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

Project # DE-FE0031908

Sreeprasad T. Sreenivasan (PI)

Ramana Chintalapalle (co-PI) Venkata Surya N. Chava (co-PI)

The University of Texas at El Paso

Acknowledgments

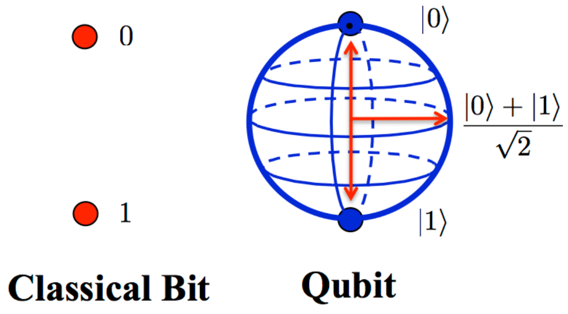
- Dr. Adam Payne (Project Manager, DOE)
- Aruna Nair, Functional Quantum Materials Laboratory (FQML), UTEP
- Center for Integrated Nanotechnologies (CINT), Albuquerque, NM
- Prof. Trevor Thornton, Director - ASU Nanofab

U.S. DEPARTMENT OF ENERGY
Office of Fossil Energy

NATIONAL ENERGY TECHNOLOGY LABORATORY

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*(3), 192-196 (2007)

DiVincenzo criteria

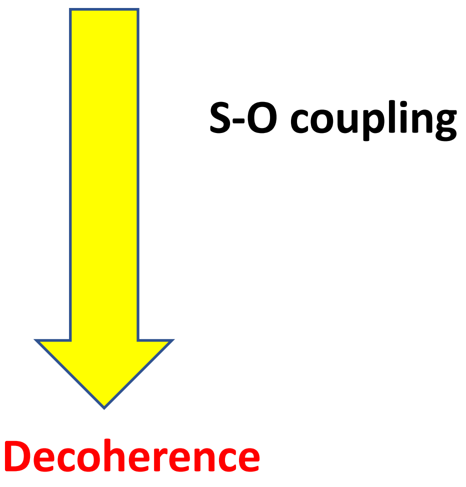
1. Long coherence time
2. Efficient initialization
3. Scalable
4. Readout
5. Universal quantum gates

Progress of Physics, 48(9-11), 771-783. (2000)

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%

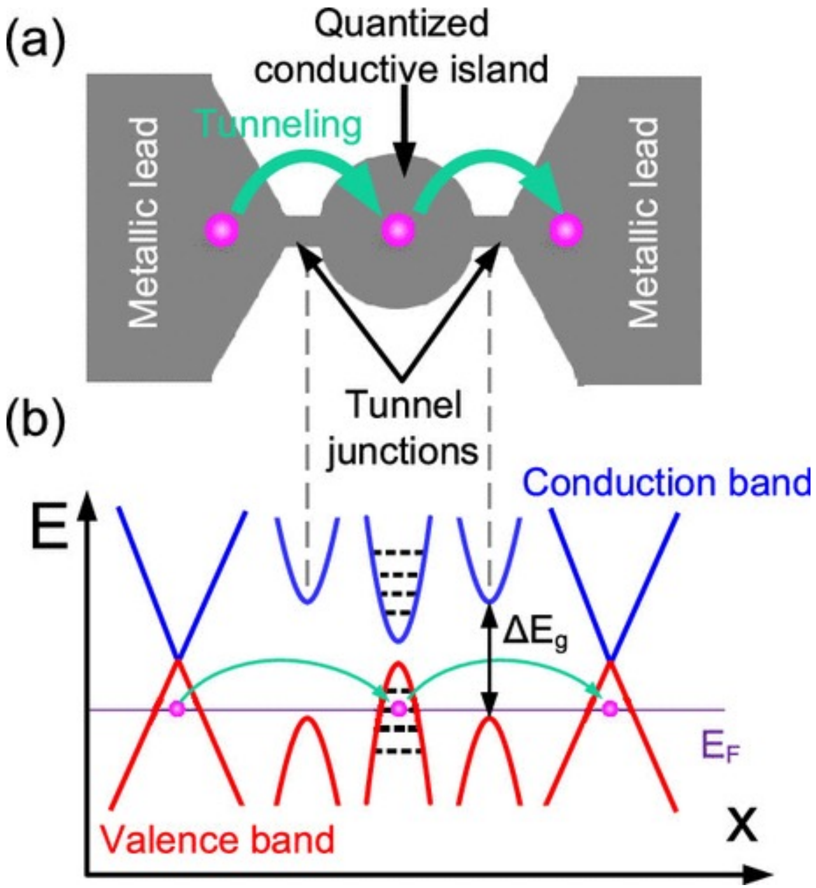


Advantages of Graphene

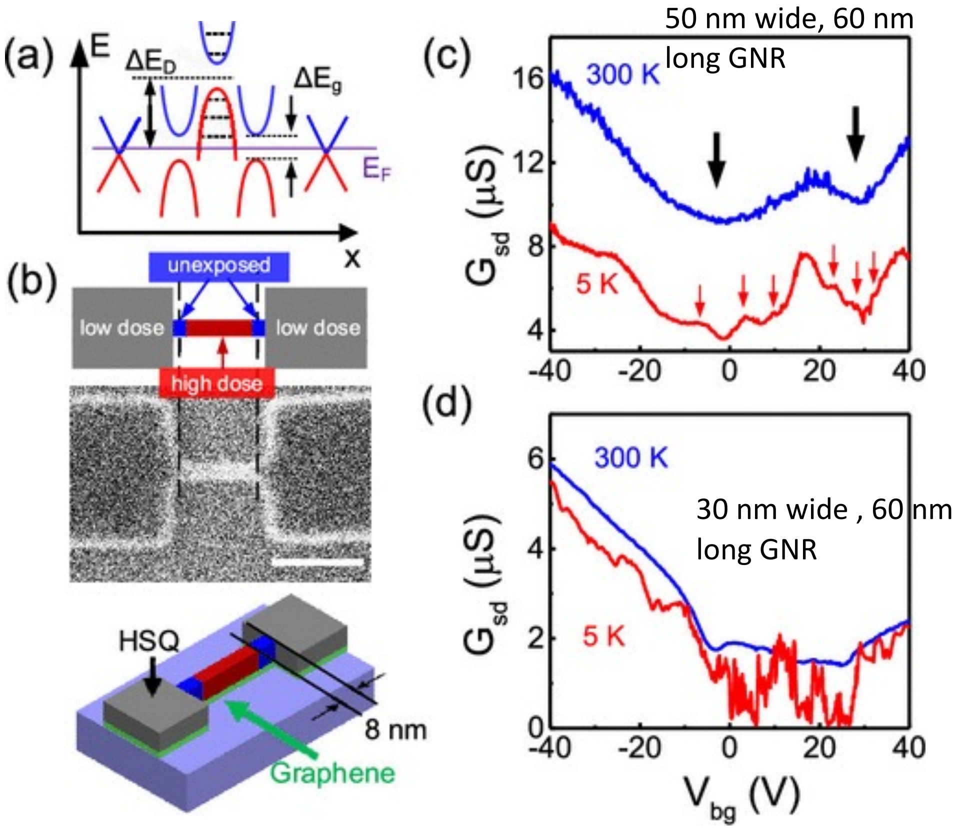
1. Very low nuclear spin
2. Weak spin-orbit coupling
3. Scalable material platform

Nature Physics 3.3 (2007): 192-196.

Quantum Dots in “Graphene”



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



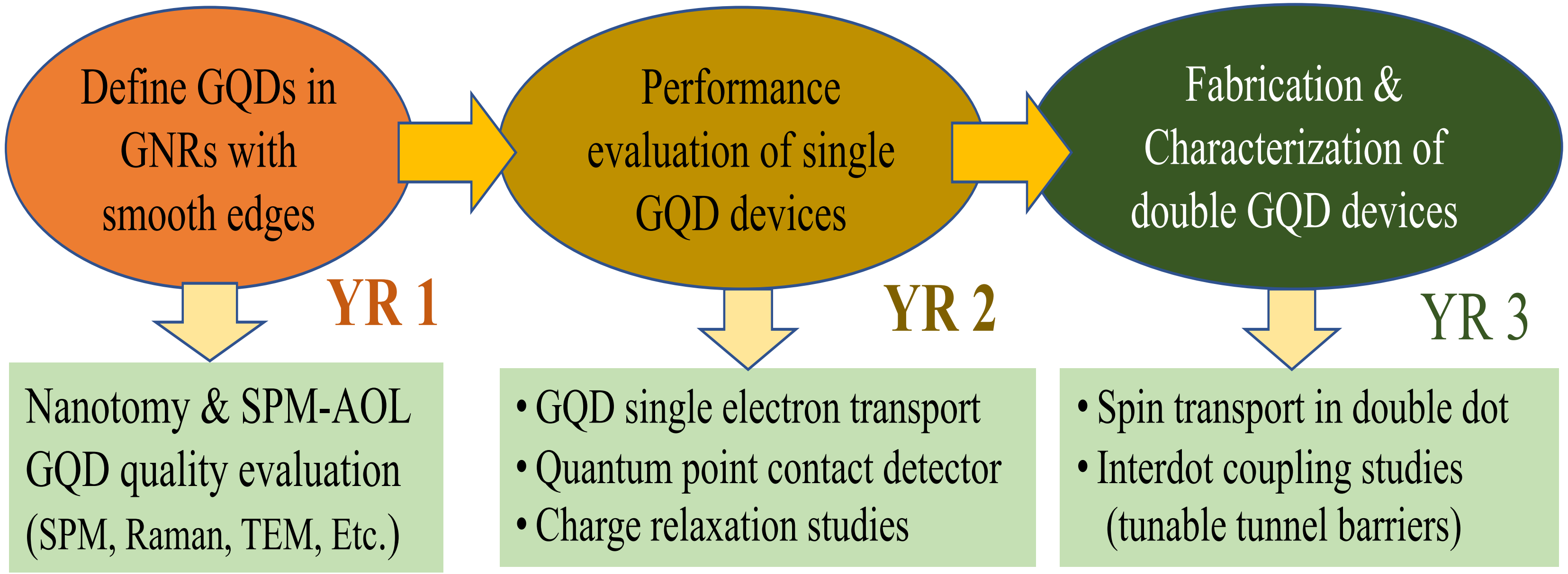
ACS nano 13.7 (2019): 7502-7507.

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

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**											

CURRENT PROGRESS AND RESULTS

Preparation of GNRs: Part-I

Chemically unzipped CNTs: Material Synthesis and Characterization

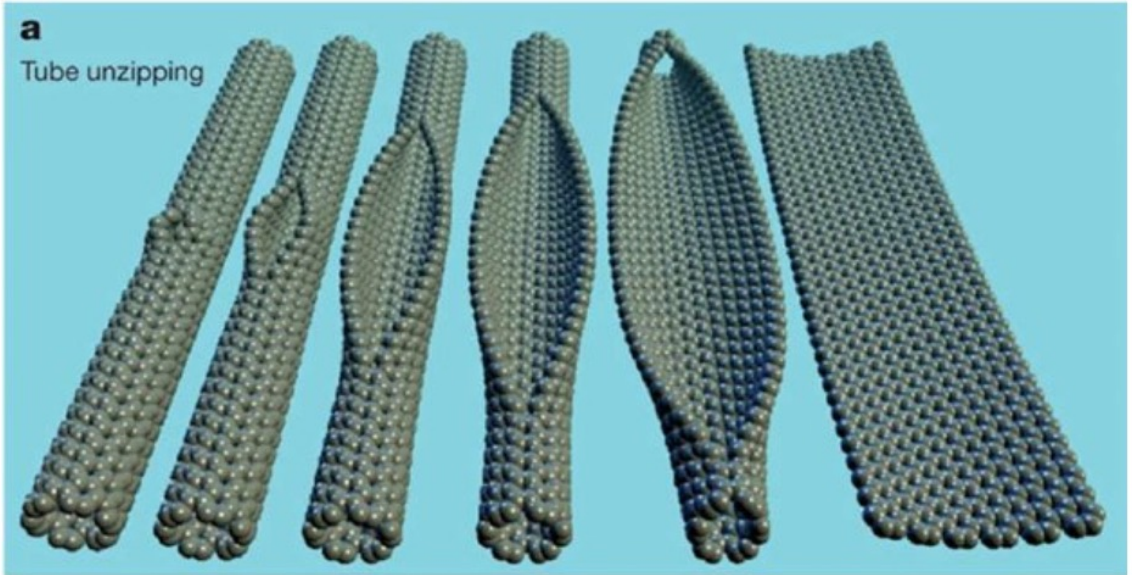
- **Unzipping of CNTs produces semiconducting GNRs**

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

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

MWCNTS/SWCNTS $\xrightarrow[\text{2 steps, oxidation and reduction}]{\text{Electrochemical Unzipping}}$

Unzipping of Carbon Nanotubes (CNTs)



James, Dustin K., and James M. Tour, *Macromolecular Chemistry and Physics*, *213*(10-11), 1033-1050

Kosynkin, D., et. al, *Nature* 458**,** 872–876 (2009)

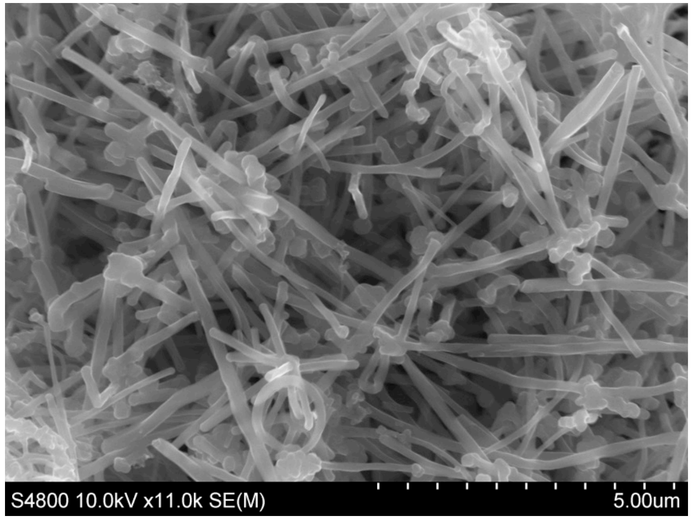
Tuo Wang, et. al, Carbon, 158, 2020, 615-623,

Dhanraj B. Shinde, et. al., *Journal of the American Chemical Society* 2011 *133* (12), 4168-4171

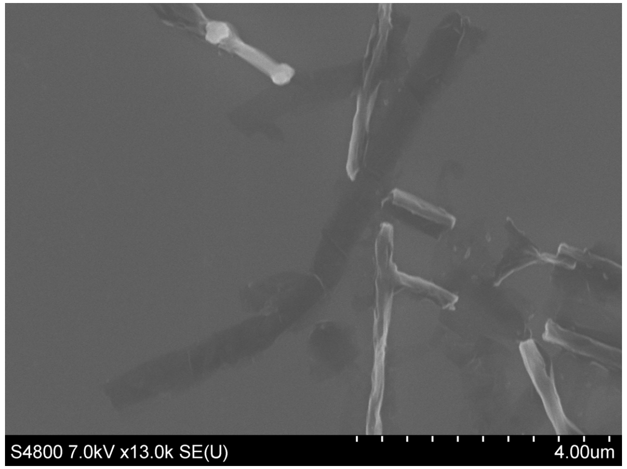
Scanning Electron Microscopy (SEM) Results

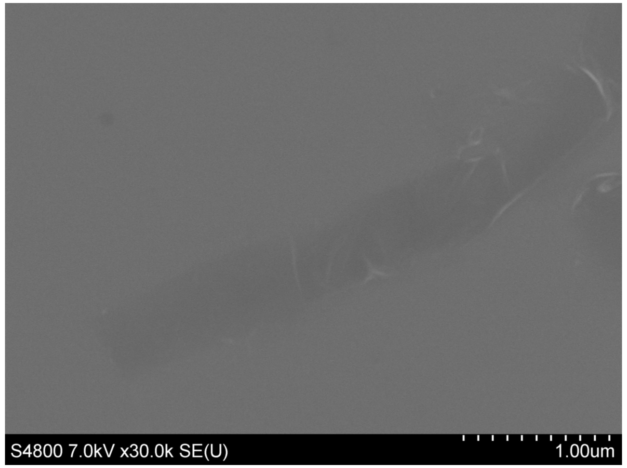
Unzipped MWCNTs

Pristine MWCNT

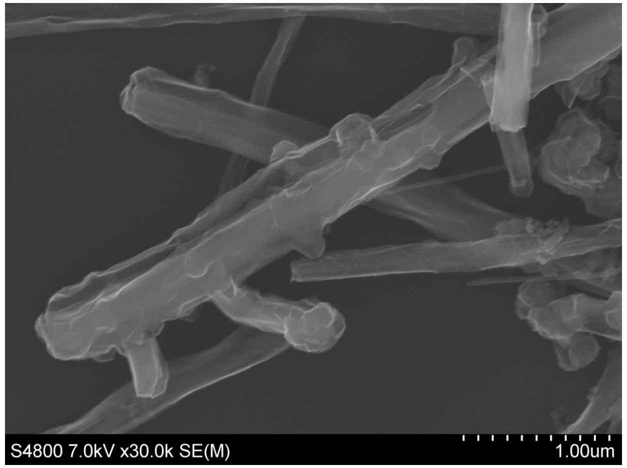


$KMnO_4$

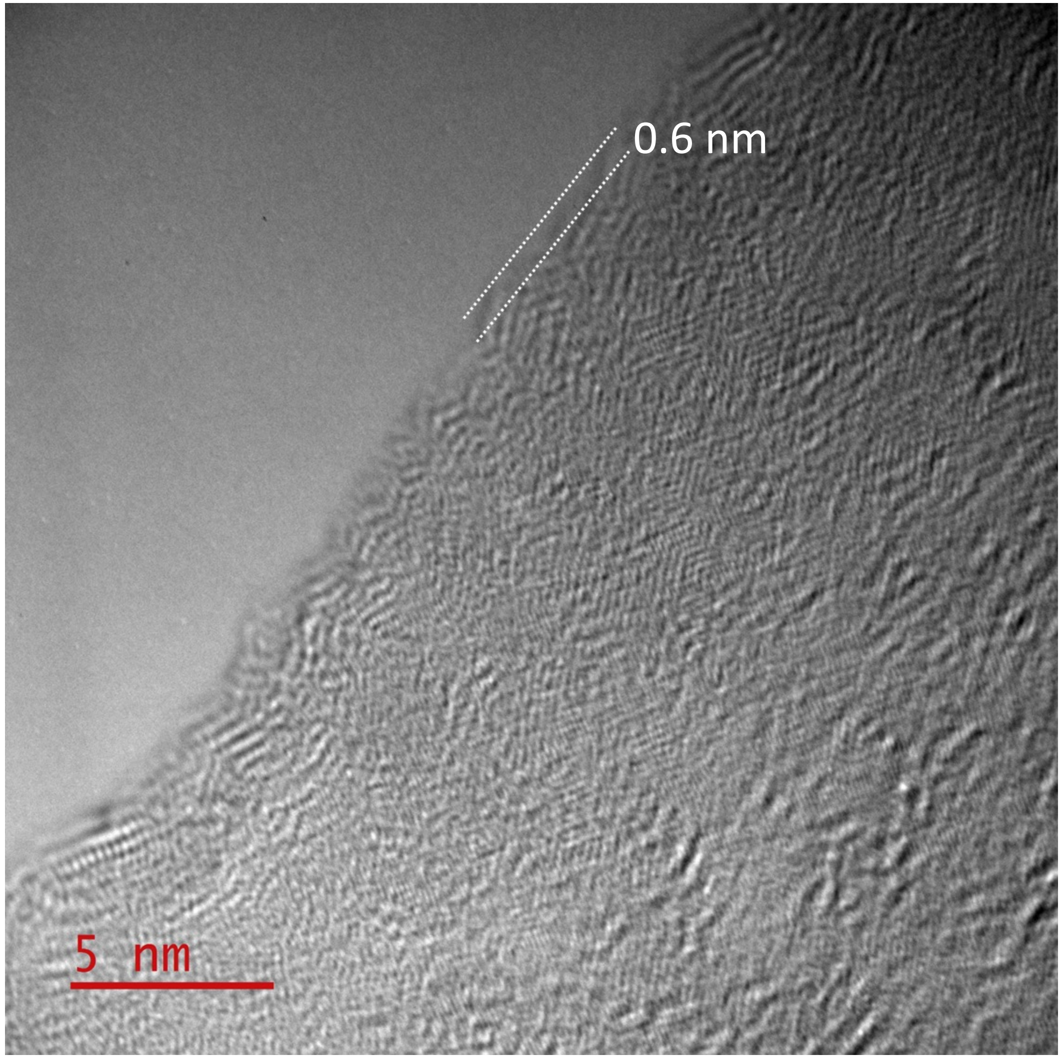


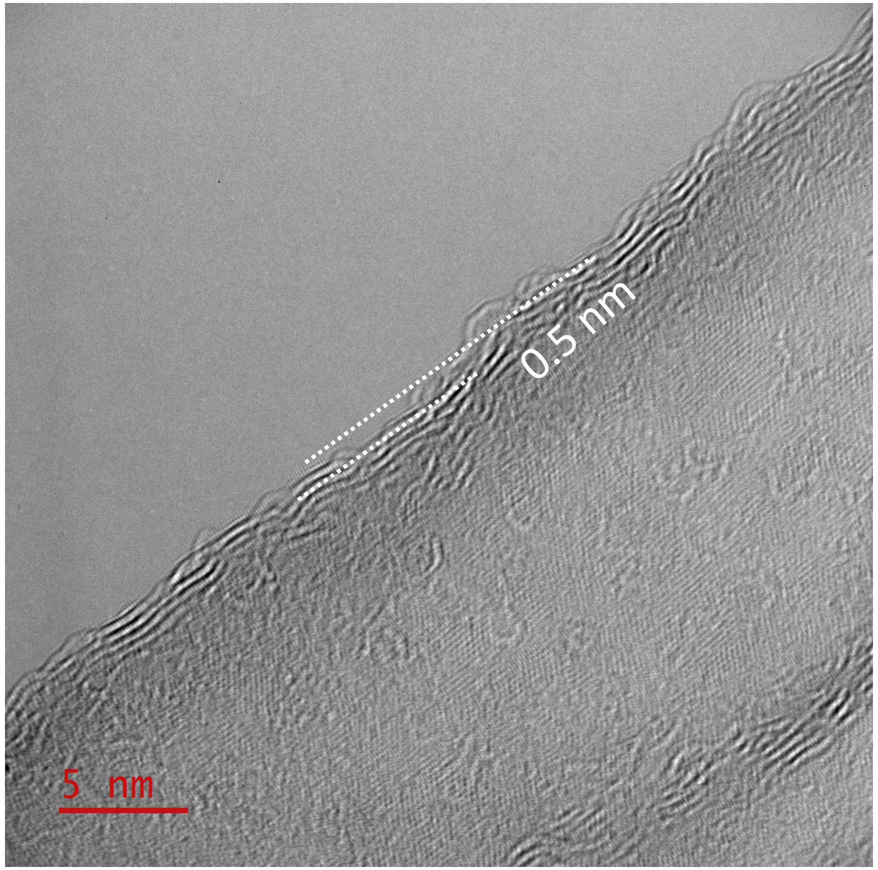


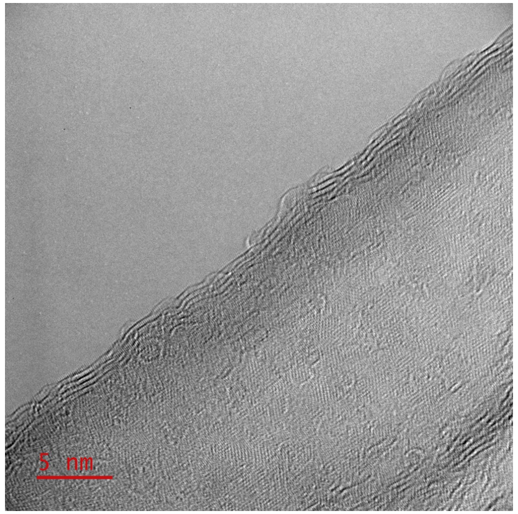
Ammonium persulfate

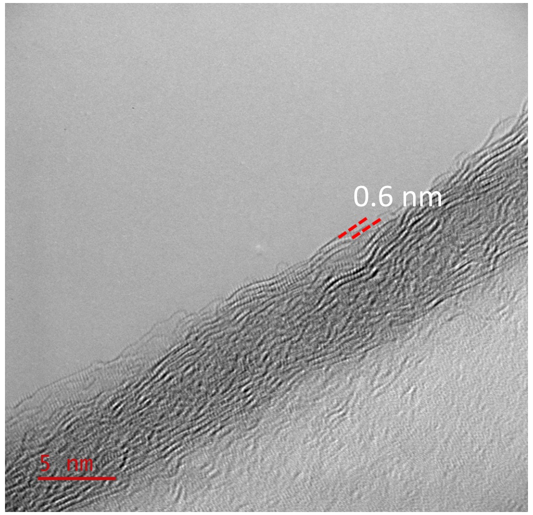


Transmission Electron Microscopy (TEM) Results



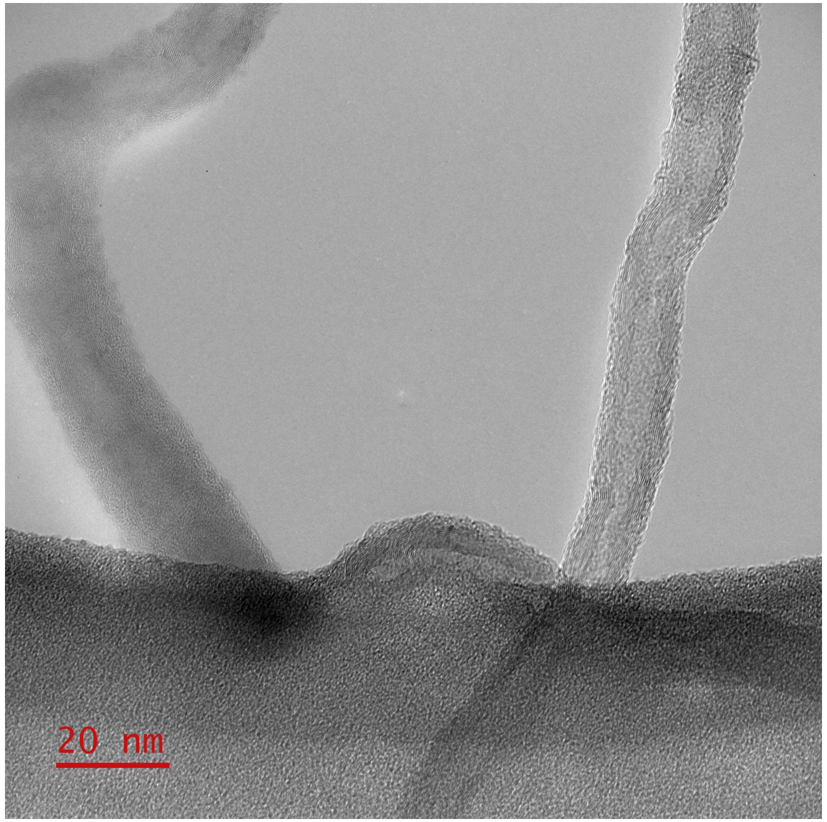


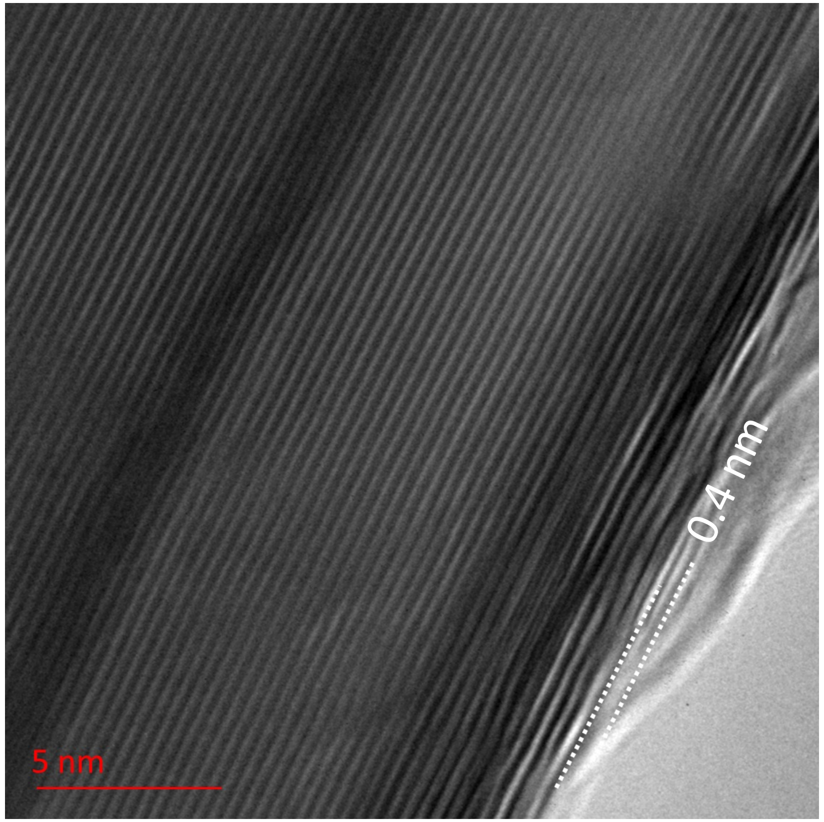




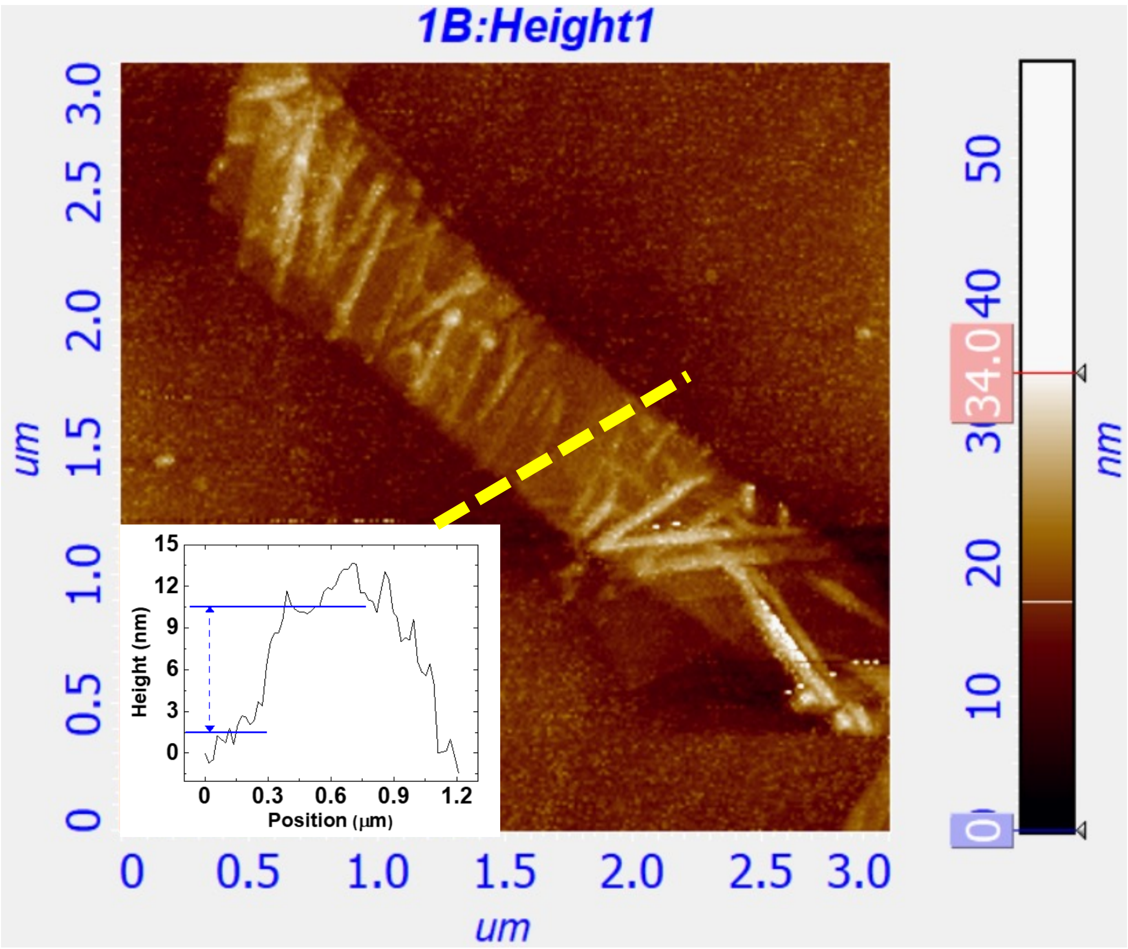
Transmission Electron Microscopy (TEM) Results

(C) UMWCNT - $(NH_4)_2S_2O_8$

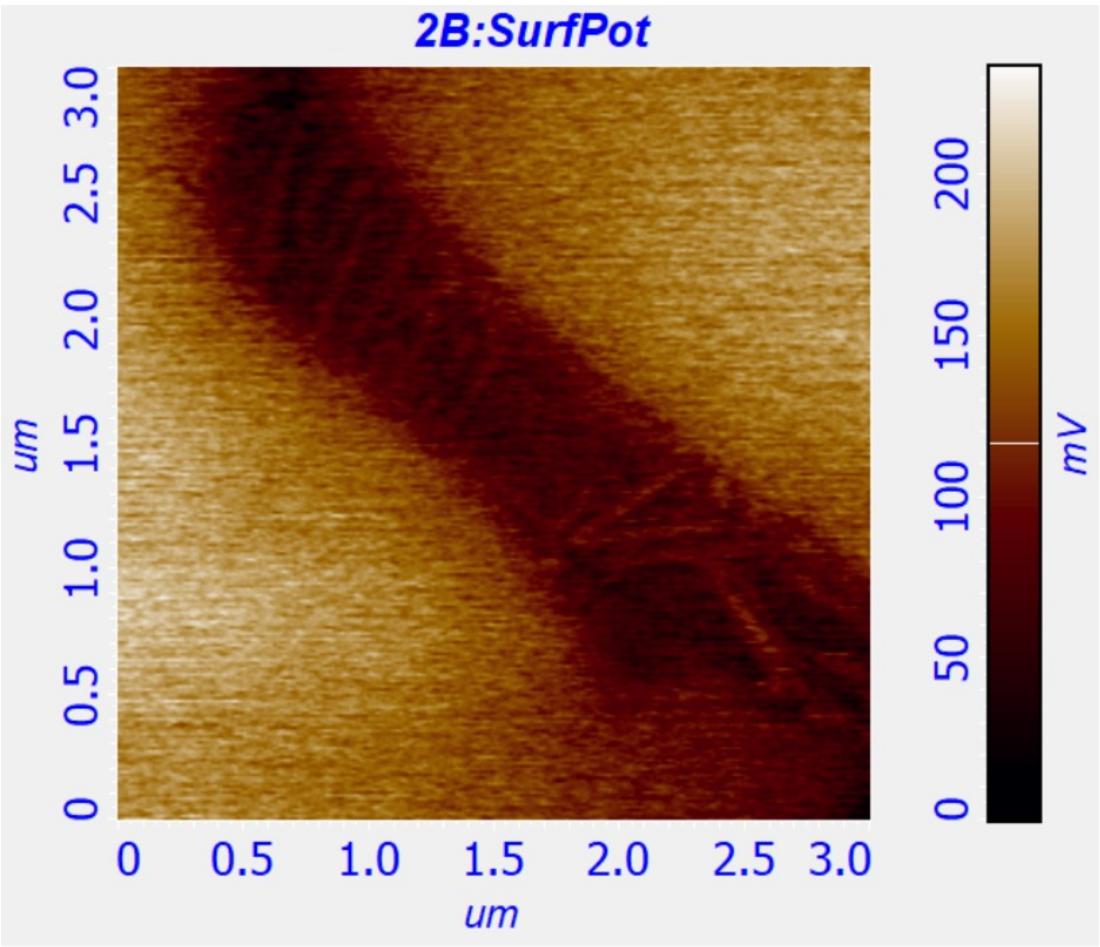




Topography

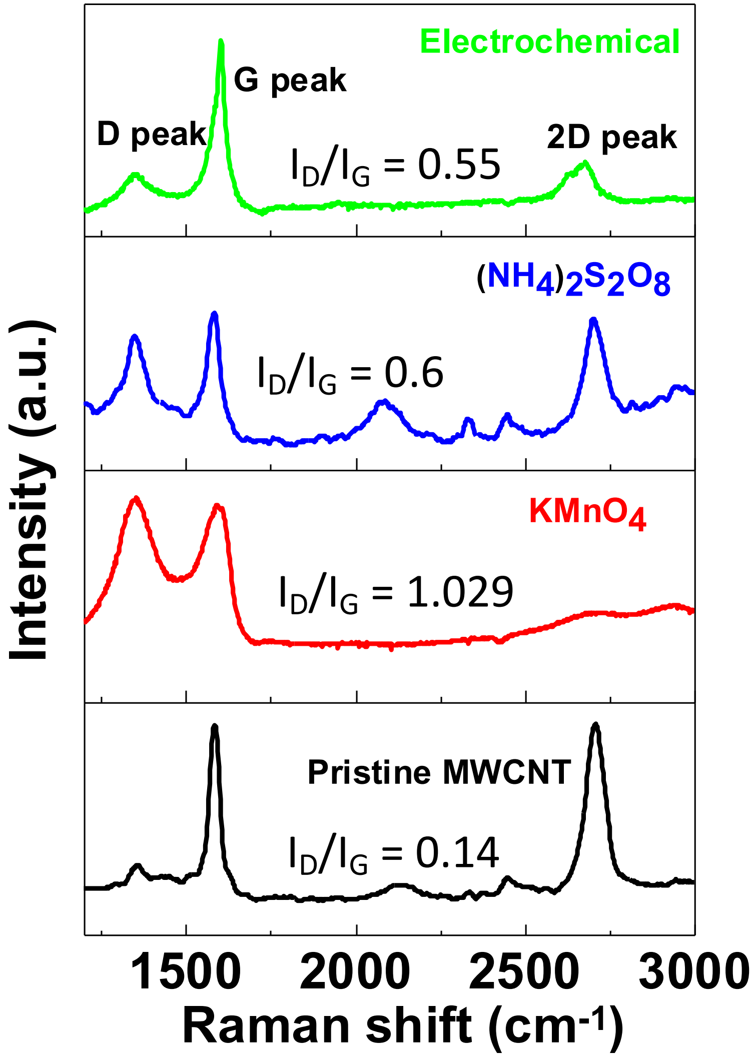


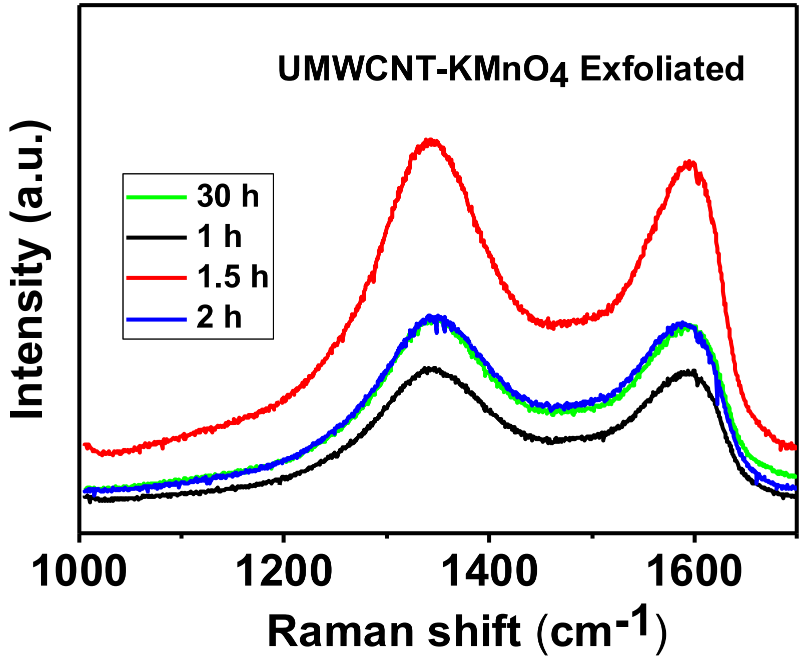
Surface Potential



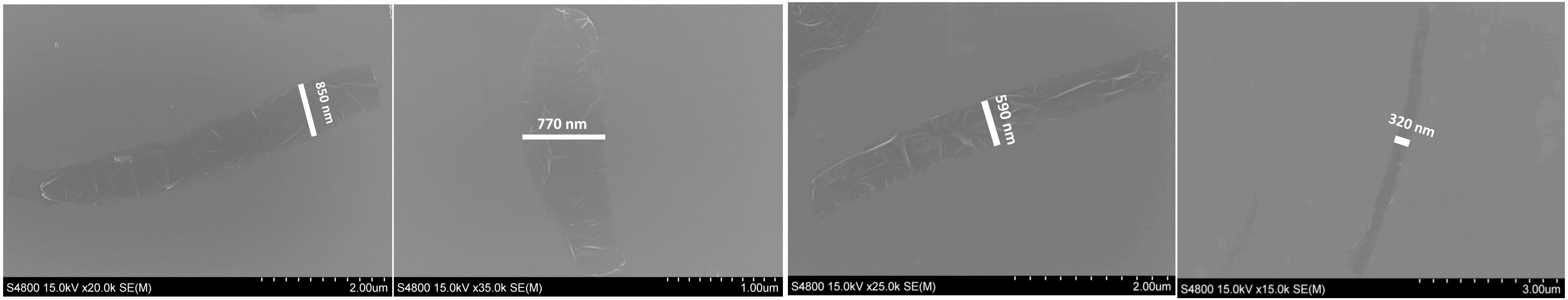
Raman spectroscopic investigation of unzipped MWCNTs

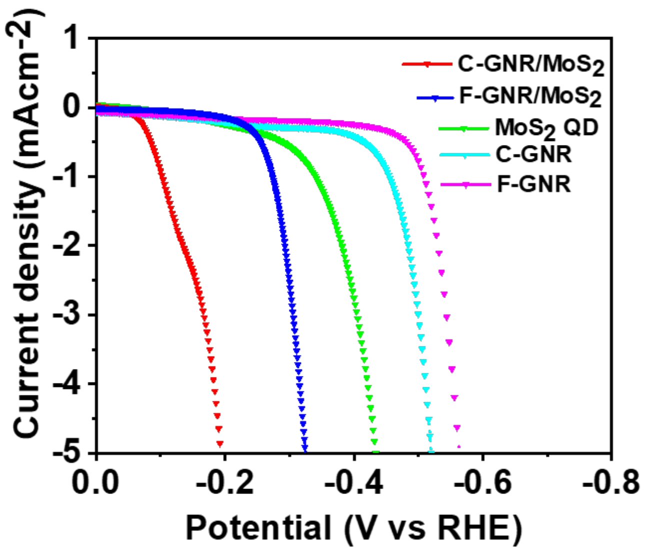
- Existence of D band in an indication of the defects present
- I_D/I_G values are used to compare the amount of defects
- Unzipping using $(NH_4)_2SO_8$ appears to produce less defects compared to $KMnO_4$





Part-I: Outcome





1. “Platinum-like Hydrogen Evolution Reaction Onset for GNR/MoS2 Heterostructure through curvature-dependent Electron Density Modulation and Enhanced Interfacial Charge Transfer”, Aruna N. Nair, Mohamed F Sanad, Venkata S.N. Chava, and Sreeprasad T. Sreenivasan, (Submitted).
2. “Graphene Nanoribbon-Fullerene (GNR-C_{60}) Heterostructure for Nitrogen Reduction Reaction”, Aruna N. Nair and Sreeprasad T. Sreenivasan, 240th Electrochemical Society (ECS) Meeting, Oct 10-14, 2021

PROJECT SCHEDULE

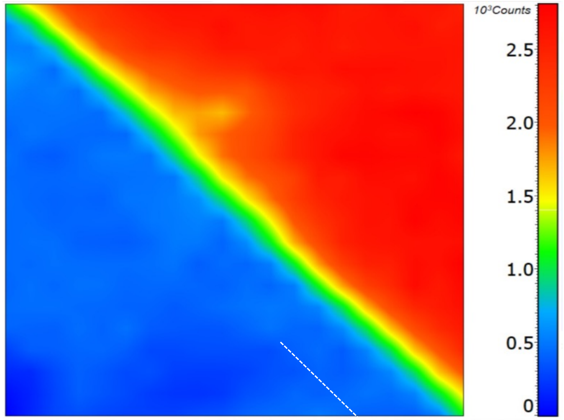
		Yr1				Yr2				Yr3			
S. No.	**Task Title**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
1	Project Management and Planning	ϕ											
2	Preparation of GNRs with prescribed width and smooth edges		ϕ		ϕ								
3	Device fabrication and characterization of a single-electron transistor					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												ϕΔ
	ϕ-Milestones	**Δ-Go/No-Go Decision points**											

Preparation of GNRs: Part-2

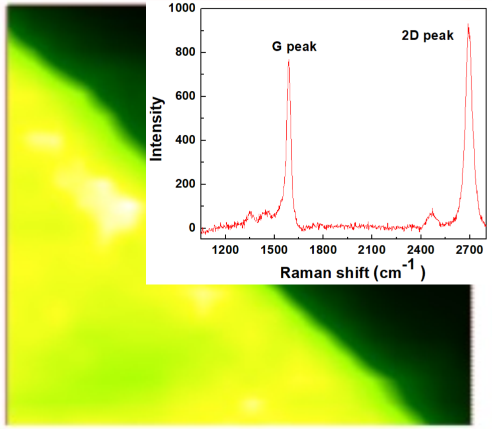
CVD graphene synthesis and material characterization

Two zone CVD furnace

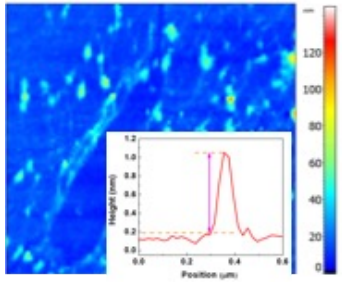
Integrated setup for SPM and Raman characterization

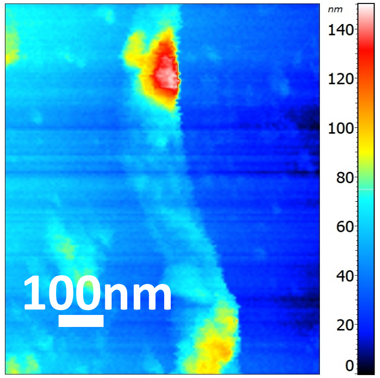


Raman spectrum 2D map

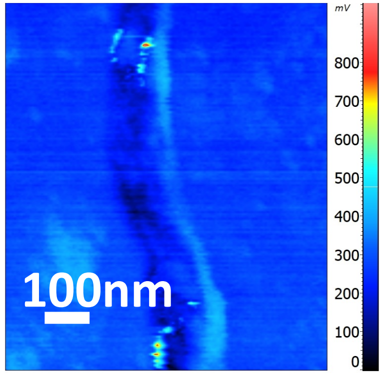


G peak



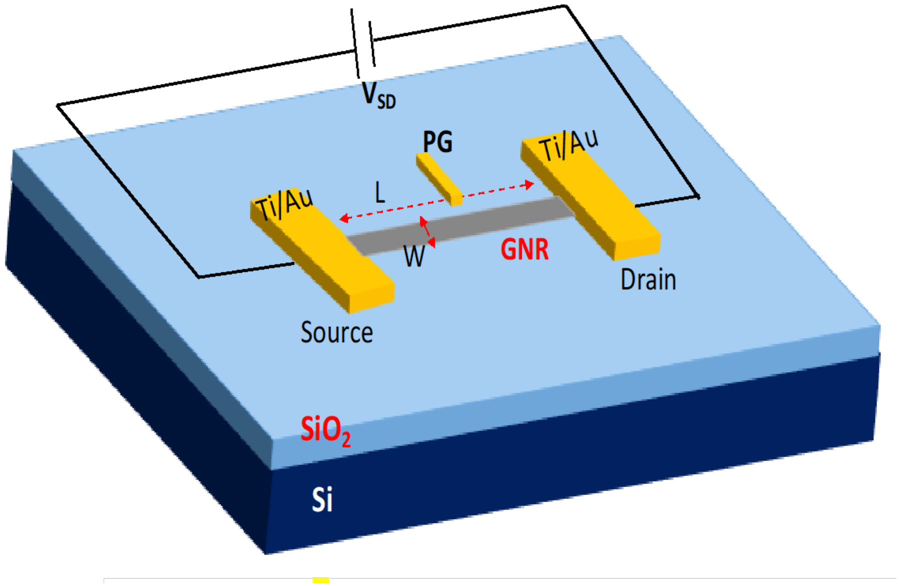


2D Height map



2D KPFM map

Electron beam lithography (EBL) for CVD graphene patterning into GNRs

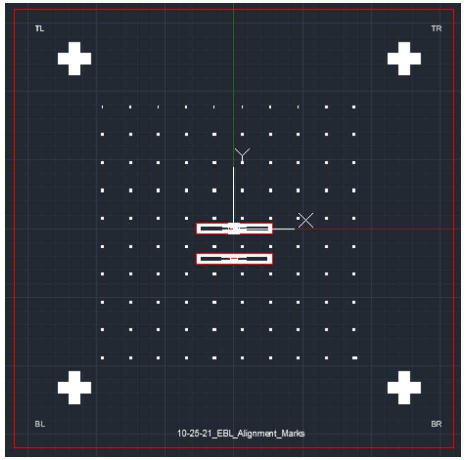


GNR FET device

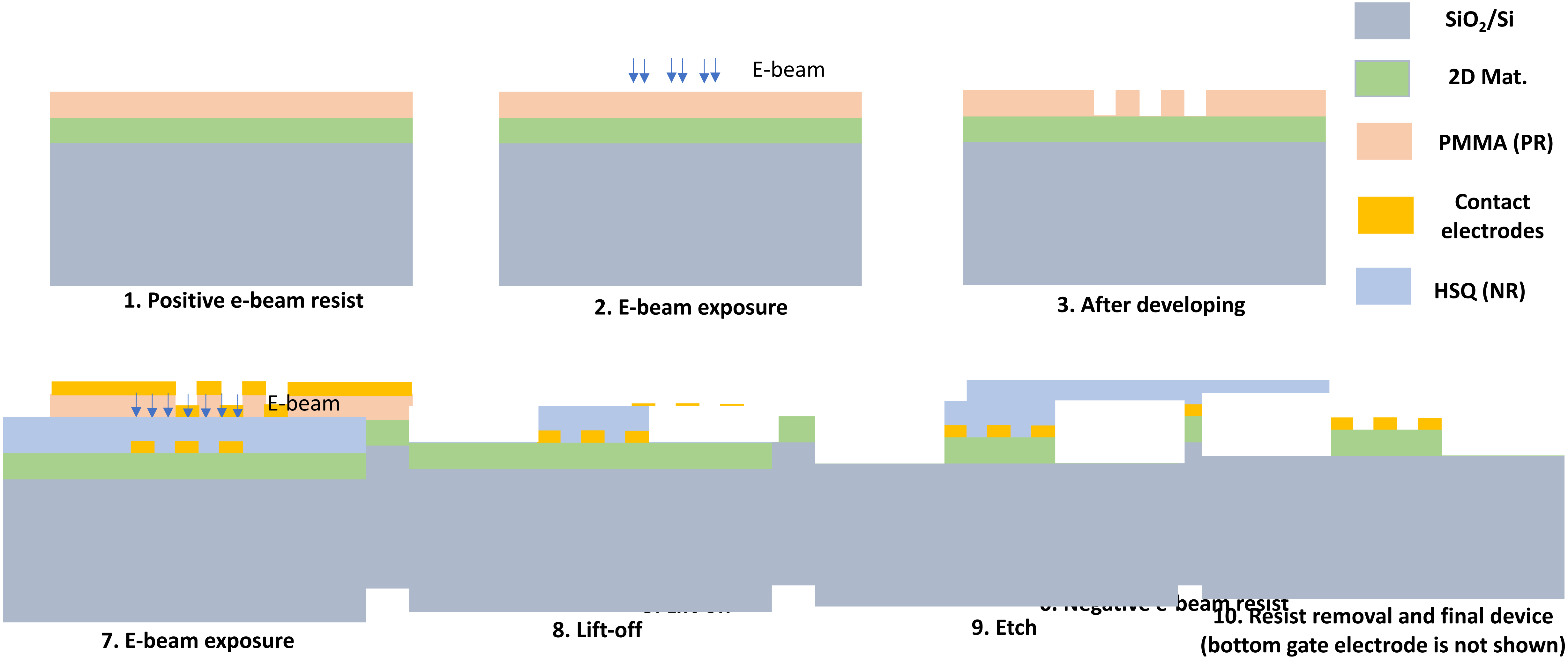
Process flow

1. Substrate with graphene
2. Design mask-file (CAD)
3. Prepare (coat) substrate for photo/e-beam lithography
4. Expose PR under UV light/e-beam
5. Develop
6. Optical inspection

Mask layout



GNR Device Fabrication Process Flow



GNR FET Device Fabrication Process Details

- Starting substrates will require metal alignment keys for EBL alignment and for reference to 2D material location
- The SEM will be used to identify 2D particle location for probe pattern placement with reference to alignment keys

Step 1. Coat PMMA positive EBL resist – PMMA 950 A6

Step 2. Exposure on EBL – Align to keys and expose probe pattern in PMMA, (Exposure dose ~600uC/cm^2)

Step 3. Develop PMMA resist using MIBK:IPA

Step 4. Deposit Cr/Au metal for probe pattern lift-off

Step 5. Lift-off metal/resist using acetone

Step 6. Coat negative resist – maN-2403

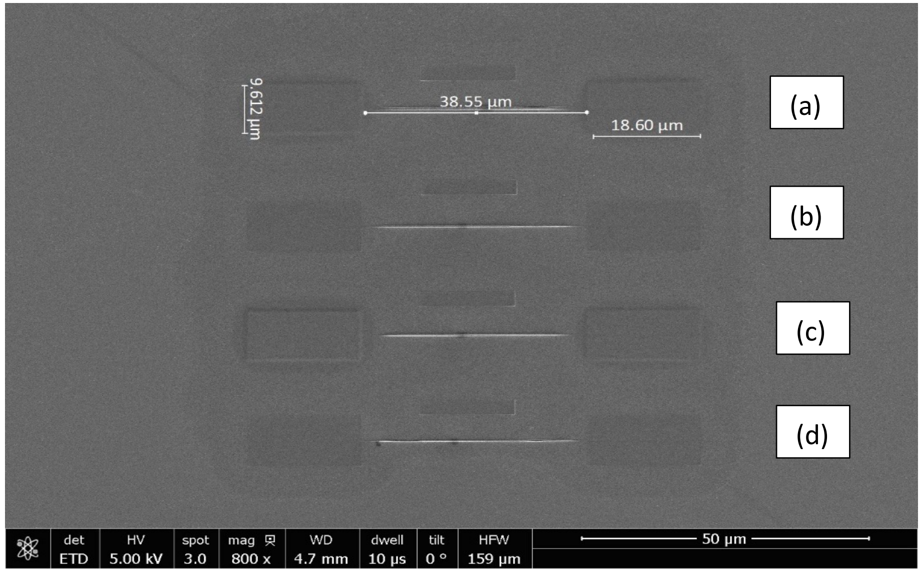
Step 7. Exposure on EBL – Align to keys, expose pattern in maN-2403 to protect probed graphene (Exp ~ 250uC/cm^2)

Step 8. Develop maN-2403 resist

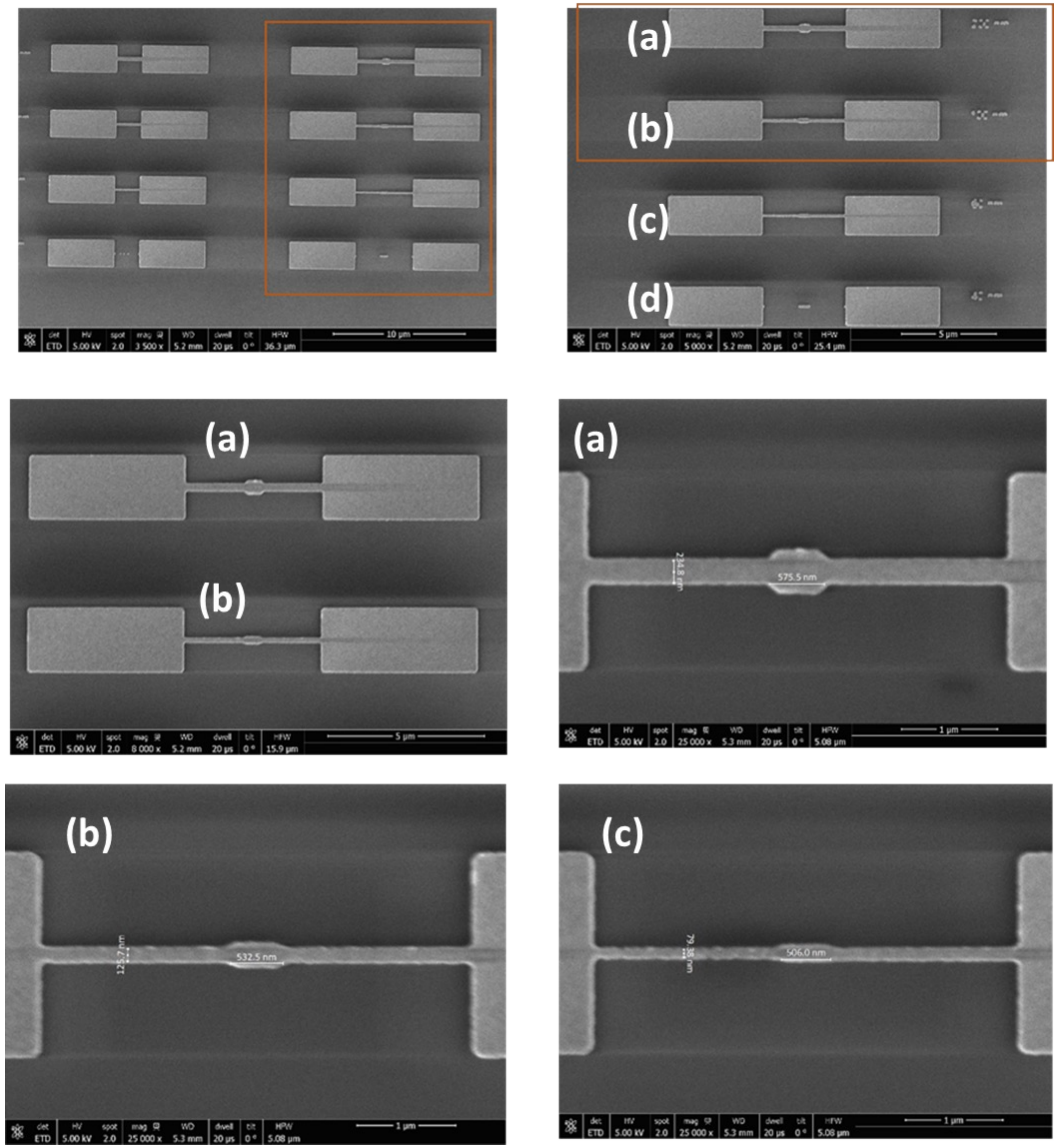
Step 9. Etch excess graphene (RIE)

Step 10. Strip resist and coat backside metal

SEM images: Electron beam lithography (EBL) patterning of graphene into GNRs

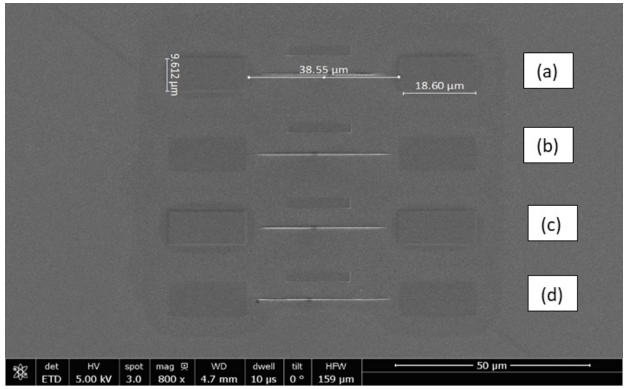


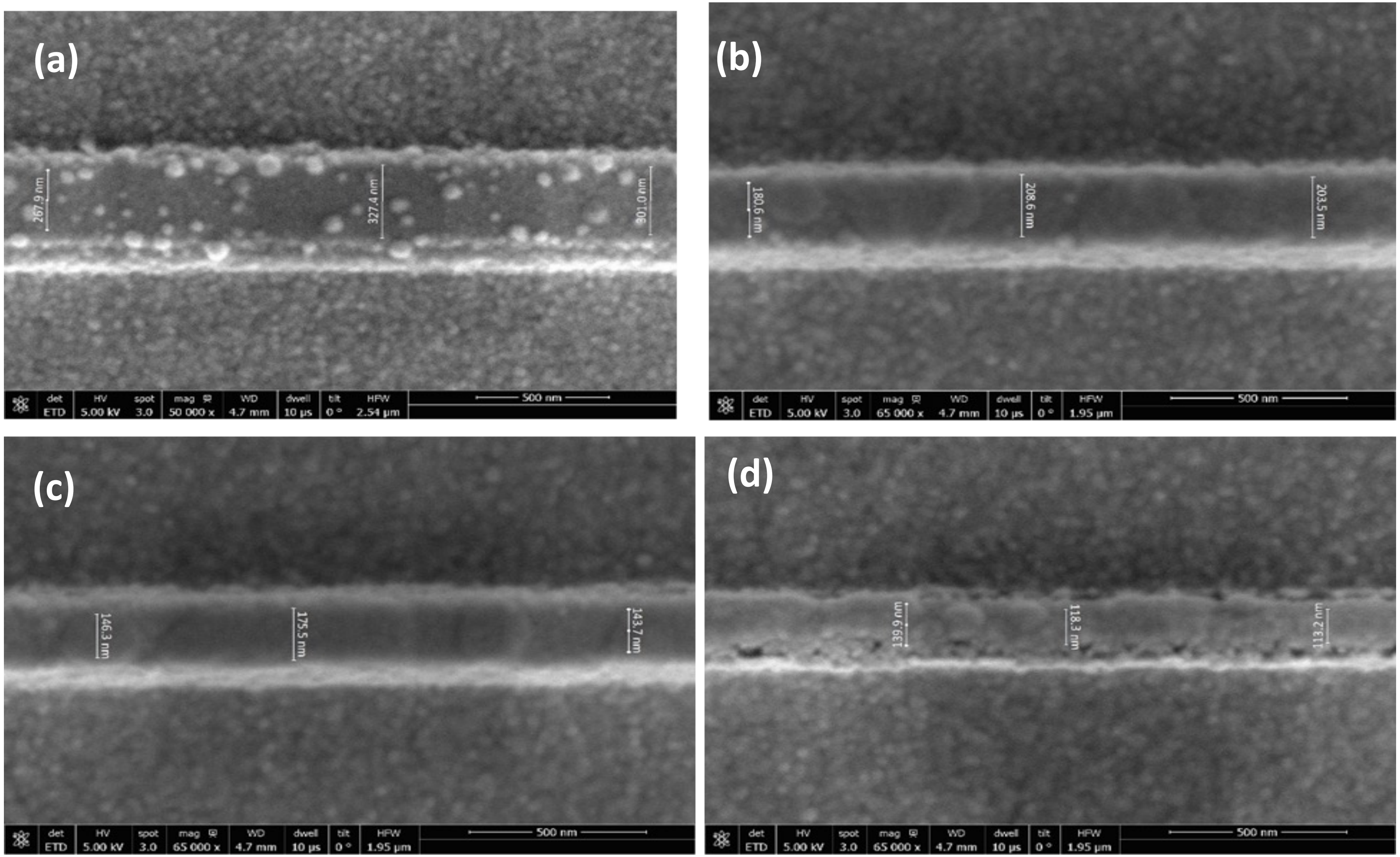
ma-N 2403 (negative) resist



PMMA (positive) resist

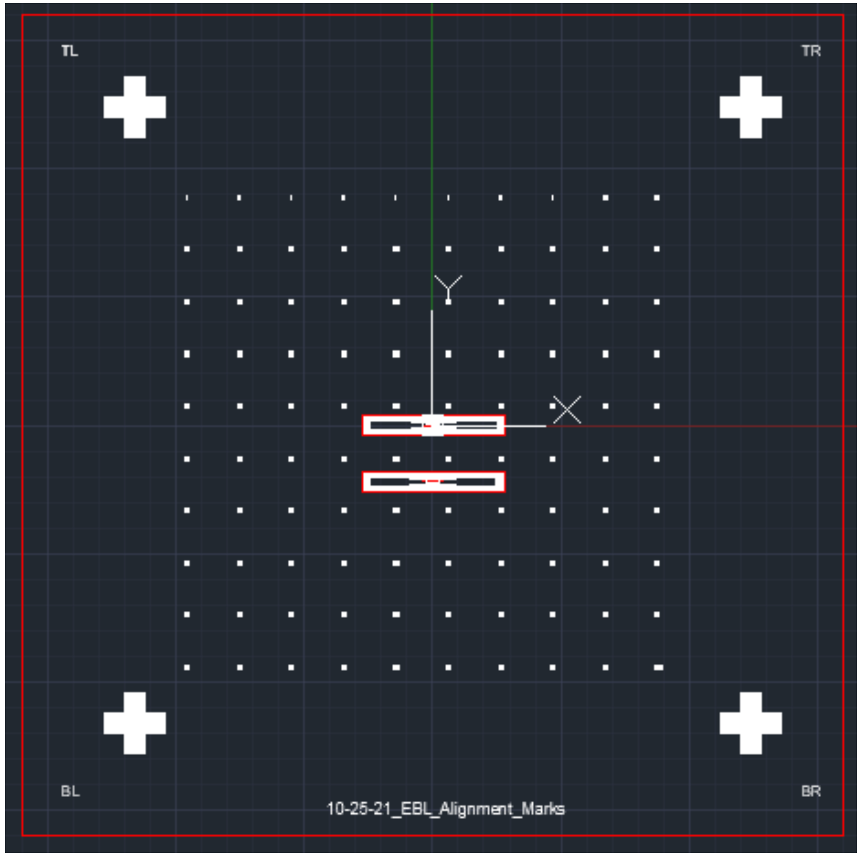
SEM images: Electron beam lithography (EBL) patterning of graphene into GNRs

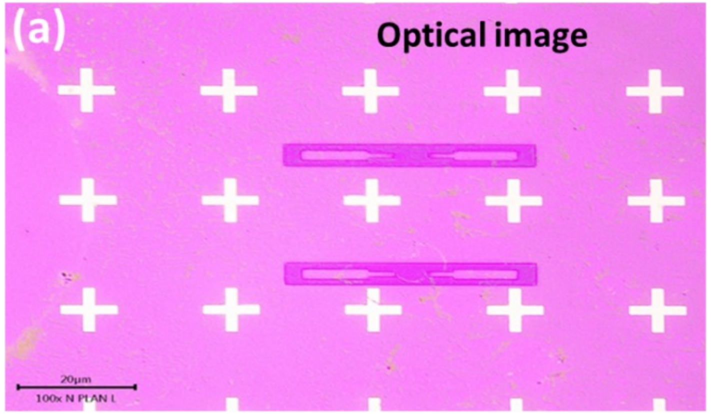


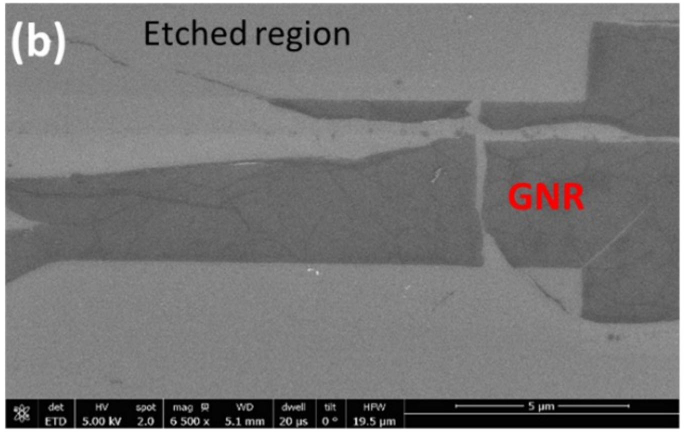


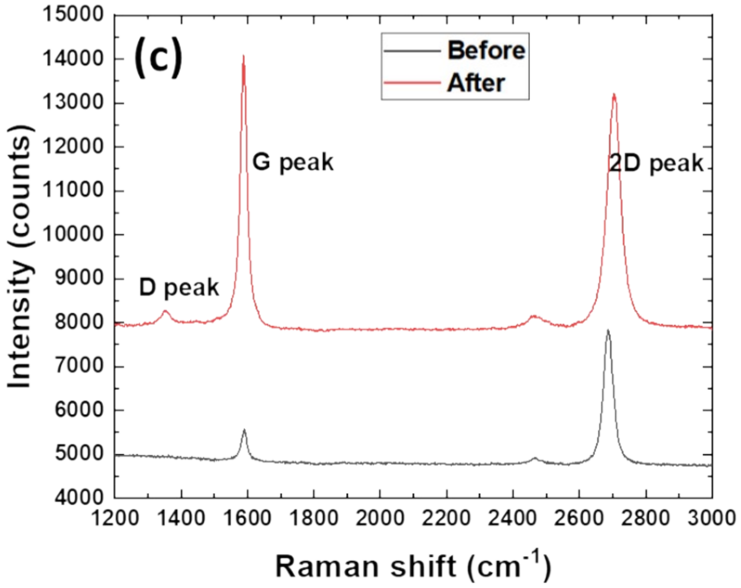
ma-N 2403 (negative) resist

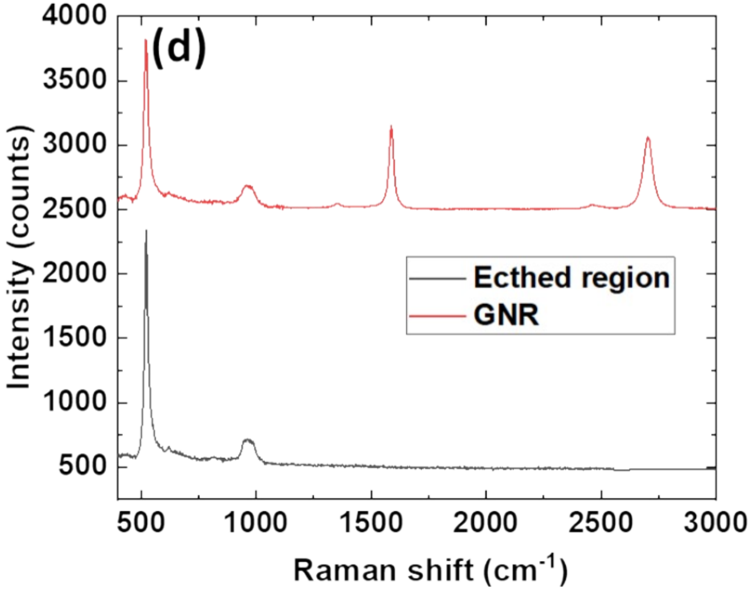
Electron beam lithography (EBL) and RIE patterning of graphene into GNRs: Microscopic and Raman study





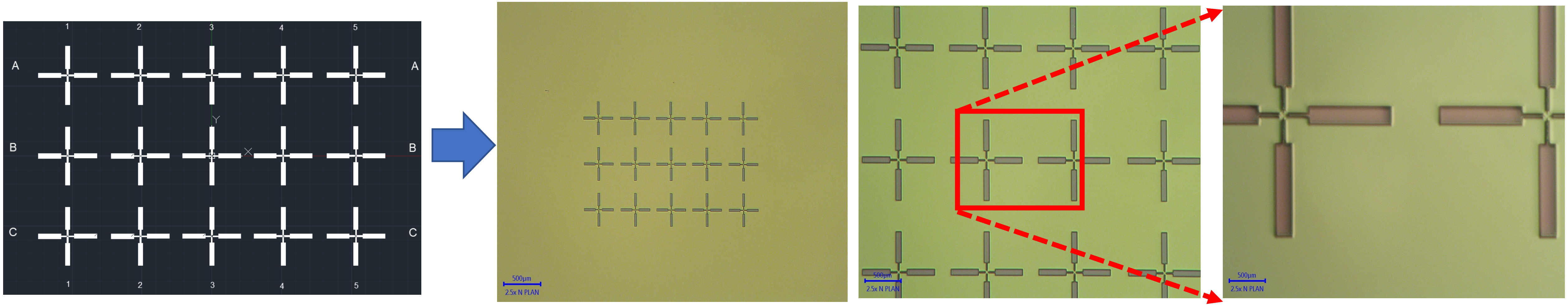




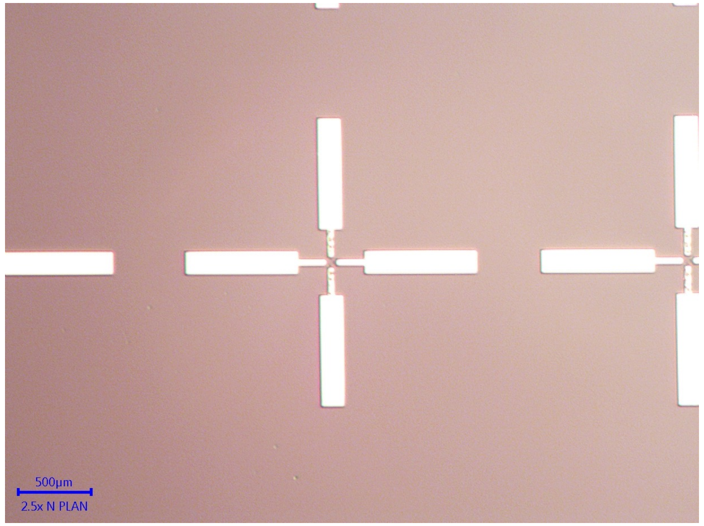


Electron beam lithography (EBL) patterning for metal electrode deposition

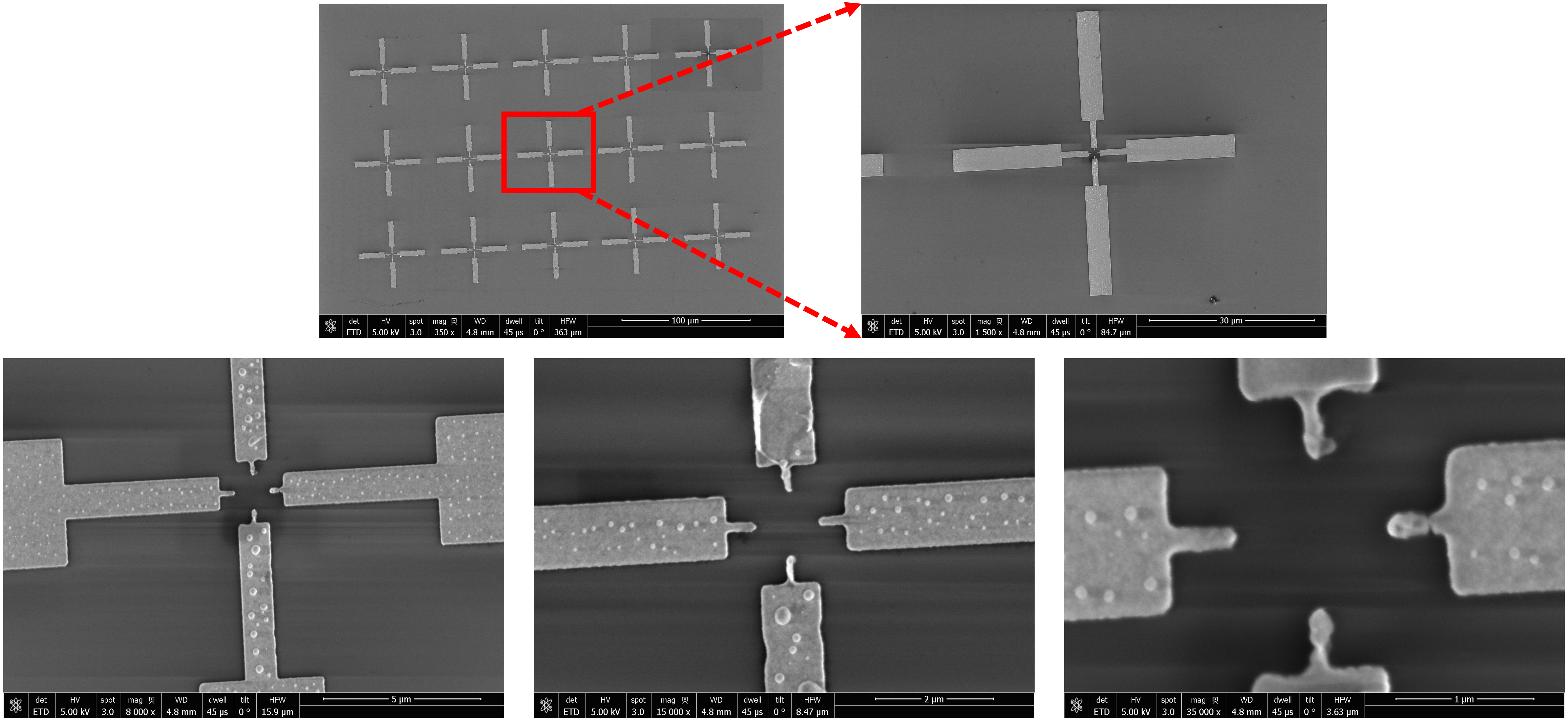
❑ After EBL Resist patterning, and development



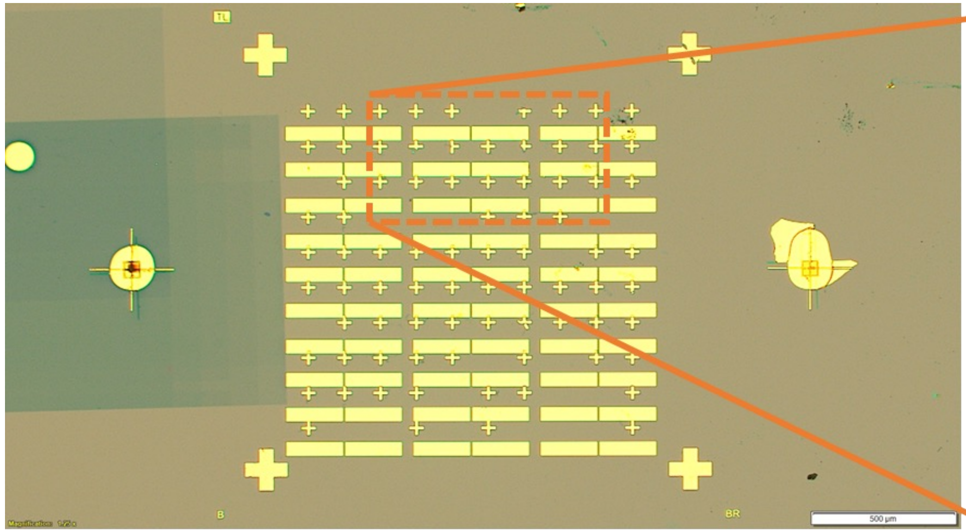
❑ After metal (Ti/Au) deposition and lift-off

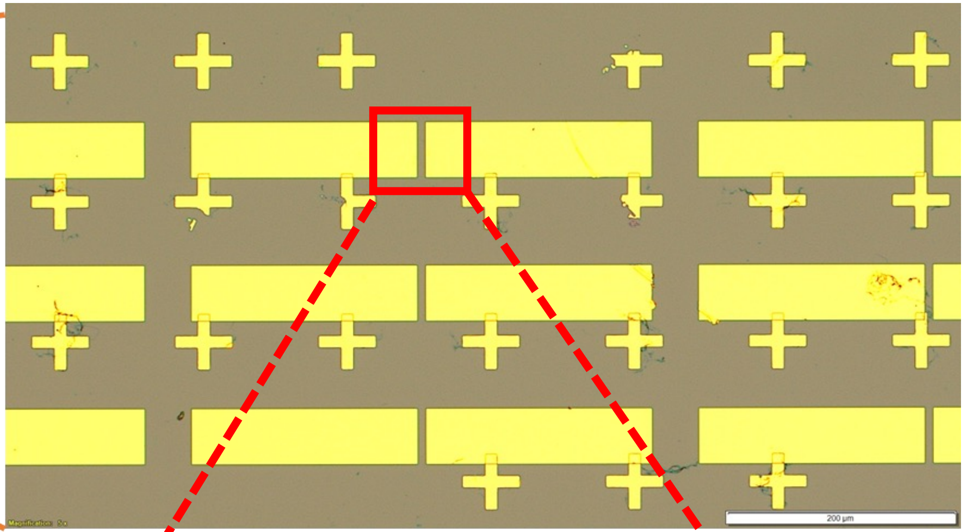


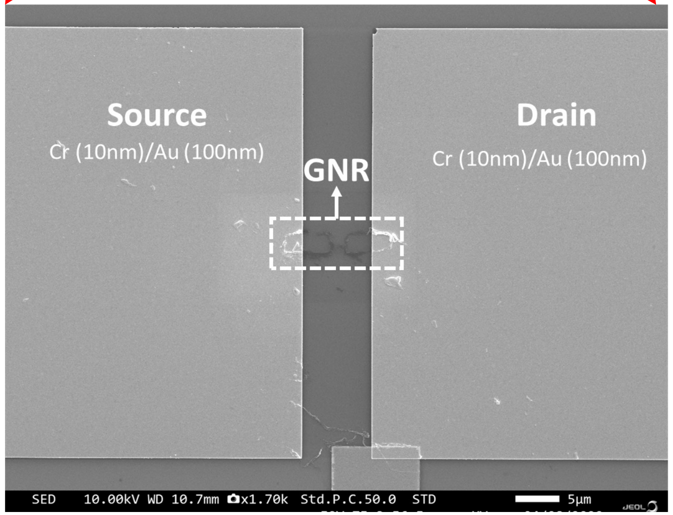
EBL patterning for metal contact electrodes: SEM images



Graphene Nanoribbon (GNR) FET device and Electrical Characterization







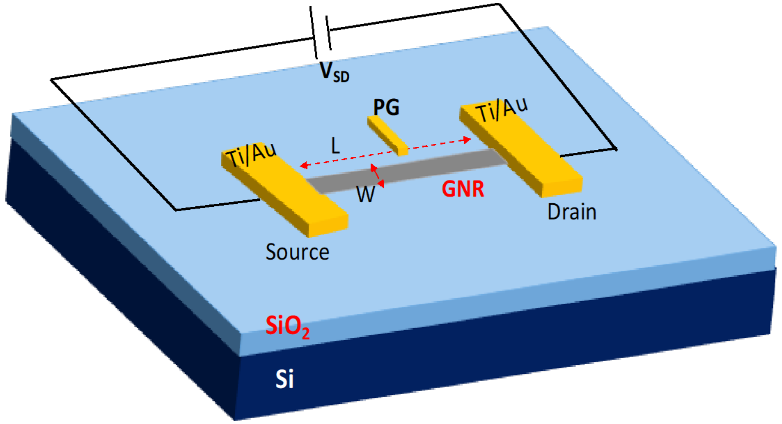
Back-gated GNR FET Device with Source and Drain metal electrodes (Cr/Au) on top

Project-II: Summary & Action Plan

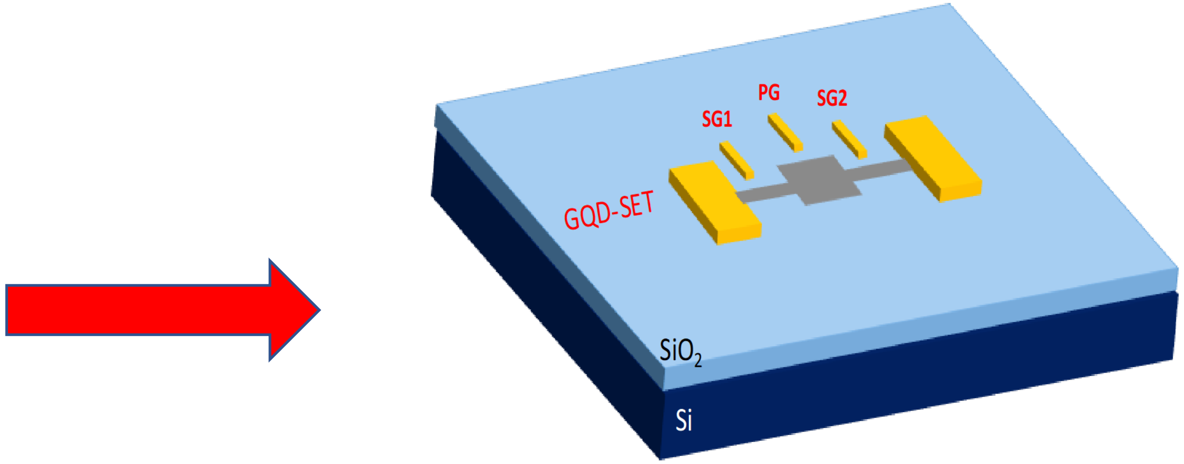
1. Achieved GNRs with widths ~60nm by patterning CVD graphene.
2. To conduct STM studies on prepared GNRs and evaluate local density of states to derive correlation between process and edge roughness (CINT/ANL).
3. Continue fabricate FET devices to study the bulk electrical properties of the GNRs.
4. Prepare a manuscript on edge roughness and LDOS for unzipped and EBL prepared GNRs.

Project-II: Summary & Action Plan

1. Fabrication of single electron transistor (SET) device using unzipped CNT (or GNR) and GNRs prepared using EBL
2. Characterize the electrical and transport properties, analyze and compare the obtained results with traditional CNT, graphene-based SET devices.
3. Prepare and submit a manuscript based on the above results.



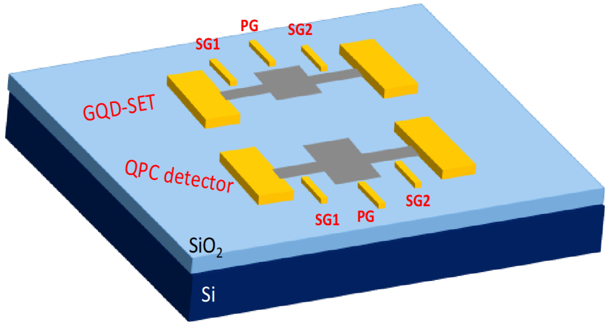
GNR FET

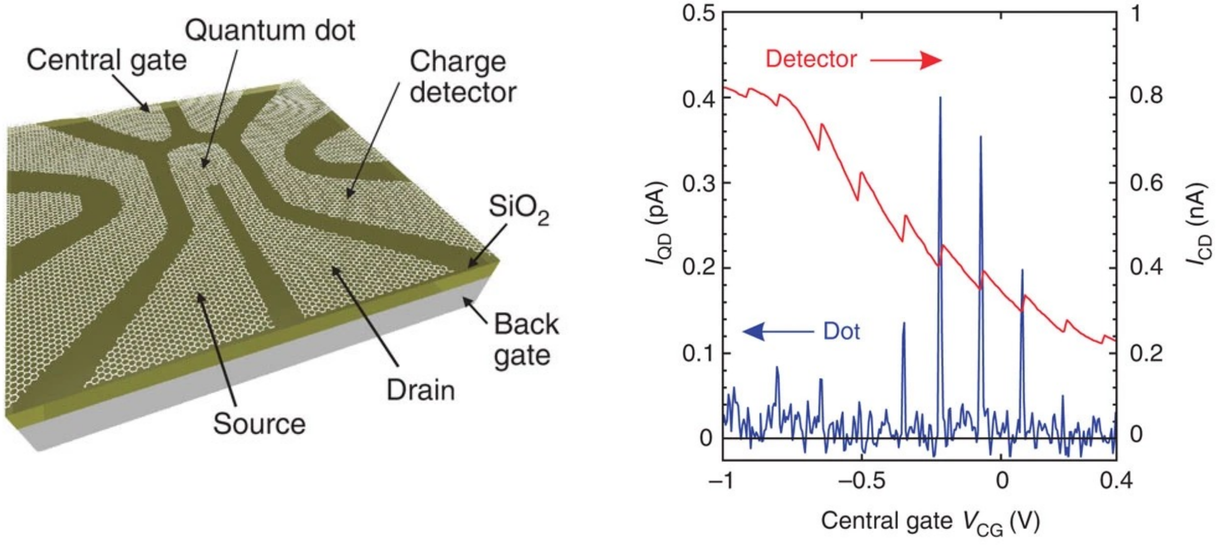


GQD SET

FUTURE WORK

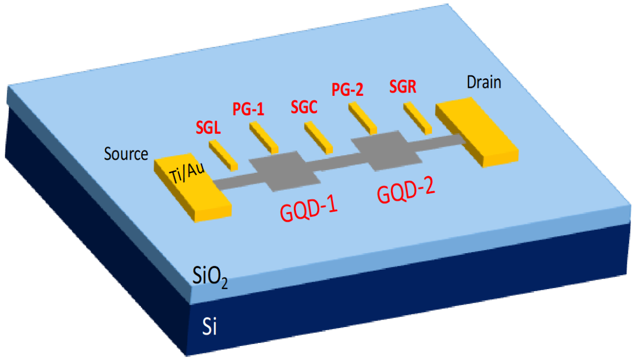
1. Characterization of SET using QPC

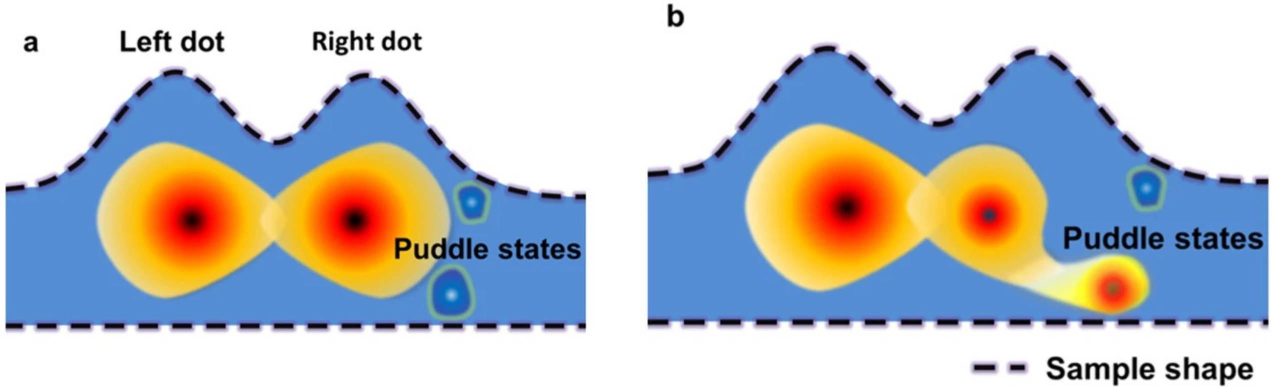




Nature communications **volume 4**, 1753 (2013)

2. Characterization of Double Quantum Dots





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

Publications

Exclusively from the project

1. “Platinum-like Hydrogen Evolution Reaction Onset for GNR/MoS2 Heterostructure through curvature-dependent Electron Density Modulation and Enhanced Interfacial Charge Transfer”, Aruna N. Nair, Mohamed F Sanad, Venkata S.N. Chava, and Sreeprasad T. Sreenivasan, (Submitted).

Acknowledged for partial support

1. M. F. Sanad, H. M. Franklin, B. A. Ali, A. R. P. Santiago, A. N. Nair, Venkata S.N. Chava, Olivia Fernandez-Delgado, Nageh K. Allam, Steven Stevenson, Sreeprasad T. Sreenivasan, Luis Echegoyen, “Cylindrical C96 Fullertubes: A Highly Active Metal Free O2-Reduction Electrocatalyst”. Angewandte Chemie (2022).
2. Mohamed F Sanad, Venkata S. N. Chava, Ahmed Shalan, Lissette G. Enriquez, 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 & Interfaces 13 (34), 40731-40741.
3. Venkata S.N. Chava, P.S. Chandrasekhar, Ashley Gomez, Luis Echegoyen and Sreeprasad T. Sreenivasan, “Efficient inverted planar perovskite solar cells with enhanced open circuit voltage and fill factor using $Ti_3C_2T_x$ MXene doping of PCBM electron transporting layer”, ACS Applied Energy Materials 4 (11), 12137–12148.
4. Graphene Nanoribbon-Fullerene (GNR-C60) Heterostructure for Nitrogen Reduction Reaction, Aruna N. Nair and Sreeprasad T. Sreenivasan, 240th Electrochemical Society (ECS) Meeting, Oct 10-14, 2021

Thank You!