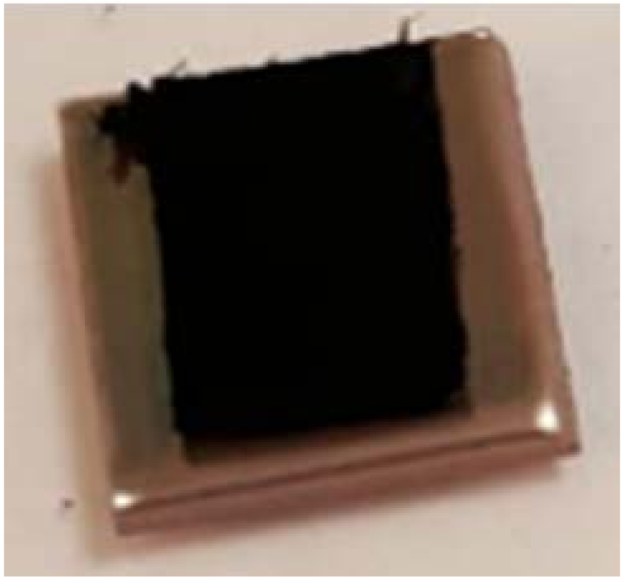


3. Accomplishments
- Fabricating VACNT-Cu structures

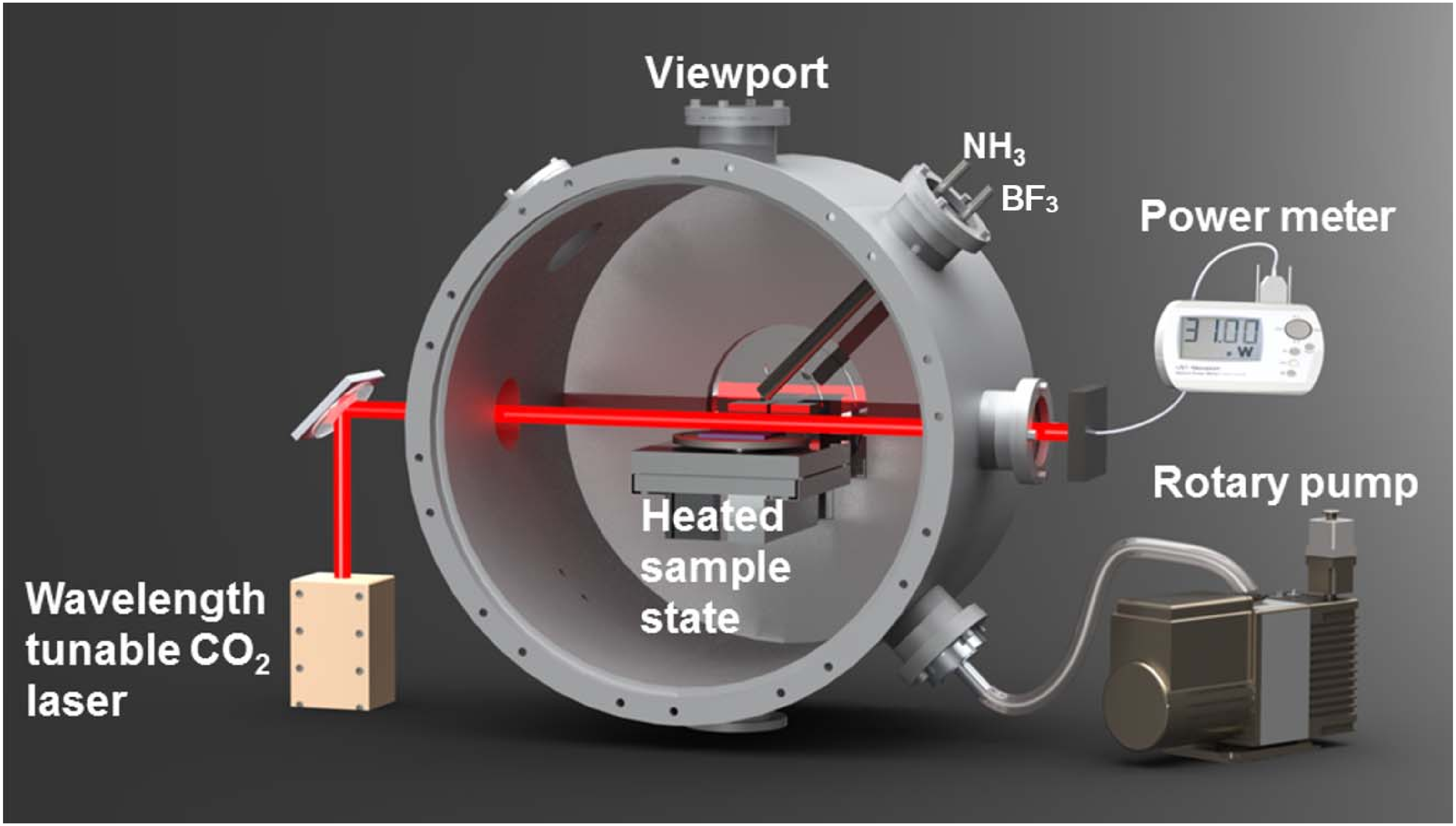


3. Accomplishments
- Fabricating VACNT-Cu structures

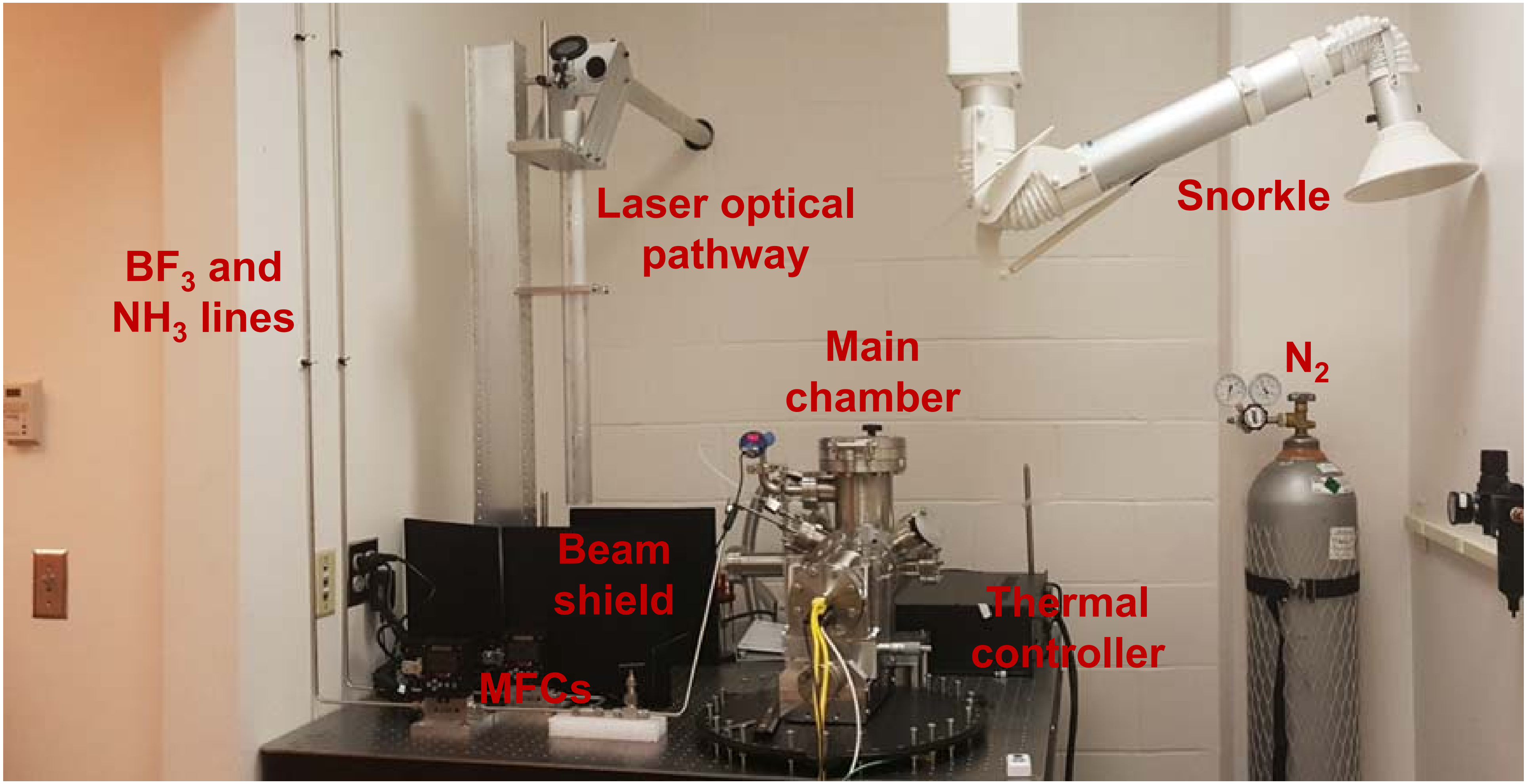
VACNT-Cu structures were fabricated via using a nickel carbide interfacial layer.



3. Accomplishments
- Building a LCVD system for growing BN

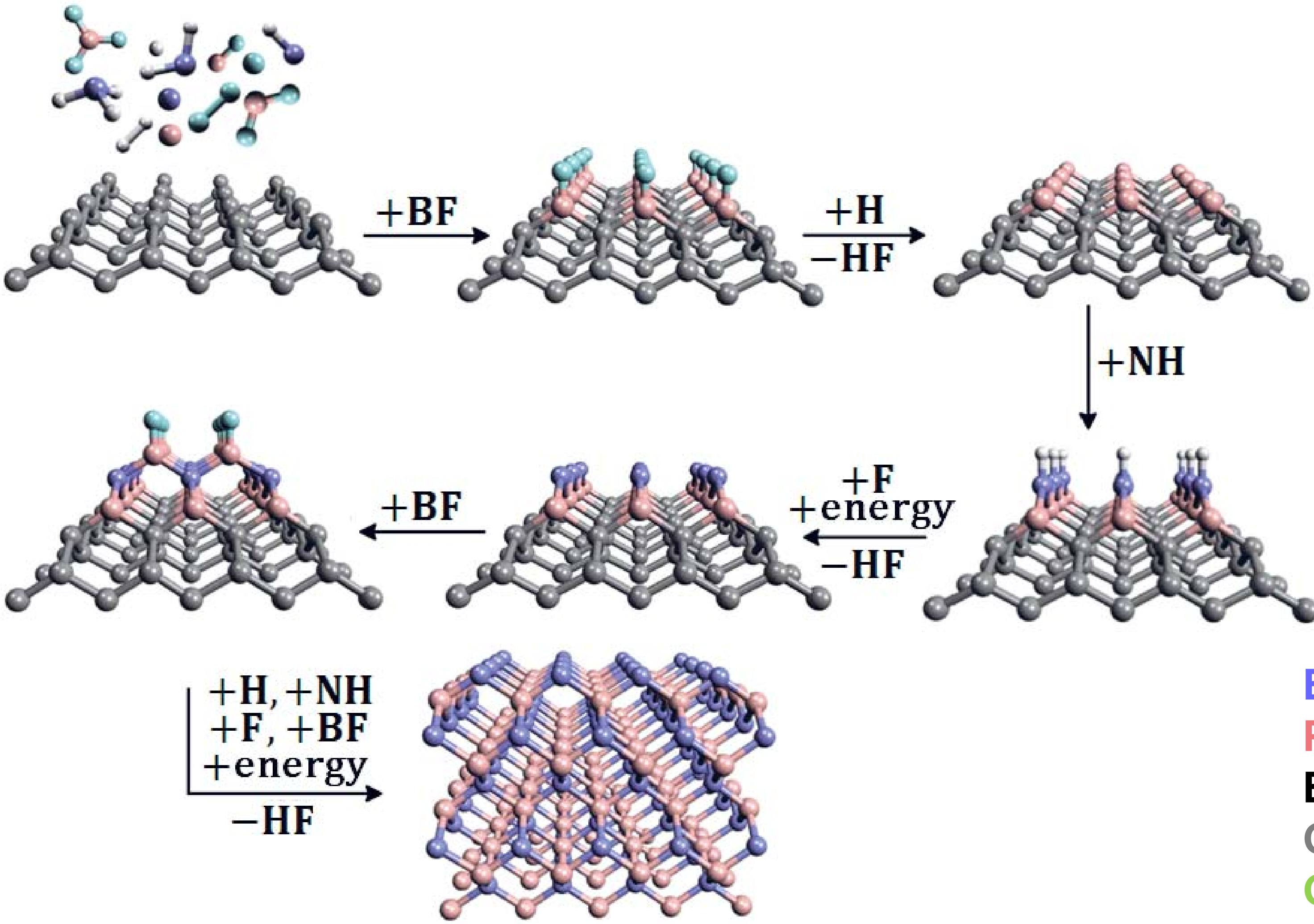


3. Accomplishments
- Building a LCVD system for growing BN



3. Accomplishments

- Building a LCVD system for growing BN

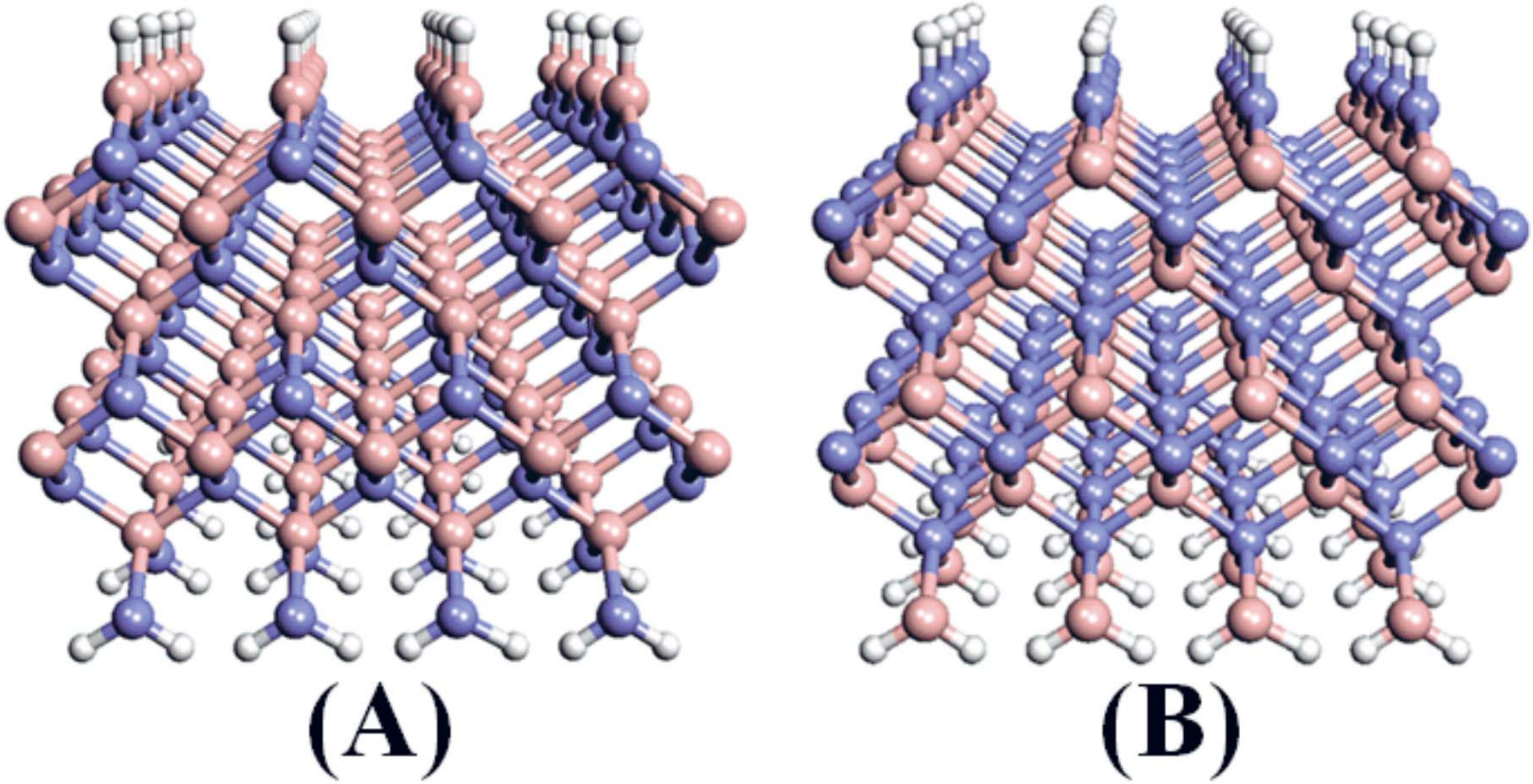


Blue ball: N
Pink ball: B
Black ball: Si
Grey ball: H
Green ball: F

Growing c-BN from BF_x and NH_x species (x = 0, 1, 2, 3) in an H/F-saturated gas

Johan Karlsson, Theoretical Routs for c-BN Thin Film Growth, Dissertation presented at Uppsala University

3. Accomplishments
- Building a LCVD system for growing BN

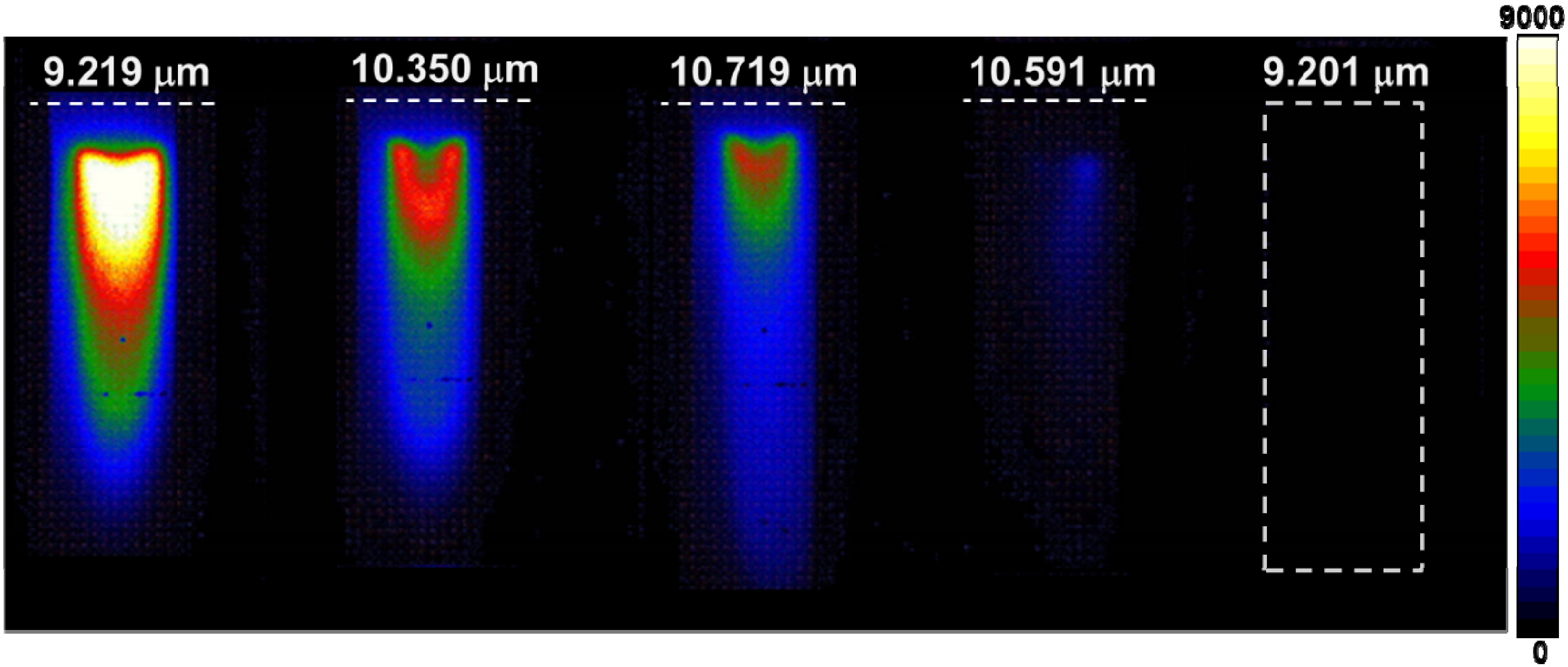


Supercells of the H- or F-covered (A) B- and (B) N-terminated c-BN(100) surfaces.

Blue ball: N
Pink ball: B
Grey ball: H or F

Johan Karlsson, Theoretical Routs for c-BN Thin Film Growth, Dissertation presented at Uppsala University

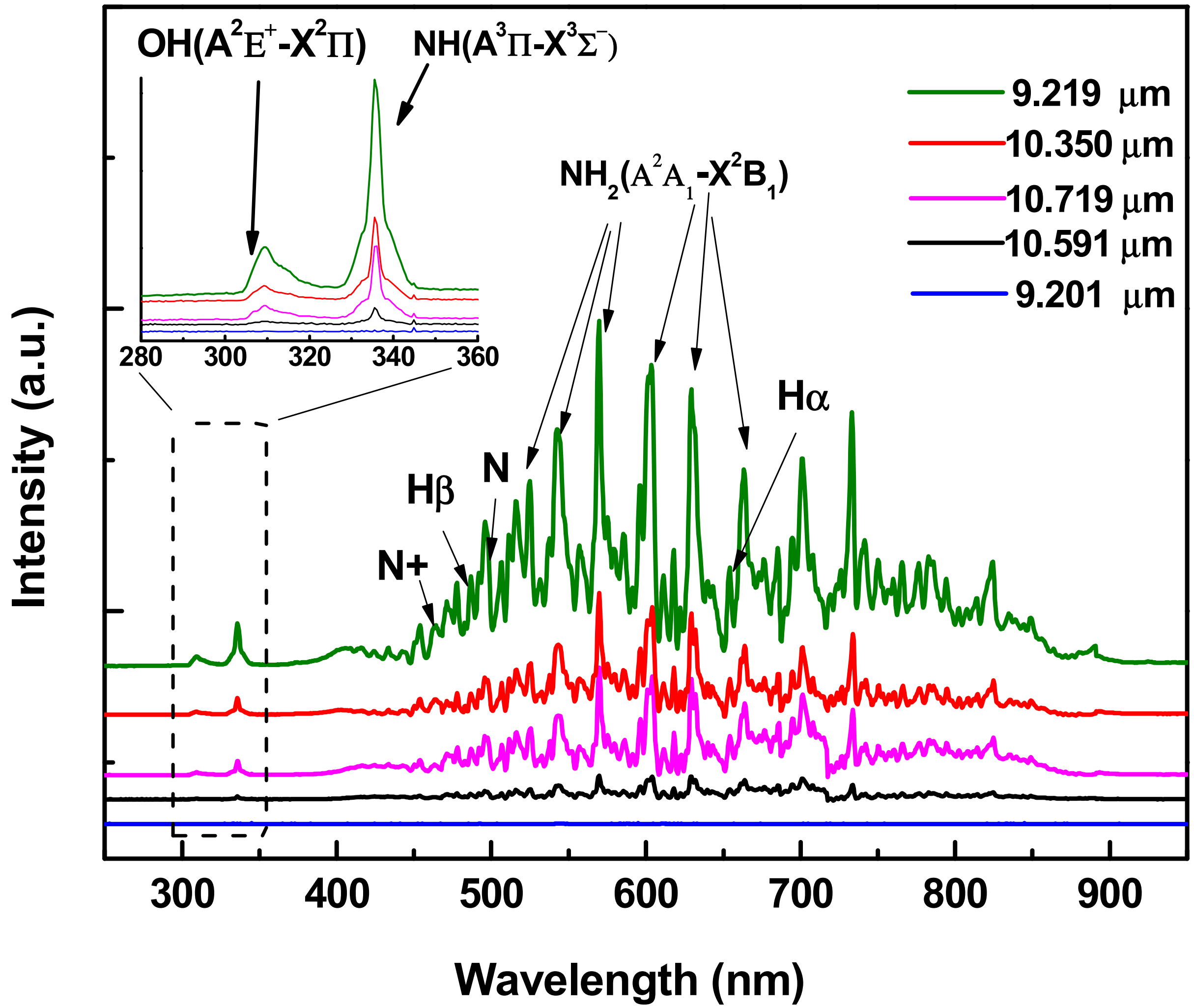
3. Accomplishments
- Building a LCVD system for growing BN



Optical images of NH_3 flows when irradiated at different laser wavelengths in open air.

3. Accomplishments

- Building a LCVD system for growing BN



OES spectra of NH_3 under laser irradiation at different wavelengths in open air.

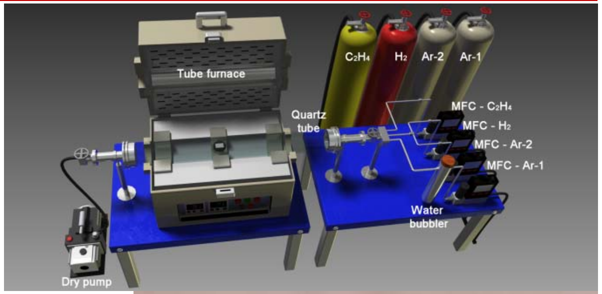
3. Accomplishments

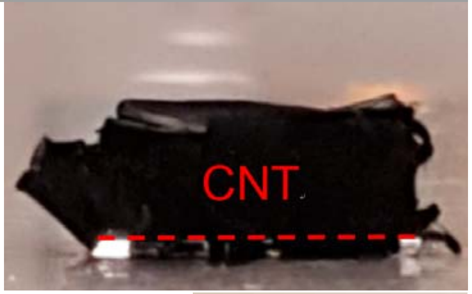
- Building a LCVD system for growing BN

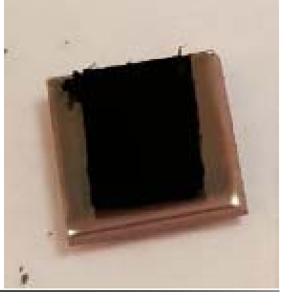
A LCVD system was established.

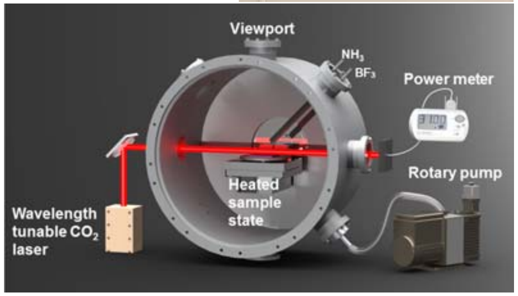
3. Accomplishments
- Summary

1) **Established a WVA-CVD system**
2) **Obtained ultralong VACNTs upto 4 mm long**
3) **Obtained VACNT-Cu structure**
4) **Establishing a LCVD system**





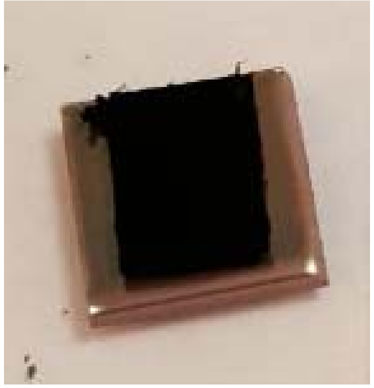




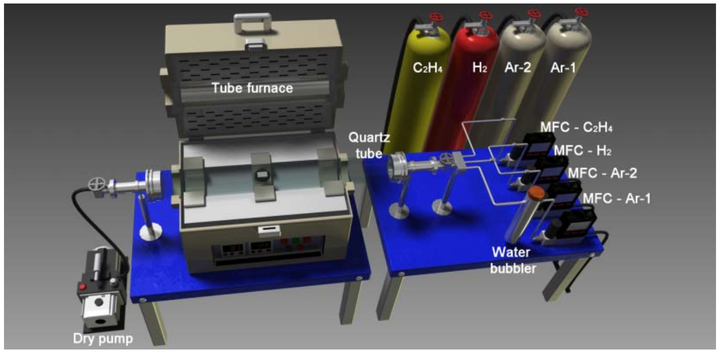
4. Deliverables

1. Ultralong VACNTs up to 4 mm

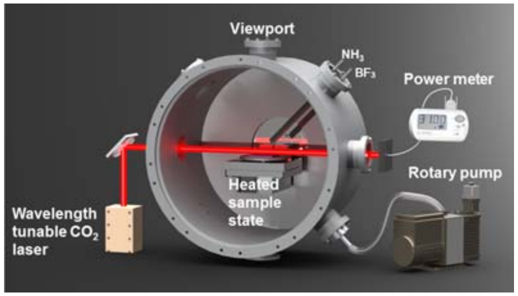
2. VACNT-Cu structure



3. WVA-CVD system



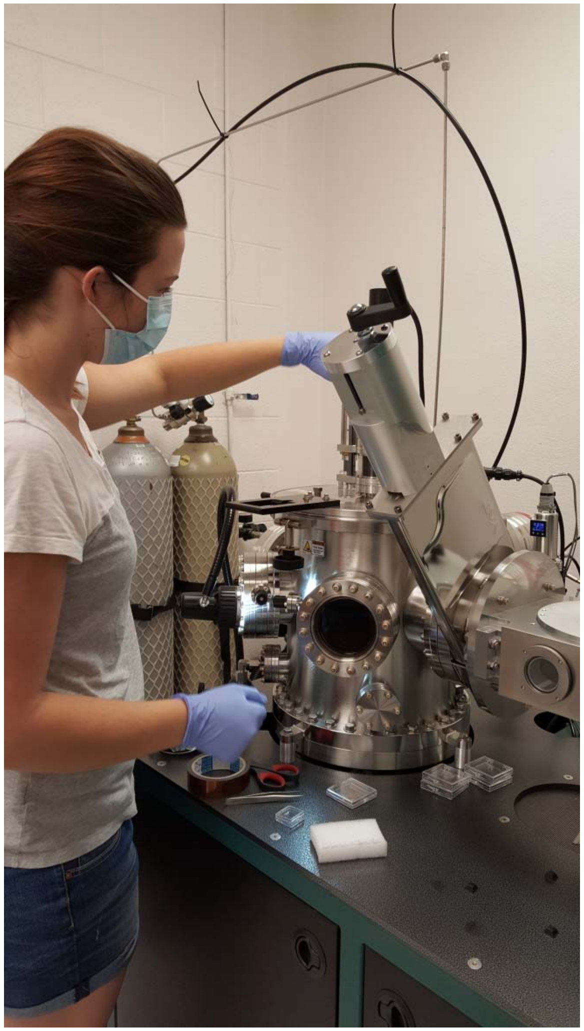
4. LCVD system



5. Planned Activities in the Next-Phase

1. Growing VACNT patterns (accommodating BN among CNTs);
2. Fabricating VACNT-Cu structure that can work at a temperature above 2000 ˚C;
3. Growing BN using the LCVD method;
4. Fabricating VACNT-BN-Cu structure;
5. Studying electrical and thermal properties of the VACNT-Cu and VACNT-BN-Cu structures; and
6. Investigating thermal stability of the VACNT-BN and VACNT-BN-Cu structures.

6. Student Training



Student	Program	Training
Qiming Zou	PhD student at UNL	Under the support of this project, he was trained with all required experiments and data analysis related to fabricating and characterizing VACNTs, BN, VACNT-Cu, and VACNT-BN-Cu .
Kamran Keramatnejad	PhD student at UNL	Growing ultralong VACNTs for fabricating well-aligned CNT sheets and fibers.
Rachel Jarvis	High-school student at Lincoln North East High School	As a Young Nebraska Scientist Summer High School Researcher, she was trained operating a mask aligner, sputtering system, and WVA-CVD system. In addition, Rachel was able to grow ultralong VACNTs.

Acknowledgements

We would like to express our heartfelt thankfulness for the Department of Energy and National Energy Technology Laboratory (Grant Number: DE-FE0023061) for the generous financial support.

Thank you!