Synthesis and Characterization of N-Doped Carbon Nanoribbons

John Glauber
Miguel Angel Ibarra
Michael Kummer
Advisor: Jessica Campos-Delgado

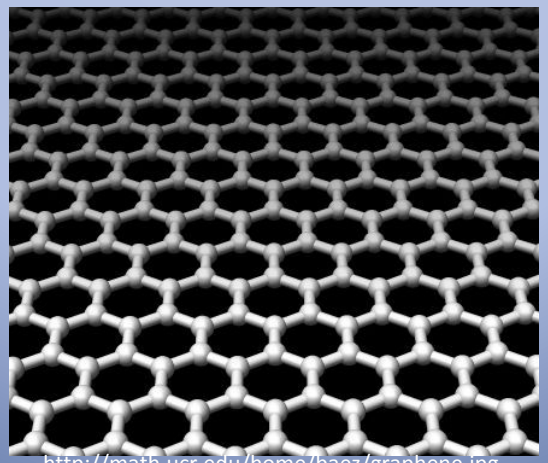
Rice University Summer 2009

Purpose

- To alter the physical and electrical properties of carbon nanoribbons by in-situ CVD nitrogen doping.
- To detect substitutional doping in the carbon lattice or at the edges with the use of:
  - Raman Spectroscopy
  - XRD
  - EDX

Importance of Graphene

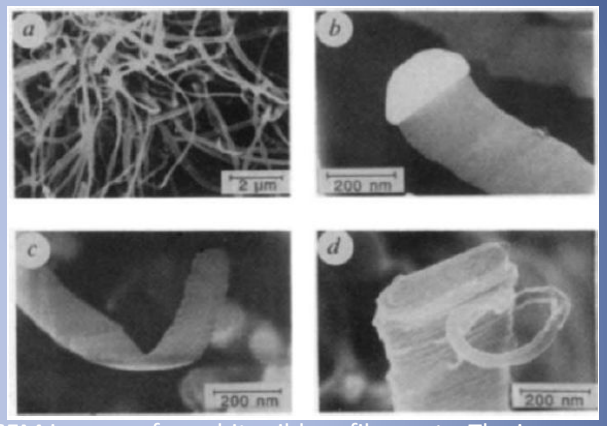
- Single sheets of sp^2 bonded carbon atoms in hexagonal lattice
- **Zero-gap semiconductor** – between a metal and a semiconductor
- **Spin orbit interaction** – spin interacts with motion



http://math.ucr.edu/home/baez/graphene.jpg

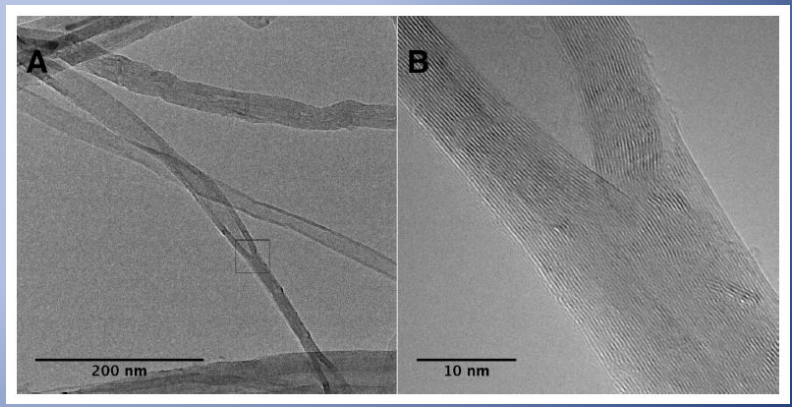
Review of Literature: Carbon Nanoribbons

- Murayama, H. et al. (1990)
  - Disproportionation of carbonmonoxide
    - Carbon monoxide / Hydrogen gas flow with Fe(CO)5
    - Iron carbides serve as catalysts. Growth occurs from tips.
    - 50 vol% products are ribbon filaments produced
    - 86% degree of graphitization
    - Ribbon layers form perpendicular to axis of growth as long as 10µm



SEM images of graphite ribbon filaments. The iron catalyst can be observed at the tip. Murayama, H. et al.

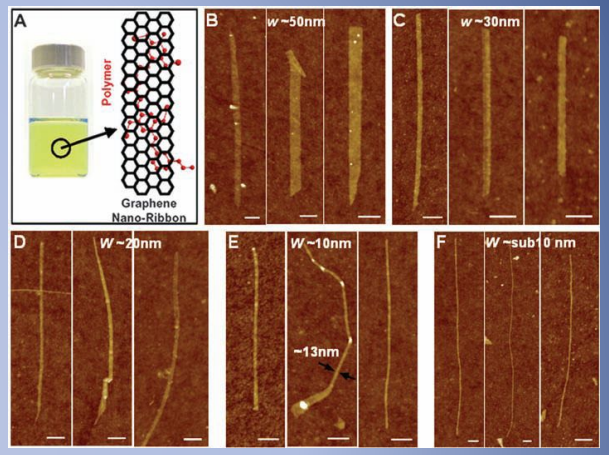
- Cano-Márquez, Abraham G. et al. (2009)
  - Intercalation and Exfoliation
    - Open ended MWCNTs intercalated by Li ion solution in NH_3
    - Exfoliated with HCl
    - Yields ~60% possible



TEM images of intercalated MWCNT. Cano-Márquez, Abraham G. et al.

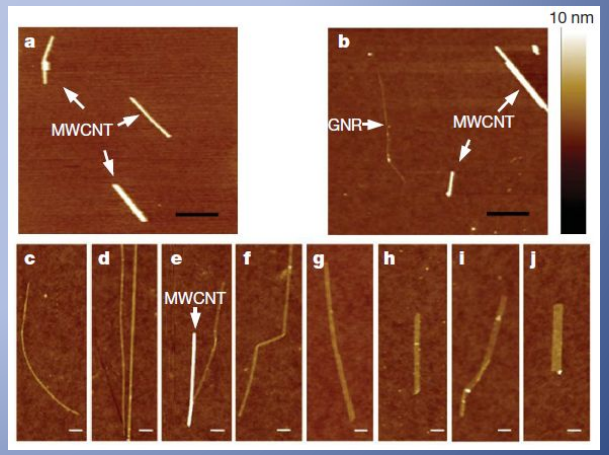
Review of Literature: Carbon Nanoribbons

- Li, Xiaolin et al. (2009)
  - Chemical exfoliation
    - Bulk graphite
    - 60s heating to 1000°C in 3% Ar-H
    - 30 min sonication DCE and PmPV
    - Analysis with AFM
    - Produced graphene nanoribbons (GNR) sub-10 nm widths



AFM images of chemically exfoliated GNRs. Li, Xiaolin et al.

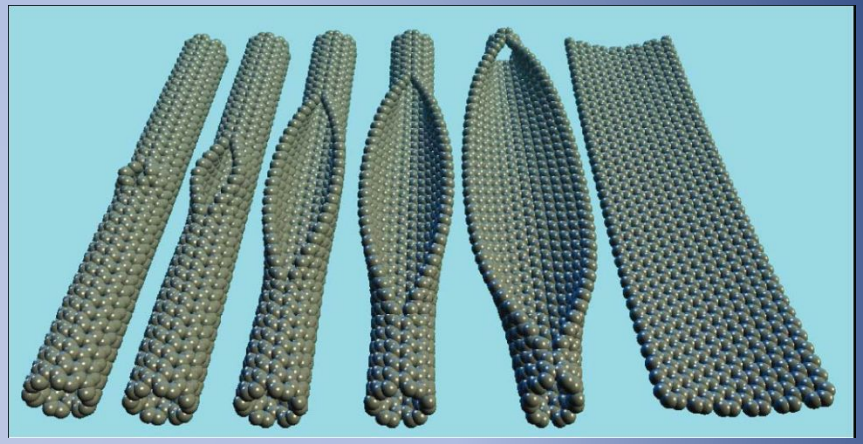
- Jiao, Liying et al. (2009)
  - Unzipping carbon nanotubes
    - Argon Plasma etching of MWCNTs
    - Immerse MWCNTs in PMMA as a protective layer
    - 10W Ar plasma longitudinally etches
    - 10s etching - 20% yield, 10-20 nm width, 2 nm thickness
    - Longer etching times single / few layer GNRs



AFM images of plasma etched carbon nanoribbons. Jiao, Living et al.

Review of Literature: Carbon Nanoribbons

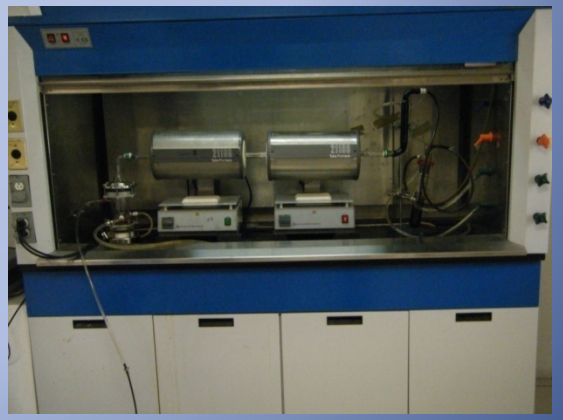
- Kosynkin, Dmitry V. et al. (2009)
  - Unzipping by solution oxidation
    - Suspend MWCNTs in H_2SO_4 and treated with $KMnO_4$
    - 80-100% of MWCNTs form nanoribbons
    - Higher degrees of oxidation with more oxidizing agents



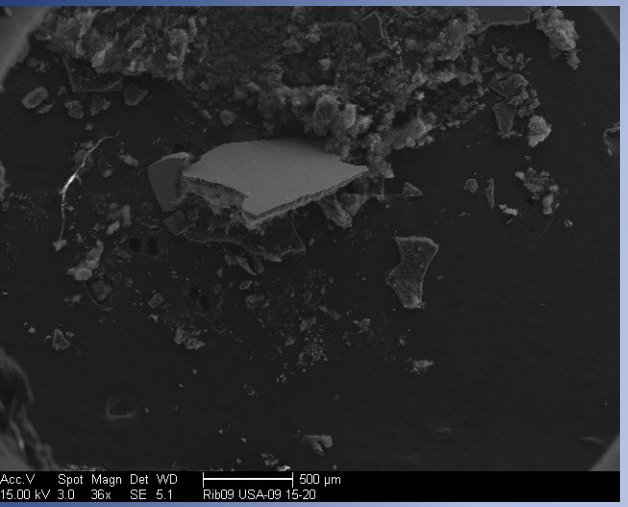
Computer rendering of the unzipping of a single layer of a MWCNT. Kosynkin, Dmitry V. et al.

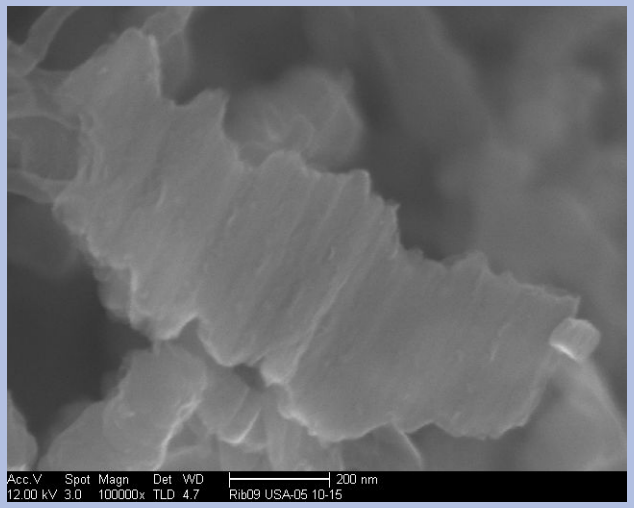
Method

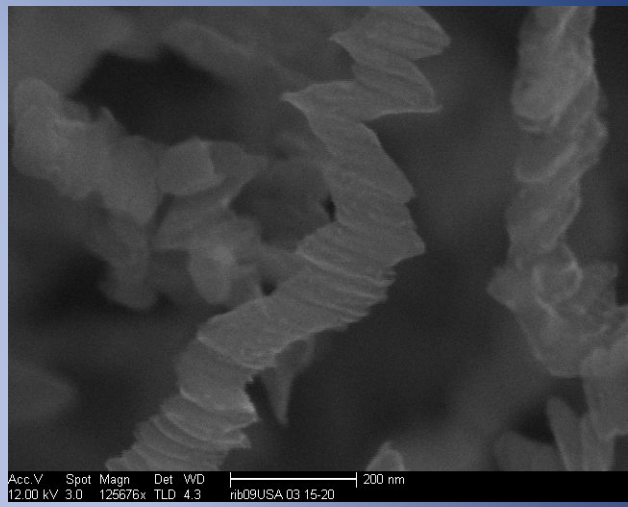
- Chemical Vapor Deposition Pyrolysis
- Solution Preparation:
  - 280 ml (98.625 wt%) Ethanol
  - 2.8035 g (1.25 wt%) Ferrocene
  - 266 µL (0.125 wt%) Thiophene
- Furnace Temperature:
  - 950°C
- Flux Rates:
  - Heat/Cool: 0.2 L/min
  - Synthesis: 0.8 L/min
- Ultrasonic Generator:
  - Wavelength: 590
  - Frequency: 568
- Synthesis Duration:
  - 30min

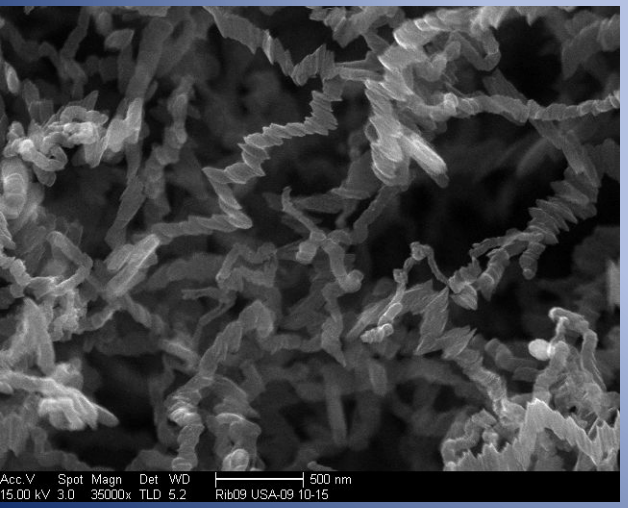


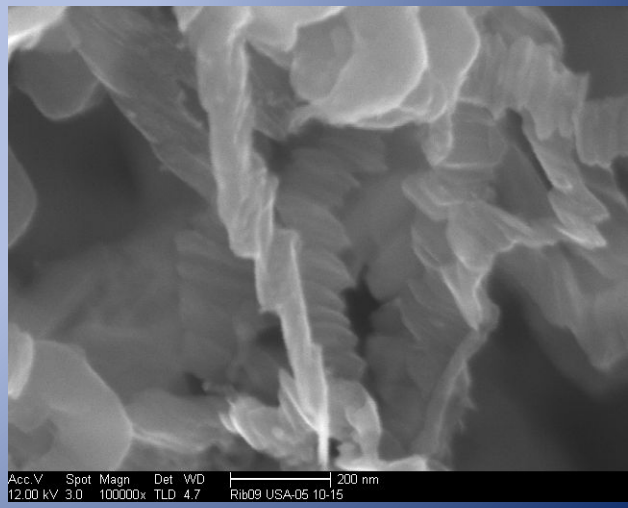
SEM Characterization



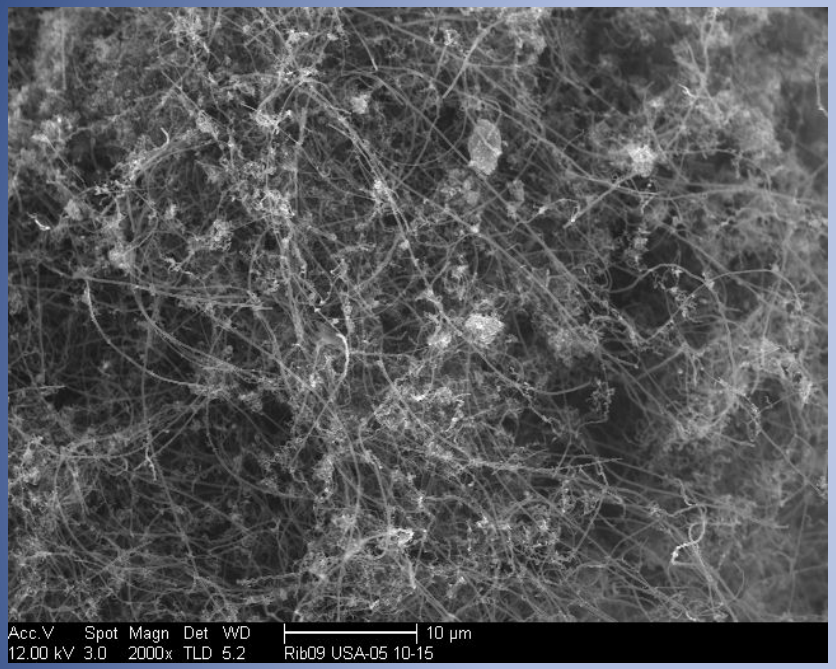


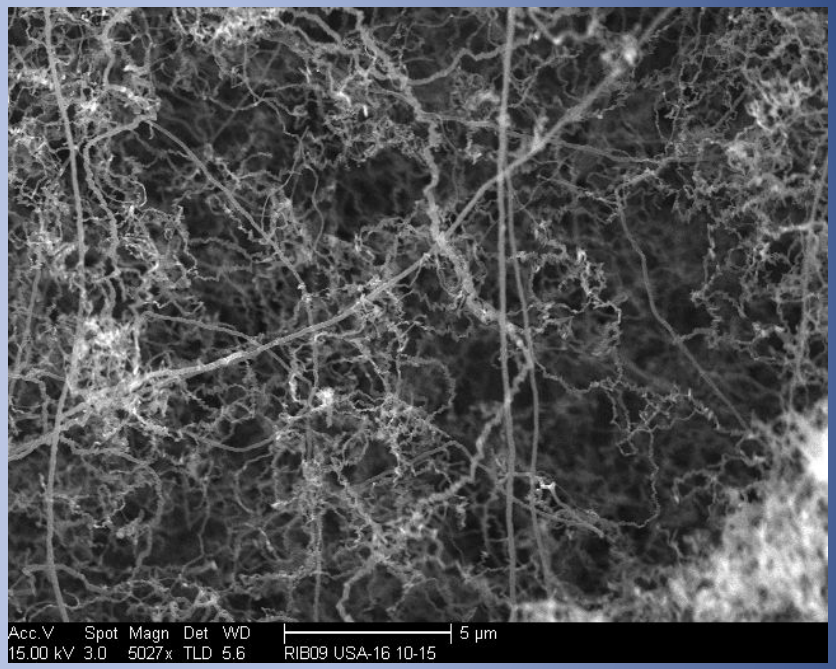






SEM images of pristine carbon nanoribbons synthesized by the CVD pyrolysis process

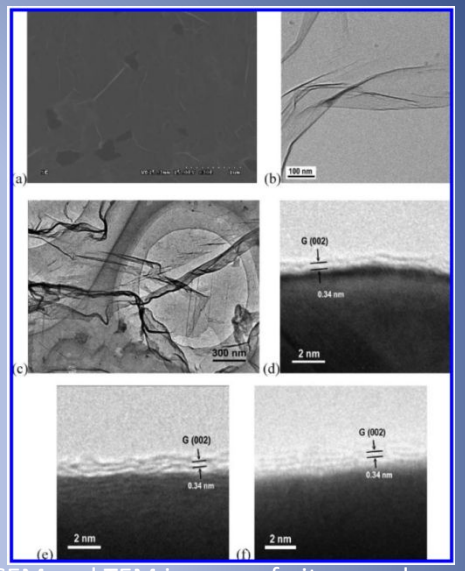




Evidence of fiber and tube growth in pristine carbon nanoribbon sample.

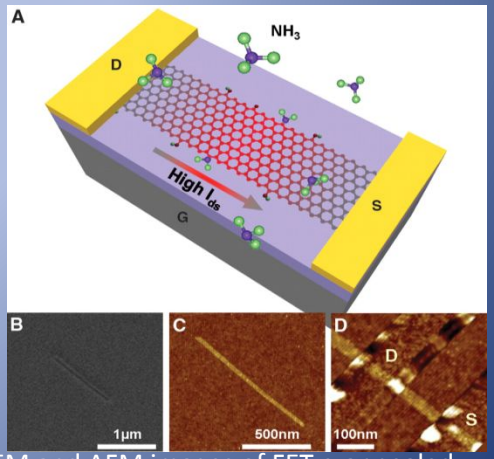
Review of Literature: N-Doped Nanoribbons

- Wei, Dacheng et al. (2009)
  - CVD synthesis
    - Cu film on Si substrate used as catalyst
    - Ar/H flow during heating
    - CH_4 and NH_3 flow for 10min of synthesis.
    - Cooled in H_2 environment
    - Produced few layer graphene
    - Nitrogen substituted into lattice
      - Pyrrolic and pyridinic N atoms detected



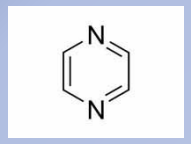
SEM and TEM images of nitrogen doped graphene. Wei, Dacheng et al.

- Wang, Xinran et al. (2009)
  - Electrical annealing in NH_3 environment
    - High vacuum environment
    - N doping occurs at edges with C atom being substituted
    - Clear N signal detected by XPS
    - P- and N-doping due to oxygen functionalization



SEM and AFM images of FET e-annealed GNR device. Wang, Xinran et al.

Physical Properties

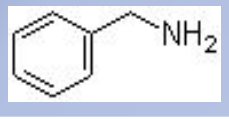


Pyrazine

Molecular Formula	$C_4H_4N_2$
Molar Mass	80.09 g/mol
Appearance	White crystals
Density	1.031 g/cm^3
Melting point	52 °C
Boiling point	115 °C
Solubility in water	Soluble

Adapted from:
http://en.wikipedia.org

Physical Properties

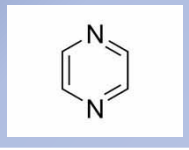


Benzylamine

Molecular Formula	C_7H_9N
Molar Mass	107.15 g mol^{-1}
Appearance	Colorless liquid
Density	0.981 g/mL
Melting Point	-30 °C (22°F)
Boiling Point	183 °C (361.4°F)
Solubility in water	3.24 g / 100 g water @ 25 °C
Solubility in methanol	methanol 9.16 M

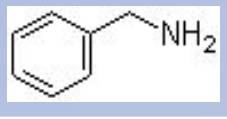
Adapted from: http://en.wikipedia.org

Method of Production: In-Situ N-Doped nanoribbons

Pyrazine ($C_4H_4N_2$) 

Pyrazine Concentration (wt %)	**0.125**	**1**	**3**
Ferrocene Concentration (wt %)	1.25	1.25	1.25
Thiophene Concentration (wt %)	0.125	0.125	0.125
Furnace Temperature (°C)	950	950	950
Synthesis Duration (min)	30	30	30
Argon Flux Rates (L/min)	Purge: 0.2 L/min Synthesis: 0.8 L/min	Purge: 0.2 L/min Synthesis: 0.8 L/min	Purge: 0.2 L/min Synthesis: 0.8 L/min

Method of Production: In-Situ N-Doped nanoribbons

Benzylamine (C_7H_9N) 

Benzylamine Concentration (wt %)	**3**	**5**	**10**
Ferrocene Concentration (wt %)	1.25	1.25	1.25
Thiophene Concentration (wt %)	0.125	0.125	0.125
Furnace Temperature (°C)	950	950	950
Synthesis Duration (min)	30	30	30
Argon Flux Rates (L/min)	Purge: 0.2 L/min Synthesis: 0.8 L/min	Purge: 0.2 L/min Synthesis: 0.8 L/min	Purge: 0.2 L/min Synthesis: 0.8 L/min

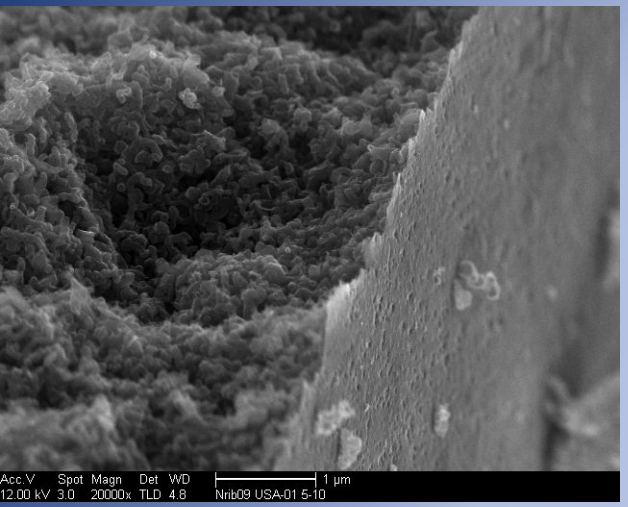
Characterization Methods

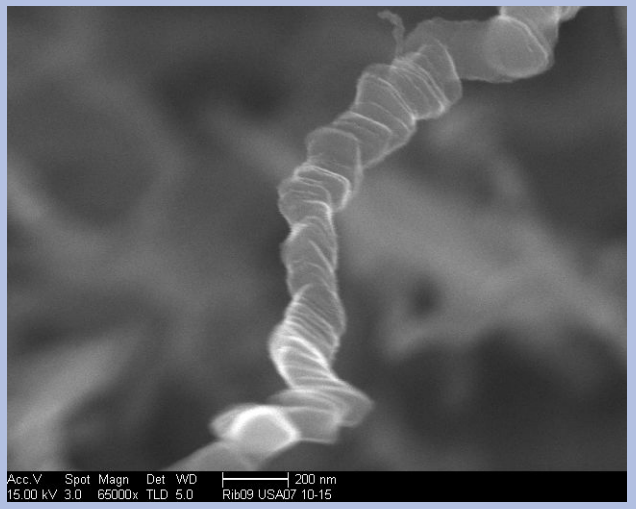
- SEM
- TEM
- XRD
- Raman
- PPMS

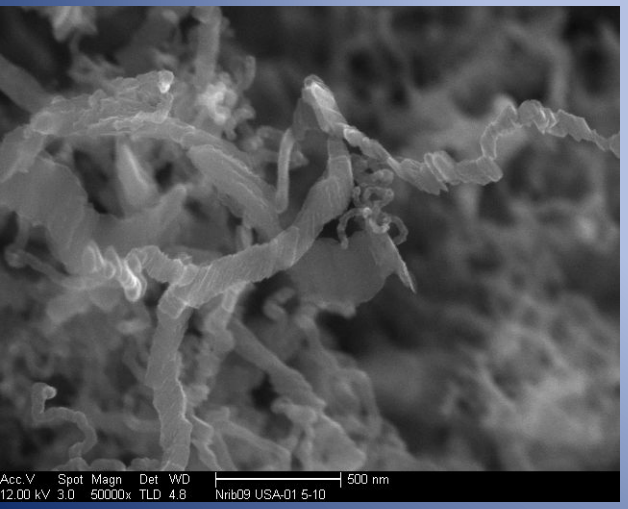
0.125% Pyrazine; 1.0% Pyrazine; 3.0% Pyrazine

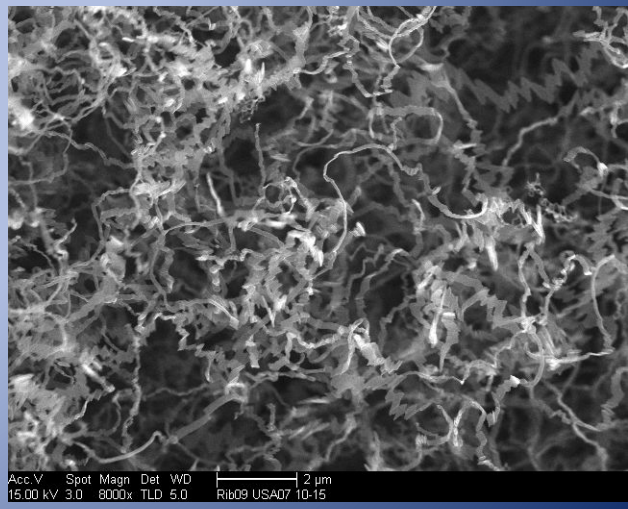
SEM

0.125 wt% Pyrazine

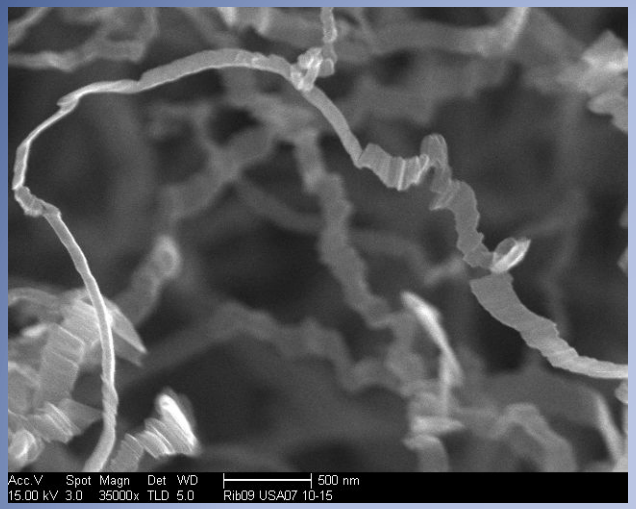


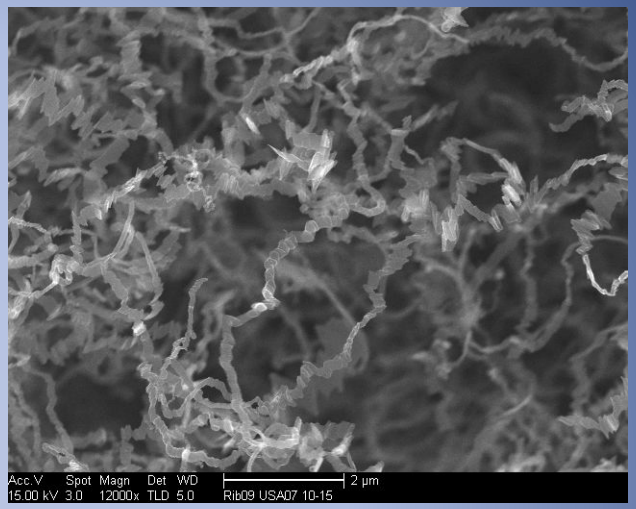


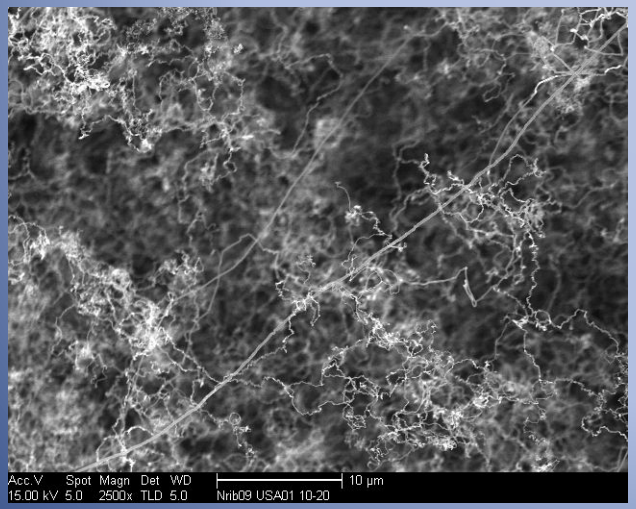


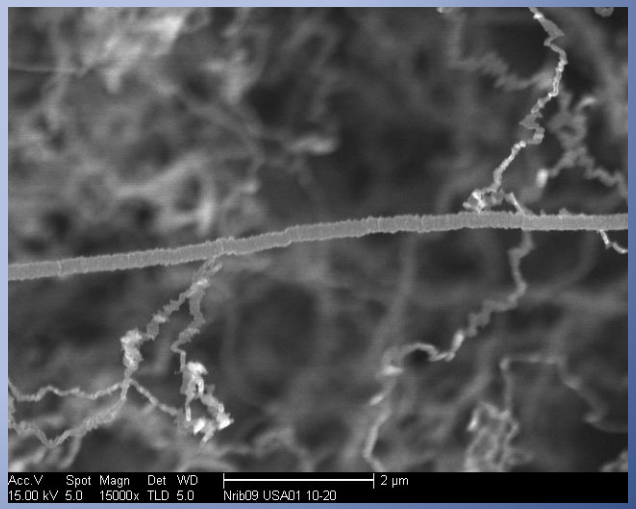


SEM images of carbon nanoribbons doped with 0.125 wt% pyrazine.

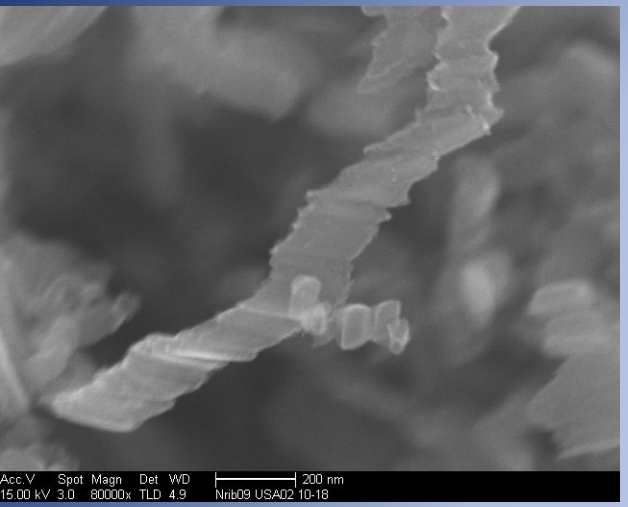

Acc.V Spot Magn Det WD 500 nm
15.00 kV 3.0 35000x TLD 5.0 Rib09 USA07 10-15

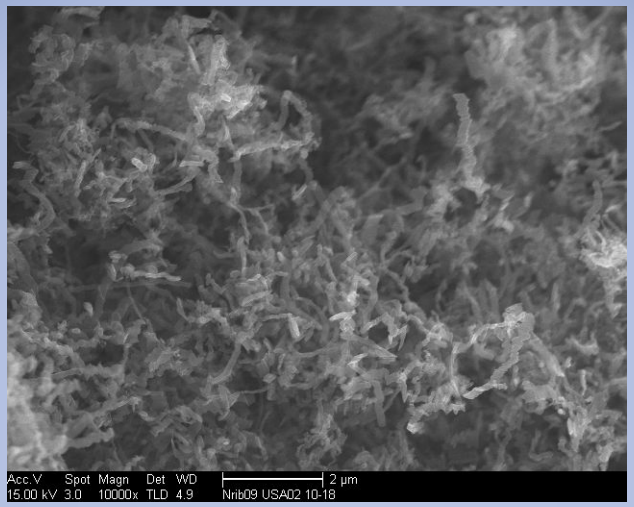

Acc.V Spot Magn Det WD 2 µm
15.00 kV 3.0 12000x TLD 5.0 Rib09 USA07 10-15

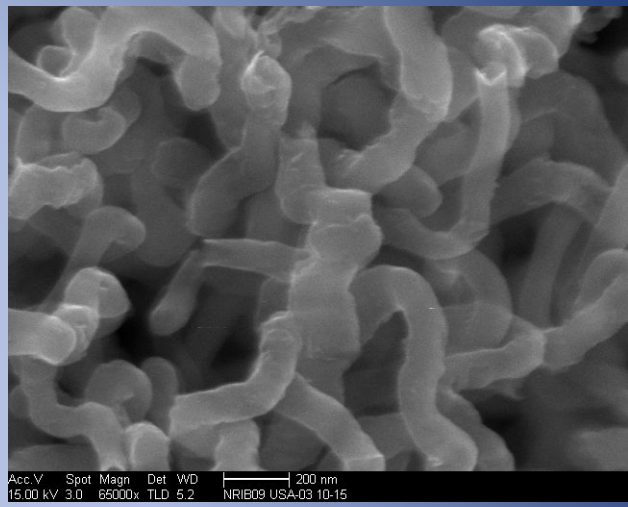

Acc.V Spot Magn Det WD 10 µm
15.00 kV 5.0 2500x TLD 5.0 Nrib09 USA01 10-20

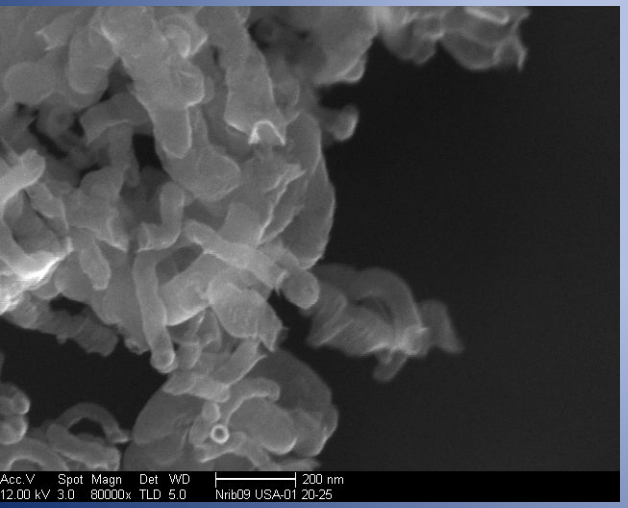

Acc.V Spot Magn Det WD 2 µm
15.00 kV 5.0 15000x TLD 5.0 Nrib09 USA01 10-20

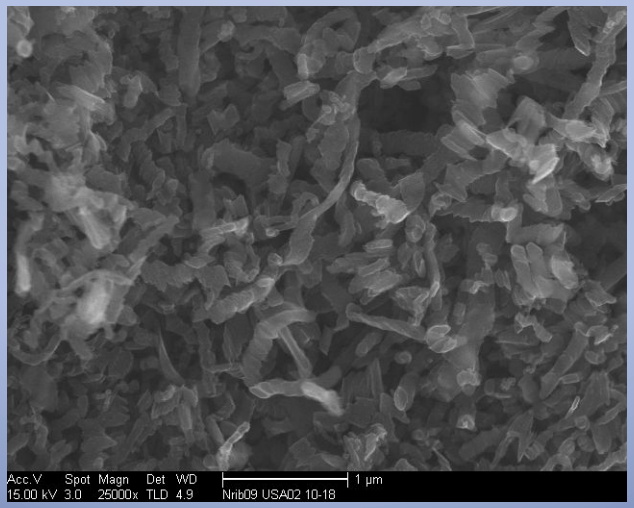
1.0 wt% Pyrazine

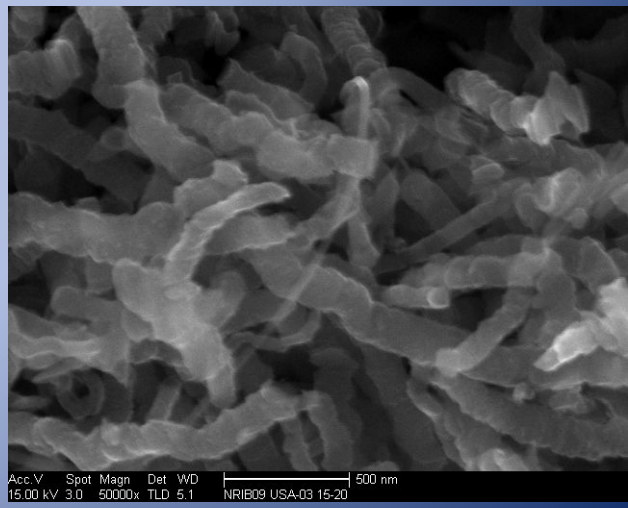






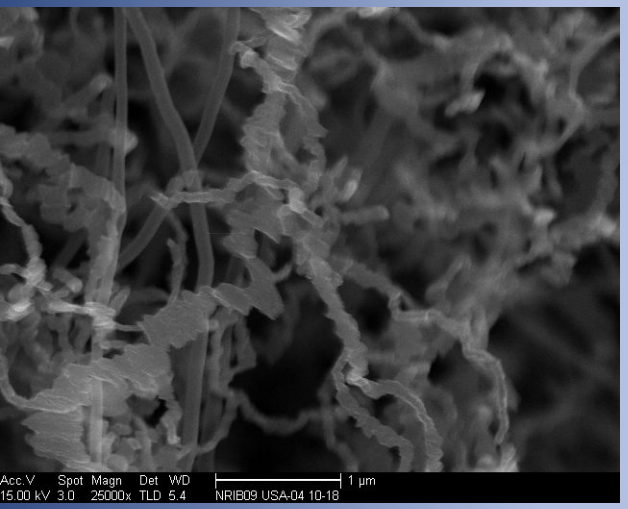


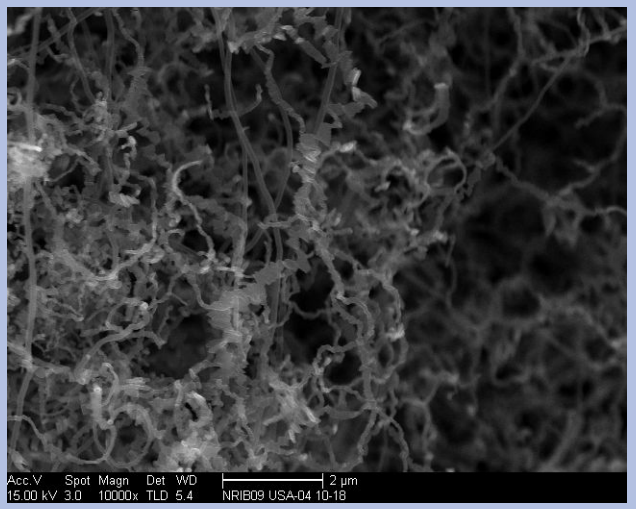


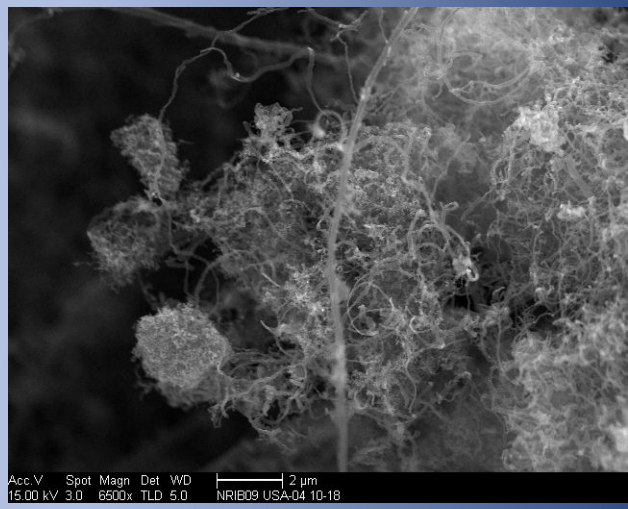


SEM images of carbon nanoribbons doped with 1.0 wt% pyrazine. Higher concentrations of worm and tube growth are apparent.

3.0 wt% Pyrazine





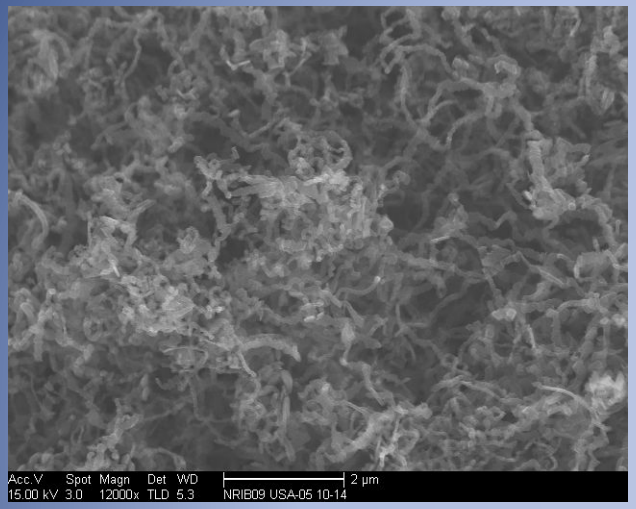


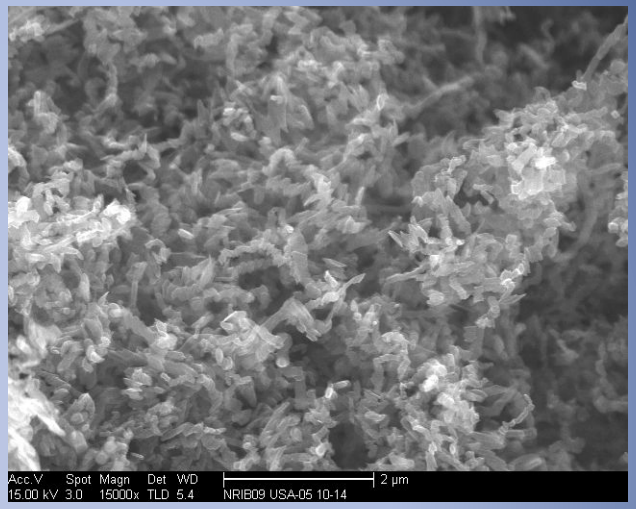
SEM images of carbon nanoribbons doped with 3.0 wt% pyrazine. Higher concentrations of tube and fiber growth are apparent.

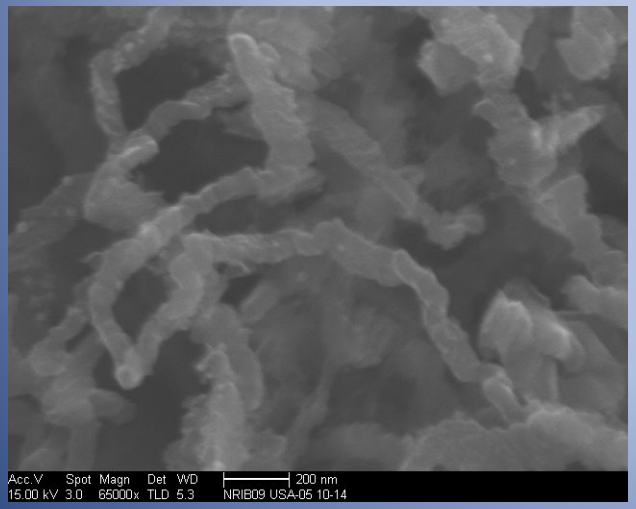
3.0 wt% Benzylamine, 5.0 wt% Benzylamine, 10.0 wt% Benzylamine

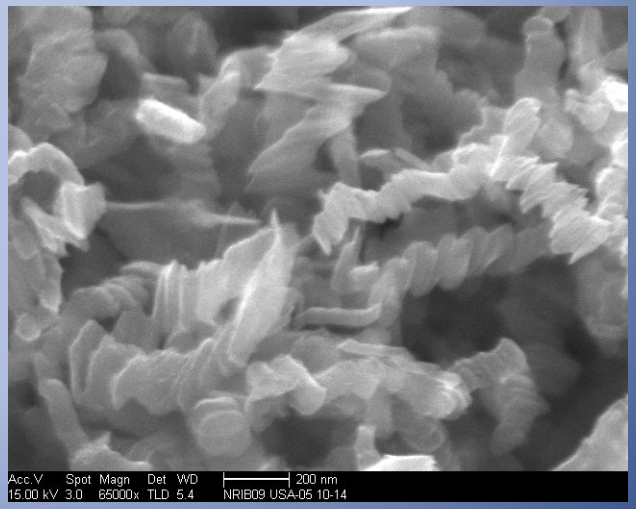
SEM

3.0 wt% Benzylamine



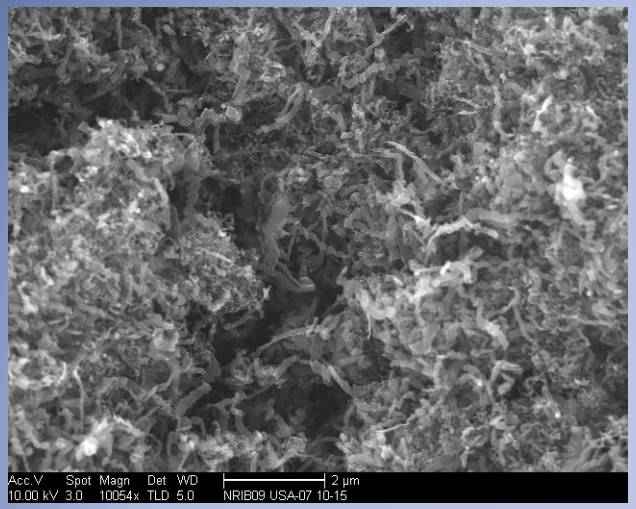


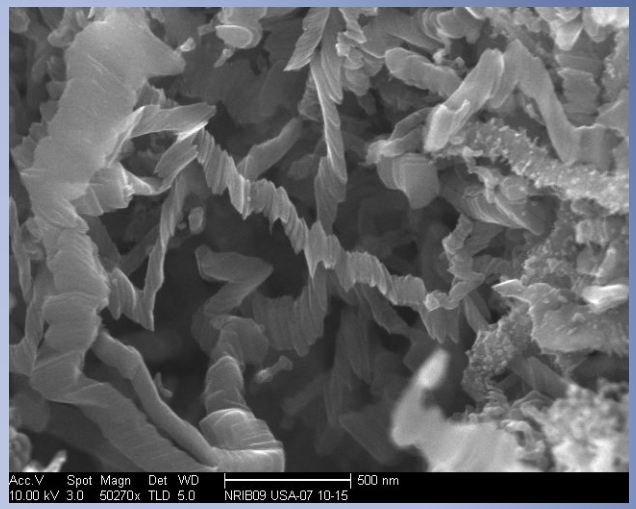


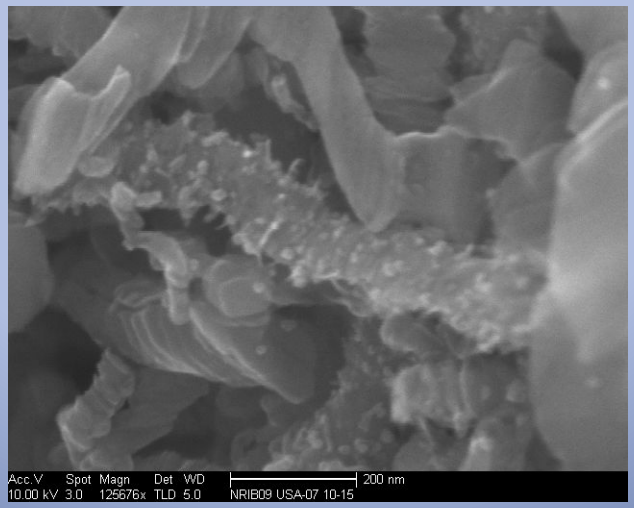


SEM images of carbon nanoribbons doped with 3.0 wt% benzylamine.

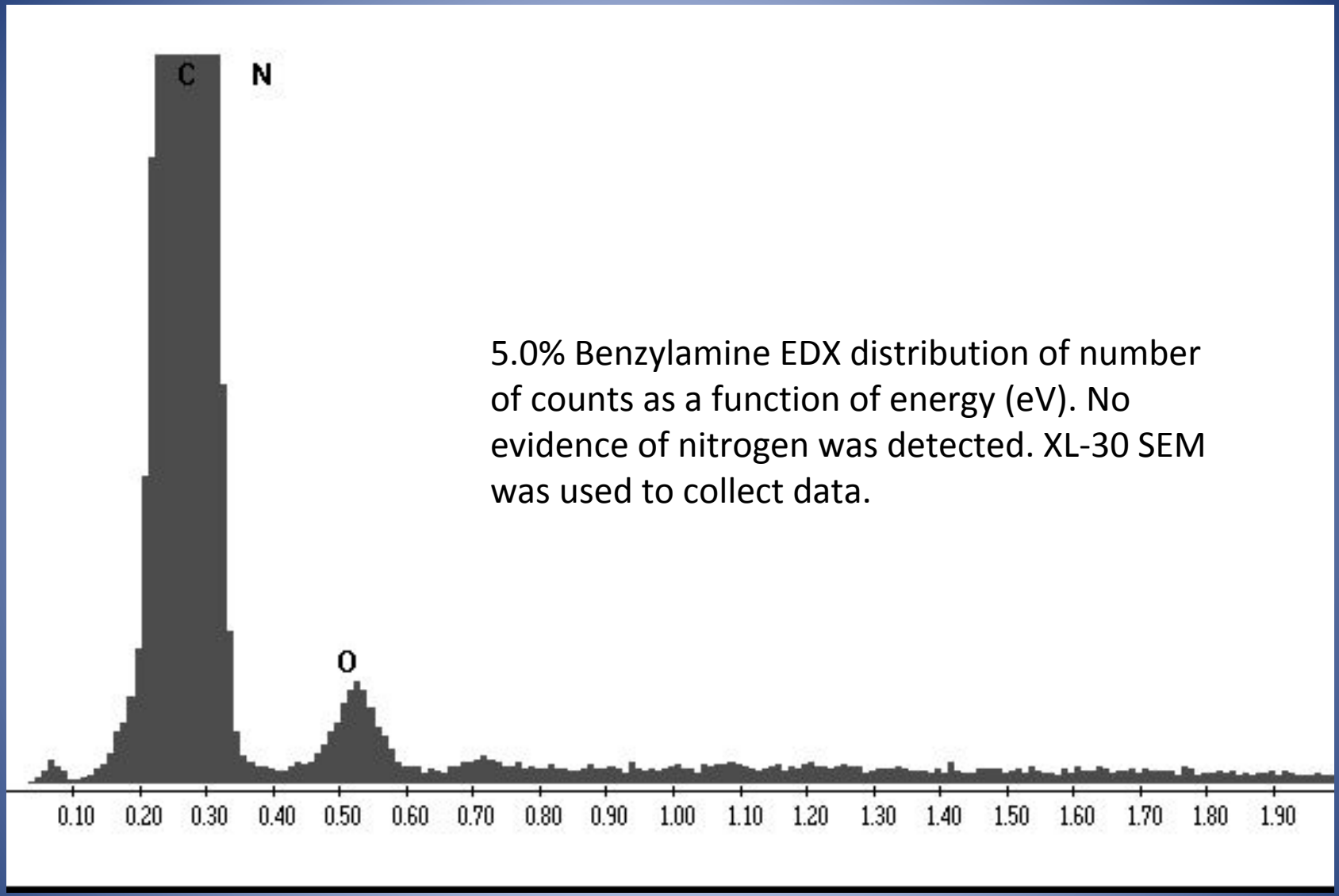
5.0 wt% Benzylamine





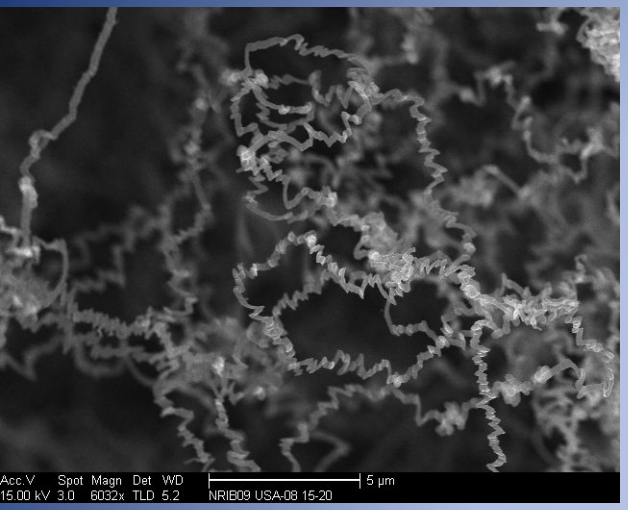


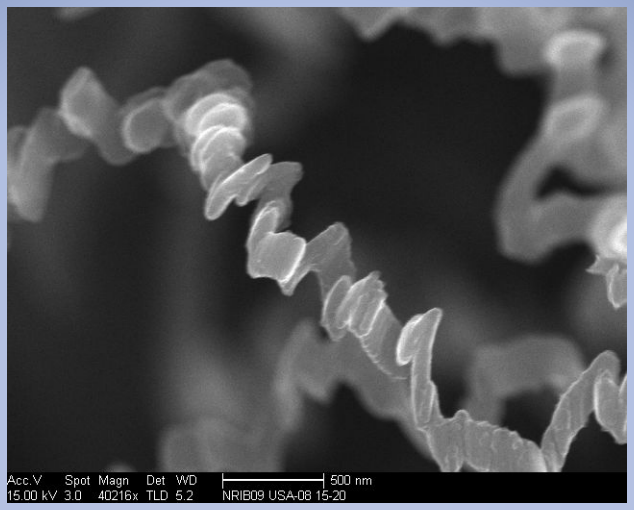
SEM images of carbon nanoribbons doped with 5.0 wt% benzylamine. Evidence of carbonaceous growth can be detected.

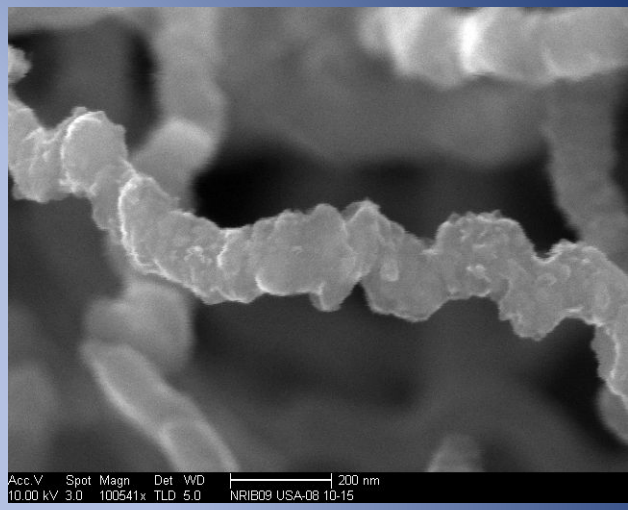


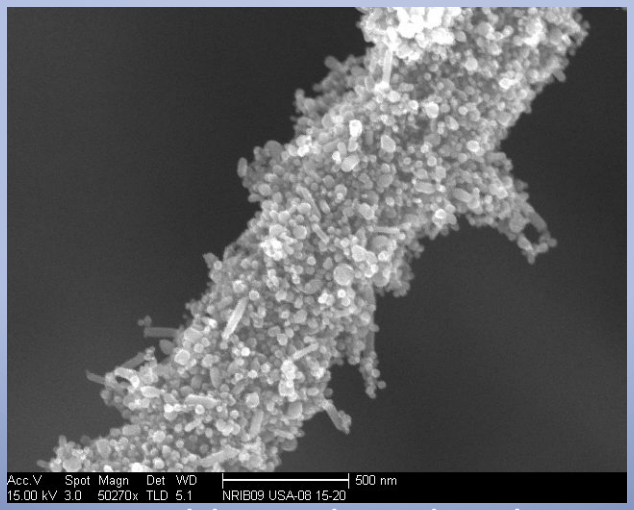
5.0% Benzylamine EDX distribution of number of counts as a function of energy (eV). No evidence of nitrogen was detected. XL-30 SEM was used to collect data.

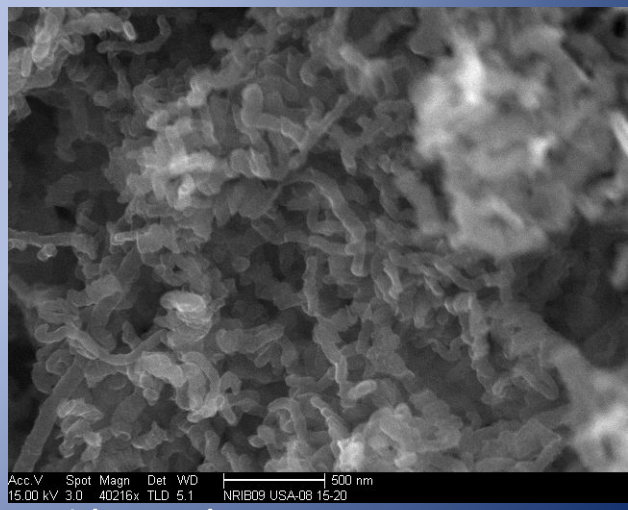
10.0 wt% Benzylamine







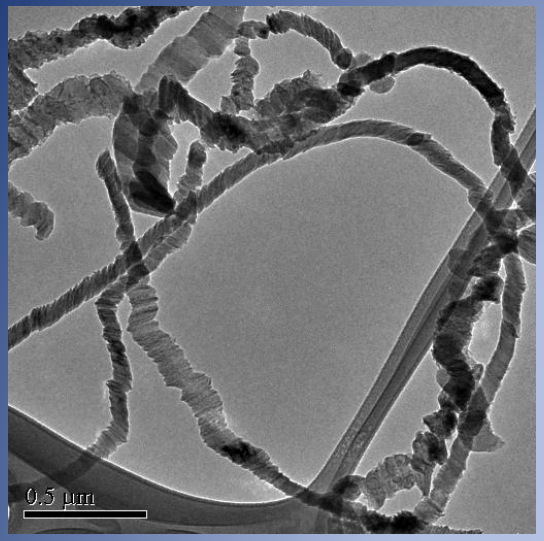


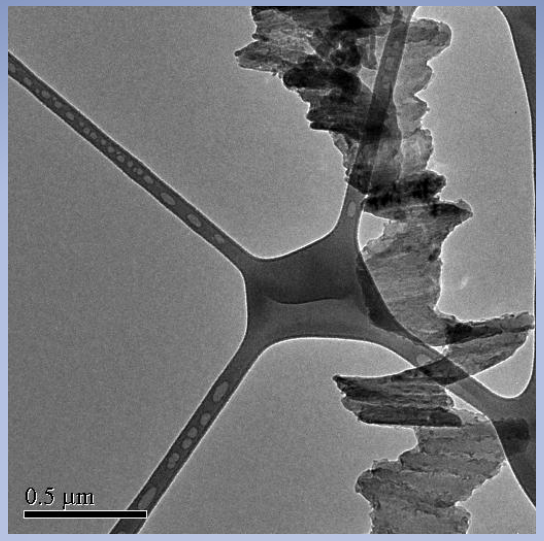


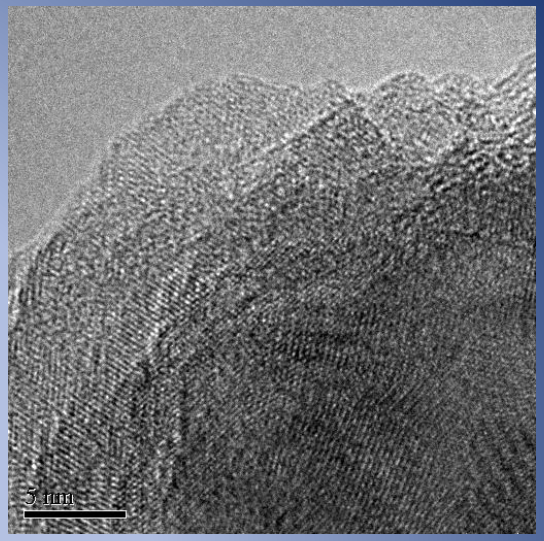
SEM images of carbon nanoribbons doped with 10.0 wt% benzylamine. Evidence of fibers and carbonaceous growth can be detected.

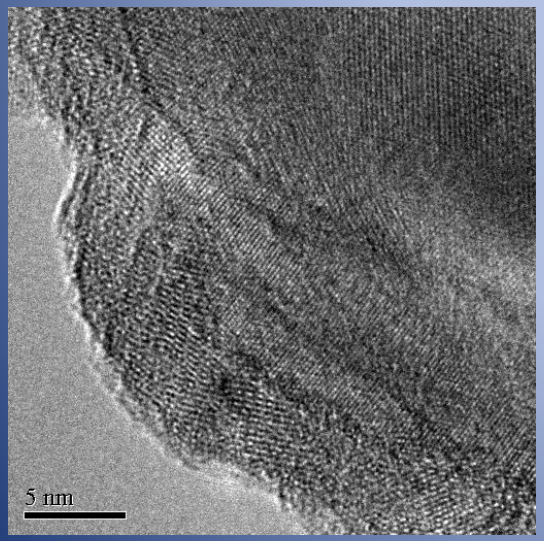
3% Pyrazine

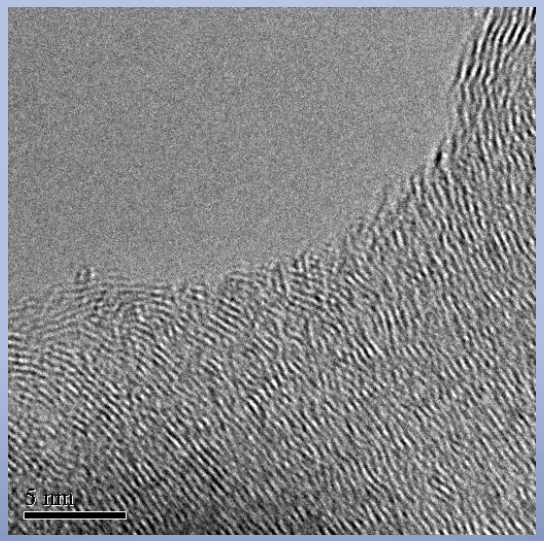
TEM

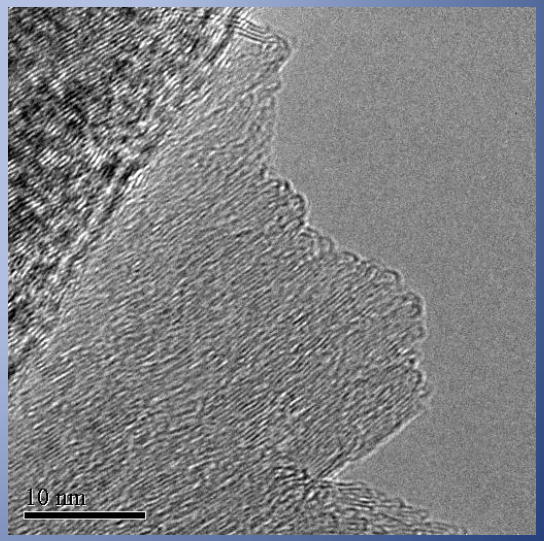

0.5 µm

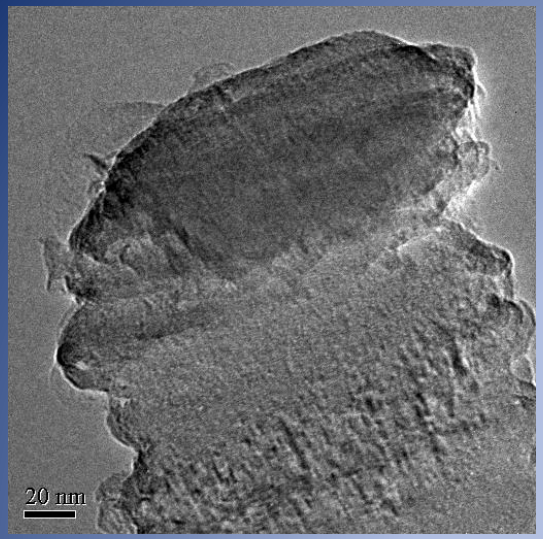

0.5 µm

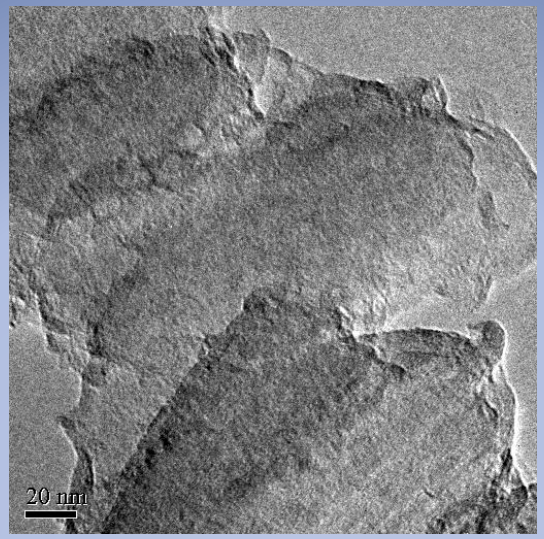

5 nm

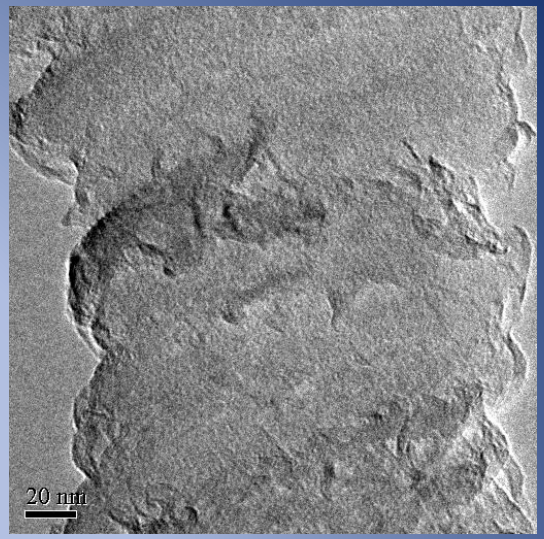

5 nm

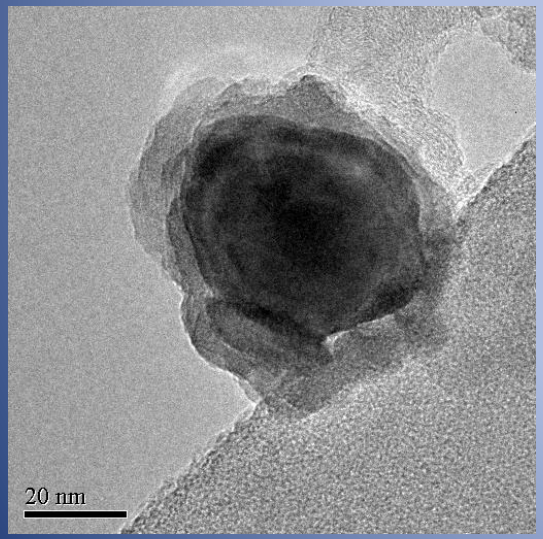

5 nm

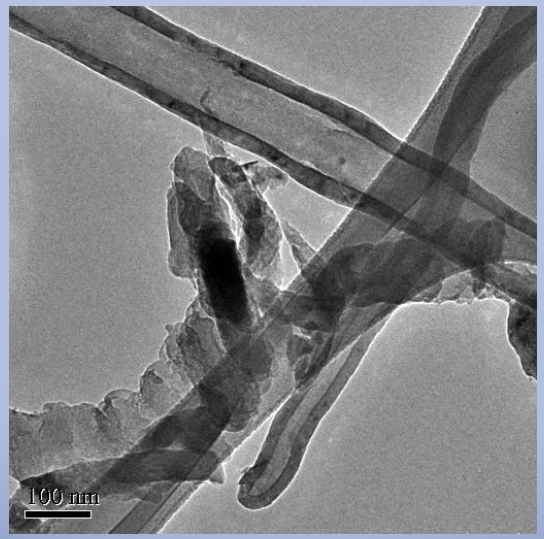

10 nm

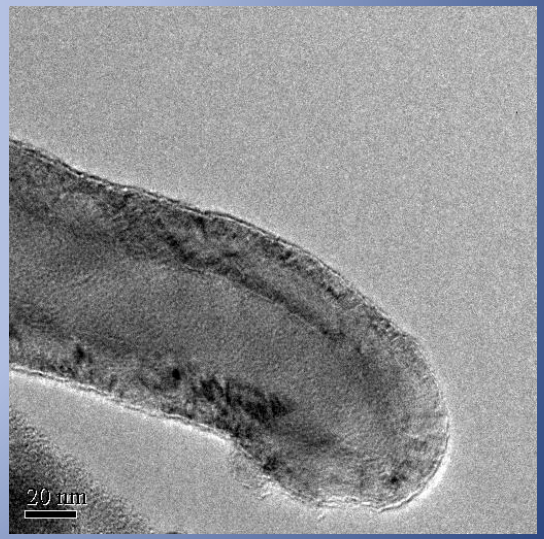

20 nm


20 nm

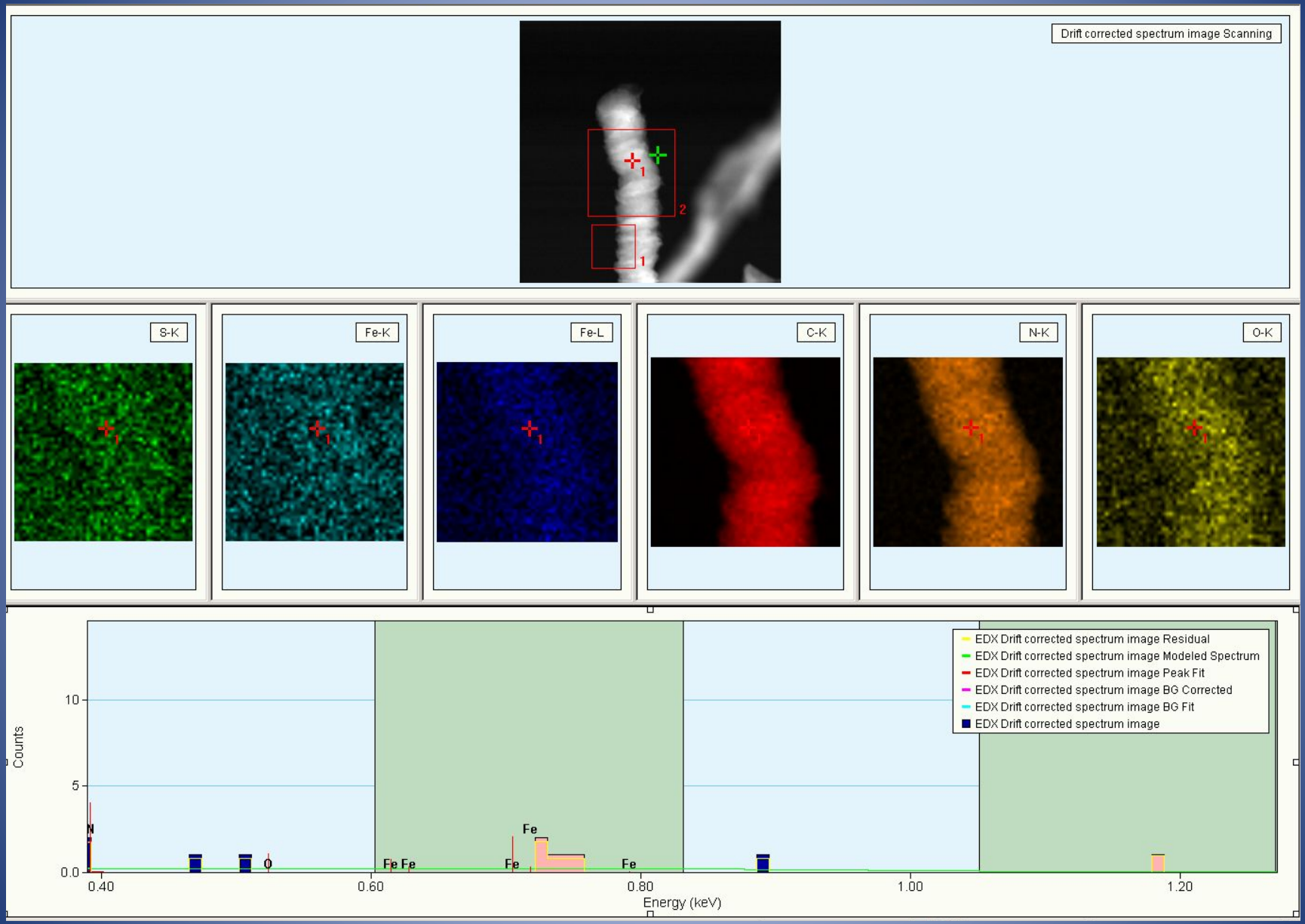

20 nm


20 nm

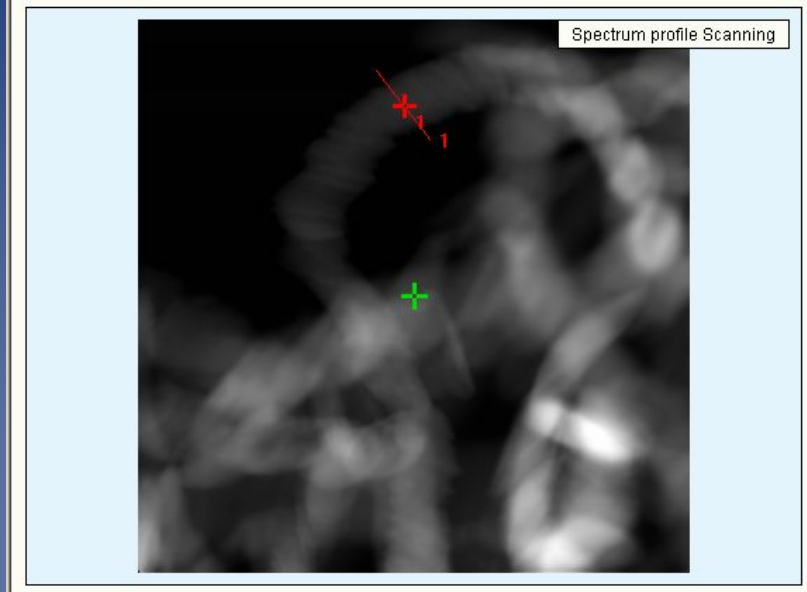

100 nm

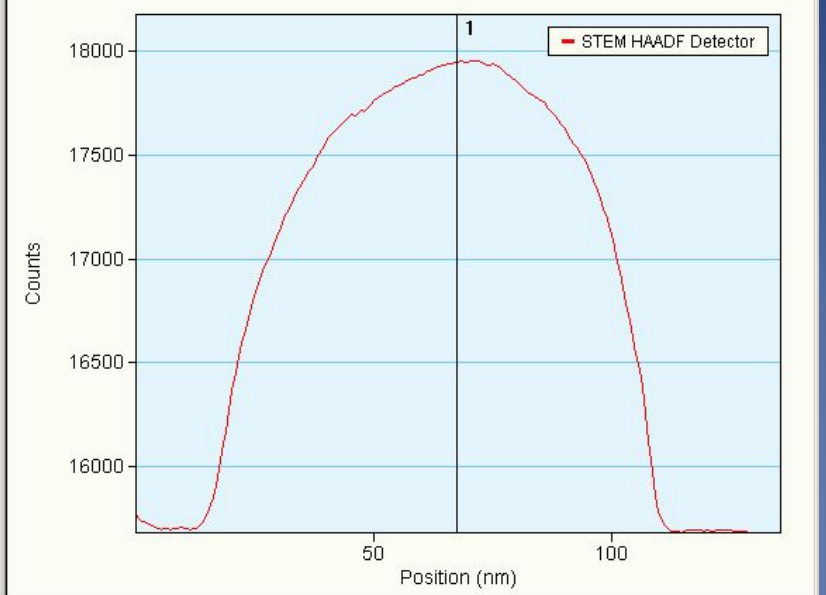

20 nm

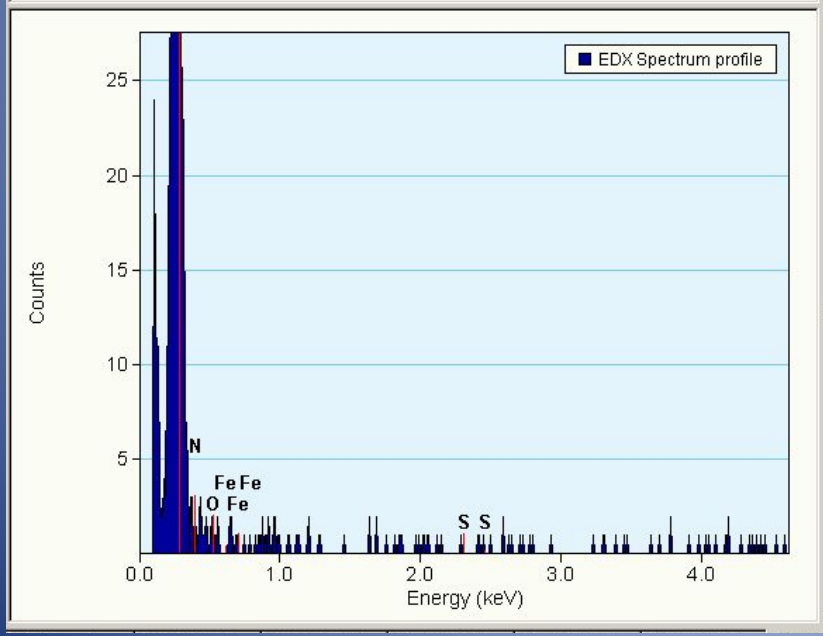
EDX Line Scan of 3% Pyrazine

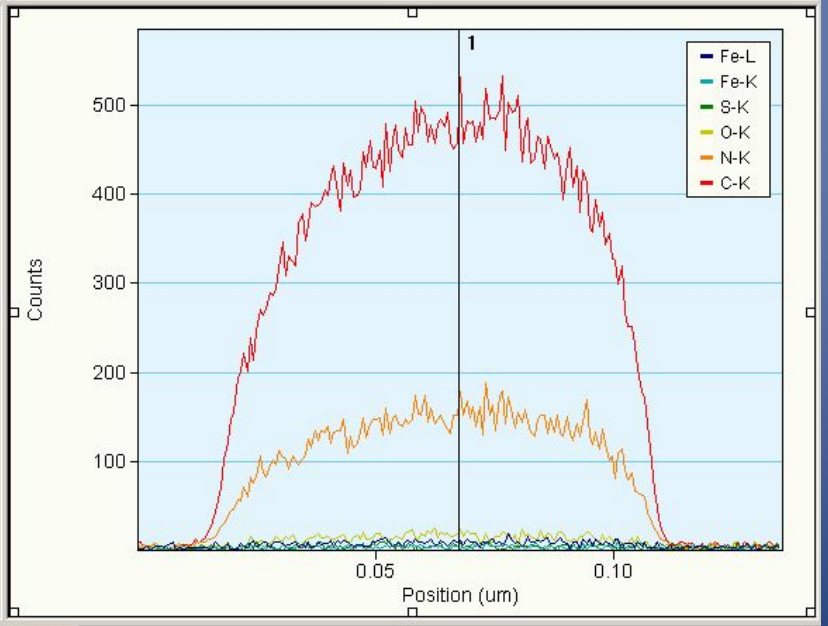


EDX Line Scan of 3% Pyrazine

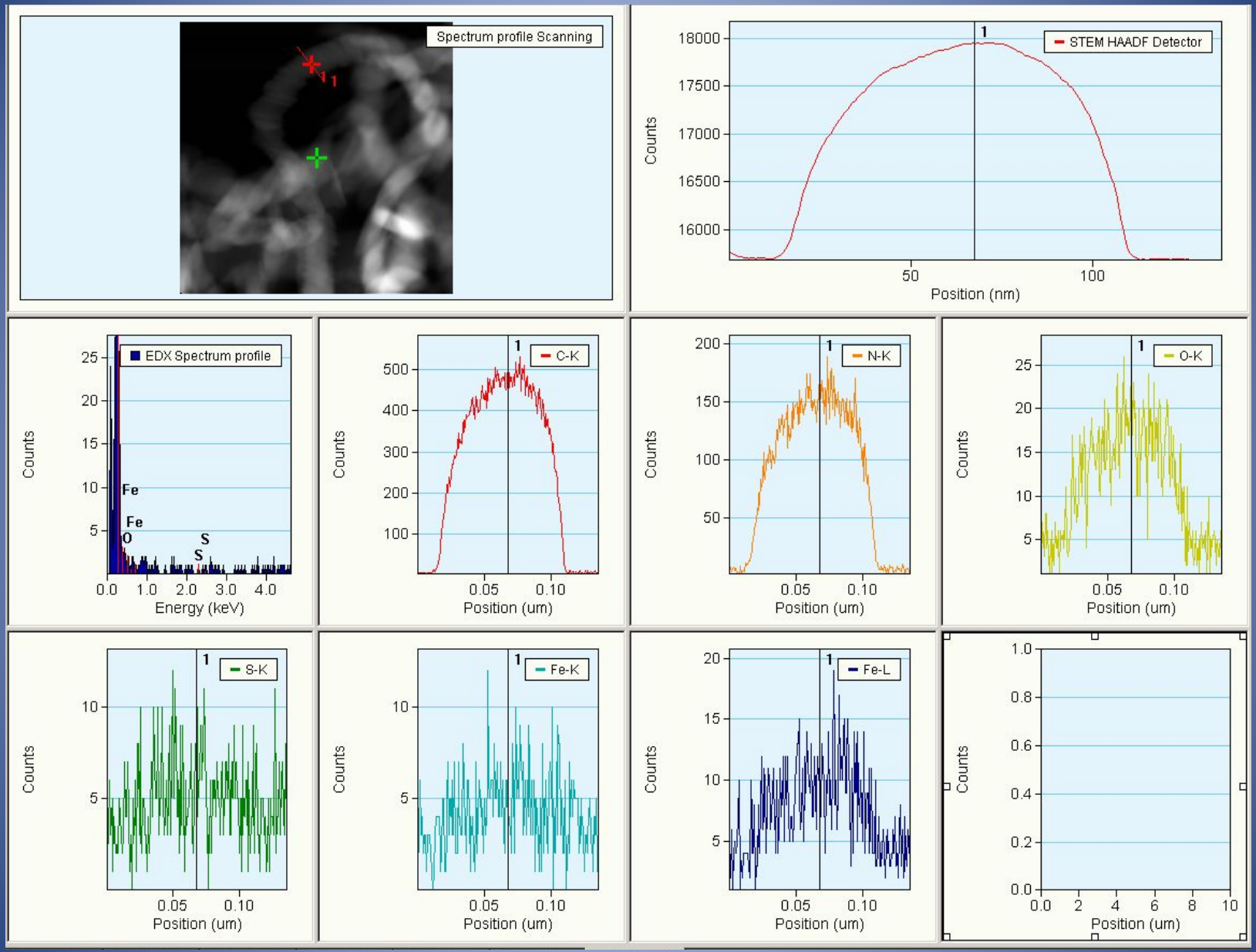








EDX Line Scan of 3% Pyrazine

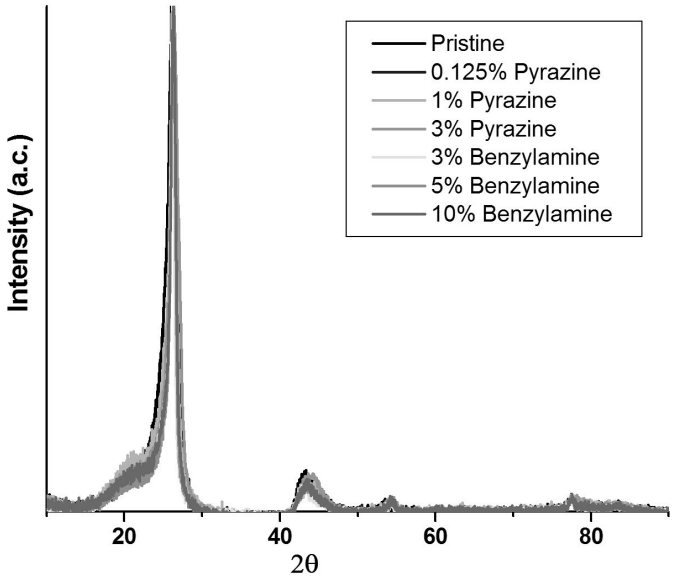


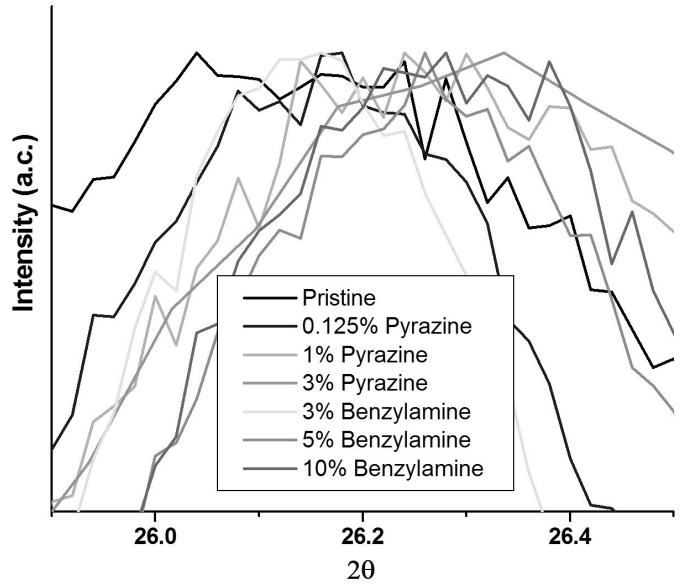
Rice University Summer 2009

Pristine; 0.125%, 1.0%, 3.0% Pyrazine; 3.0%, 5.0%, 10.0% Benzylamine

XRD

Bragg's Law: nλ=2d sin(θ)





Normalized graphs of intensity as a function of angle for x-ray diffraction with pristine and nitrogen doped carbon nanoribbons. The graph on the right shows a close up of the 002 peak.

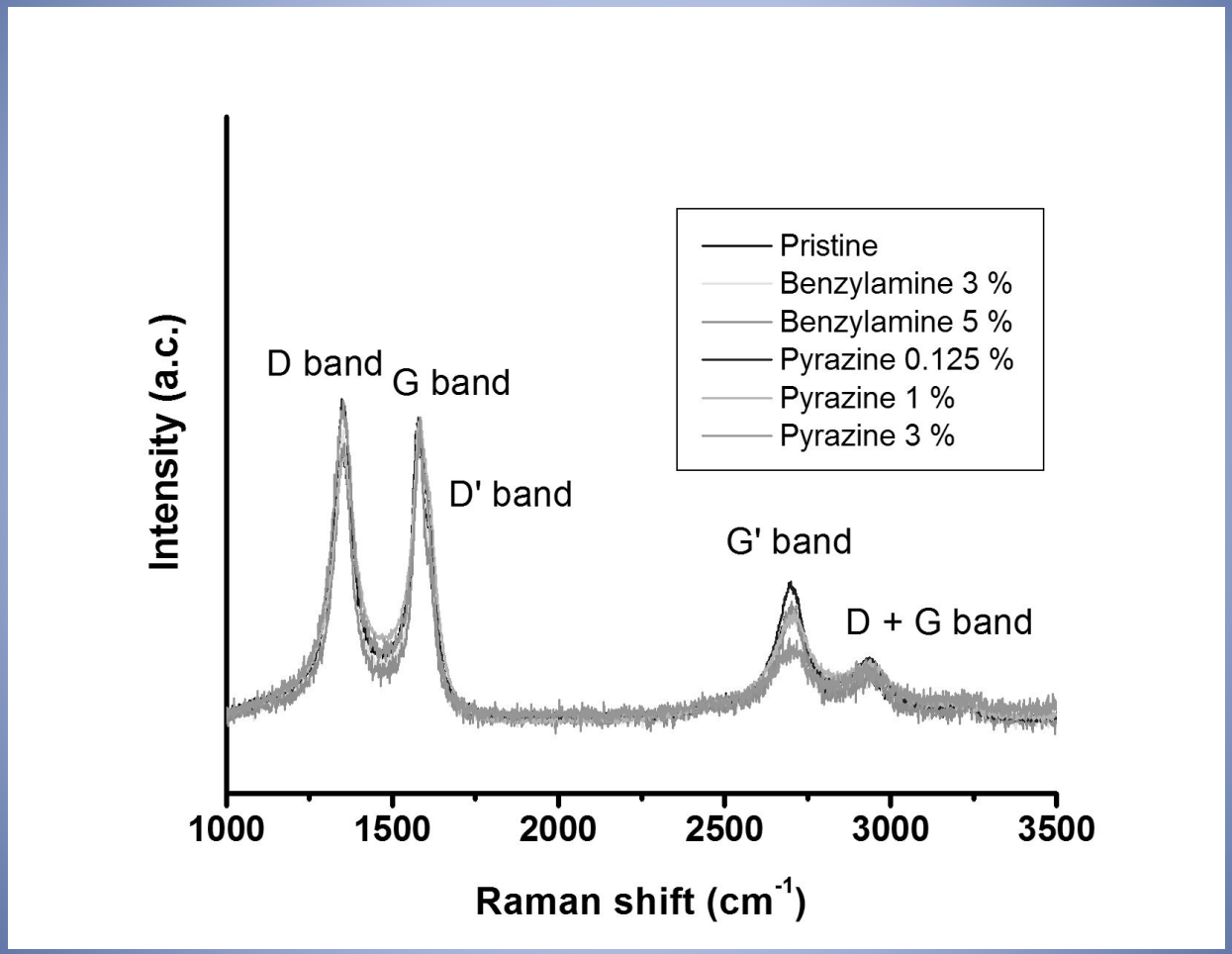
Spacing Between Graphitic Planes

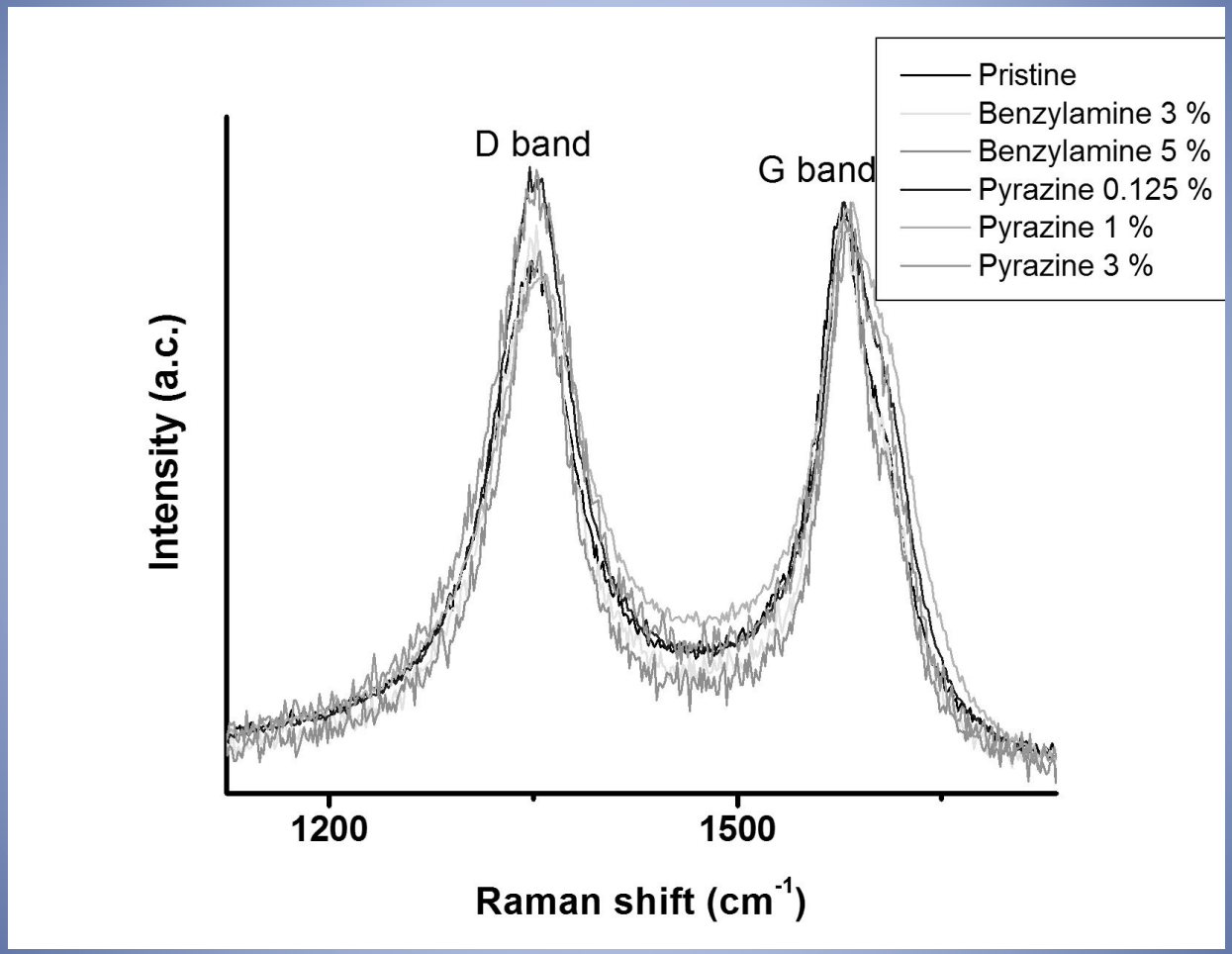
Sample	d spacing (Å)
Pristine	3.400
Pyrazine 0.125%	3.393
Pyrazine 1.0%	3.381
Pyrazine 3.0%	3.375
Benzylamine 3.0%	3.392
Benzylamine 5.0%	3.383
Benzylamine 10.0%	3.381

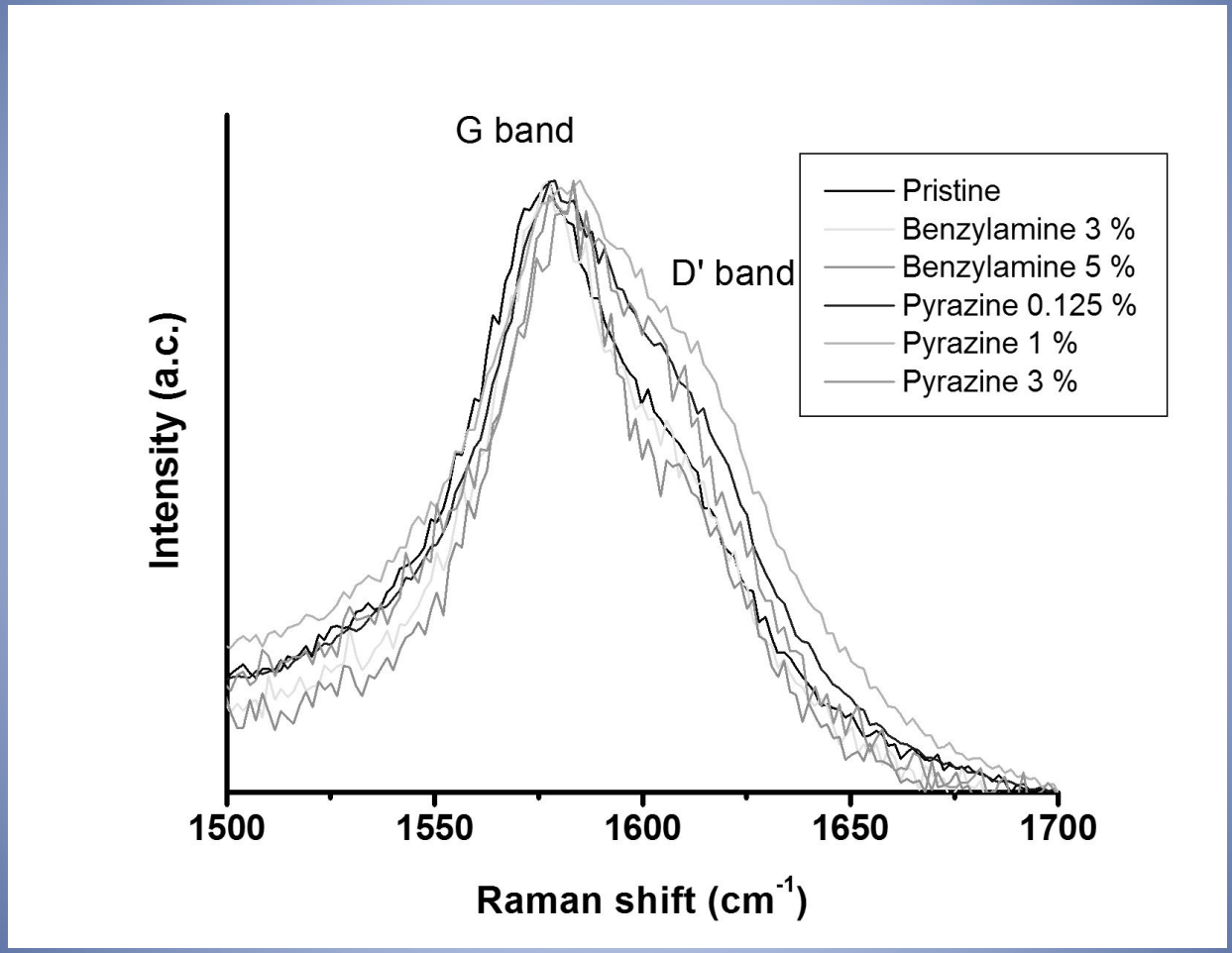
NOTE: All d spacing values were determined by averaging data from the first and second order peaks. The wavelength of the x-rays was 1.54 Å.

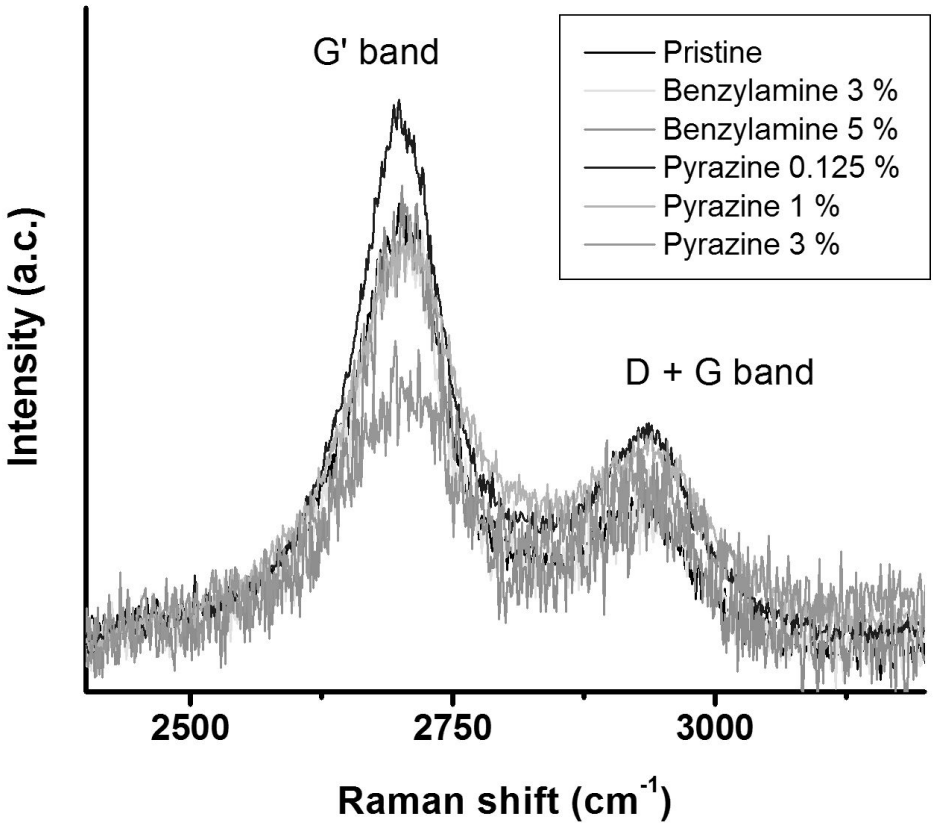
Pristine; 0.125% Pyrazine; 1.0% Pyrazine; 3.0% Pyrazine; 3.0% Benzylamine; 5.0% Benzylamine

RAMAN


Intensity (a.c.)
D band
G band
D' band
G' band
D + G band
Pristine
Benzylamine 3 %
Benzylamine 5 %
Pyrazine 0.125 %
Pyrazine 1 %
Pyrazine 3 %
1000
1500
2000
2500
3000
3500
Raman shift (cm-1)


Pristine
Benzylamine 3 %
Benzylamine 5 %
Pyrazine 0.125 %
Pyrazine 1 %
Pyrazine 3 %
D band
G band
Intensity (a.c.)
1200
1500
Raman shift (cm-1)

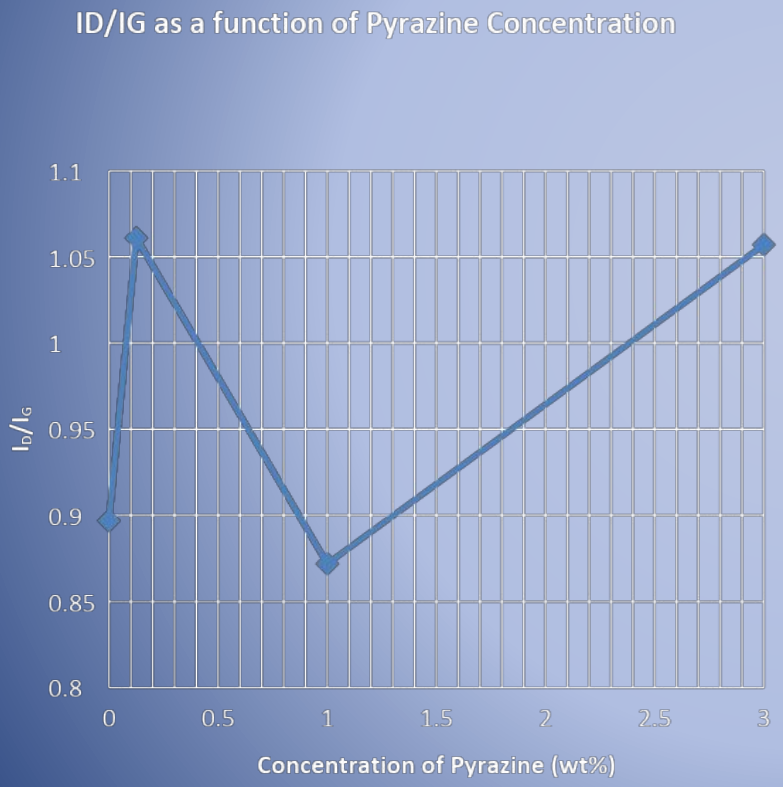

G band
D' band
Pristine
Benzylamine 3 %
Benzylamine 5 %
Pyrazine 0.125 %
Pyrazine 1 %
Pyrazine 3 %
Intensity (a.c.)
1500
1550
1600
1650
1700
Raman shift (cm-1)

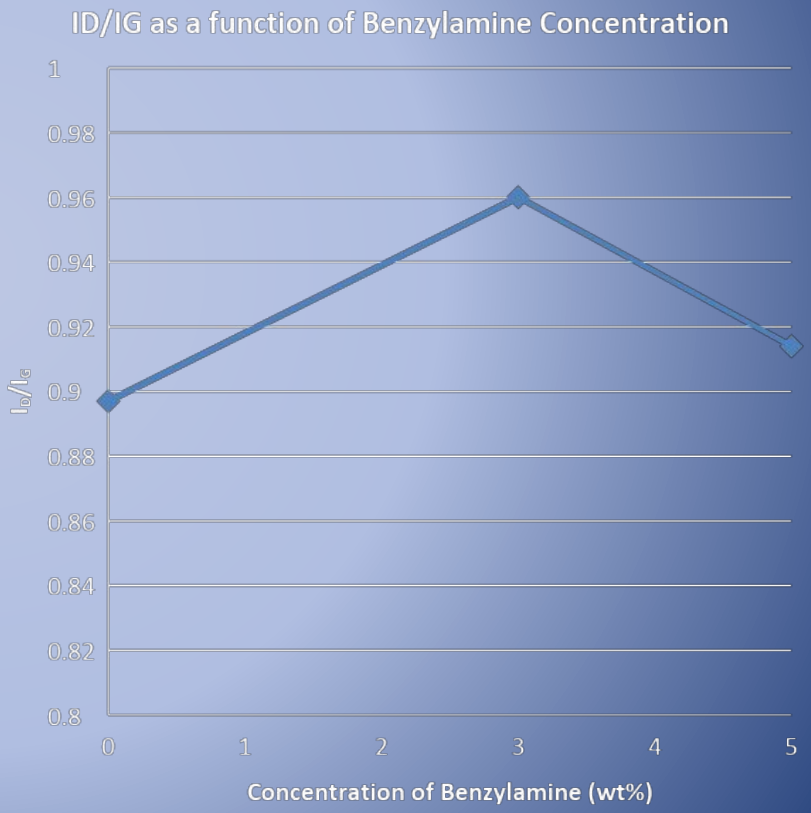

G' band
D + G band
Pristine
Benzylamine 3 %
Benzylamine 5 %
Pyrazine 0.125 %
Pyrazine 1 %
Pyrazine 3 %
Intensity (a.c.)
2500
2750
3000
Raman shift (cm-1)

D and G Band Intensity Ratio

Sample	I_D/I_G
Pristine	0.897
Pyrazine 0.125%	1.061
Pyrazine 1.0%	0.872
Pyrazine 3.0%	1.057
Benzylamine 3.0%	0.960
Benzylaminne 5.0%	0.914

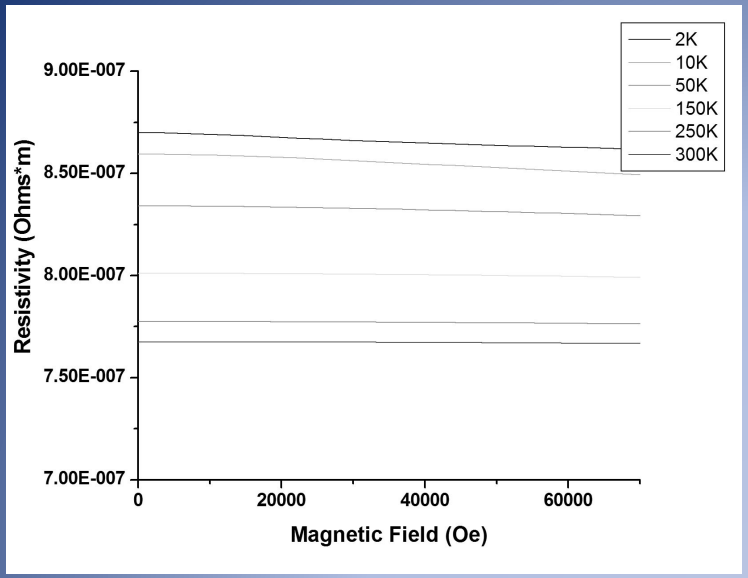
D and G Band Intensity Ratio



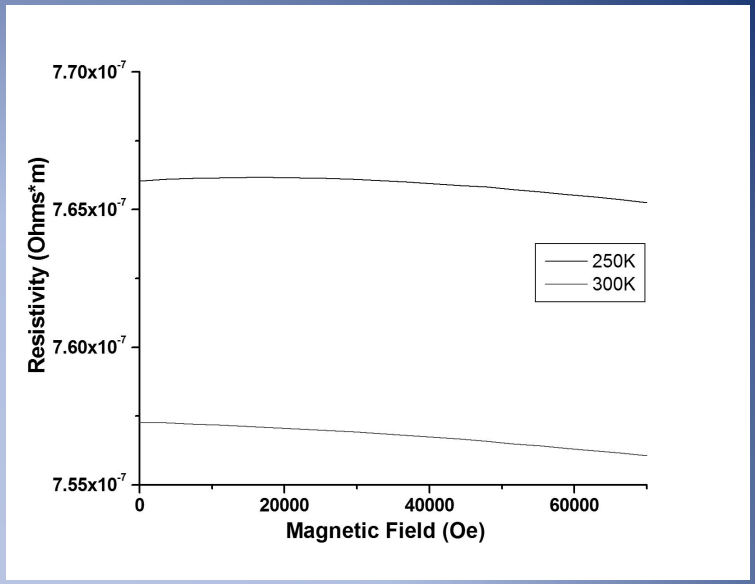


Pristine

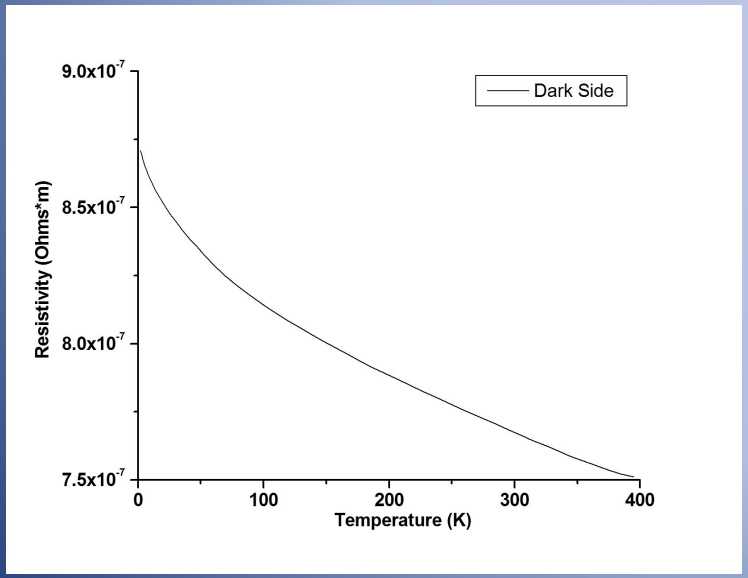
PPMS



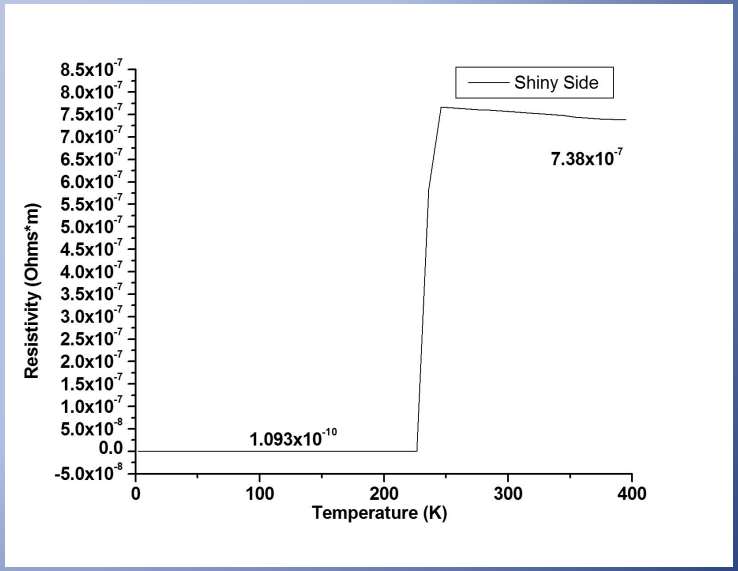
Resistivity as a function of magnetic field for the dark side of a pristine carbon nanoribbons.



Resistivity as a function of magnetic field for the shiny side of a pristine carbon nanoribbons.



Resistivity as a function of temperature for the dark side of a pristine carbon nanoribbons.



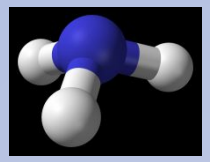
Resistivity as a function of temperature for the shiny side of a pristine carbon nanoribbons.

Future Work

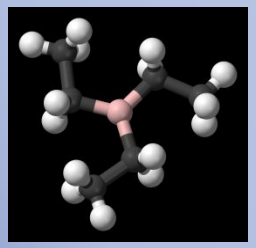
- Conduct further trials to determine ideal concentration for doping
- Additional characterization to search for evidence of N-doping
  - Electron Diffraction
  - Thermogravimetric Analysis (TGA)
  - X-ray Photoelectron Spectroscopy (XPS)
  - Electron Energy Loss Spectroscopy (EELS)

Future Work

- Post synthesis treatment:
  - Ammonia (NH_3)



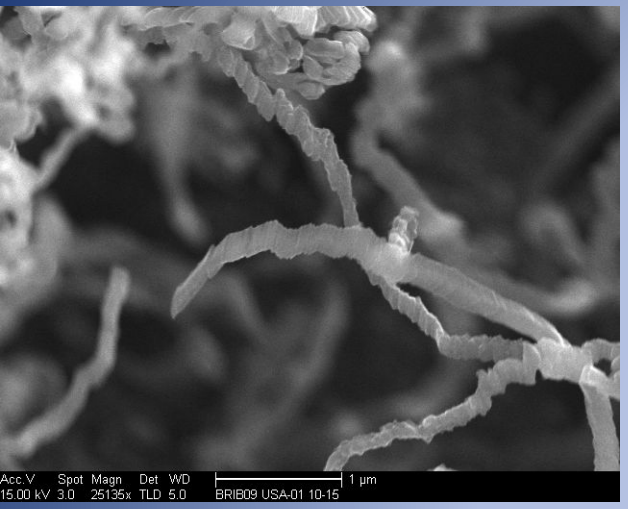
- Boron Doping:
  - TEB

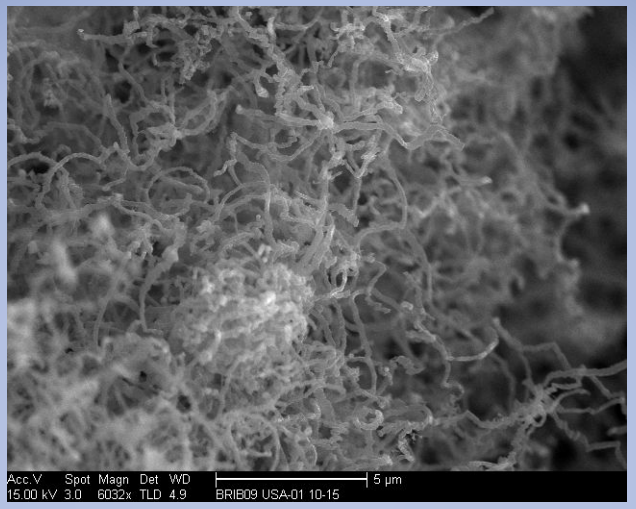


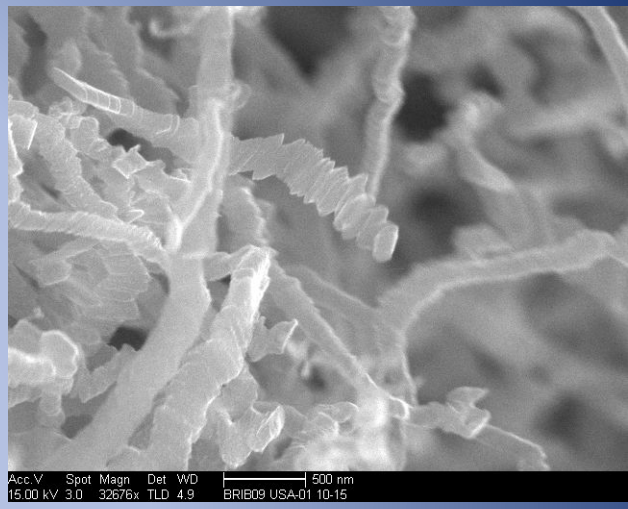
0.125 wt% Triethylborane, 1.0 wt% Triethylborane

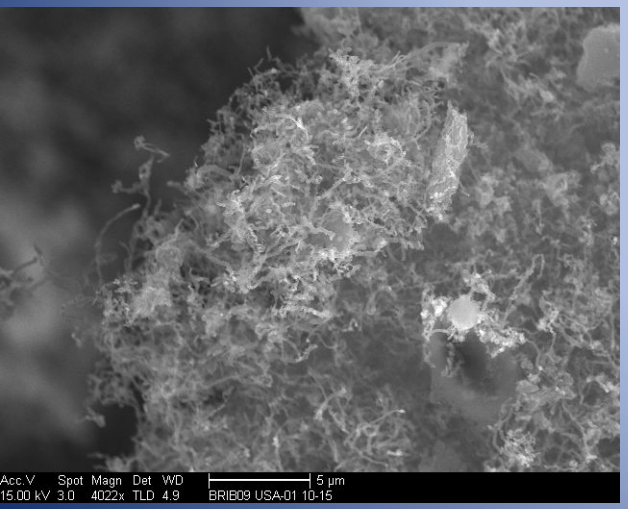
SEM

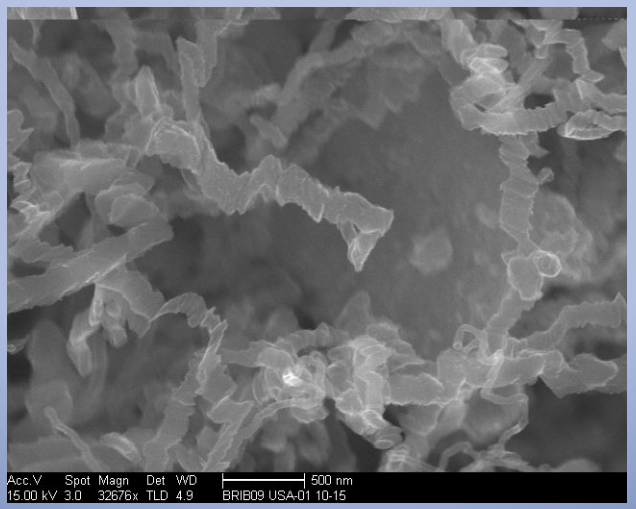
0.125 wt% Triethylborane

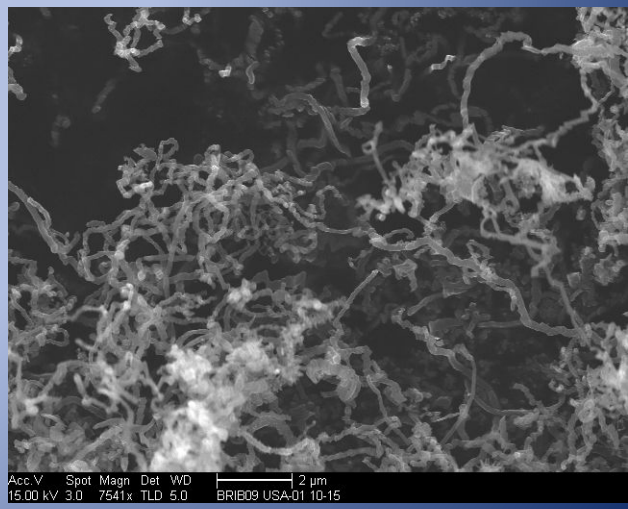






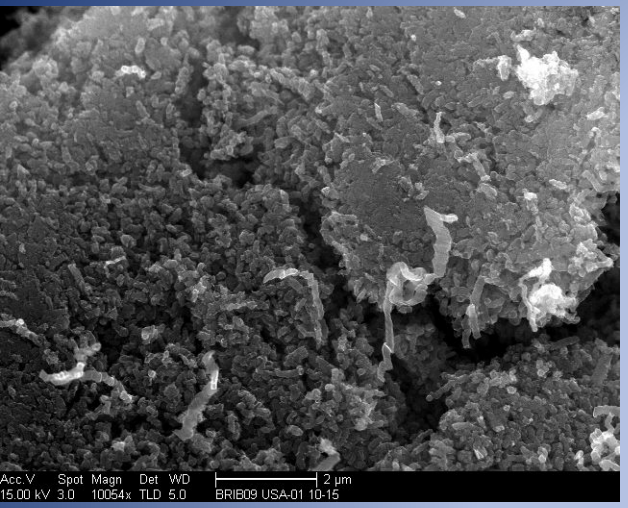


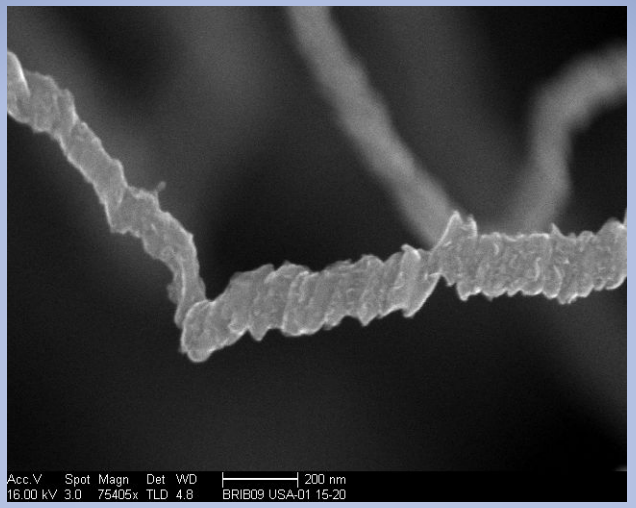


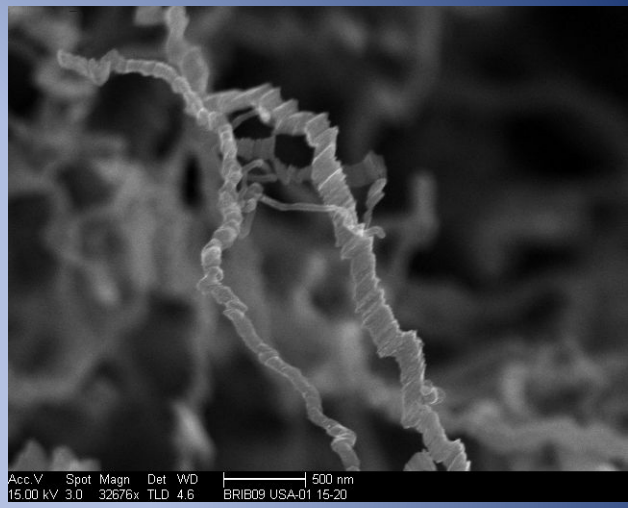


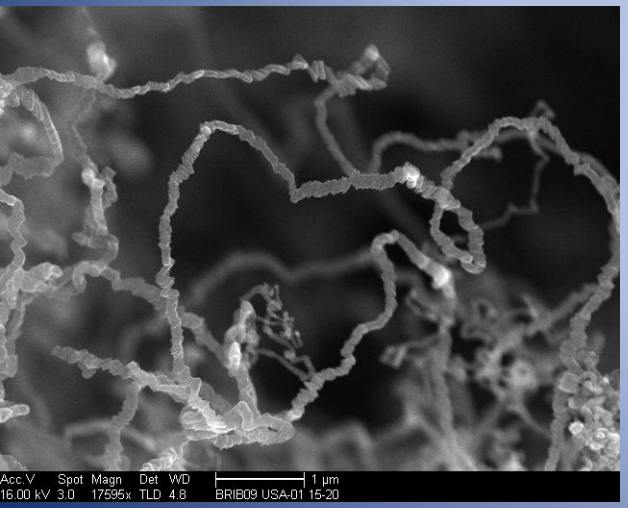
SEM images of carbon nanoribbons doped with 0.125 wt% triethylborane.

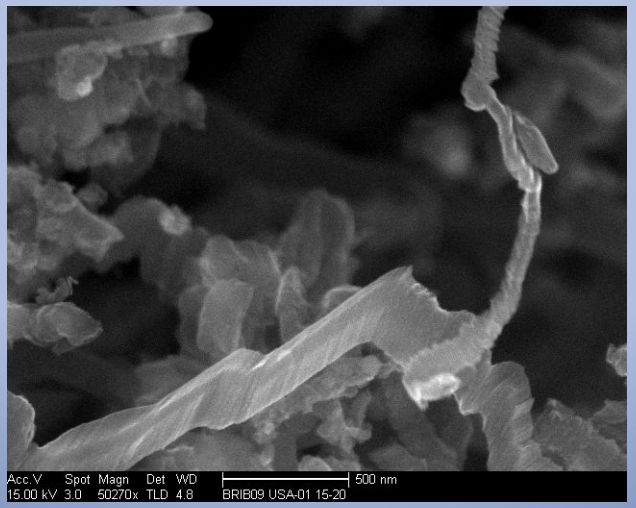
0.125 wt% Triethylborane

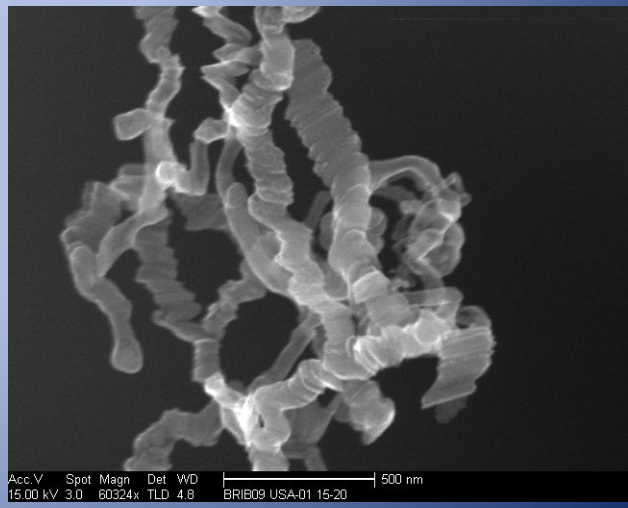






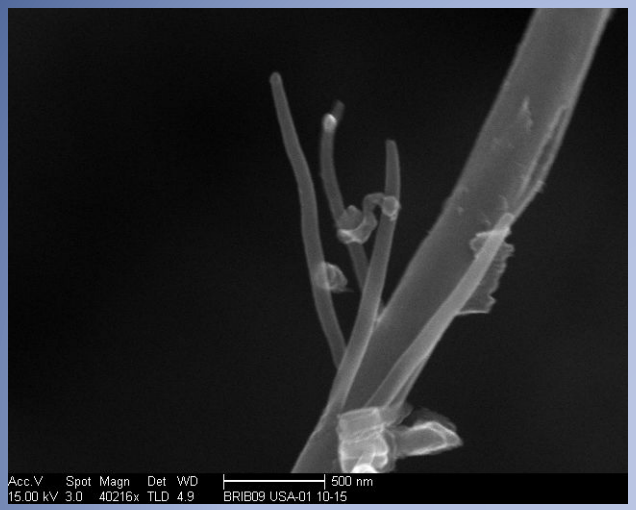


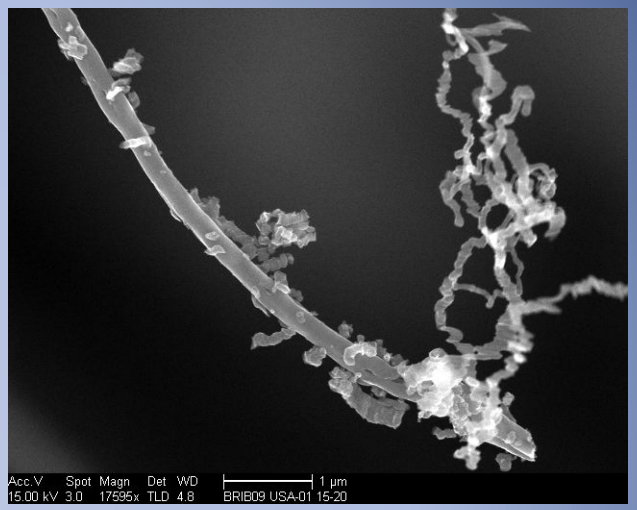


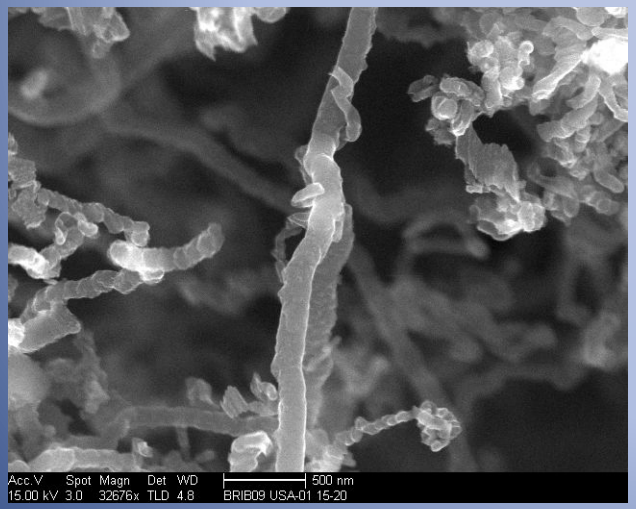


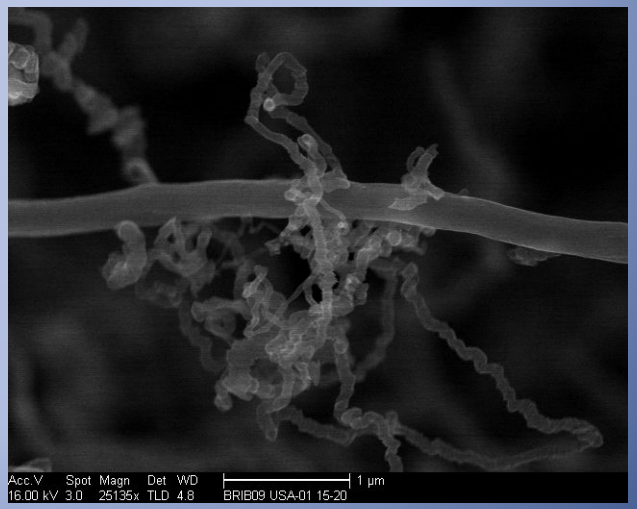
SEM images of carbon nanoribbons doped with 0.125 wt% triethylborane.

0.125 wt% Triethylborane



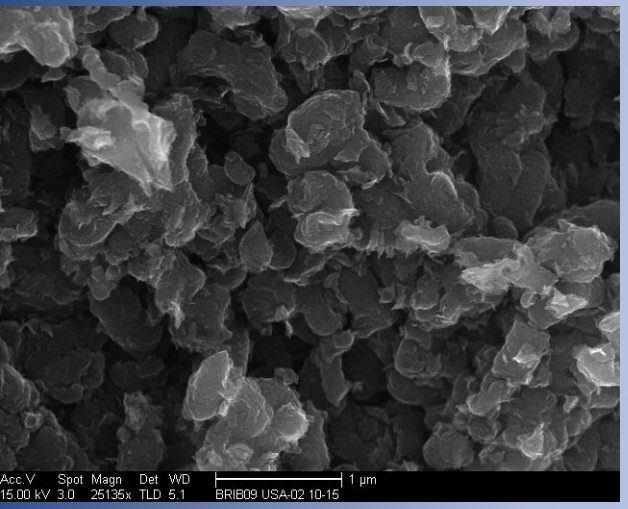


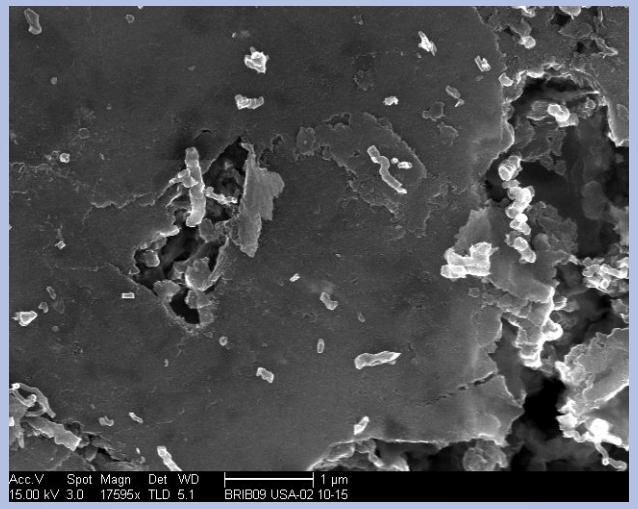


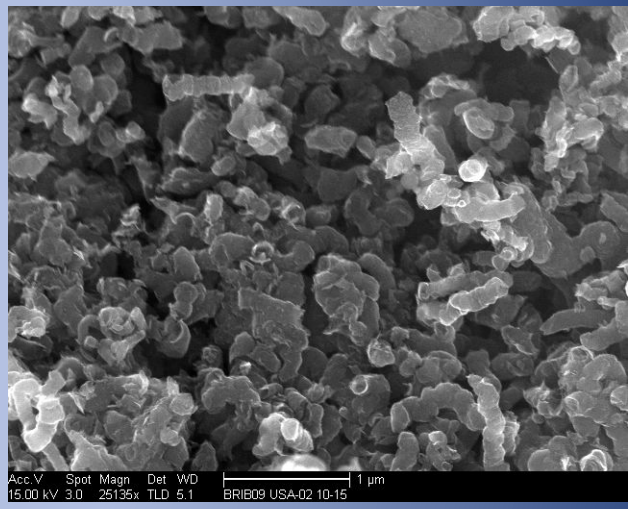


SEM images of carbon nanoribbons doped with 0.125 wt% triethylborane. Evidence of tube and fiber growth.

1.0 wt% Triethylborane

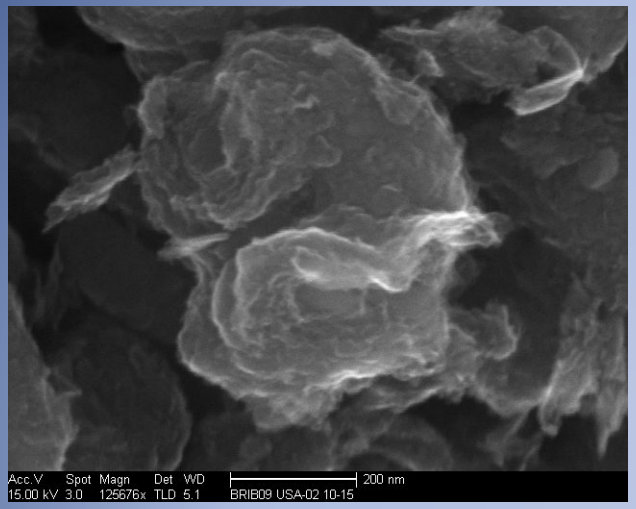


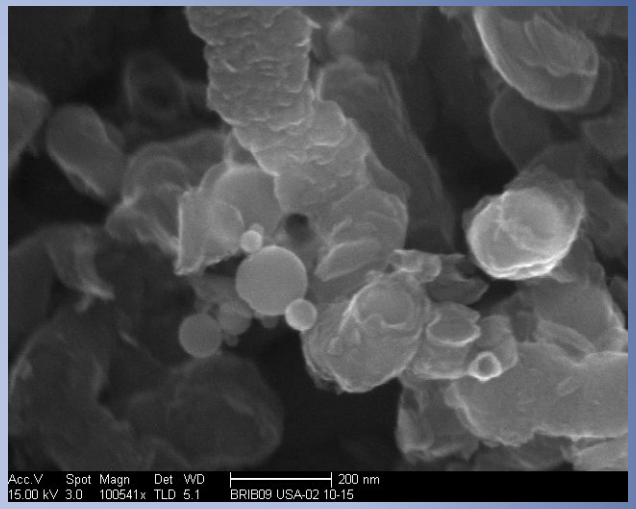


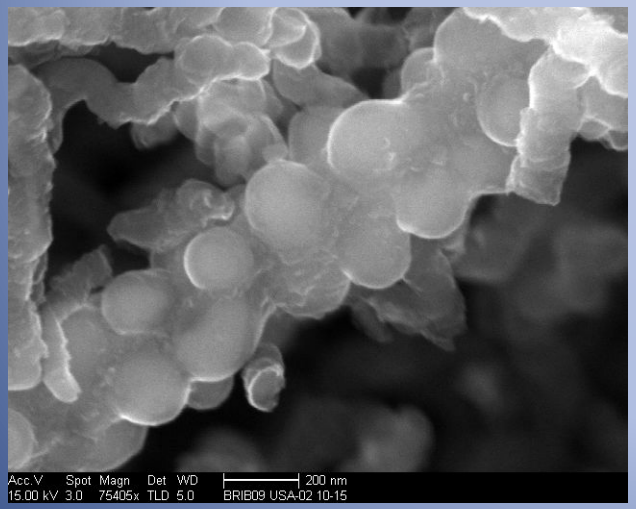


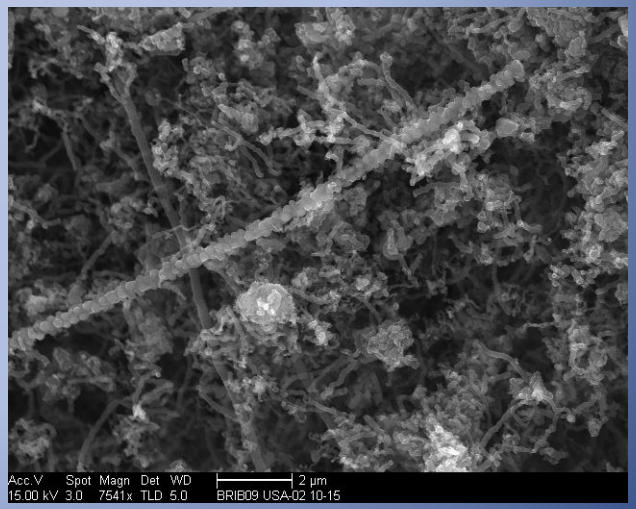
SEM images of carbon nanoribbons doped with 1.0 wt% triethylborane.

1.0 wt% Triethylborane









SEM images of carbon nanoribbons doped with 1.0 wt% triethylborane.

Acknowledgements

Prof. M. Terrones; Prof. H. Terrones; Prof. P. Ajayan; Prof. E. Muñoz; D. Ramirez; H. Martínez; S. Vega; A. Morelos; V. Gonzalez; A. Botello; Rice University; IPICYT

Works Cited

1. Hongjie Dai et al. “Chemically Derived, Ultrasmooth Graphene Nanoribbon Semiconductors.” *Science* 29 Feb 2008: vol. 19, 1229-1231
2. Jiao, Liying et al. “Narrow graphene nanoribbons from carbon nanotubes.” *Nature* 16 April 2009: vol. 458, 877-880
3. Cano-Márquez, Abraham G. et al. “Ex-MWNTs: Graphene Sheets and Ribbons Produced by Lithium Intercalation and Exfoliation of Carbon Nanotubes” *Nano Letters* 2009: vol. 9, no. 4, 1527-1533
4. Kosynkin, Dmitry V. et al. “Longitudinal unzipping of carbon nanotubes to form graphene nanoribbons” *Nature* 16 April 2009: vol. 458, 872-876
5. Murayama, H. and T. Maeda “A novel form of filamentous graphite” *Nature* 28 June 1990: vol. 345, 791-793
6. Wei, Dacheng et al. “Synthesis of N-Doped Graphene by Chemical Vapor Deposition and its Electrical Properties” *Nano Letters* 2009: Vol. 9. no. 5, 1752-1758
7. Wang, Xinran et al. “N-doping of Graphene through Electrochemical Reactions with Ammonia” *Science* 8 May 2009: Vol. 324. no. 5928, 768 - 771