ULTRA-LOW DISORDER GRAPHENE QUANTUM DOT-BASED SPIN QUBITS FOR CYBER SECURE FOSSIL ENERGY INFRASTRUCTURE

Project # DE-FE0031908

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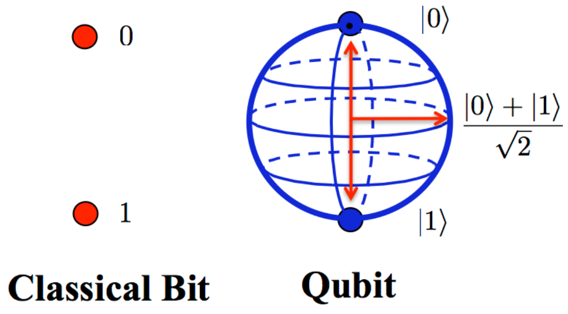
TECHNICAL BACKGROUND & MOTIVATION

Quantum Information Processing (QIP) and Quantum Bits (qubits)



https://www.bbvaopenmind.com/en/technology/digital-world/towards-the-quantum-computer-qubits-and-qudits/

https://physicsworld.com/a/quantum-communications-boosted-by-solid-memory-devices/

Physical Implementation of Qubits

- Atoms, ions, molecules
- Electronic and nuclear magnetic moments
- Charges in semiconductor quantum dots
- Charges and fluxes in superconducting circuits
- **Spin**

Nature Physics 3, (2007) 192-196.

DiVincenzo criteria

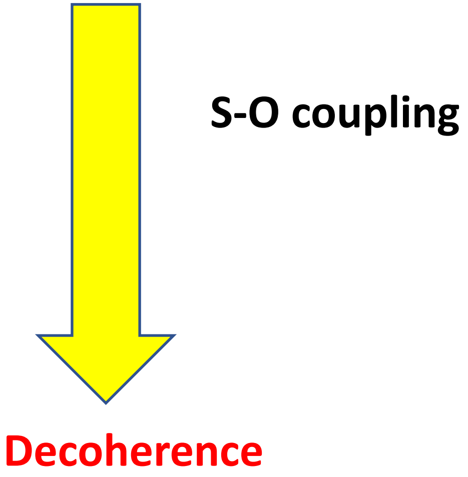
1. Long coherence time
2. Efficient initialization
3. Scalable
4. Readout
5. Universal quantum gates

Progress of Physics 48, (2000) 771-783.

GQDs for Spin Qubits

Coherence time depends on spin-orbit and hyperfine interactions in the material

III	IV	V	VI
5 B 10 (3) 20% 11 (3/2) 80%	6 C 12 (0) 99% 13 (1/2) 1%	7 N 14 (1) 99.6% 15 (1/2) 0.4%	8 O 16 (0) 99.76% 17 (5/2) 0.04% 18 (0) 0.20%
13 Al 27 (5/2) 100%	14 Si 28 (0) 92% 29 (1/2) 5% 30 (0) 3%	15 P 31 (1/2) 100%	16 S 32 (0) 95% 33 (3/2) 1% 34 (0) 4%
31 Ga 69 (3/2) 60% 71 (3/2) 40%	32 Ge 72 (0) 27% 73 (9/2) 8% 74 (0) 36%	33 As 75 (3/2) 100%	34 Se 77 (1/2) 8% 78 (0) 24% 80 (0) 50% 82 (0) 9%
49 In 113 (9/2) 5% 115 (9/2) 95%	50 Sn 118 (0) 24% 119 (1/2) 9% 120 (0) 33%	51 Sb 121 (5/2) 57% 123 (7/2) 43%	52 Te 125 (1/2) 7% 126 (0) 19% 128 (0) 32% 130 (0) 34%

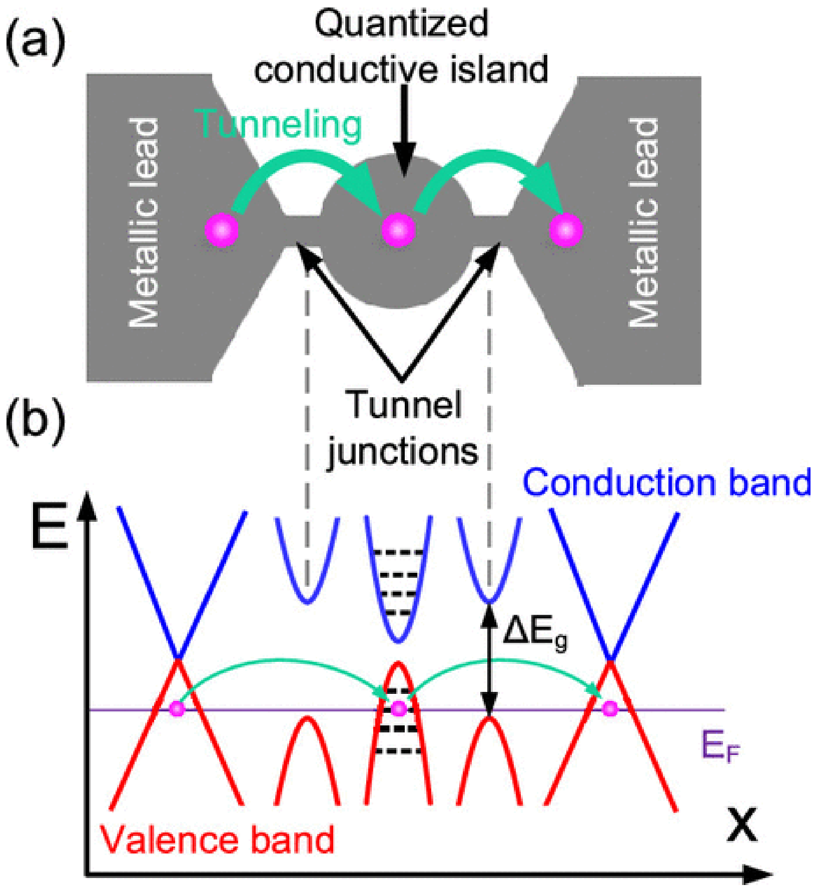


Advantages of Graphene:

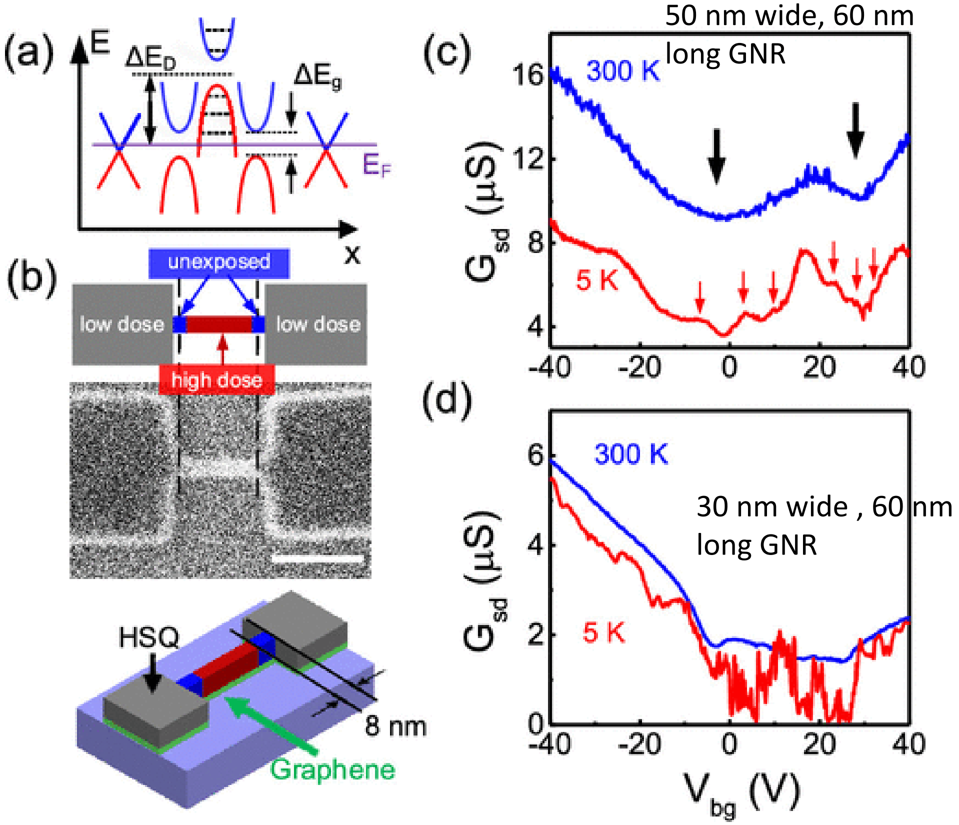
1. Very low nuclear spin
2. Weak spin-orbit coupling

Nature Physics 3, (2007) 192-196.

Quantum Dots in Graphene



- **Fabrication residues**
- **Substrate defects**
- **Edge effects (disorder)**



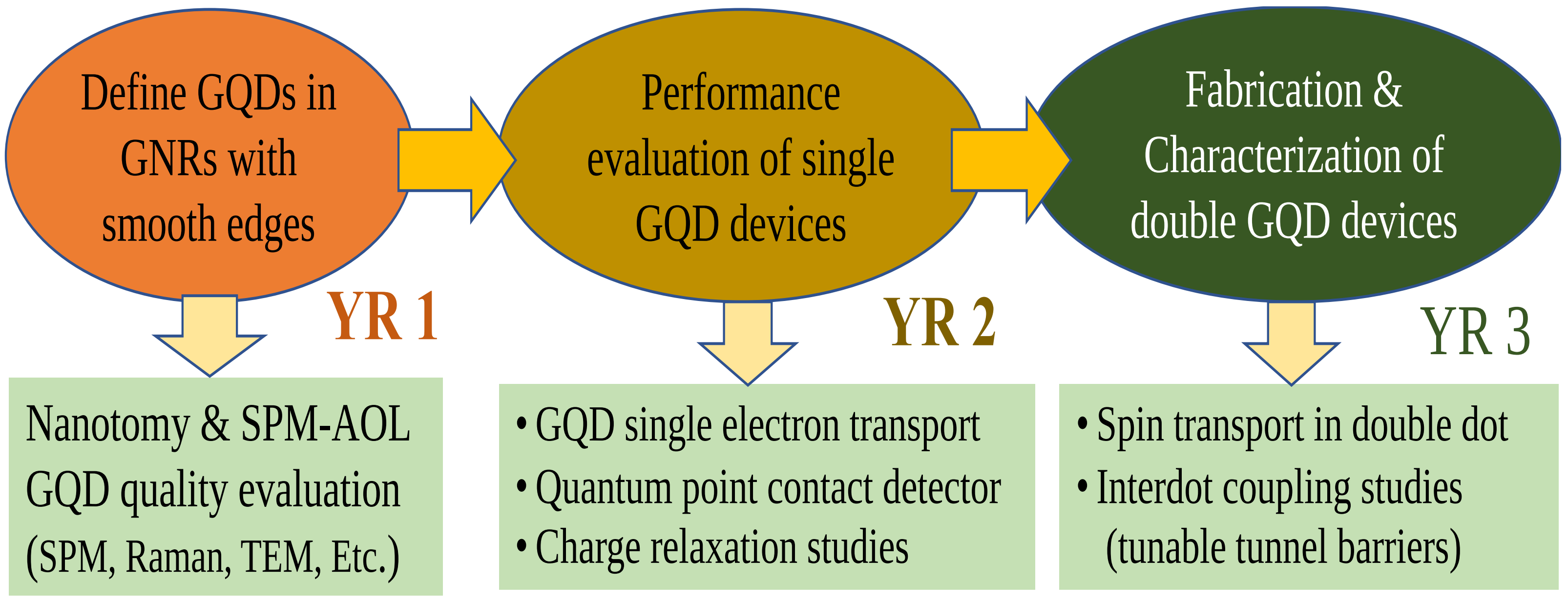
ACS Nano 13, (2019) 7502-7507.

Project Objectives

Objective 1: Define GQDs on GNR with ultralow local defects

Objective 2: Low-temperature characterization of quantum transport and spin relaxation times in GQDs

Objective 3: Develop double GQD-based qubit platform and characterize coupling effects



Outline of the overall effort of the proposed project

CURRENT PROGRESS AND RESULTS

Synthesis of GNRS and Characterization

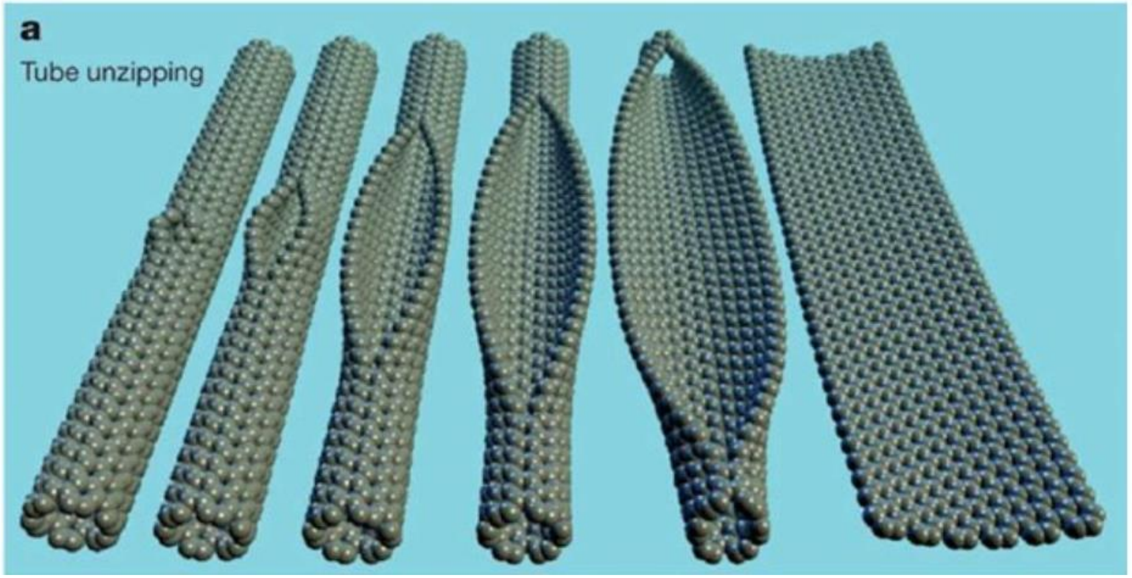
- **Unzipping of CNTs produces semiconducting GNRs**

MWCNTS/SWCNTS $\xrightarrow[75^{o}C,\ 2h]{KMnO_4}$

MWCNTS/SWCNTS $\xrightarrow[80^{o}C,\ 24h]{(NH_4)_2S_2O_8}$

MWCNTS/SWCNTS —— Electrochemical Unzipping ——> 2 steps, oxidation and reduction

Unzipping of Carbon Nanotubes (CNTs)

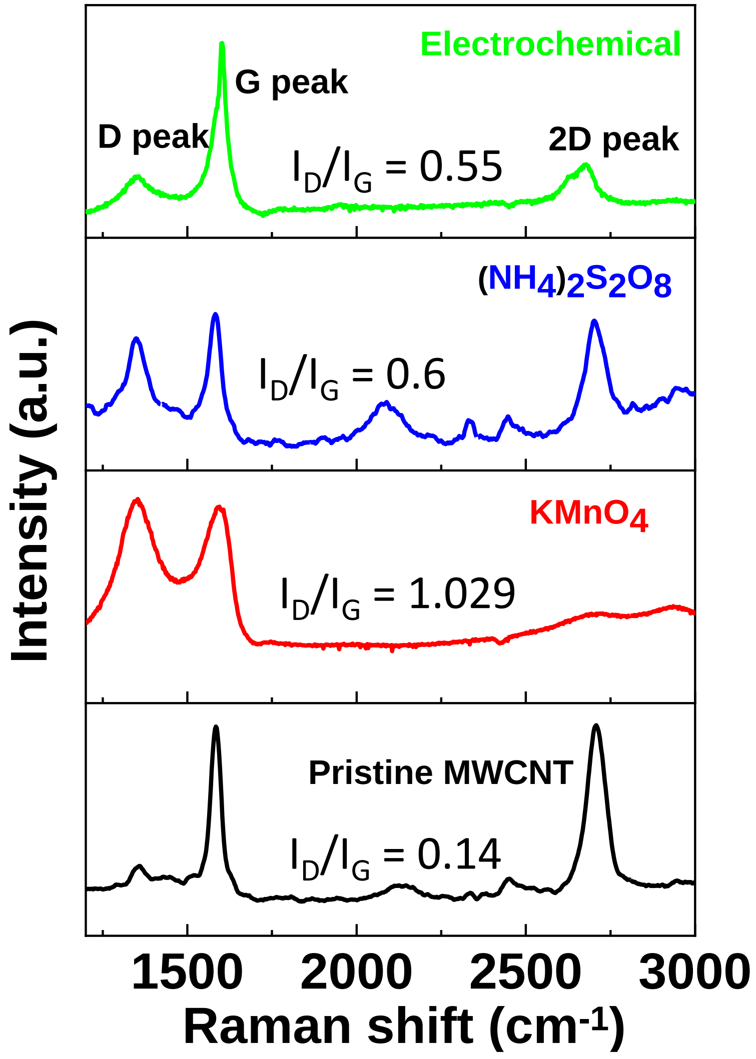


Nature 458, (2009) 872–876. Carbon 158, (2020) 615-623.

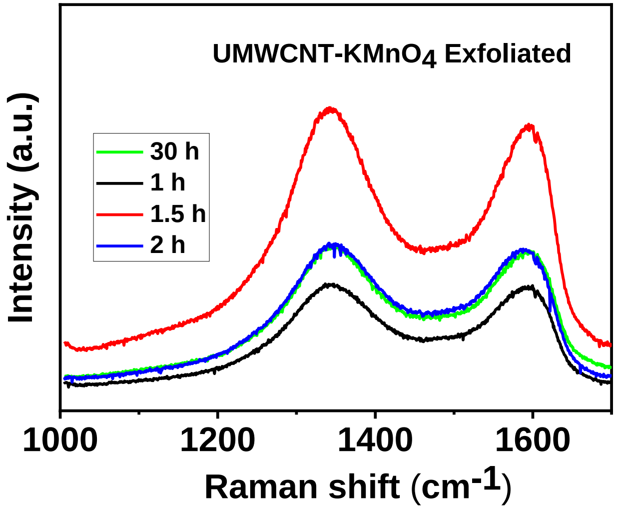
Journal of the American Chemical Society 133, (2011) 4168-4171.

Macromolecular Chemistry and Physics 213, (2012) 1033-1050.

Raman Spectroscopic Investigation of Unzipped MWCNTs

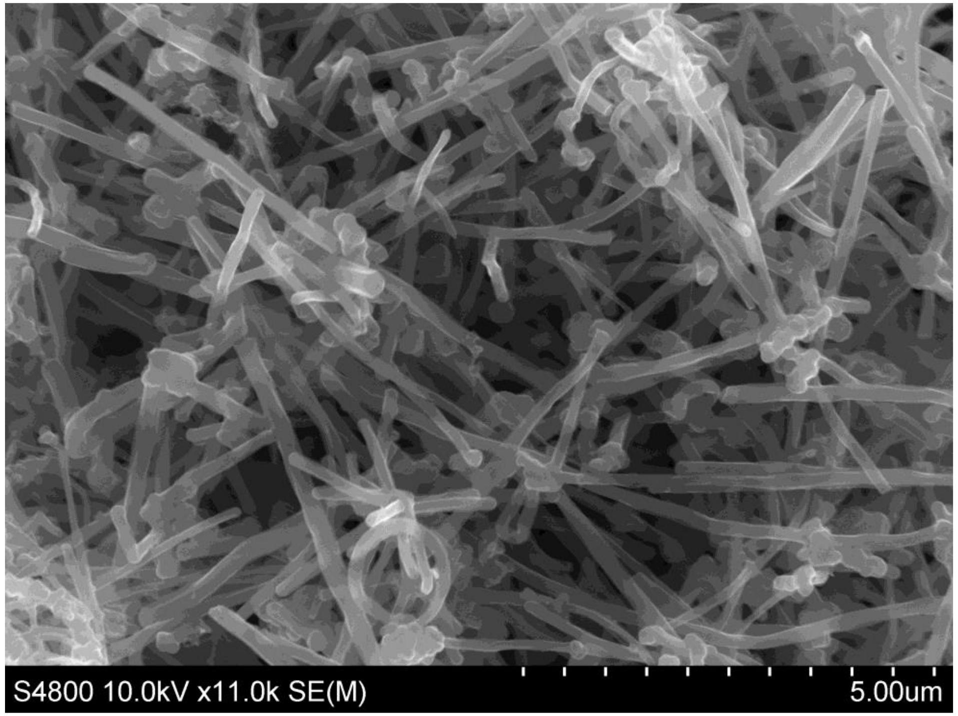


Sample	I_D/I_G	L_D (nm)	n_D x 10^{11} (cm^{-2})
MWCNT	0.14	32.09	0.31
UMWCNT-$KMnO_4$	1.03	11.84	2.31
UMWCNT-$(NH_4)_2S_2O_8$	0.60	15.50	1.35
EC-UMWCNT	0.55	16.19	1.23



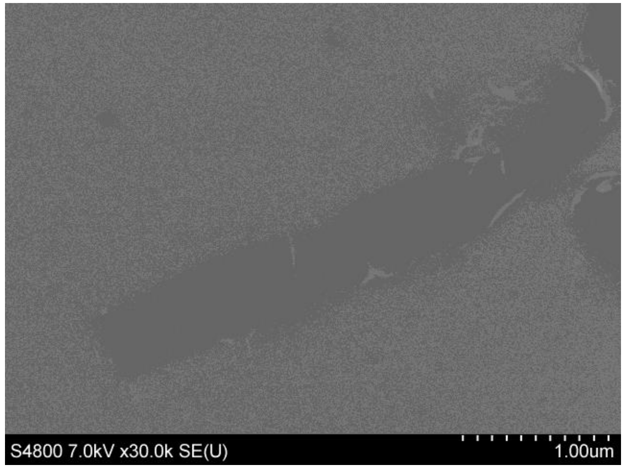
Scanning Electron Microscopy (SEM) Results

Pristine MWCNT

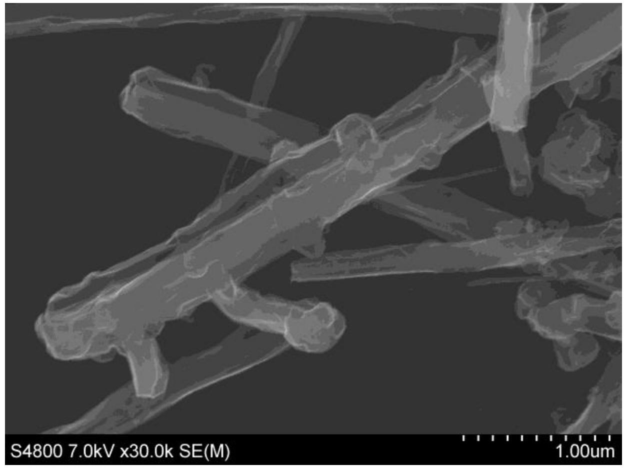


Unzipped MWCNTs

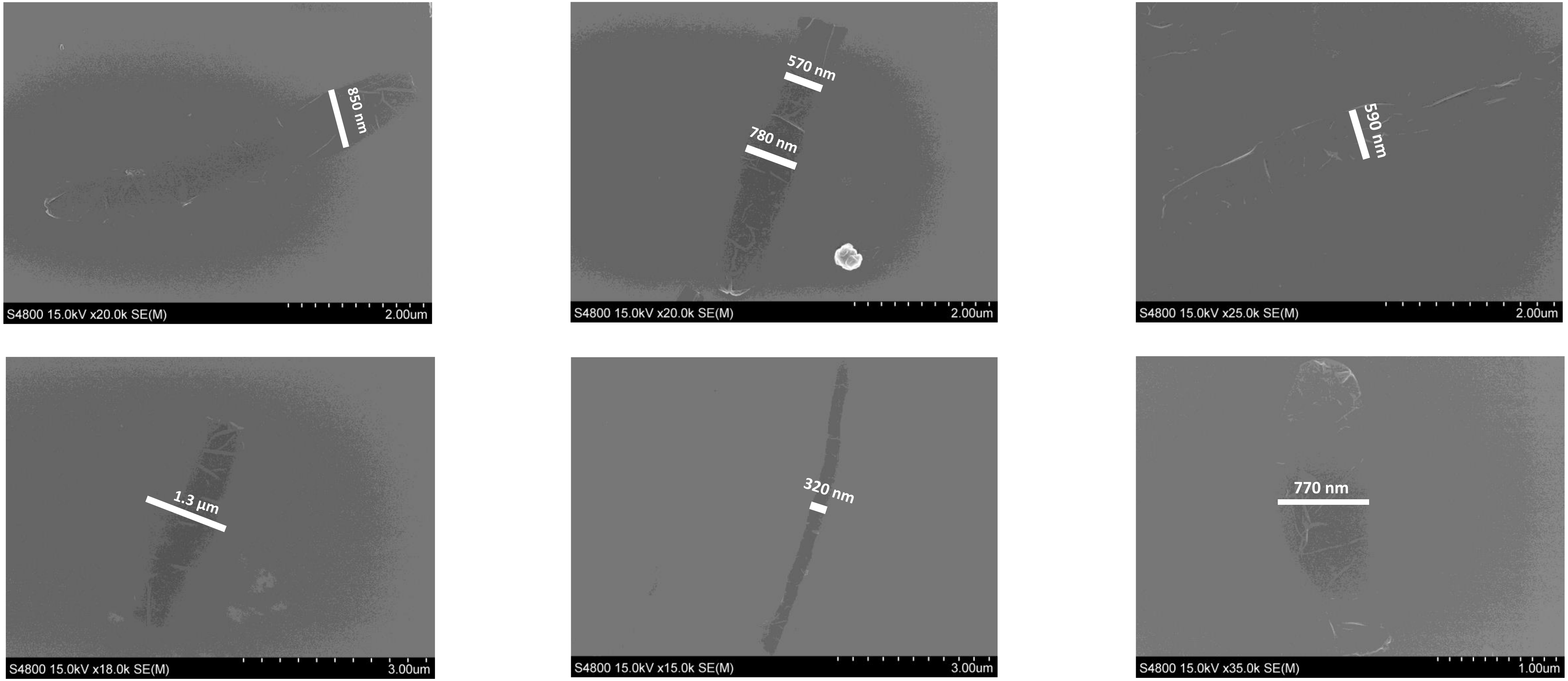
$KMnO_4$



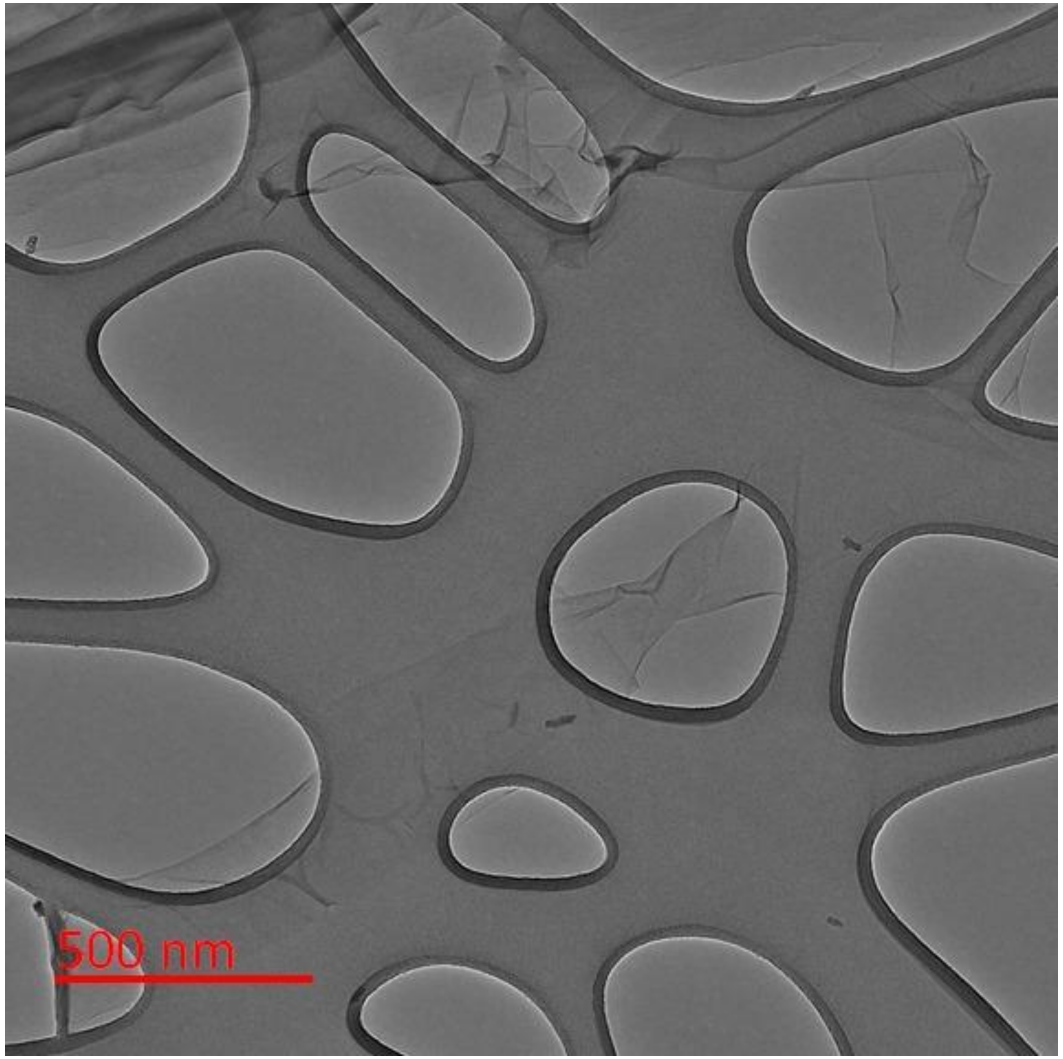
Ammonium persulfate

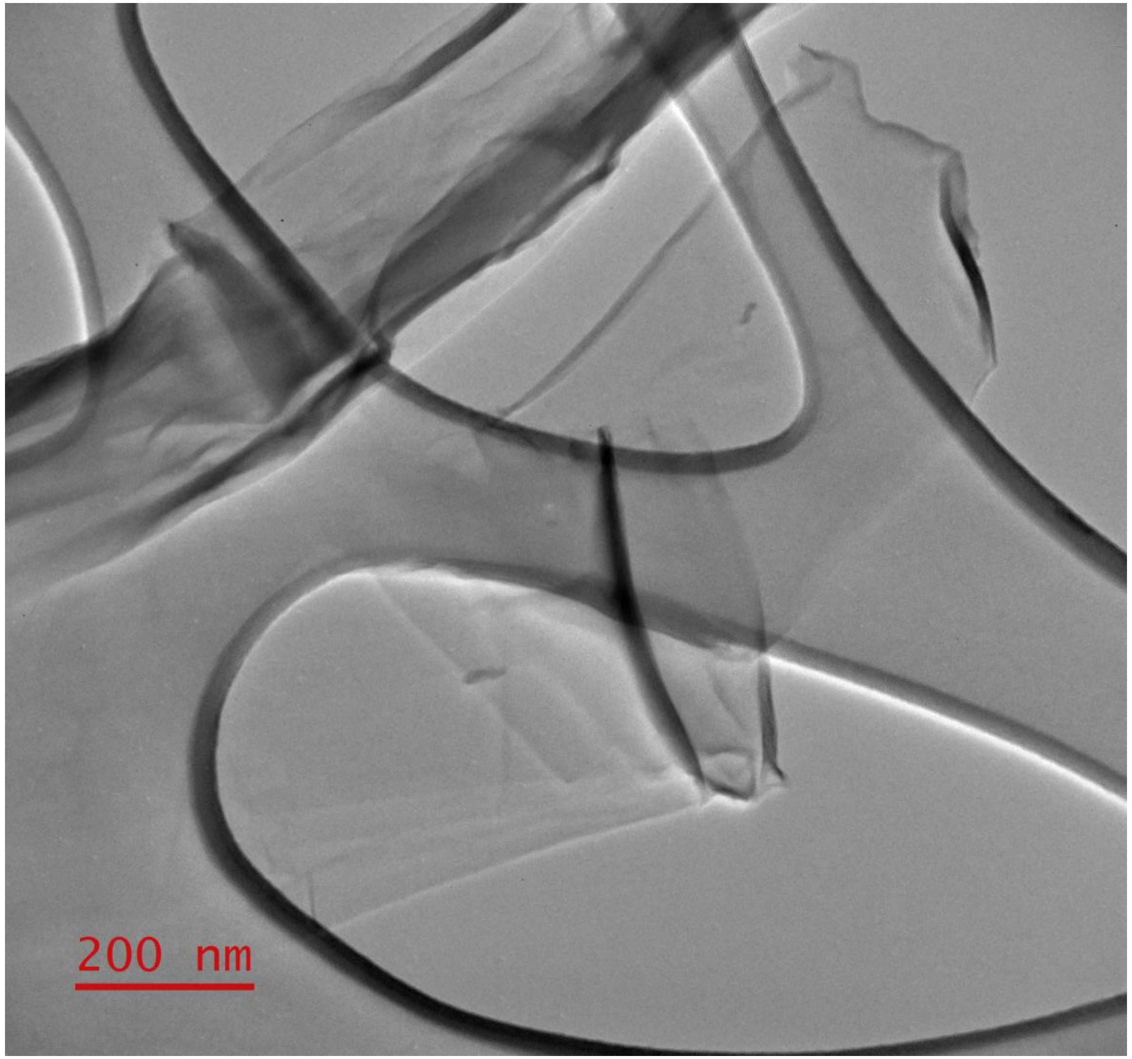


Completely Unzipped MWCNTs by $KMnO_4$ with Different Width

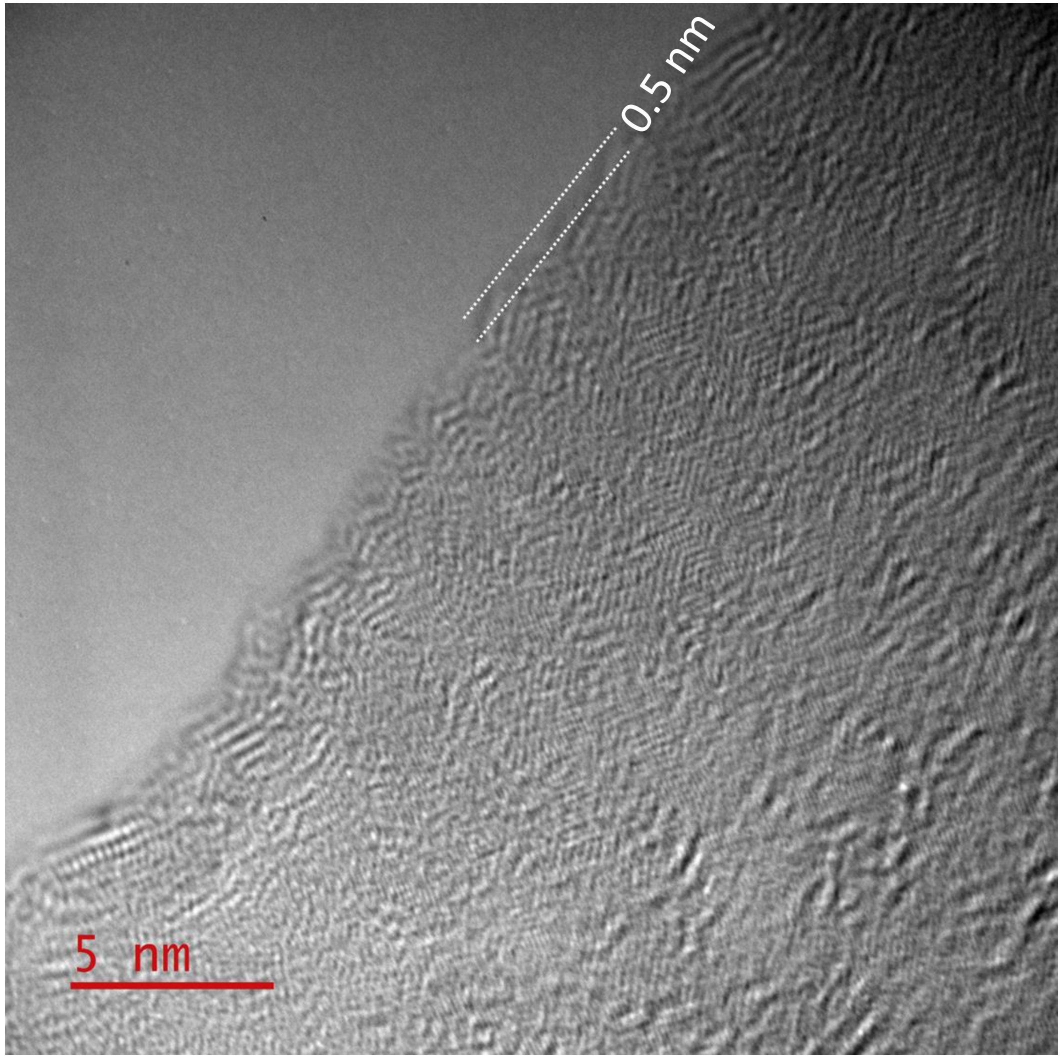


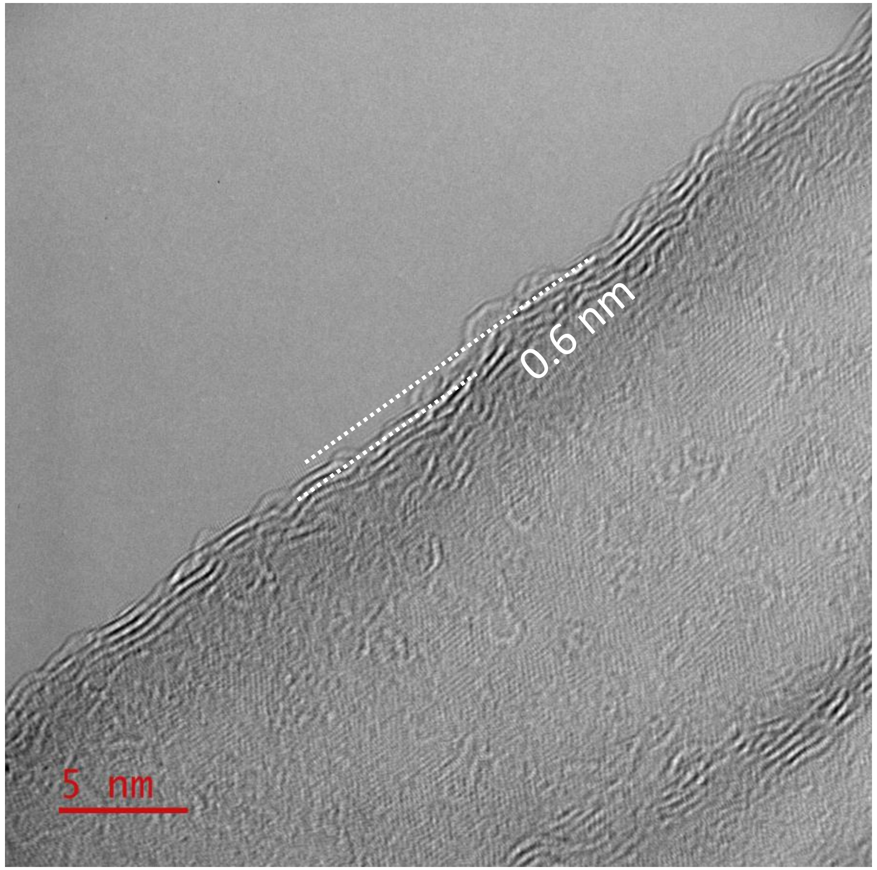
Transmission Electron Microscopy (TEM) Results

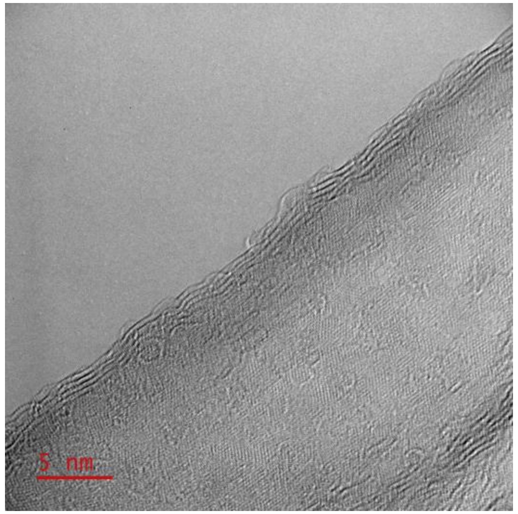


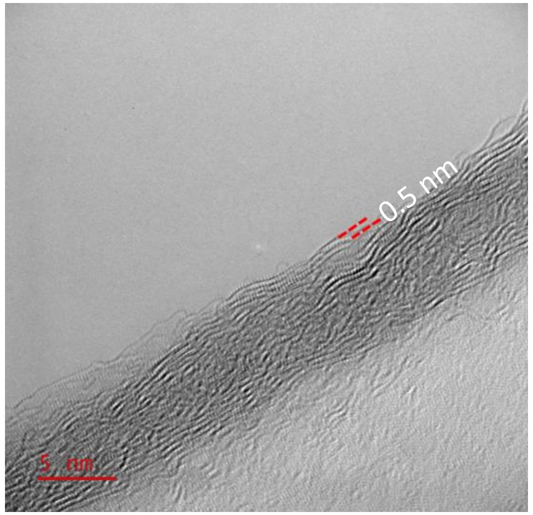


Transmission Electron Microscopy (TEM): Edge Roughness



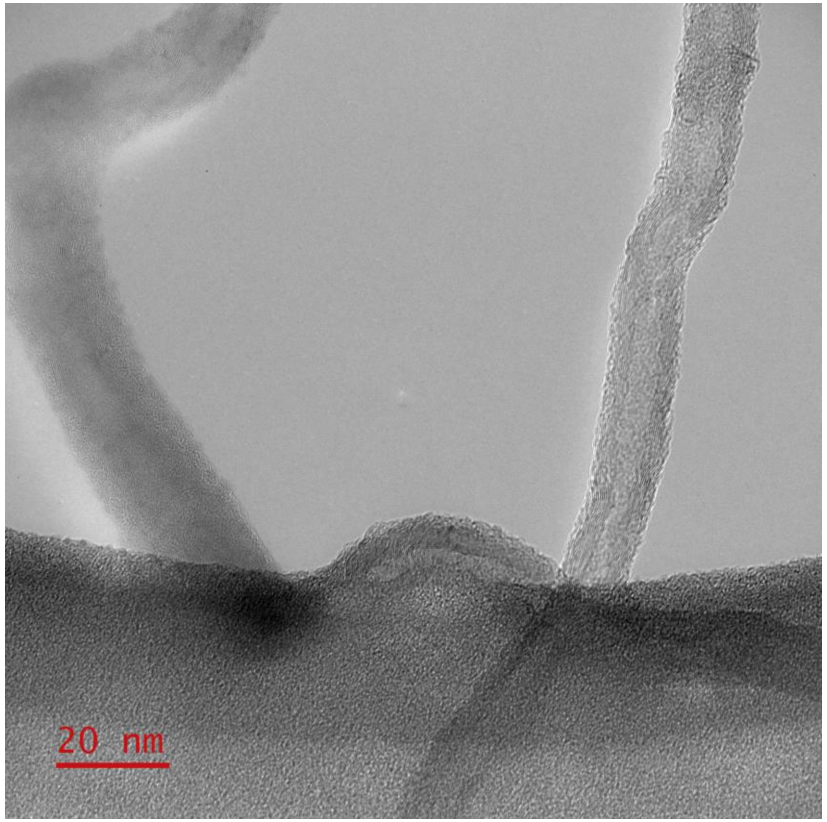


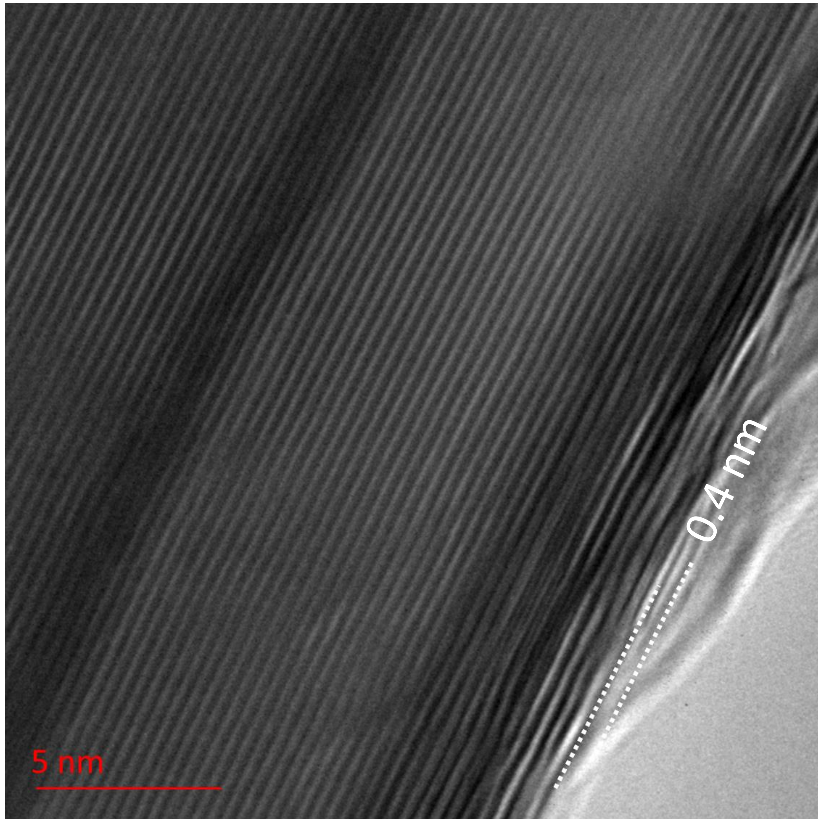




Transmission Electron Microscopy (TEM) Results

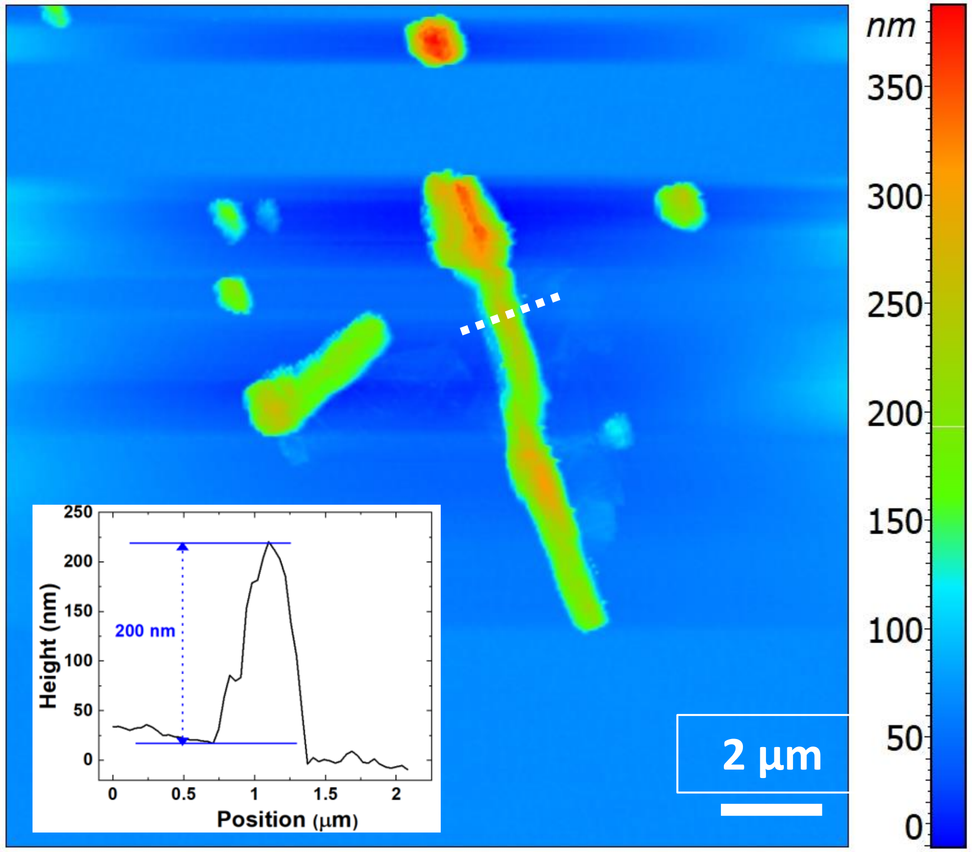
Unzipping of MWCNT by $(NH_4)_2S_2O_8$



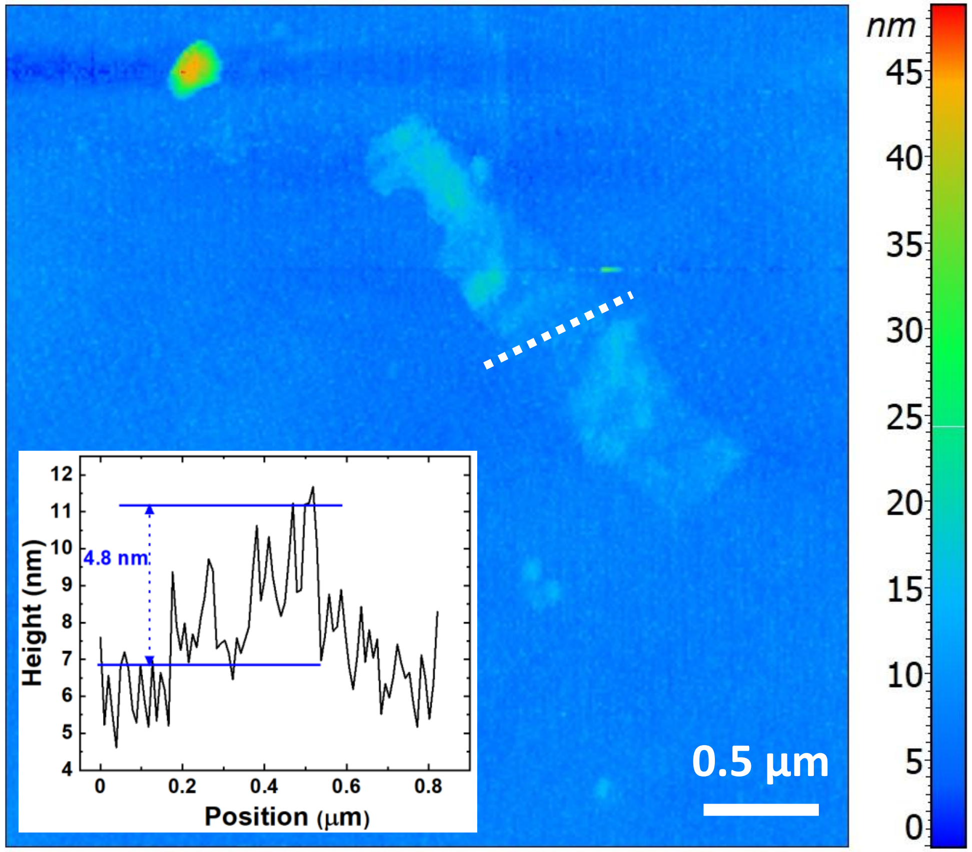


AFM Topography Analysis

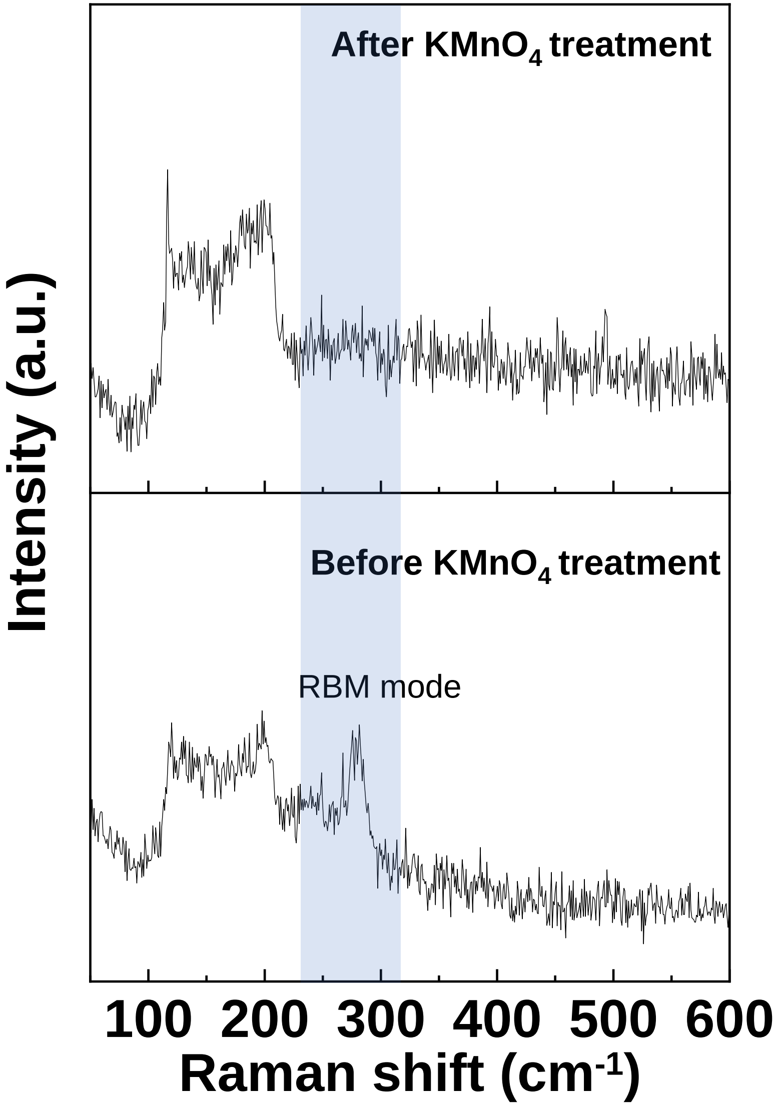
MWCNT

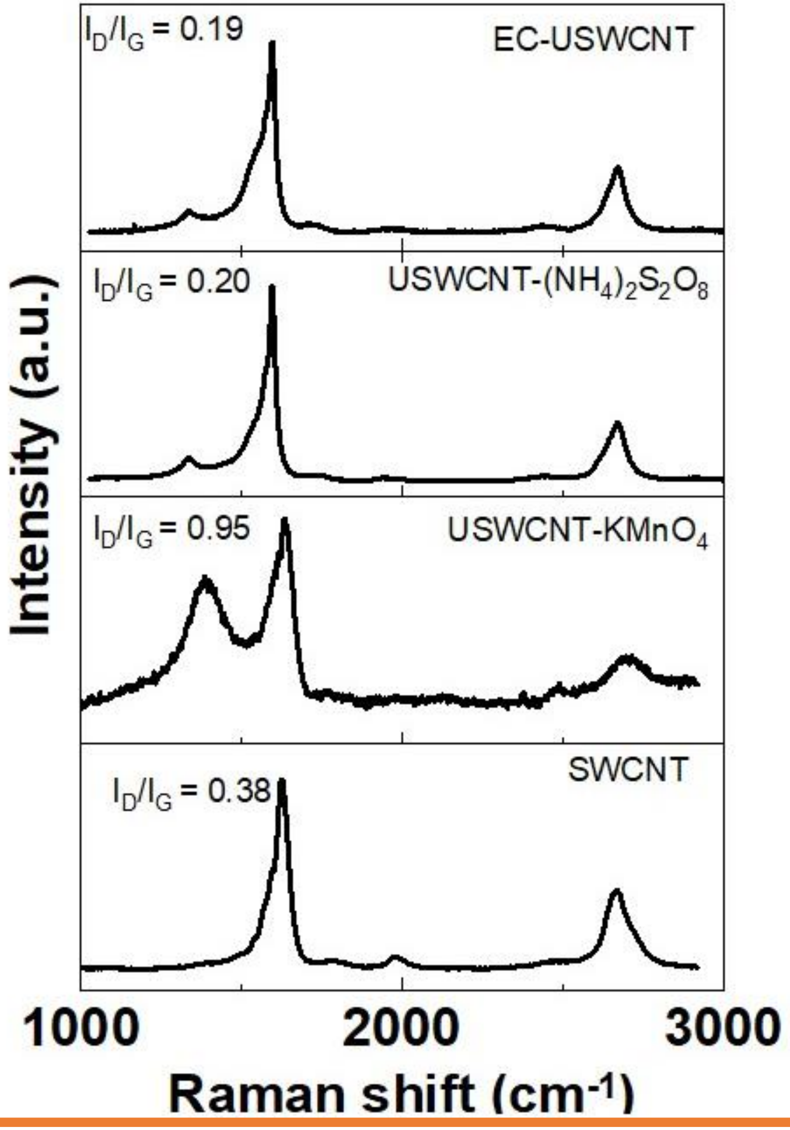


$KMnO_4$ Unzipped MWCNT

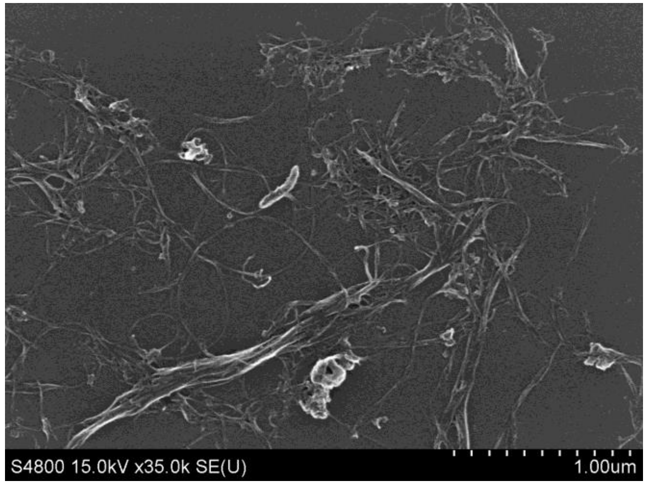


Raman Spectroscopic and SEM Investigation of Unzipped SWCNTs

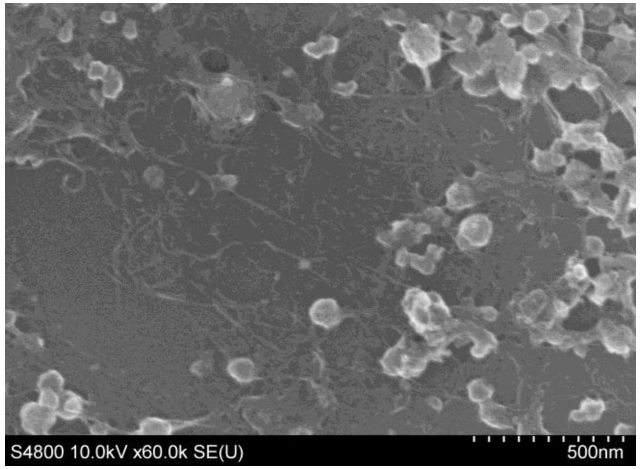




Unzipped SWCNTs



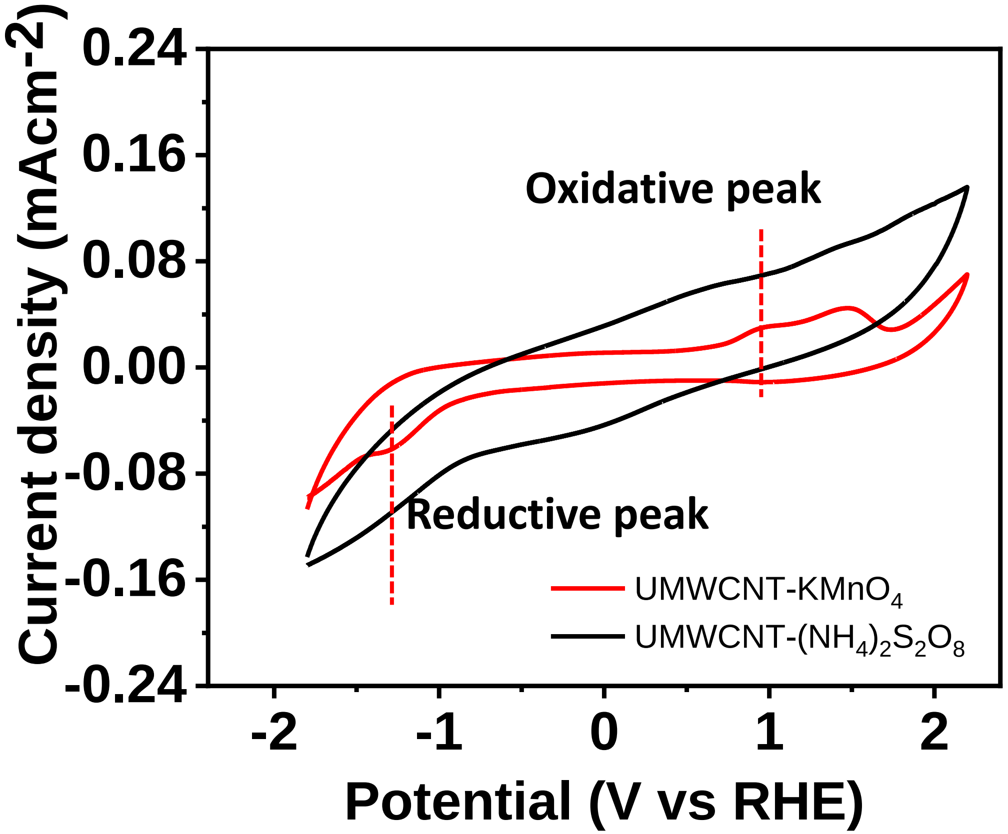
Ammonium persulfate

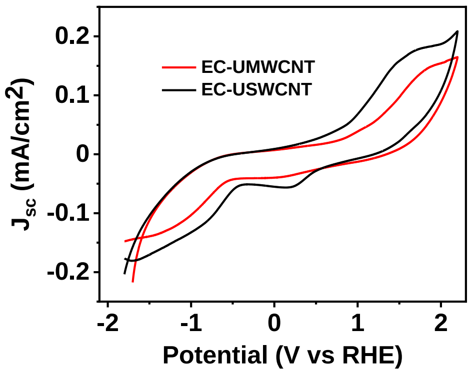


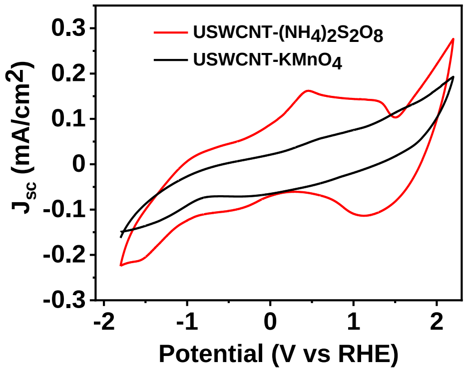
$KMnO_4$

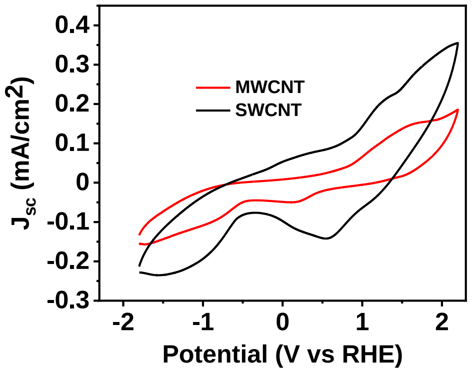
Electrochemical Estimation of Bandgap: Cyclic Voltammetry (CV)

- CV results indicates the unzipped CNTs are semiconducting in nature









$E_{1/2(ferrocene)}$ = 0.31 V, according to the equations

E_{HOMO} = -[E_{ox} – $E_{1/2(ferrocene)}$ + 4.8]eV and

E_{LUMO} = -[E_{red} – $E_{1/2(ferrocene)}$ + 4.8]eV

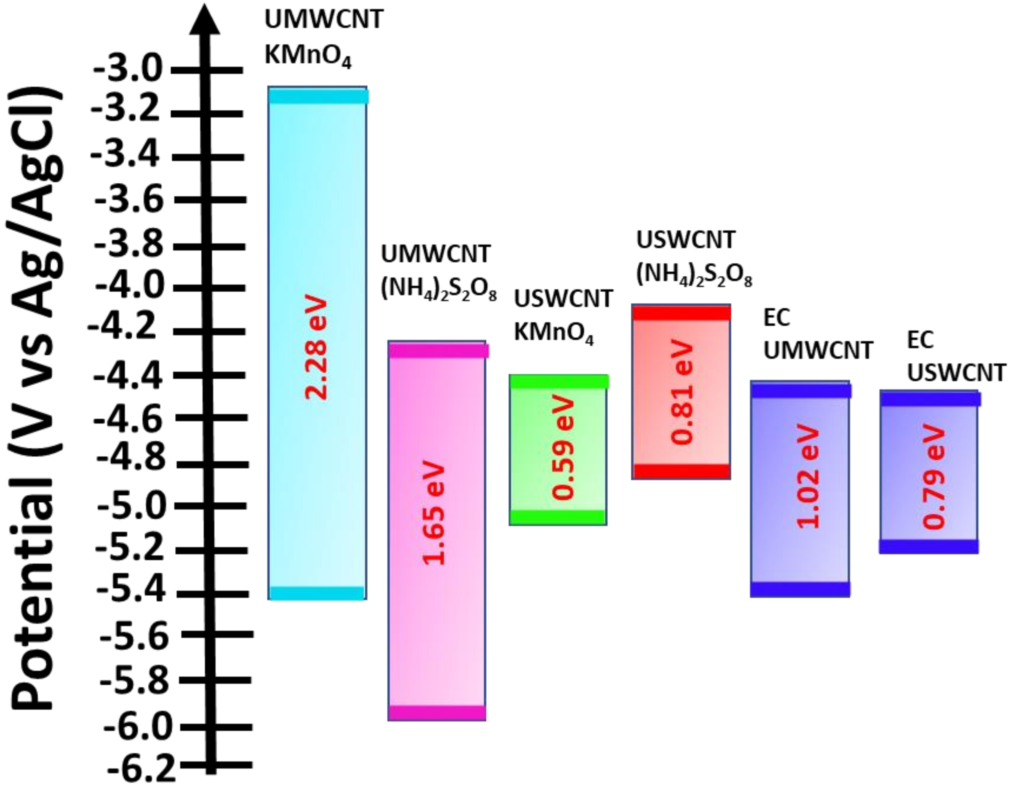
<u>UMWCNT-$KMnO_4$:</u>

E_{LUMO} = -3.14 eV , E_{HOMO} = -5.422 eV Bandgap (E_g) = 2.282 eV

<u>UMWCNT- $(NH_4)_2S_2O_8$:</u>

E_{LUMO} = -4.985 eV , E_{HOMO} = -5.748 eV, Bandgap (E_g) = 0.763 eV

Electrochemical Estimation of Bandgap



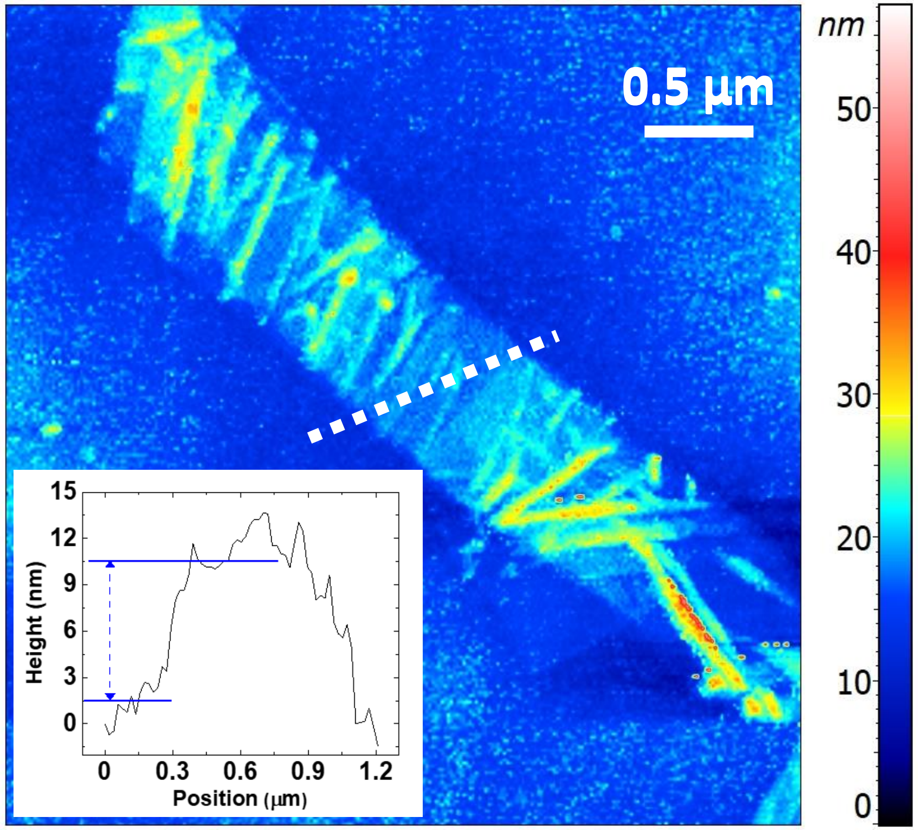
Sample	Unzipping method	Bandgap (eV)
MWCNT	N/A	1.53
SWCNT	N/A	0.69
UMWCNT	$KMnO_4$	2.28
	$(NH_4)_2S_2O_8$	1.65
	Electrochemical	1.02
USWCNT	$KMnO_4$	0.59
	$(NH_4)_2S_2O_8$	0.81
	Electrochemical	0.79

- Electrical transport characteristics are dependent on bandgap.

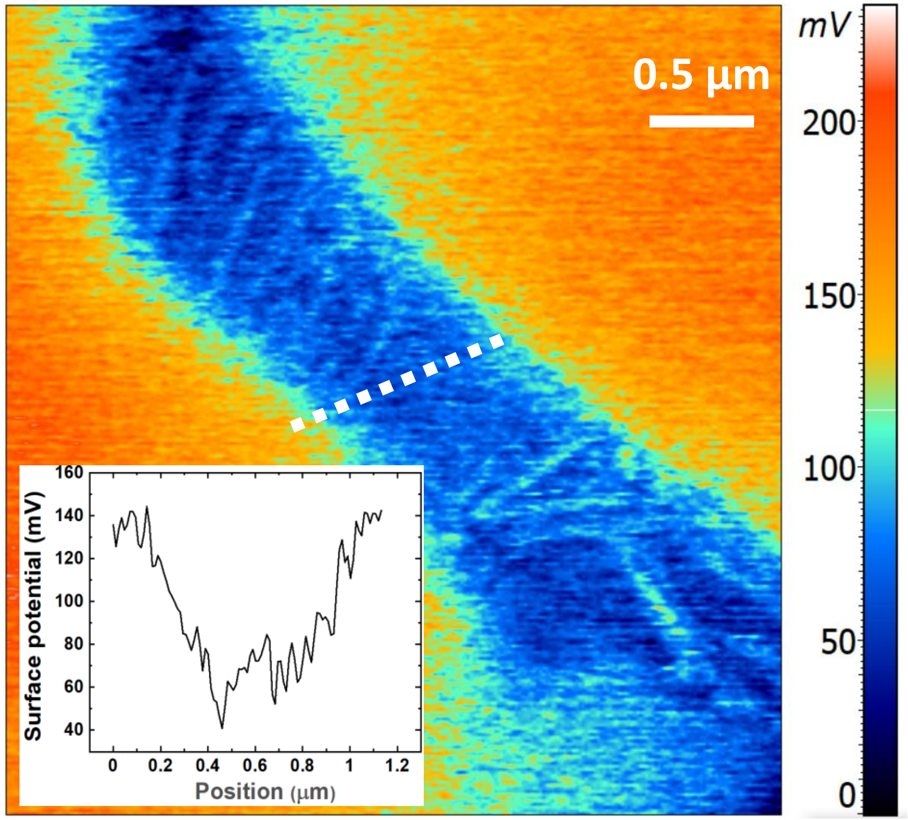
Calculation of Surface Potential and Fermi Level Using SKPFM

$KMnO_4$-UMWCNT

Topography



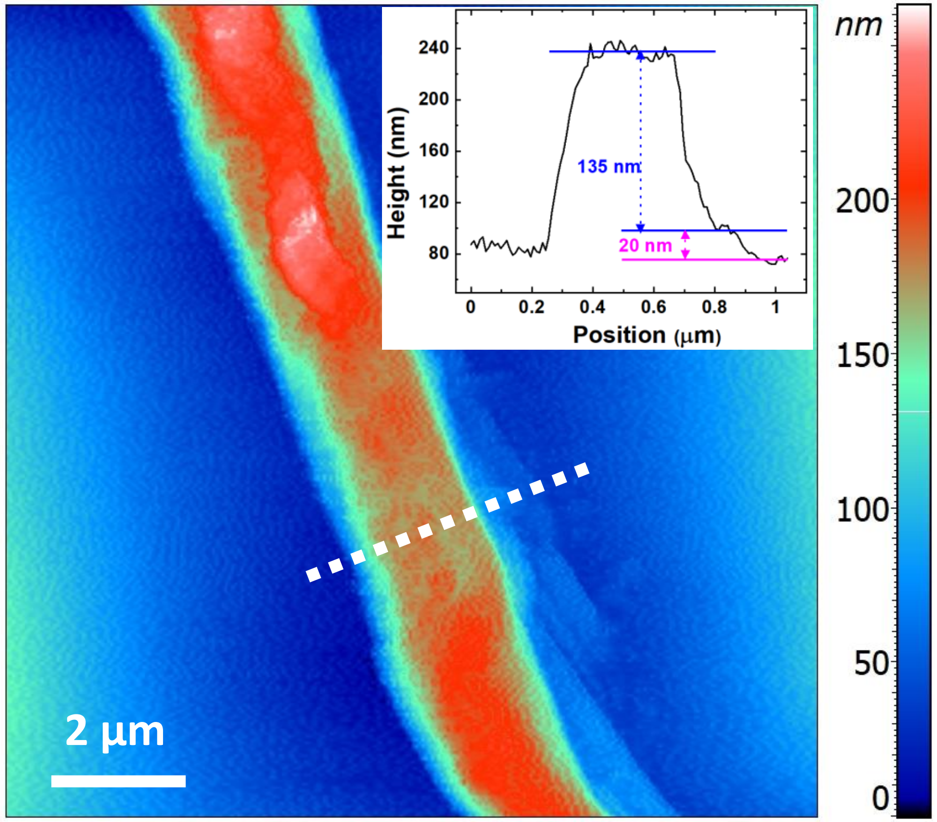
Surface Potential



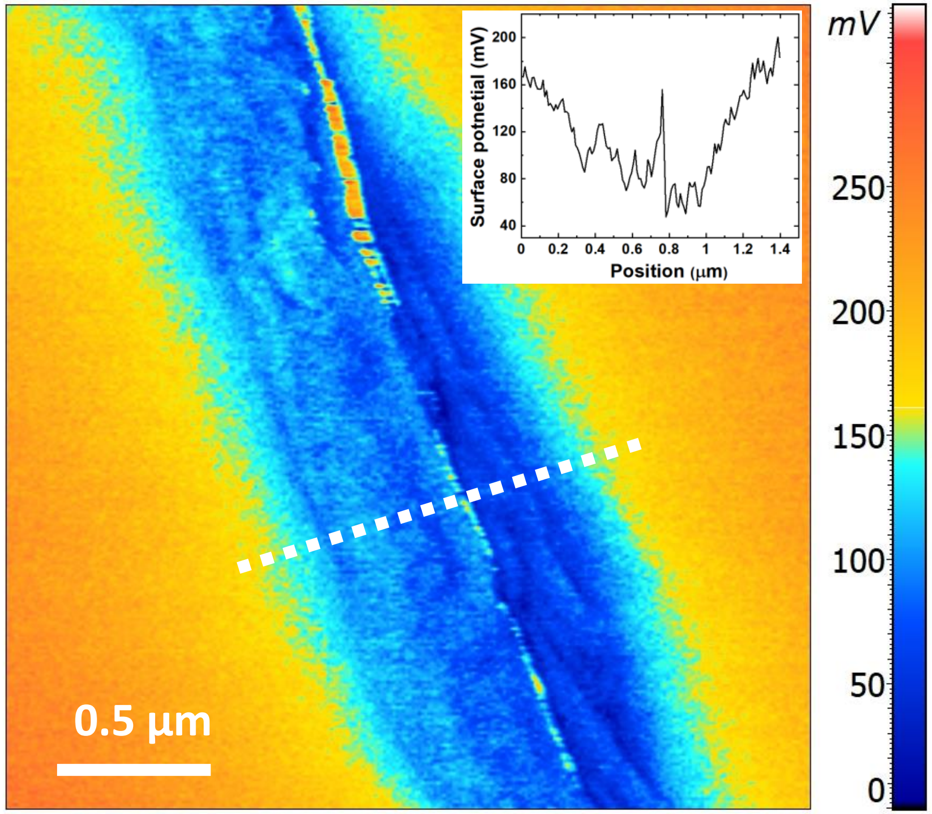
Calculation of Surface Potential and Fermi Level Using SKPFM

$(NH_4)_2S_2O_8$ UMWCNT

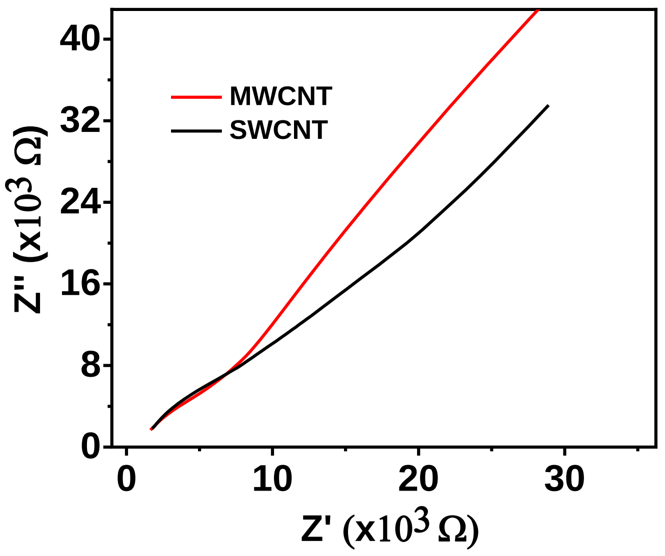
Topography

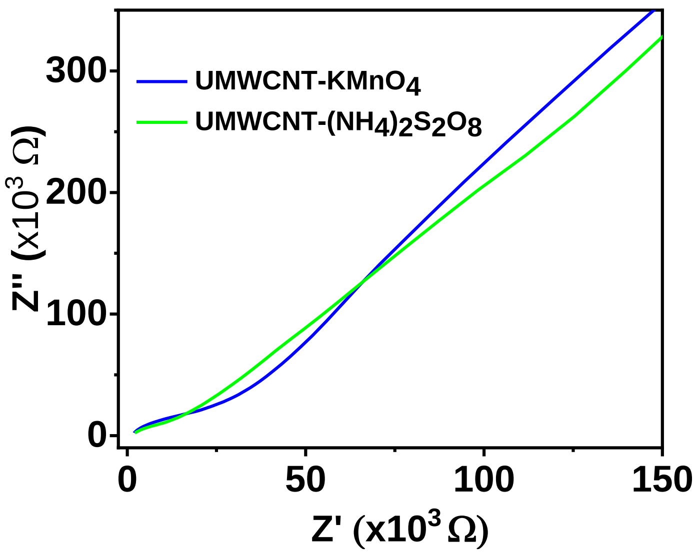


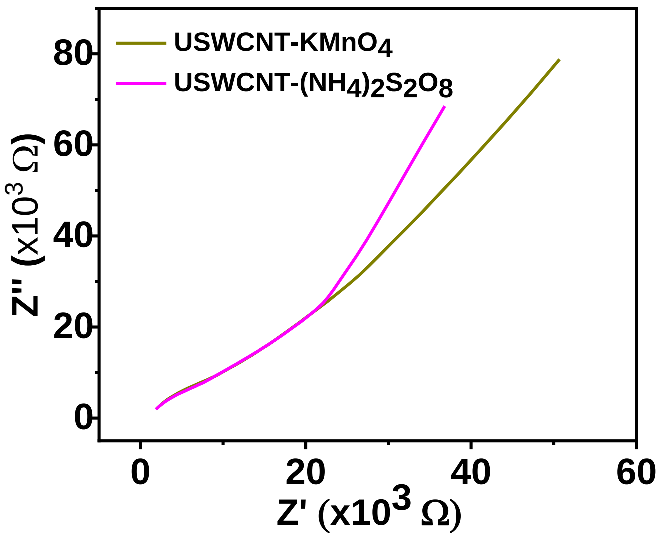
Surface Potential



Conductivity Evaluation of Unzipped CNTs Using Electrochemical Impedance spectroscopy (EIS)





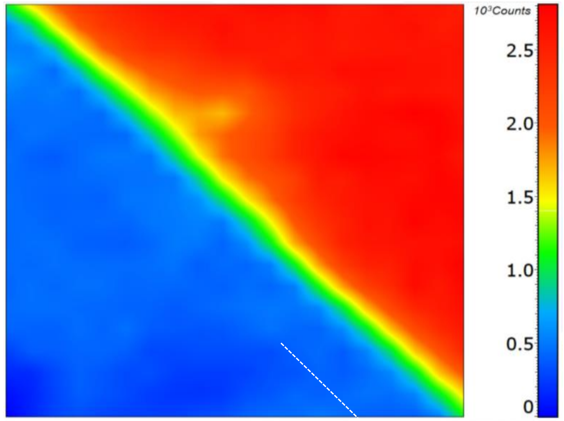


- As received SWCNT and MWCNTs are semiconducting. SWCNT is found to be more conducting compared to MWCNT.
- Same trend holds even after unzipping using $(NH_4)_2SO_8$ and $KMnO_4$
- Unzipping MWCNT/SWCNT using $(NH_4)_2SO_8$ appears to produces more conducting unzipped CNTs compared to $KMnO_4$ unzipping. Agrees well with Raman results.

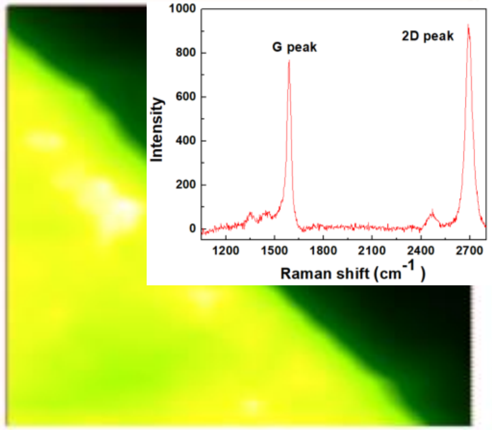
CVD Graphene Growth and Characterization

Two zone CVD furnace

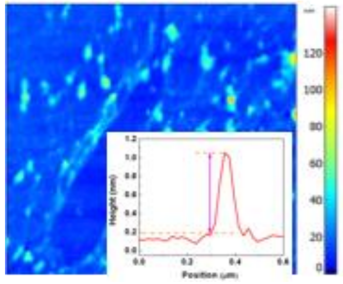
Integrated setup for SPM and Raman characterization

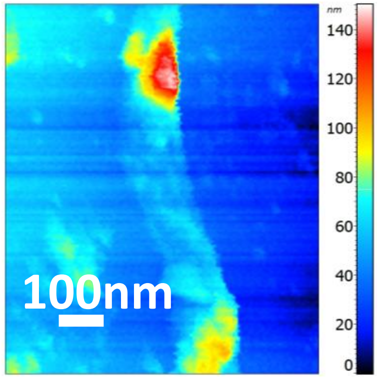


Raman spectrum 2D map

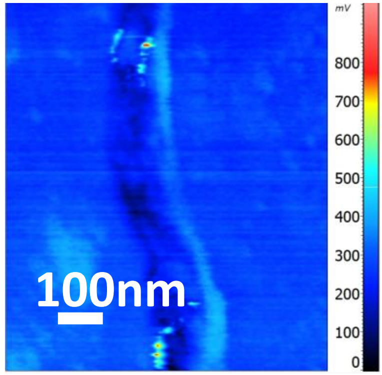


G peak





2D Height map



2D KPFM map

SUMMARY OF CURRENT PROGRESS

1. Initiated synthesis of GNRs using chemical/electrochemical unzipping of MWCNT/SWCNT
2. Characterized unzipped CNTs using different microscopic, spectroscopic and electrochemical techniques
3. Successfully prepared GNRs with different widths using $KMnO_4$ oxidation assisted unzipping of CNTs.
4. Chemical unzipping using ammonium per sulfate require further microscopic/spectroscopic studies to optimize the oxidation process conditions for producing better quality GNRs.
5. KPFM and c-AFM characterization of unzipped CNTs are currently under progress
6. Scanning probe lithography trials are in the early stage.

PROJECT SCHEDULE & MILESTONES

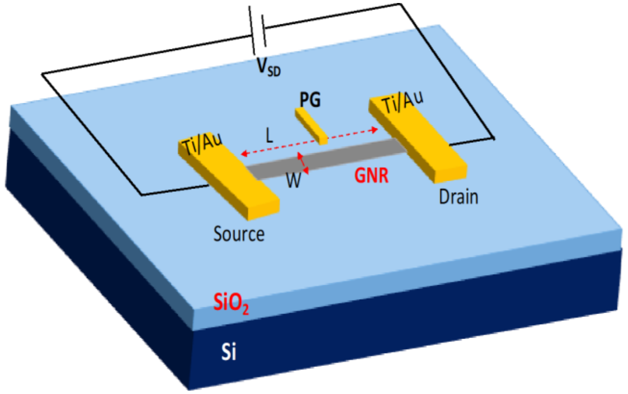
PROJECT SCHEDULE

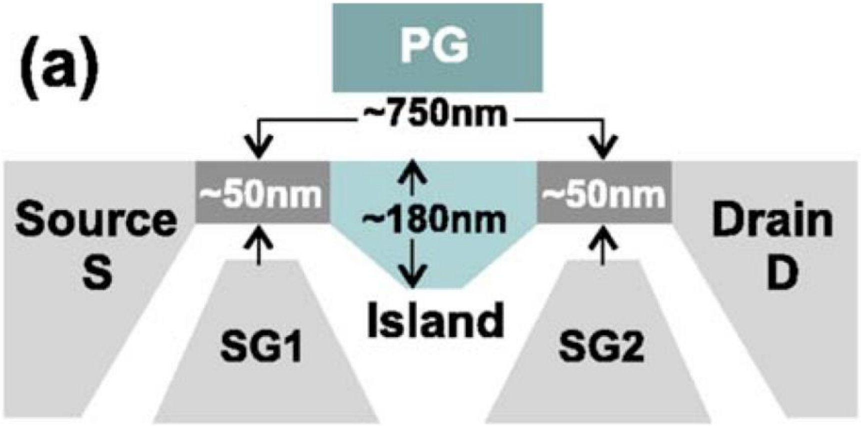
		Yr1				Yr2				Yr3			
S. No.	Task Title	1	2	3	4	1	2	3	4	1	2	3	4
1	**Project Management and Planning**	ϕ											
2	**Preparation of GNRs with prescribed width and smooth edges**		ϕ		ϕ								
3	**Device fabrication and characterization of a single-electron transistor**					ϕ	ϕ		ϕ				
4	**Characterization of GQD charge stability and charge relaxation**							ϕ		ϕ	ϕ		
5	**Fabrication and Characterization of double GQD spin qubit system**												ϕ
6	**Final Verification**												$\phi\Delta$
	ϕ-Milestones	**Δ-Go/No-Go Decision points**											

FUTURE WORK

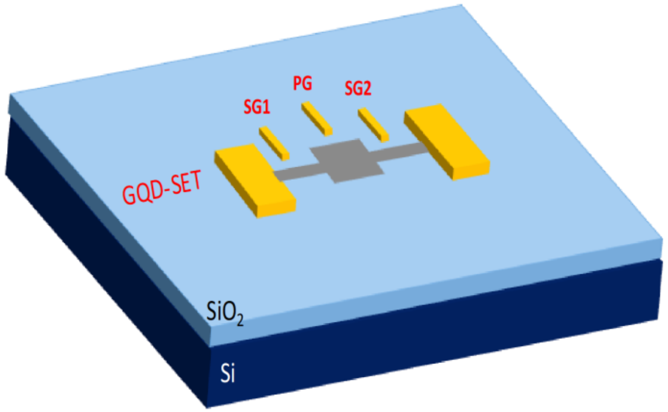
Proposed GQD-based SET and QPC Device Structure

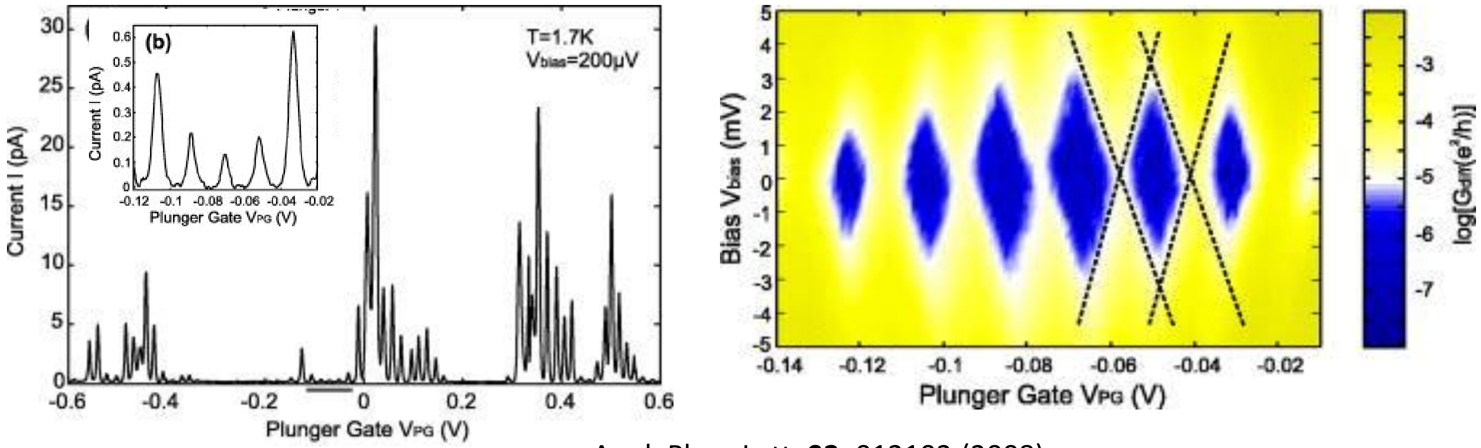
1. Electrical transport studies on GNR devices





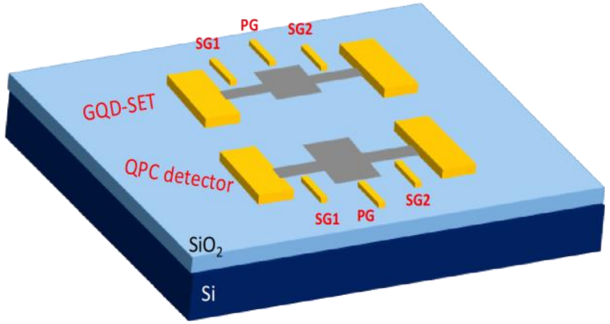
2. Characterization of SET

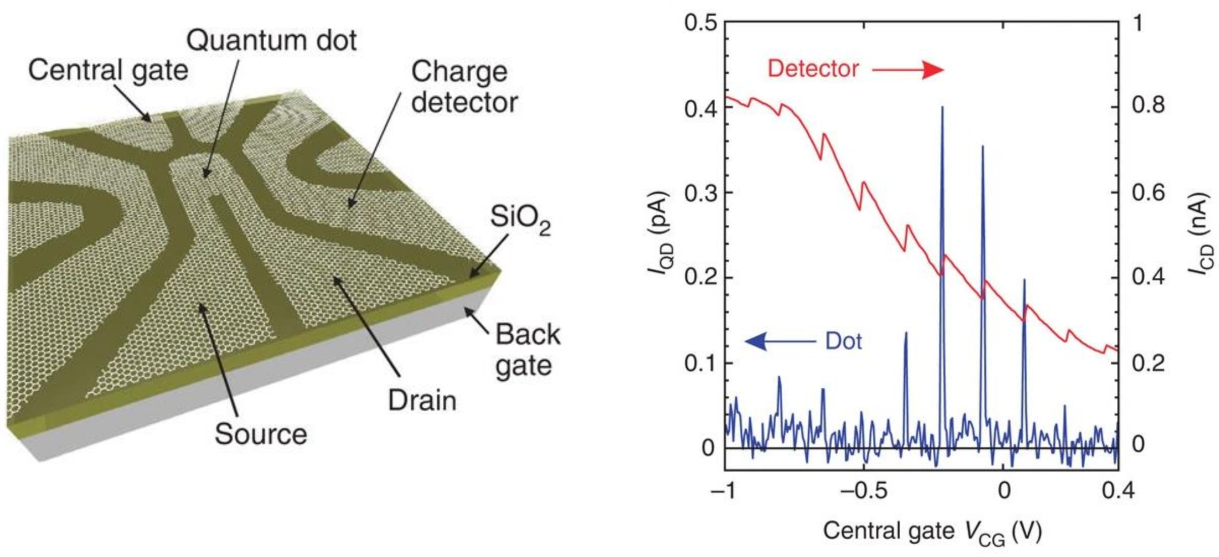




Appl. Phys. Lett. **92**, 012102 (2008)

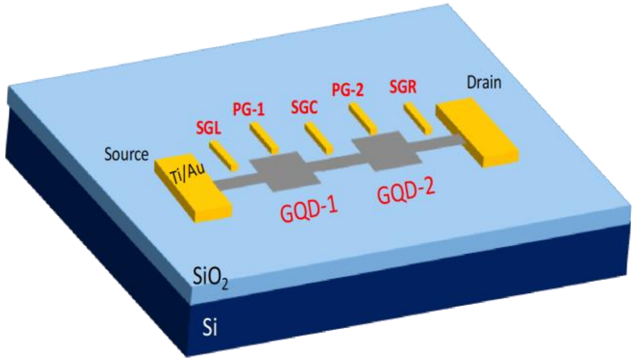
3. Characterization of SET using QPC

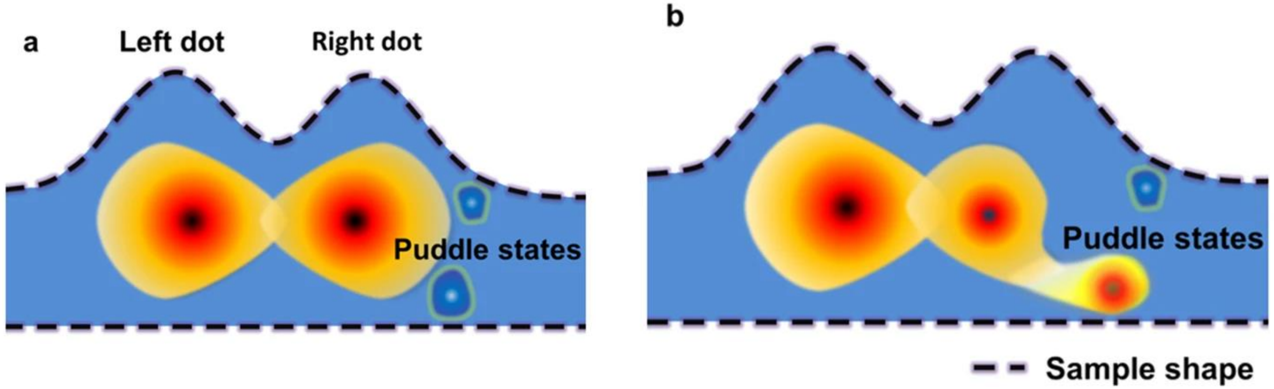




Nature communications **volume 4**, 1753 (2013)

4. Characterization of Double Quantum Dots





https://www.nature.com/articles/srep03175#Fig5

Publications

Exclusively from the project

1. Aruna N. Nair, Venkata S.N. Chava, and Sreeprasad T. Sreenivasan, "A combined microscopic, spectroscopic, and electrochemical investigation of graphene nanoribbons prepared by unzipping CNTs: Edges, Doping, and Band Structure Analysis". (*Manuscript under preparation for J. Phys. Chem. Lett.*).

Acknowledged for partial support

1. Mohamed F Sanad, Venkata S. N. Chava, Ahmed Shalan, Ting Zheng, Srikanth Pilla, Sreeprasad Sreenivasan, "Engineering of Electron Affinity and Interfacial Charge Transfer of Graphene for Self-powered Non-enzymatic Biosensor Applications", *ACS Applied Materials and Interfaces* (under review).
2. Venkata S.N. Chava, P.S. Chandrasekhar, Ashley Gomez, Luis Echegoyen, and Sreeprasad T. Sreenivasan, "MXene-based Interfacial Engineering of Efficient P-I-N Perovskite Solar Cells: A Fundamental Exploration", *Journal of Materials Chemistry A* (submitted).

Acknowledgments

- Dr. Adam Payne (Project Manager, DOE)
- Functional Quantum Materials Laboratory (FQML), UTEP
- Office of Research and Sponsored Projects (ORSP), UTEP

Acknowledgment: "This material is based upon work supported by the Department of Energy Award Number DE-FE0031908."

Thank You!