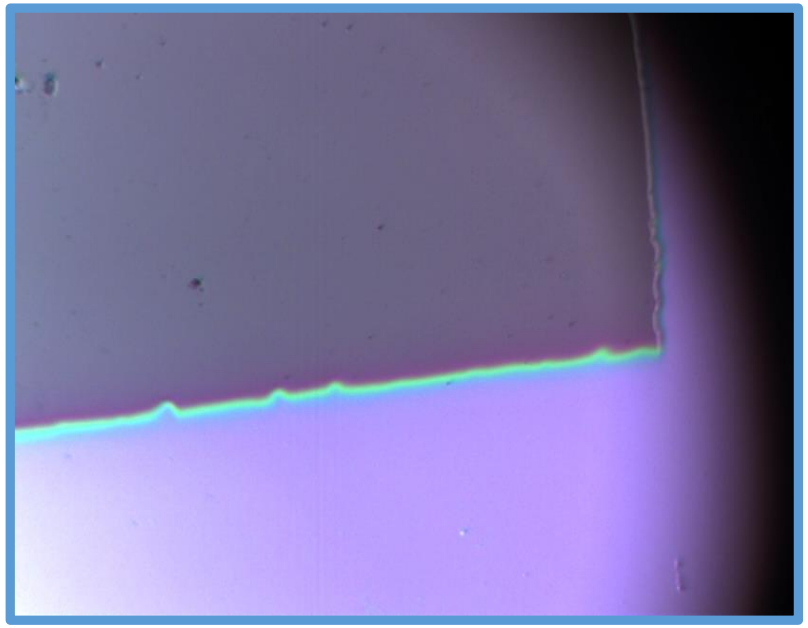
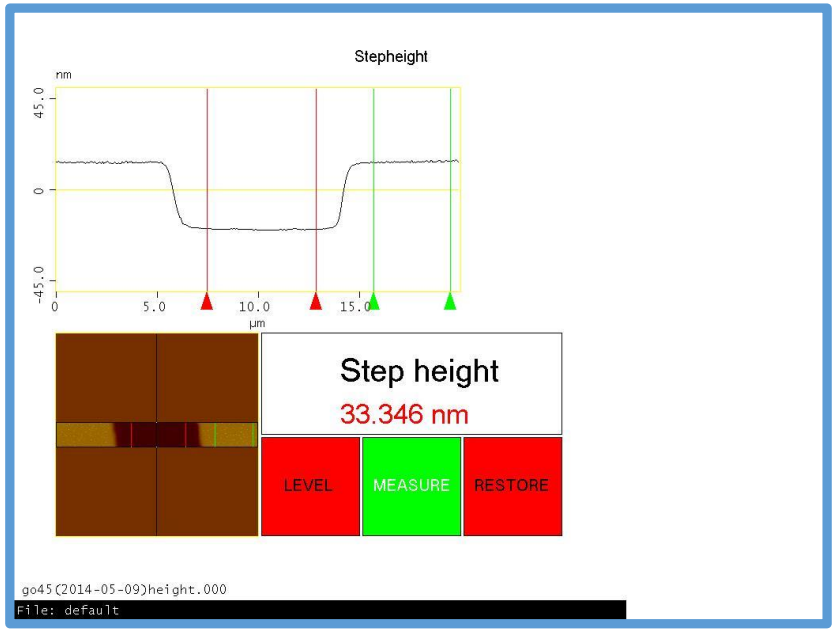
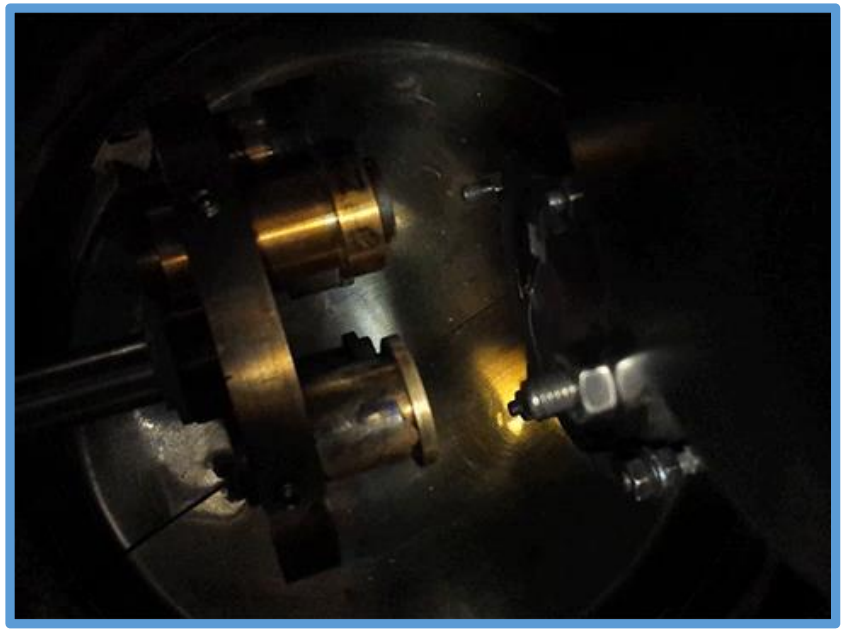
Electrical and Magneto-Transport Properties of Reduced Graphene Oxide Thin Films







Kartik Ghosh

Department of Physics Astronomy and Materials Science

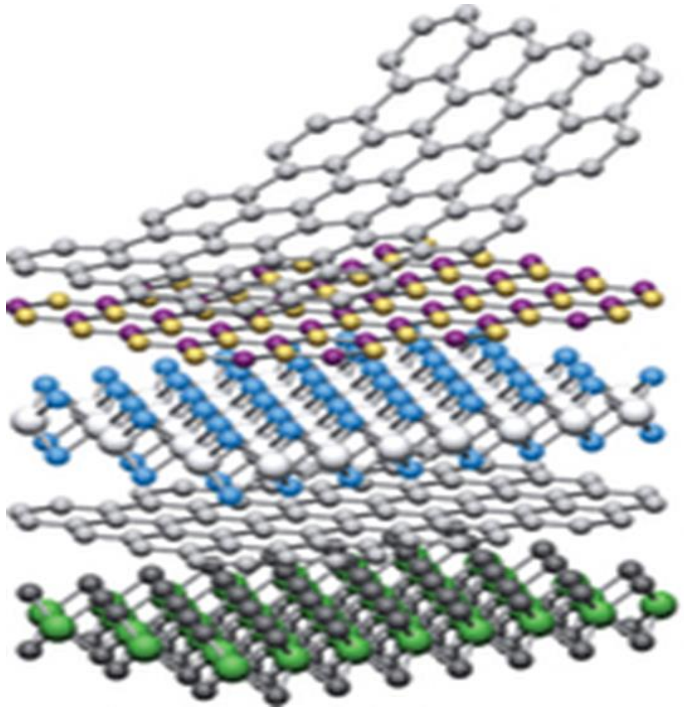
Missouri State University

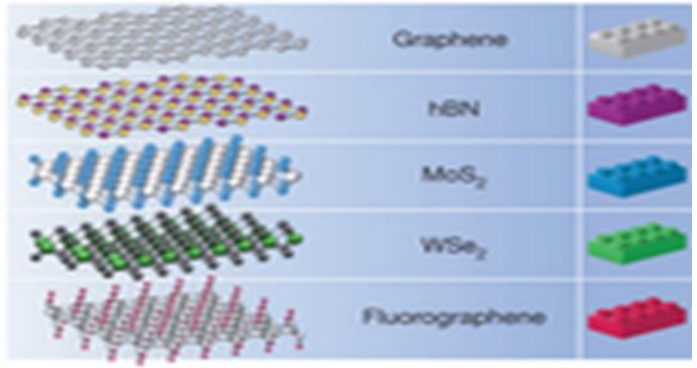
Outline

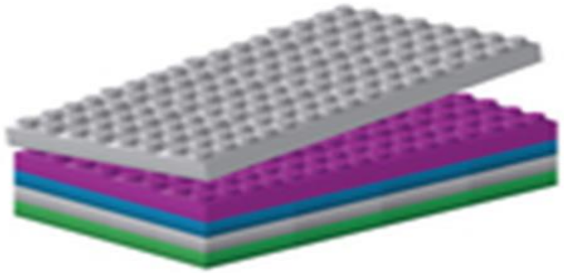
- ***Introduction***
  - 2D Materials
  - Graphene, Graphene oxide and its properties
- ***Results and Discussion***
  - Raman spectroscopy
  - XRD
  - XPS
  - Photoluminescence spectroscopy
  - Hall measurement
  - Resistance vs Temperature measurement
  - Magneto-resistance
- ***Conclusions and Future Works***

2D Material-Graphene

- Identified in 2004.
- ***Novoselov*** and ***Geim*** were awarded the Nobel Prize in Physics in 2010.
- 100 times stronger than steel, and as flexible as rubber.
- Limitation: Energy band gap.





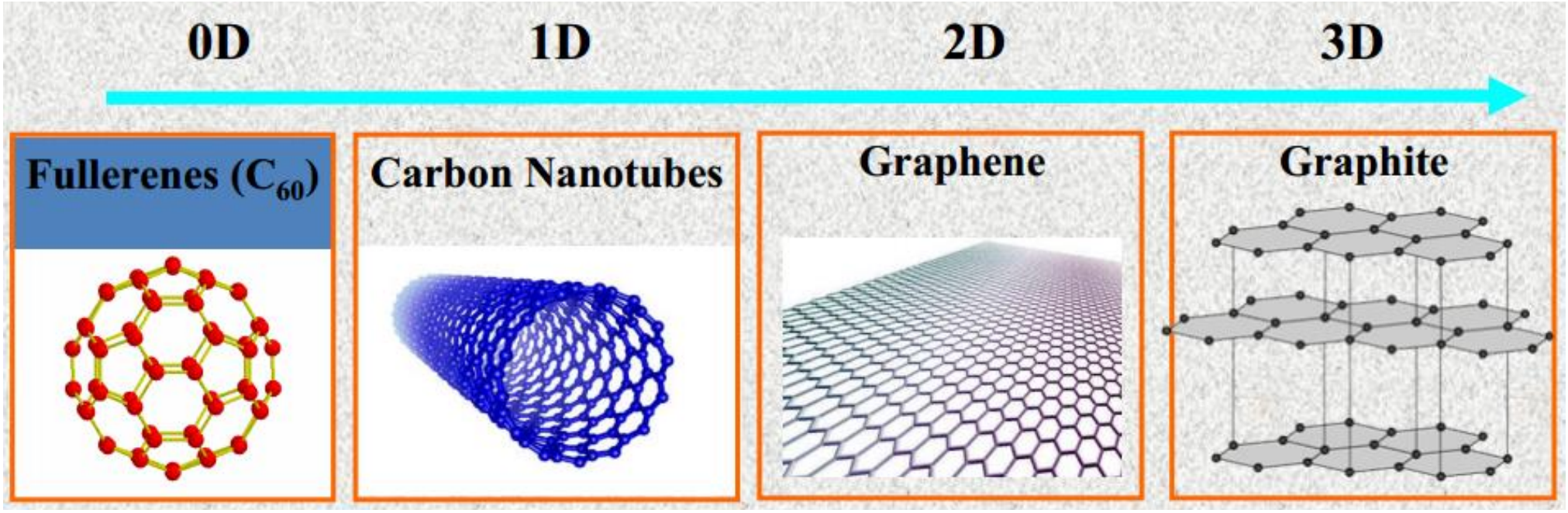


Graphene family	Graphene	hBN 'white graphene'	BCN	Fluorographene	Graphene oxide
2D chalcogenIdes	MoS_2, WS_2, $MoSe_2$, WSe_2	Semiconducting dichalcogenides: $MoTe_2$, WTe_2, ZrS_2, $ZrSe_2$ and so on		Metallic dichalcogenides: $NbSe_2$, NbS_2, TaS_2, TiS_2, $NiSe_2$ and so on	
				Layered semiconductors: GaSe, GaTe, InSe, Bi_2Se_3 and so on	
2D oxides	Micas, BSCCO	MoO_3, WO_3	Perovskite-type: $LaNb_2O_7$, $(Ca,Sr)_2Nb_3O_{10}$, $Bi_4Ti_3O_{12}$, $Ca_2Ta_2TiO_{10}$ and so on	Hydroxides: $Ni(OH)_2$, $Eu(OH)_2$ and so on	
	Layered Cu oxides	TiO_2, MnO_2, V_2O_5, TaO_3, RuO_2 and so on		Others	

AK Geim et al. Nature 499 (2013)

What is Graphene

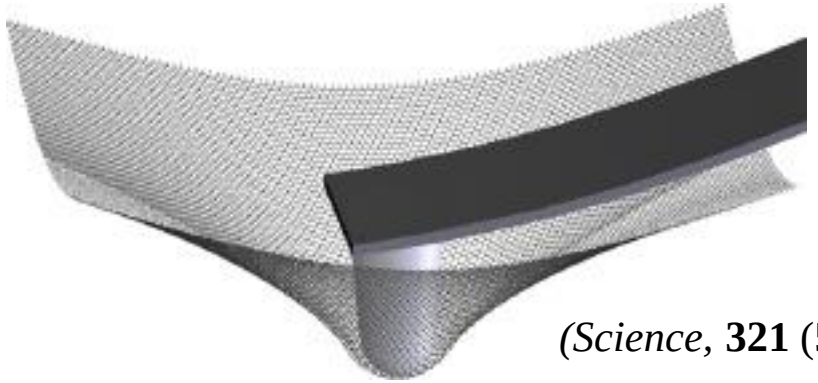
- Graphene is a flat monolayer of carbon atoms tightly packed into a 2D honeycomb lattice.
- By definition: Graphene must be sufficiently isolated from its surrounding environment so that it can be considered free standing.



Properties of graphene

Mechanical properties

- High Young's modulus (~1,100 Gpa)
-High fracture strength (125 Gpa)

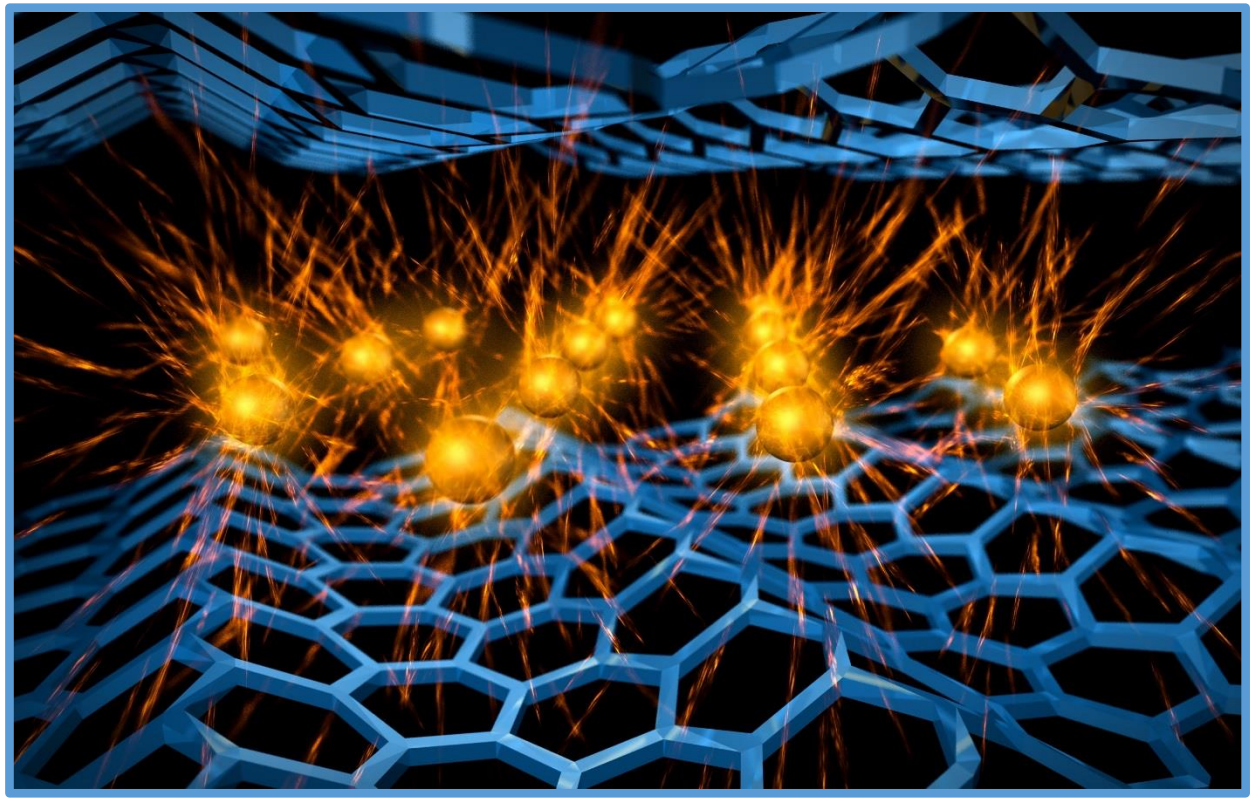


(*Science*, **321** (5887): 385)

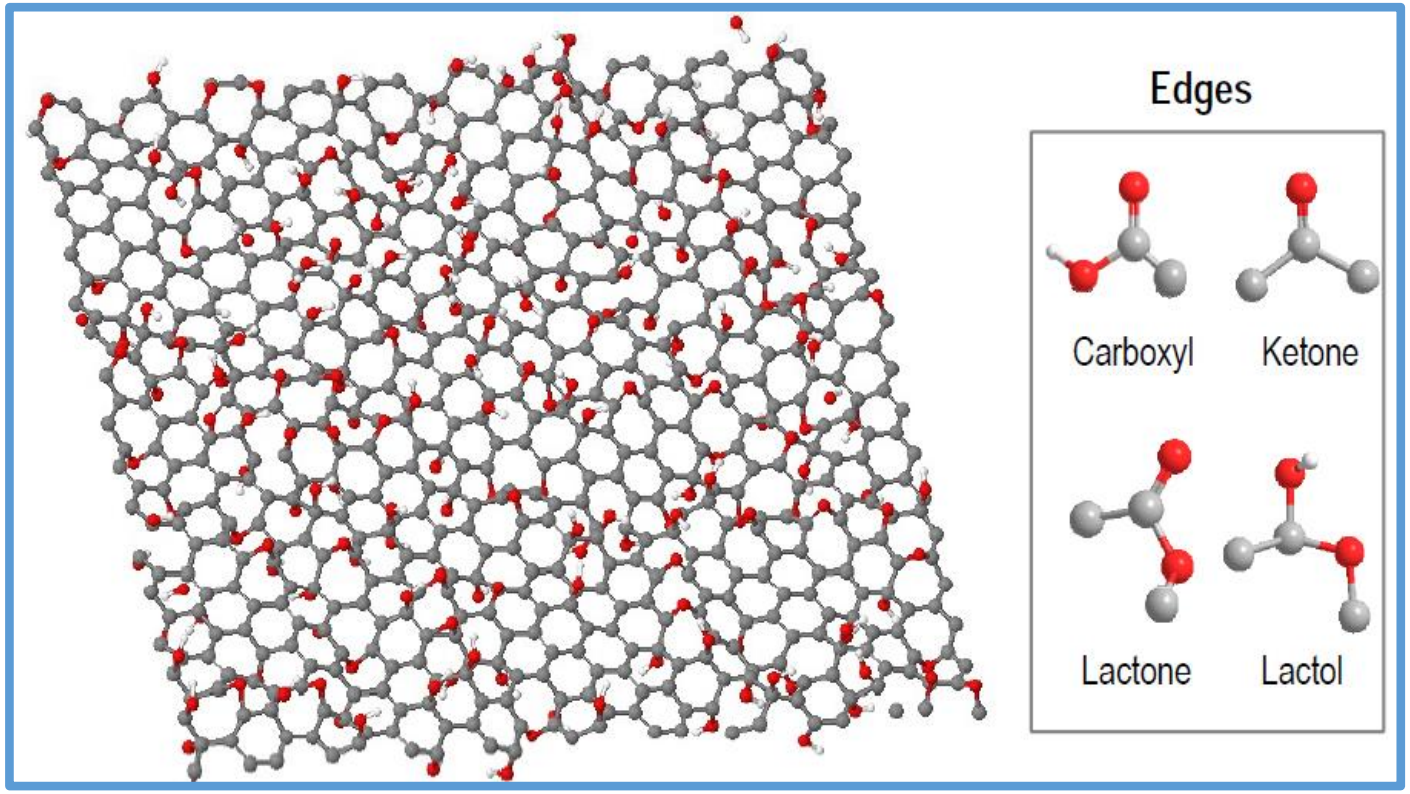
Optical properties

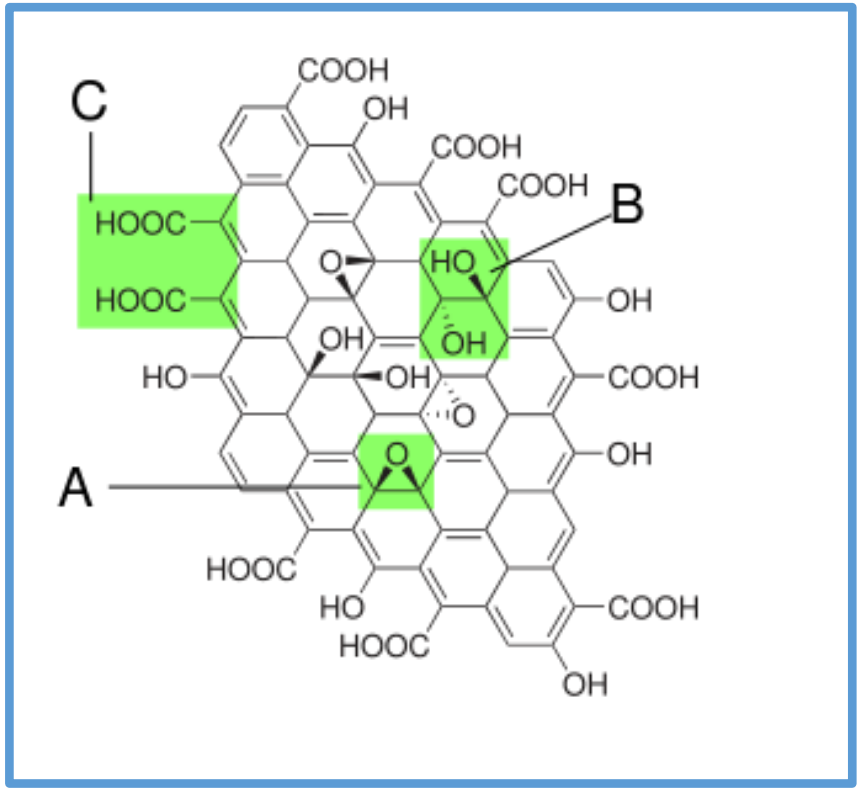
- Monolayer graphene absorbs $\pi\alpha \approx$ 2.3% of white light (97.7 % transmittance), where α is the fine-structure constant.

Electronic properties



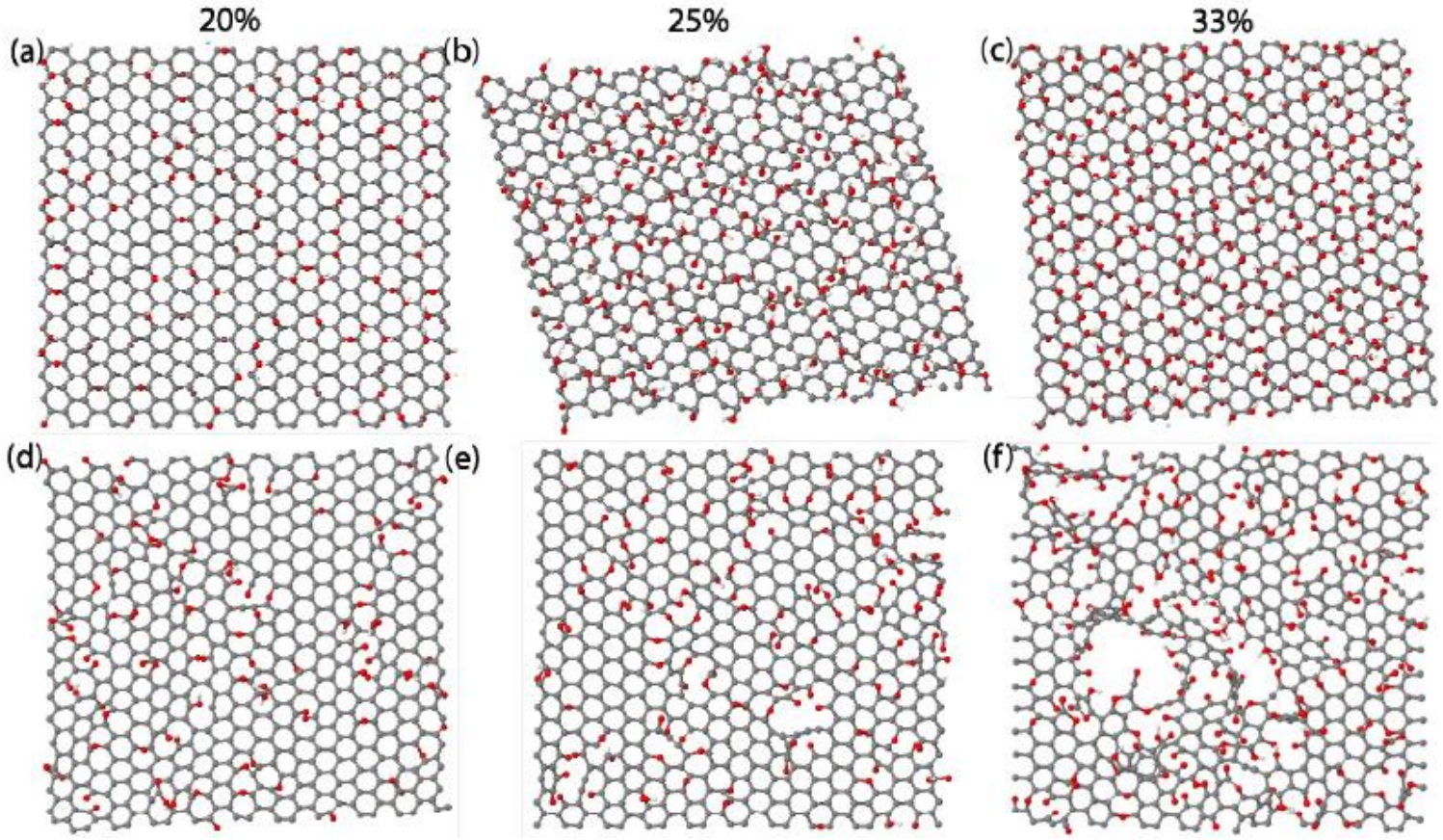
What is Graphene Oxide

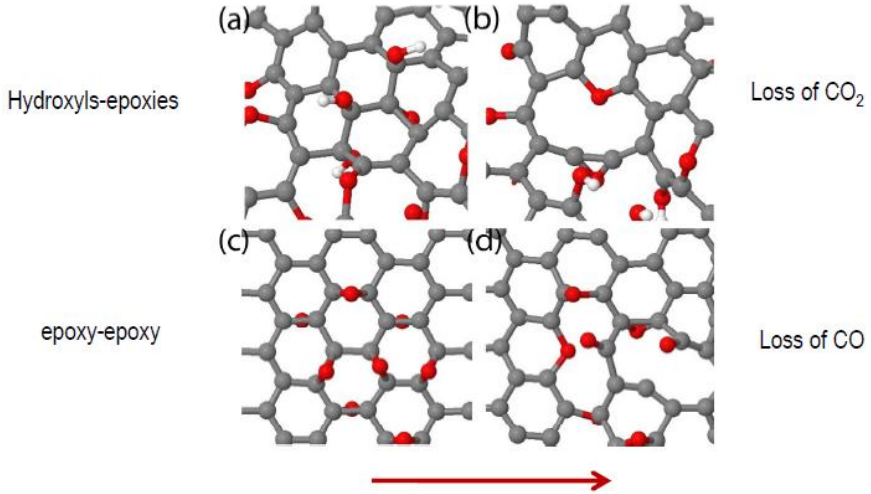




*C. Mattevi et al. Advanced Functional Materials **19**, 2577-2583 (2009)*

Evolution of ***structure*** with reduction





*C. Mattevi et al. Advanced Functional Materials **19**, 2577-2583 (2009)*

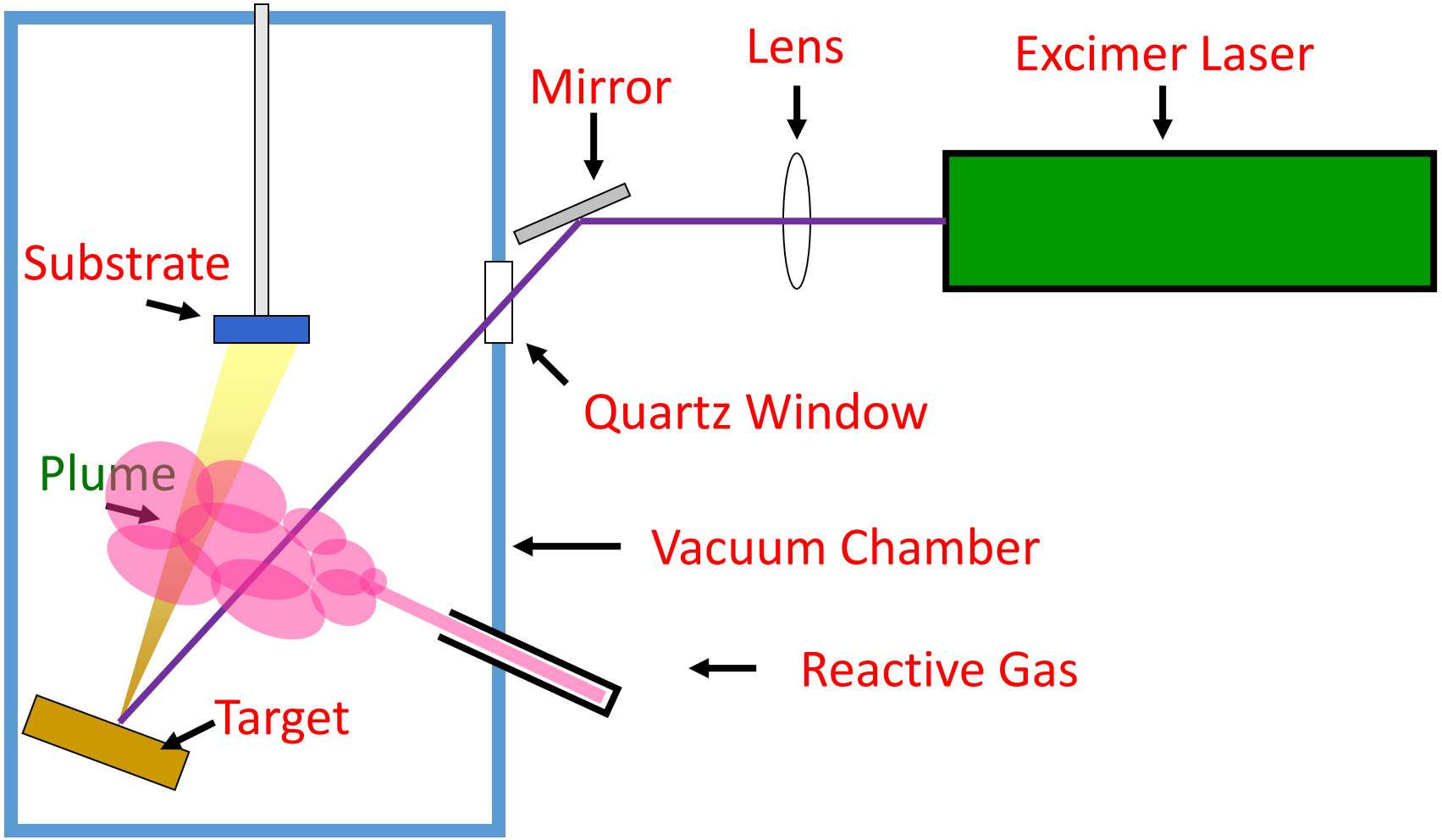
Nature Chemistry 2, 581 (2010)

Pulsed Laser Deposition



- PLD is conceptually simple: Laser beam incident on a target material– create plasma– produce the film
- PLD is versatile: Wide varieties of materials can be deposited.
- To grow complex materials

Schematic Diagram of PLD System



Motivation behind this research work

- ***How does the GO structure (chemical, atomic, electronic) evolve upon reduction?***
- ***How do the properties (optical, electrical) change on reduction?***
- ***What are the limiting factors for mobility and conductivity of rGO?***

Results and Discussion on Reduced Graphene Oxide : Our Research work

Samples using PLD

Sample ID	Number of shots
A	5000
B	100
C	10000
D	500 + 1 SLG

Target: Graphite (99.9%)

Energy density: 2 J/cm2

Temperature: 700 C

Oxygen Press: 1x10-5 Torr

Cooling: H2+Ar (1x10-4 Torr)

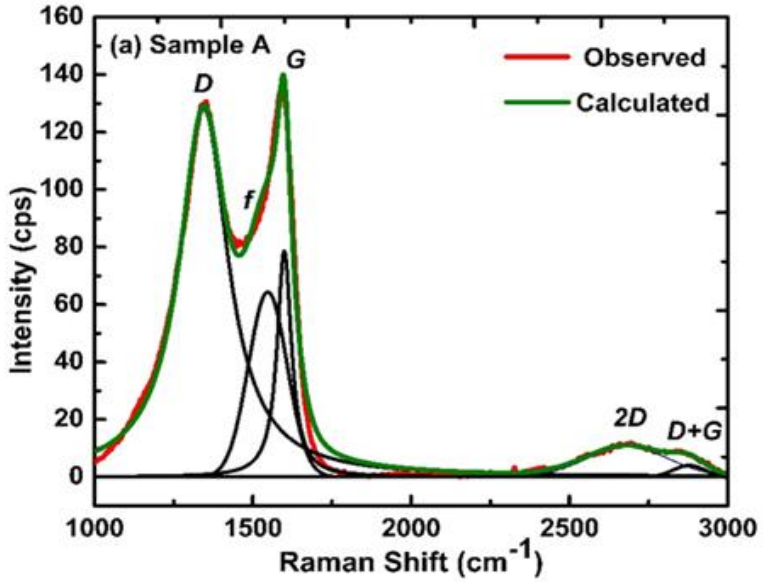
Sample ID	Number of shots SLG
A	300
B	2000
C	5000
D	10000
E	20000

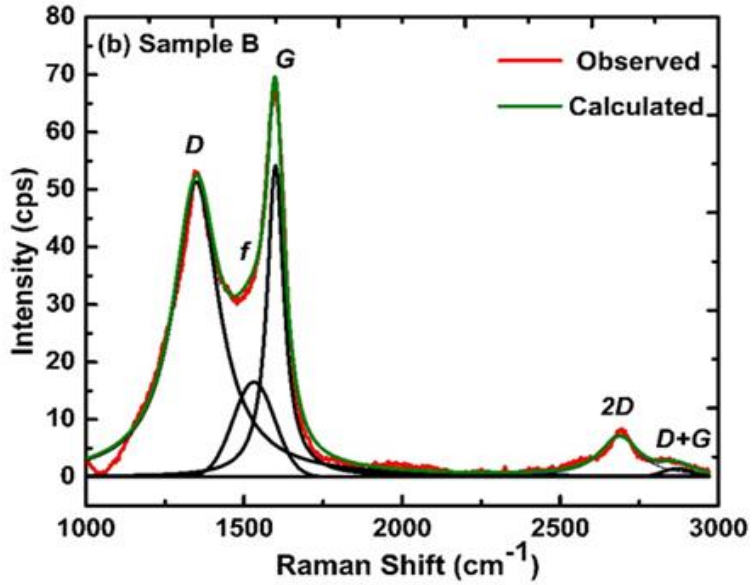
Sample ID	Number of shots
A	5000
B	100
C	10000
D	500 + 1 SLG

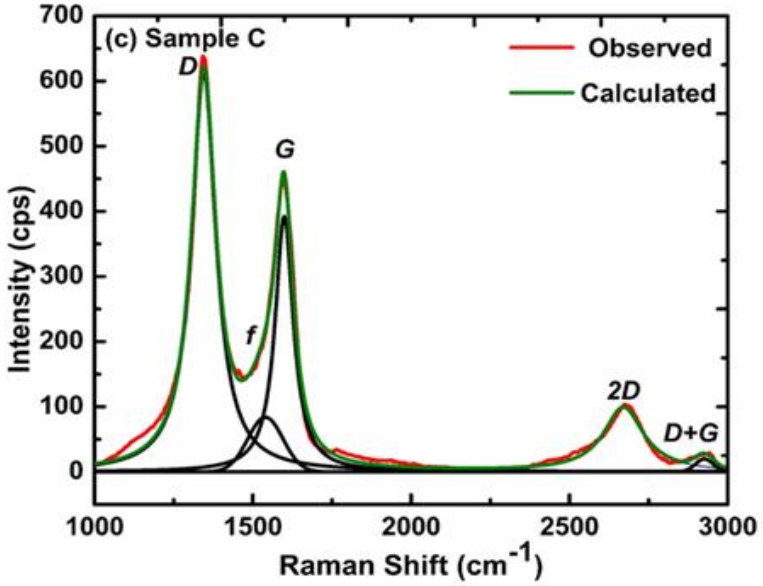
Raman vibrational modes of Graphene

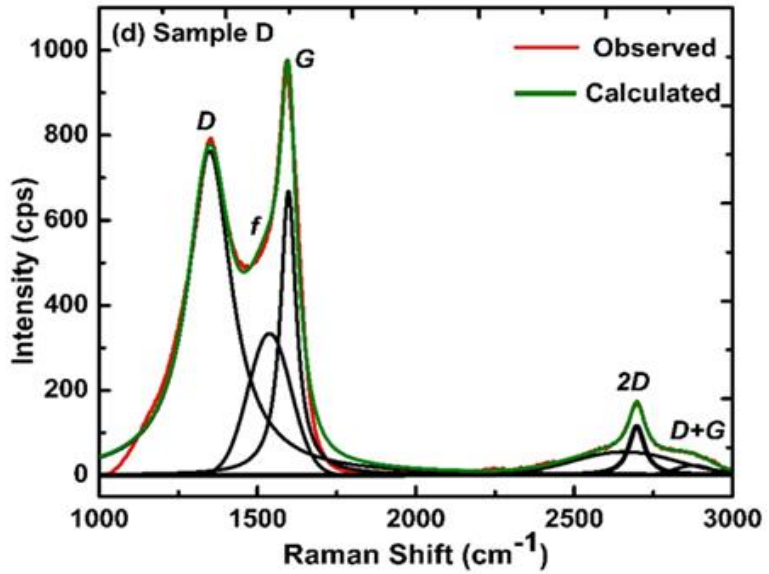
- Confirm graphene oxide by looking for the D, G and 2D peaks.
- G-band originates from the in-plane vibration of the sp^2 carbon atoms (centered around 1580 cm^{-1}): comes from C-C bond stretching mode.
- D-band (defect band) due to out-of-plane breathing mode of the sp^2 carbon atoms (centered around 1360 cm^{-1}).
- 2D-band originates from a two phonon double resonance Raman process and is an overtone of the D band.

Raman Spectroscopy of Reduced Graphene Oxide









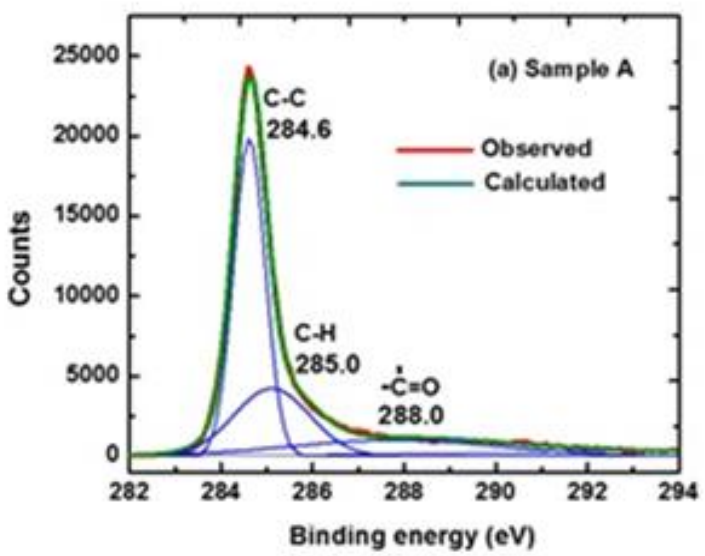
Sample ID	SP^2 cluster size (nm)
A	26.99
B	18.46
C	34.44
D	31.99

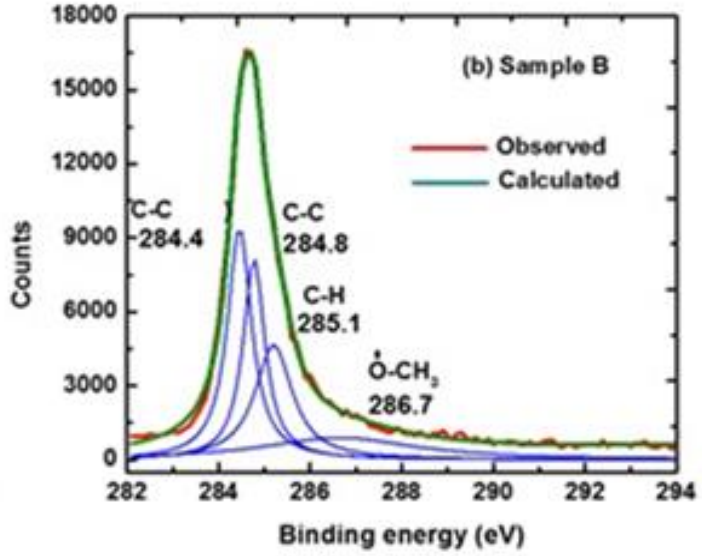
Result and Analysis of Raman Spectrum

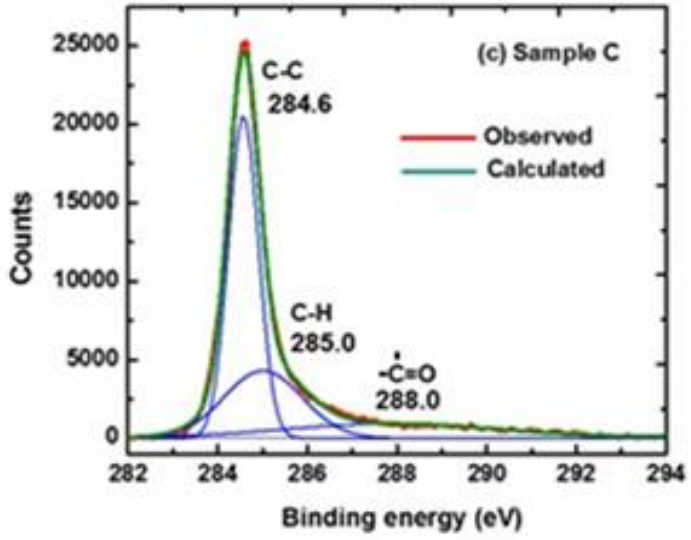
Sample ID	Peak position (cm^{-1})			FWHM (cm^{-1})			Area (cm^{-2})			I_D/I_G	I_{2D}/I_G	SP^2 cluster size (nm)
	D	G	2D	D	G	2D	D	G	2D			
A	1347.1	1590.1	2673.03	158.544	92.42	270.94	2293.7	16329	4636.94	0.96	0.059	26.99
B	1351.23	1595.08	2693.51	103.90	83.77	97.43	6804.11	7101.06	1214.83	.78	0.15	18.46
C	1345.29	1595.76	1678.45	88.25	82.99	121.51	86917.8	48760.8	18408.7	34.44	0.23	34.44
D	1353.39	1591.98	2698.21	186.809	90.53	37.72	399362	239895	16975.1	0.66	0.201	31.99

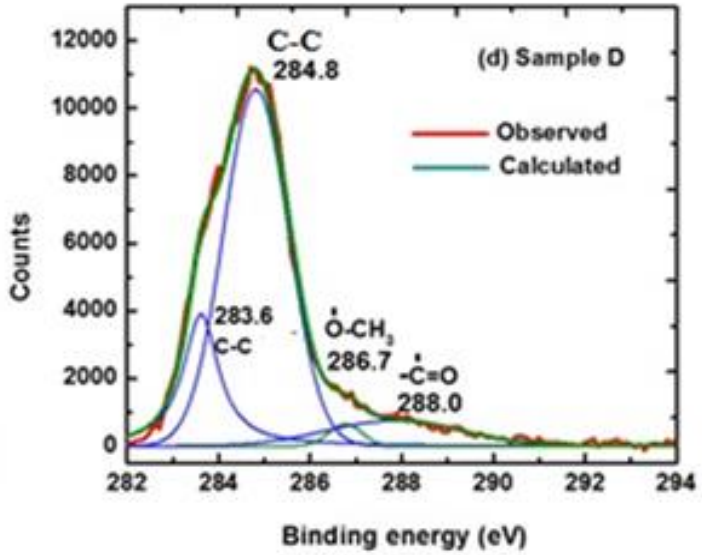
$$L_D^2(nm^2) = (1.8 * 10^{-9})\,\lambda_L^4\,\left(\frac{I_D}{I_G}\right)^{-1}$$

XPS of Reduced Graphene Oxide





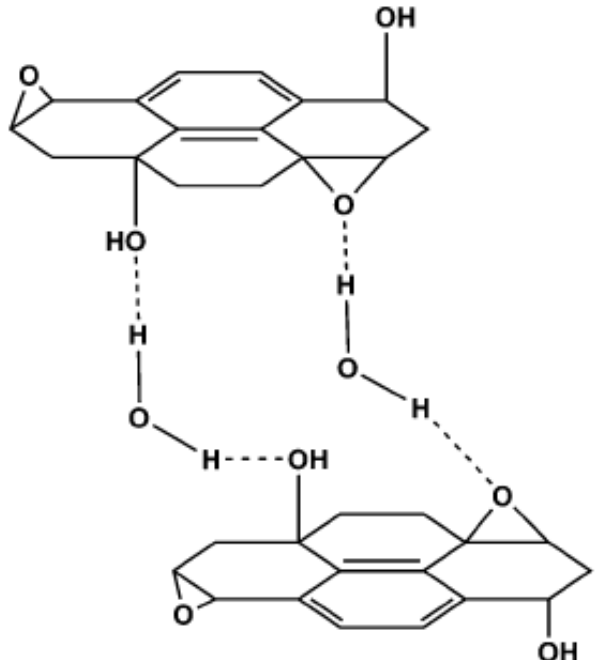




sp^2/sp^3:
54 %, 57%, 54%, and 87%
A, B, C, and D, respectively.

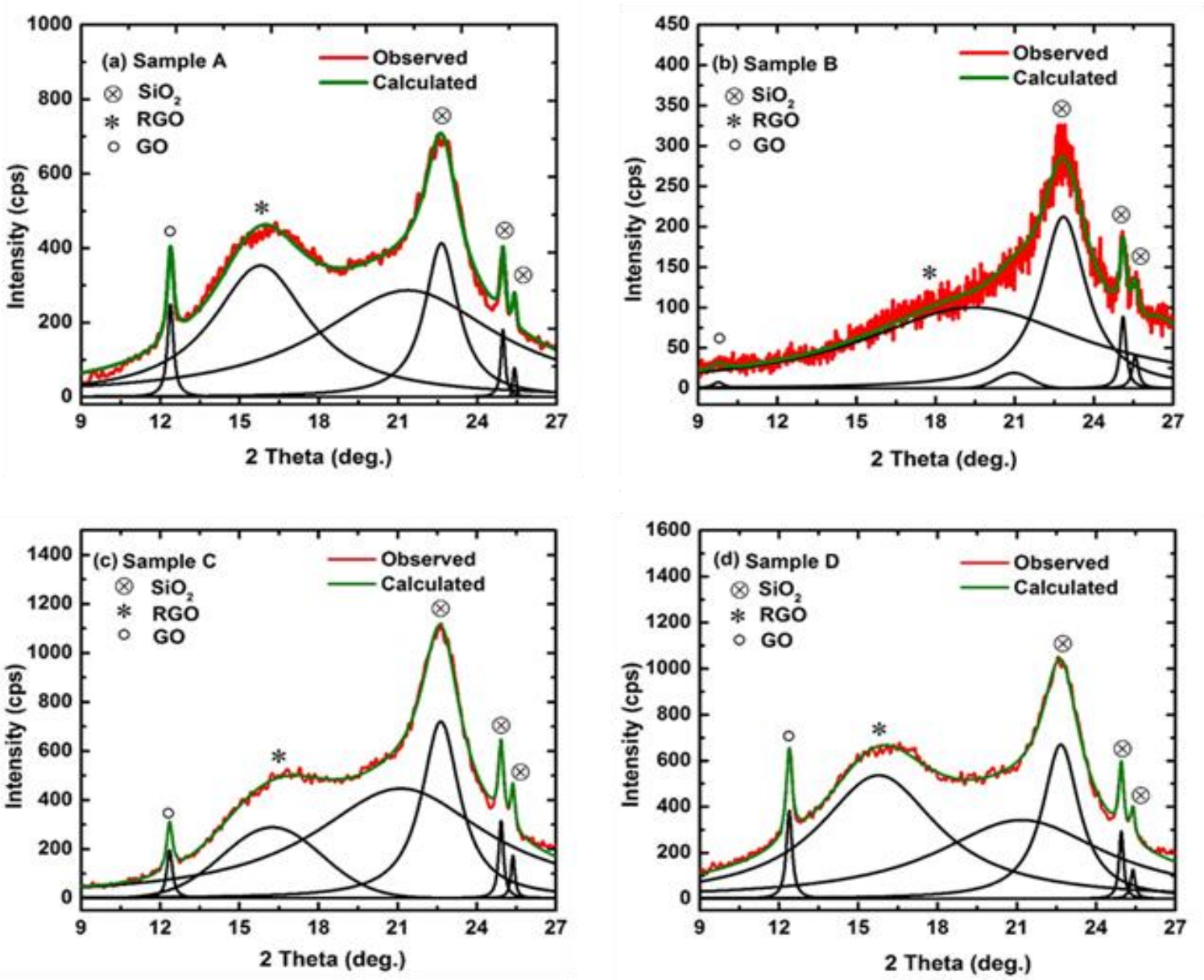
XRD Analysis of Graphene Oxide

- The structure of the Graphene oxide prepared mainly depends on the synthesis process and also on the extent of reduction.
- GO individual sheets are held together by the strong hydrogen bonding present between the layers.
- **Interlayer distances can be confirmed by the XRD analysis**.

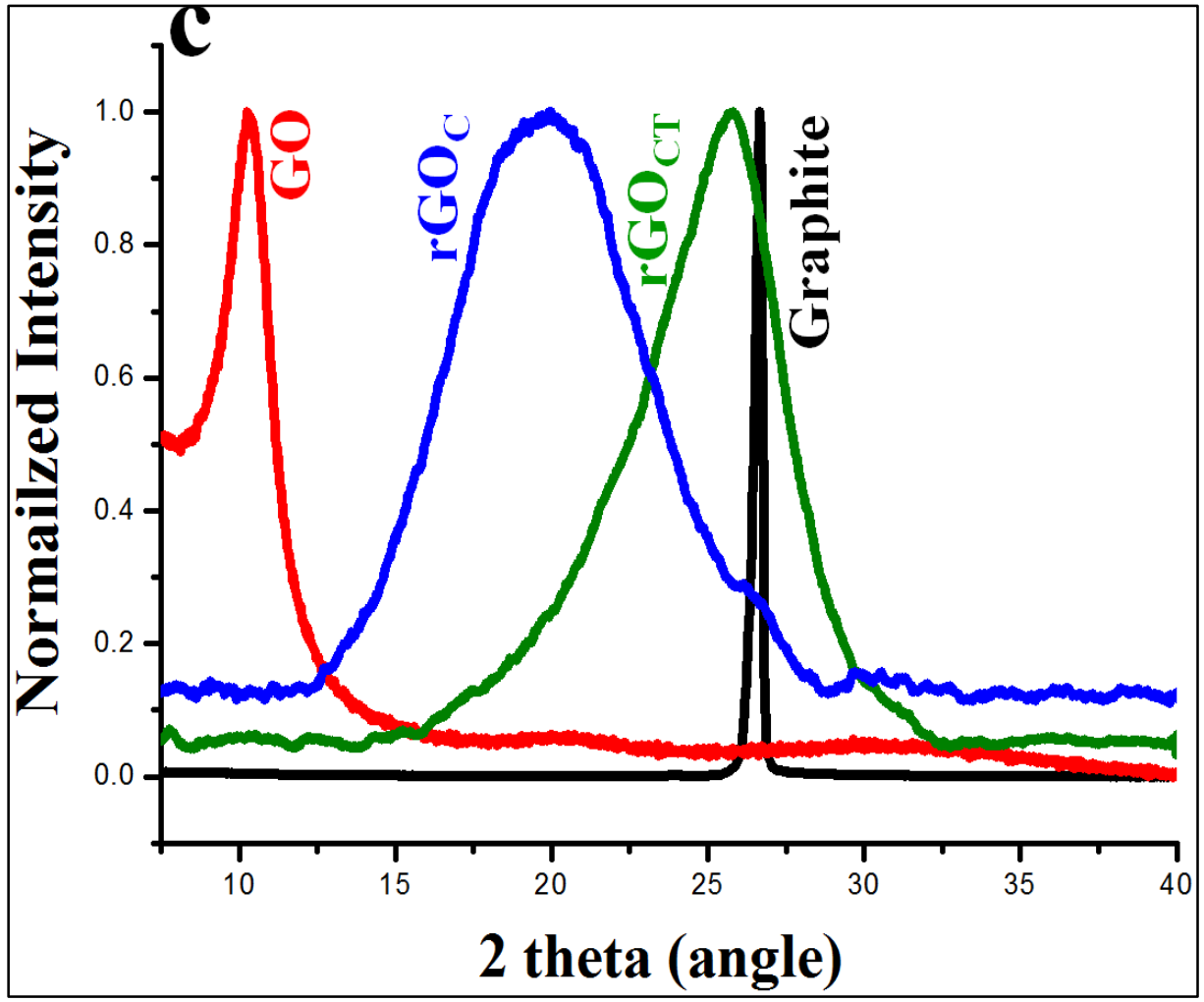


A.Lerf, H. He, Forster and J.klinowski, J.phys.Chem.B. 102 4477 (1998).

XRD Reduced Graphene Oxide



Previous Study on XRD analysis of Graphene Oxide

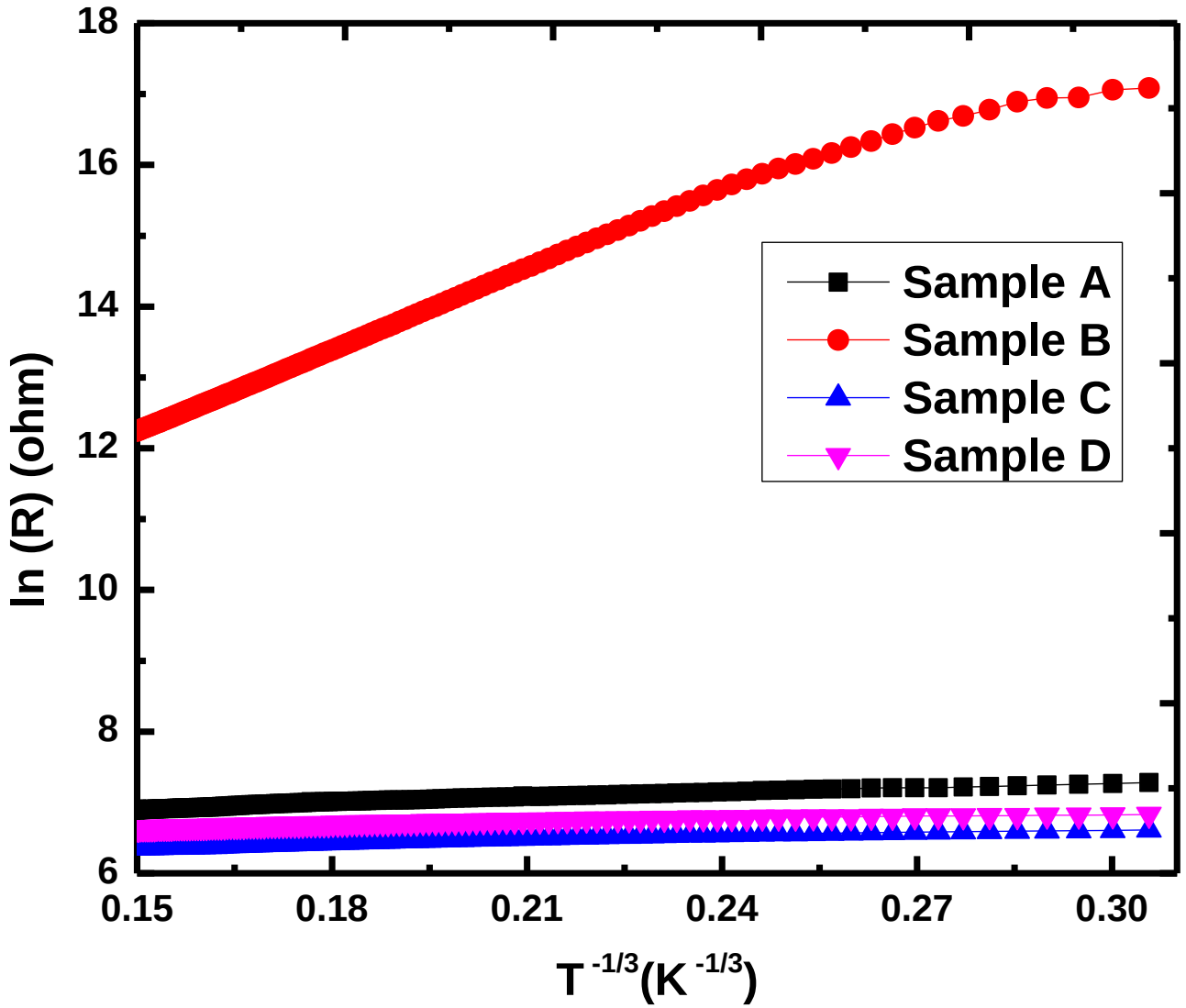


S. Some, Y. Kim, Y. Yoon, H. Yoo, S. Lee, Y. Park & H. Lee SCIENTIFIC REPORTS.3 1929 (2013).

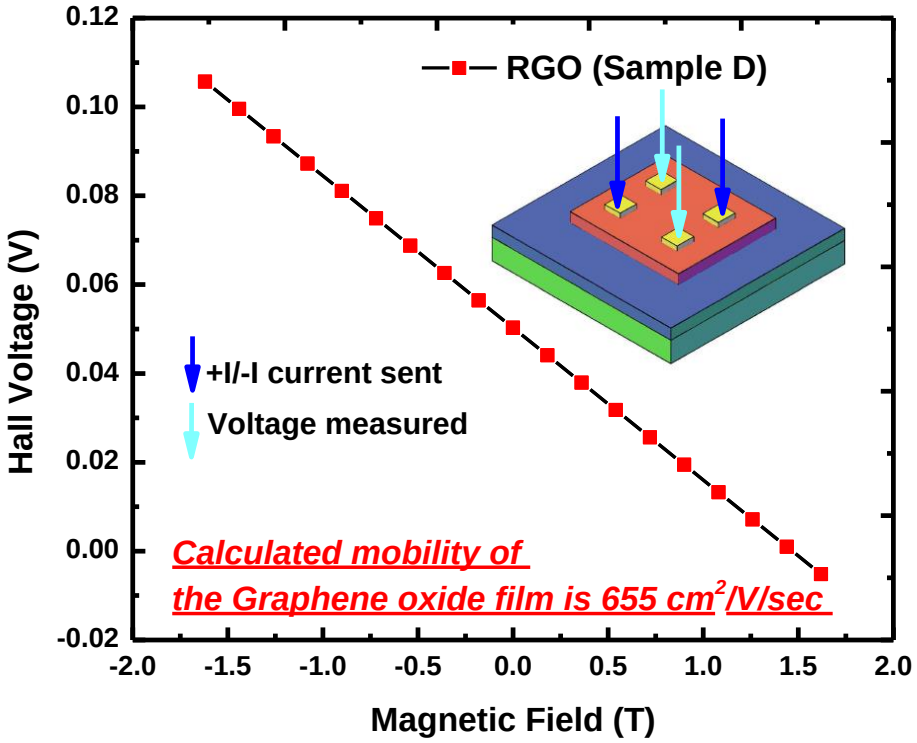
Structural parameters of GO and RGO samples obtained from XRD data.

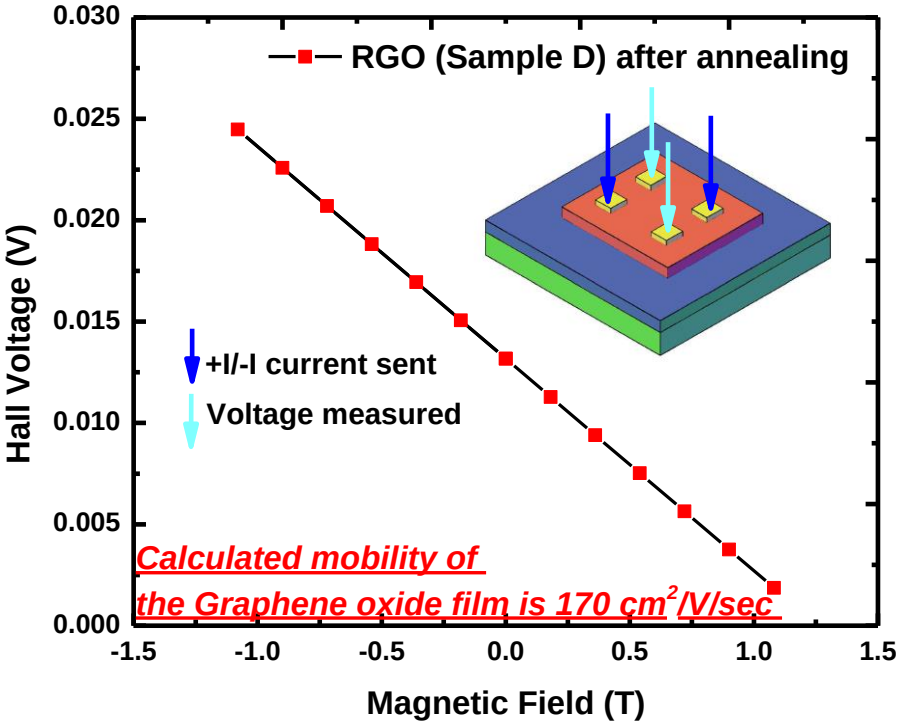
	Sample A		Sample B		Sample C		Sample D	
	RGO	GO	RGO	GO	RGO	GO	RGO	GO
Peak Position (deg)	15.86	12.38	19.37	9.77	16.22	12.36	15.78	12.38
d (Å)	5.587	7.143	4.57	9.045	5.45	7.15	5.61	7.14
FWHM(deg)	4.182	1.51	9.87	2.03	4.183	1.77	5.23	1.67
Crystallite size (Å)	19.4	53.5	8.25	39.71	19.39	45.64	15.50	48.37
Number of layers	3.47	7.48	1.80	4.39	3.55	6.37	2.76	6.77

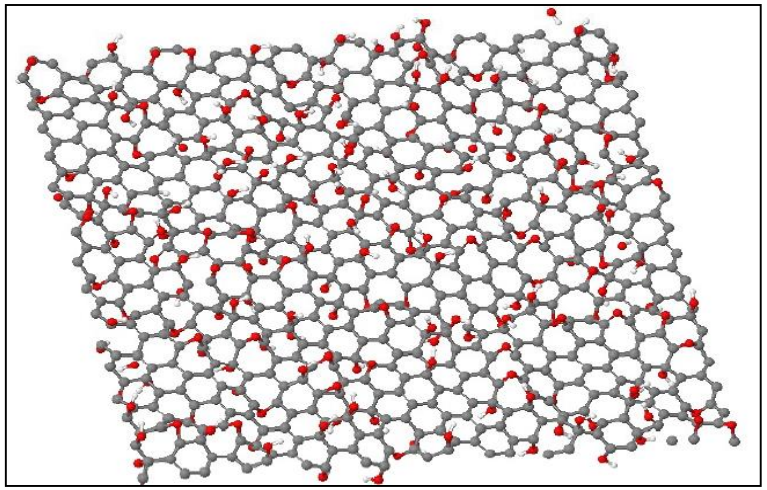
Resistance Vs Low Temperature Measurement

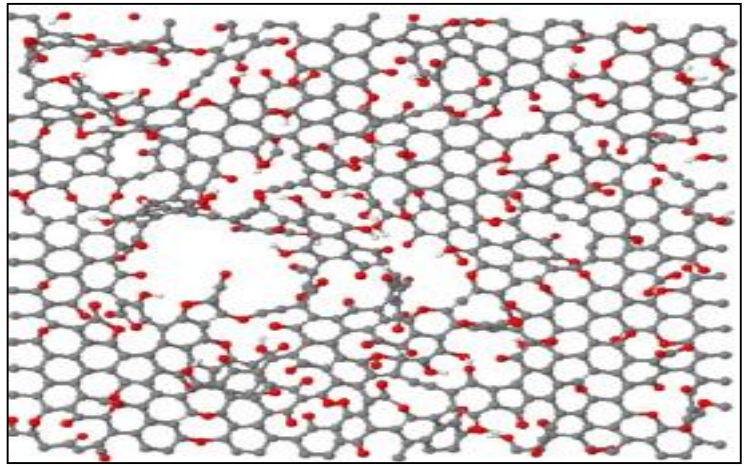


Hall Mobility of Reduced Graphene Oxide







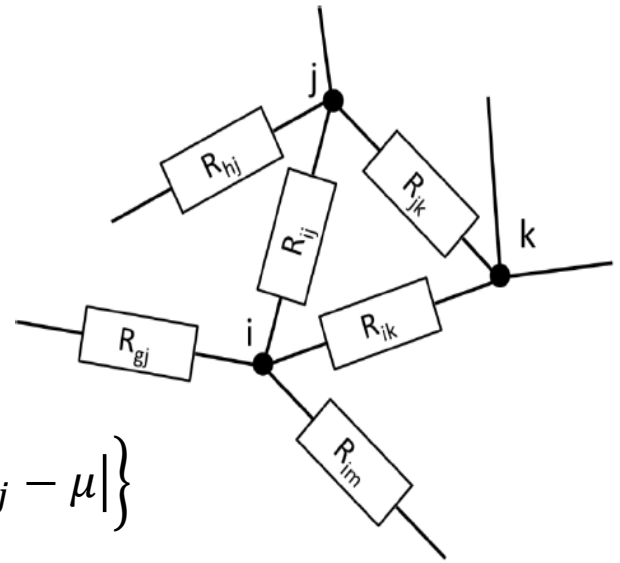


H. C. Schniepp, J. Phys. Chem.B, 2006,110,8535

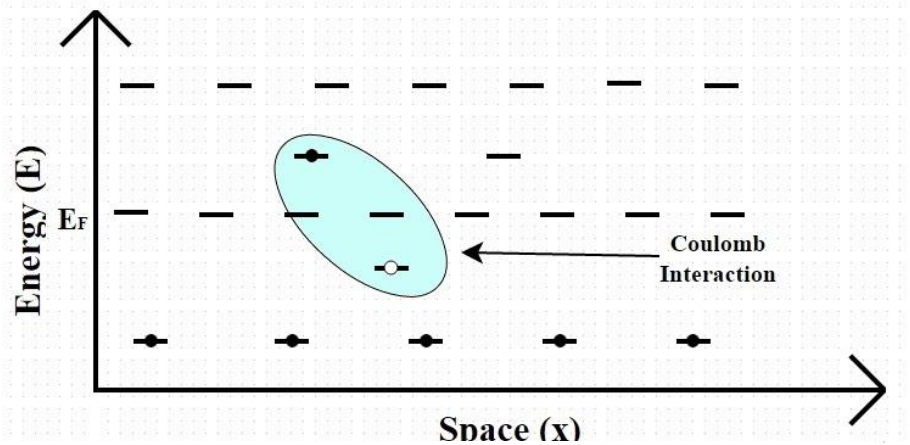
Hopping mechanism

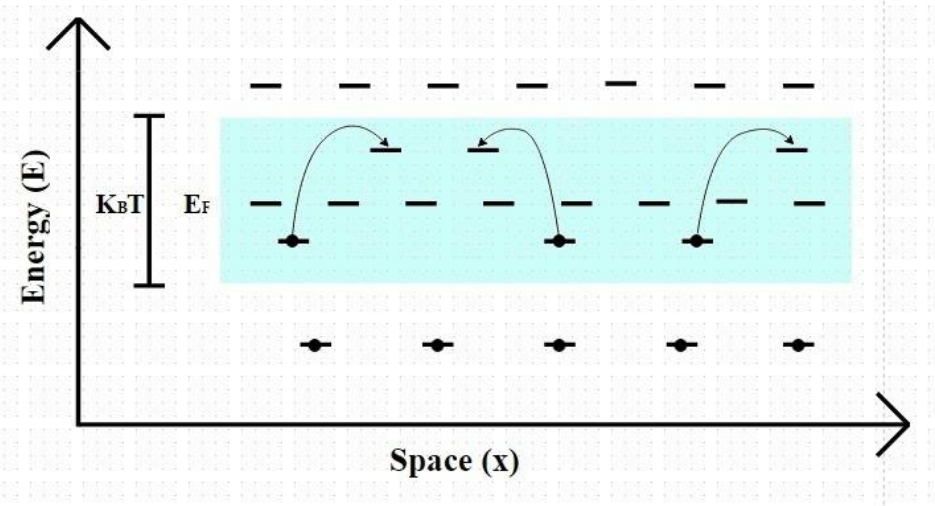
$$R(T) = R_0\, e^{\left(\frac{T_0}{T}\right)^p} \qquad R(T) = R_0 \exp\left(\frac{E_0}{K_b T}\right)$$

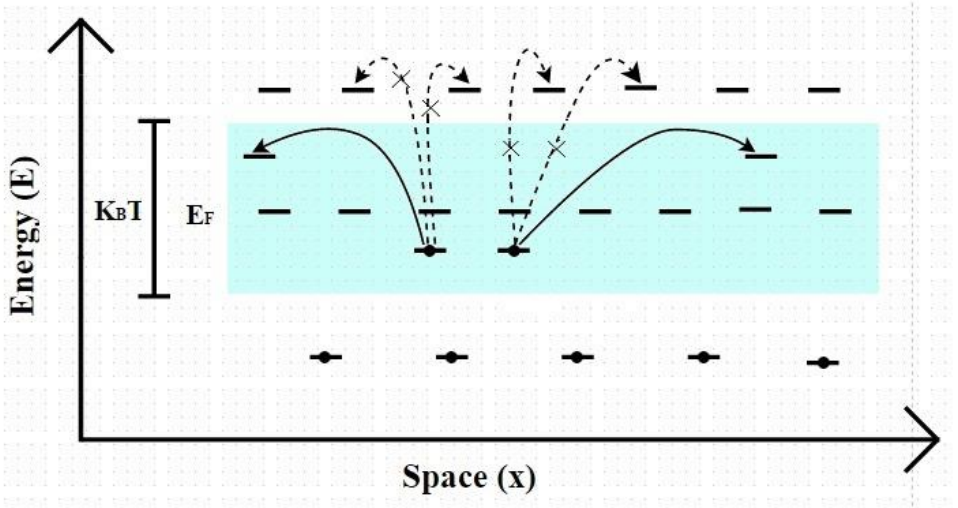
$$R_{ij} = R_{ij}^0 \exp\left\{\frac{2r_{ij}}{a}\right\} \exp\left\{\frac{\epsilon_{ij}}{K_B T}\right\}$$



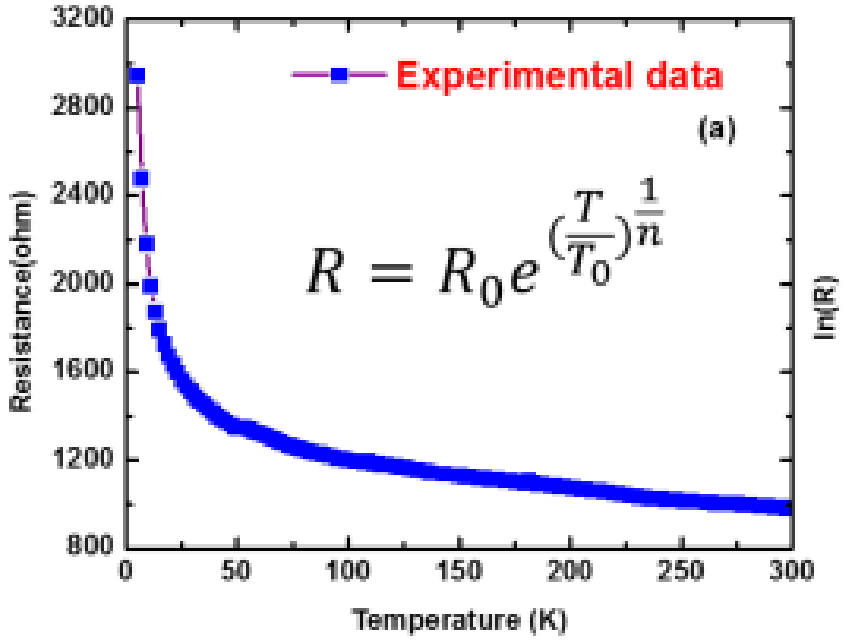
$$\epsilon_{ij} = \frac{1}{2}\left\{\left|\epsilon_i - \epsilon_j\right| + \left|\epsilon_i - \mu\right| + \left|\epsilon_j - \mu\right|\right\}$$

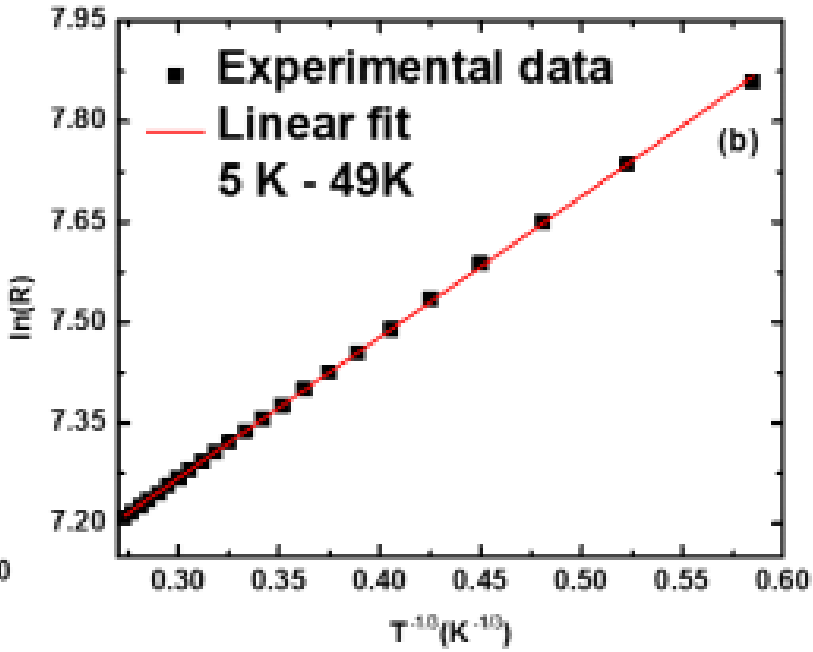


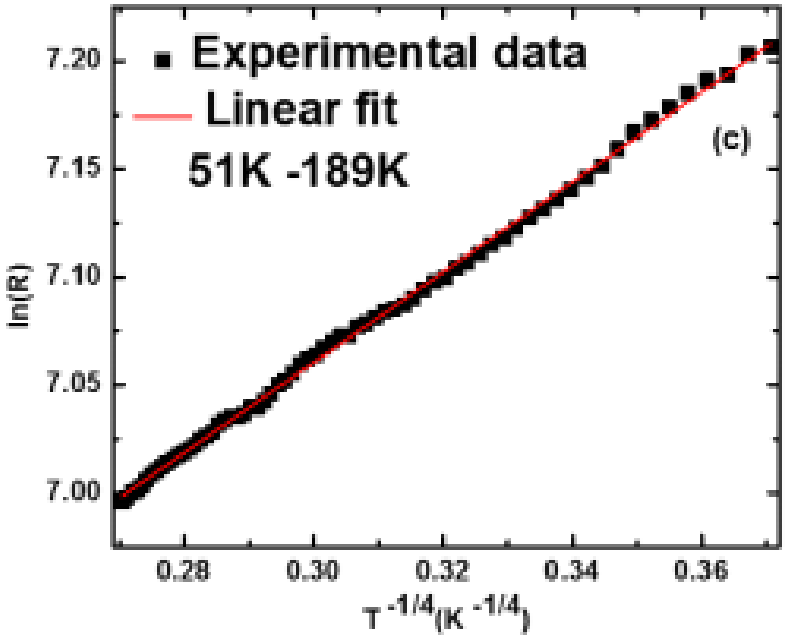


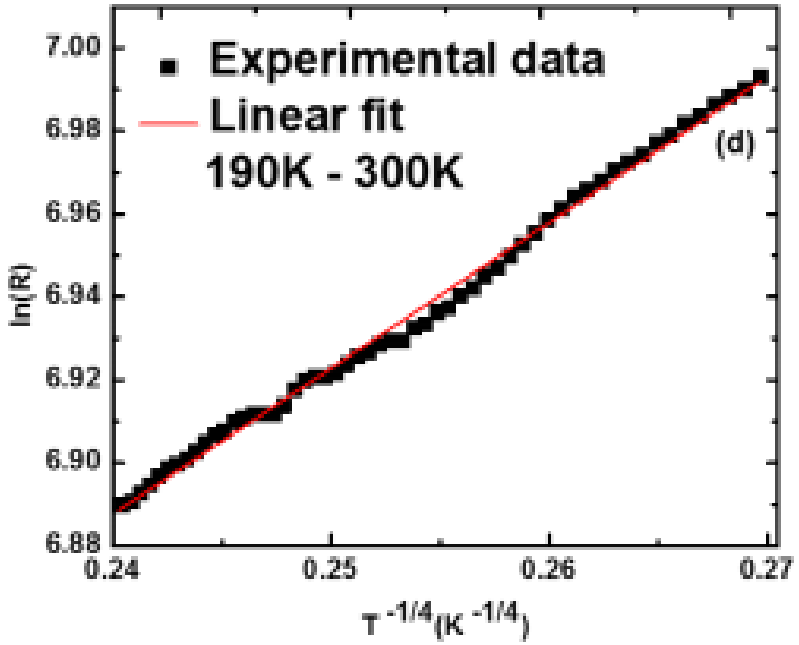


Resistance Vs Low Temperature Measurement (Sample D)

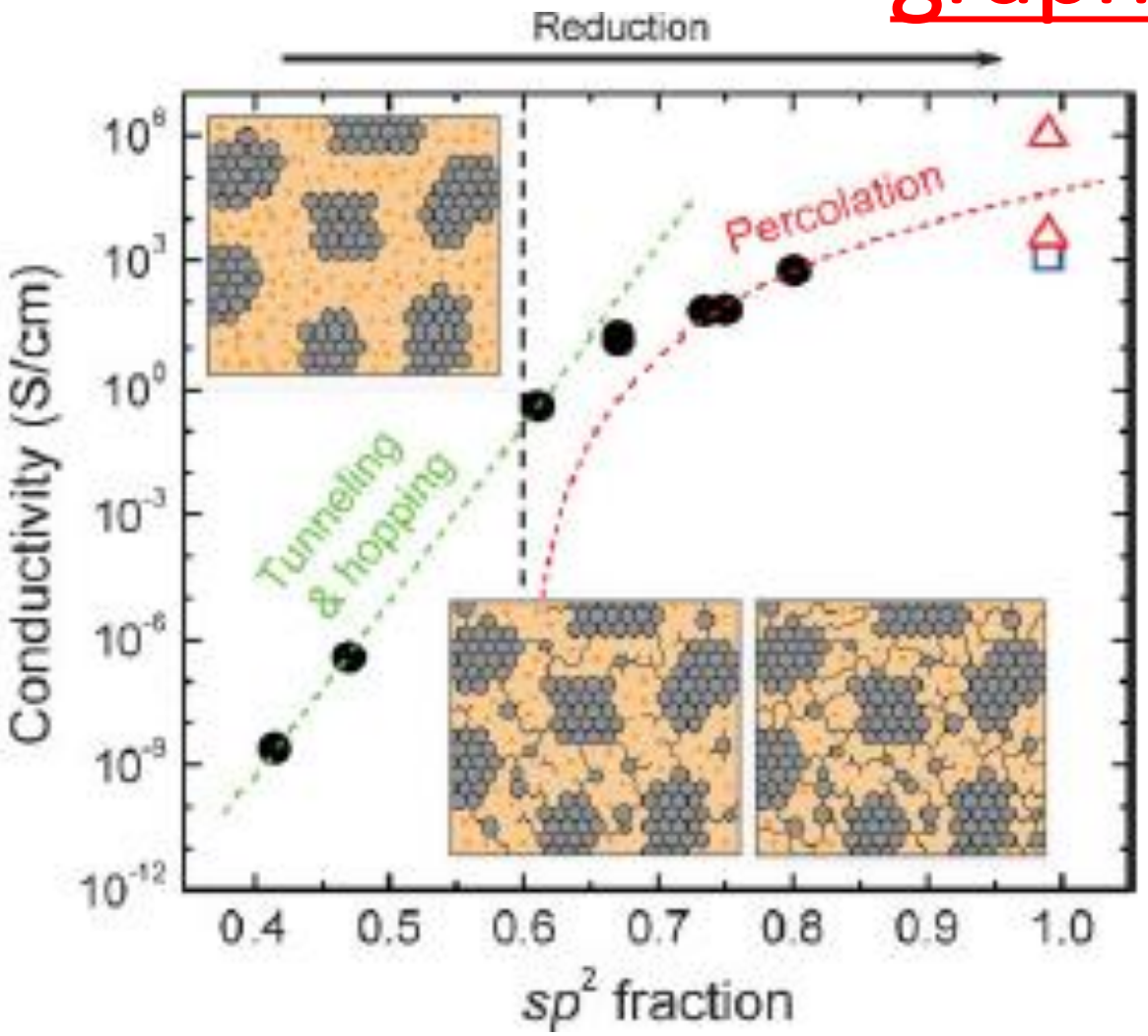




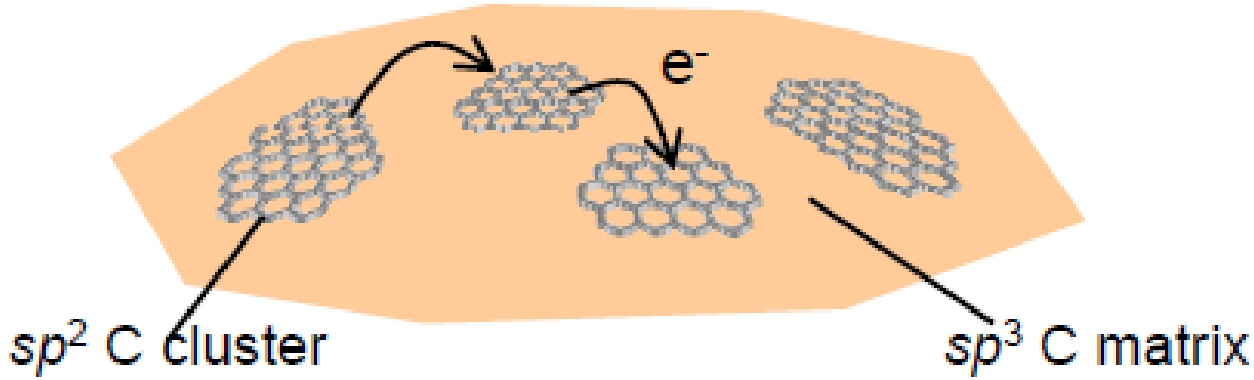




Mechanism of electrical conduction in graphene oxide

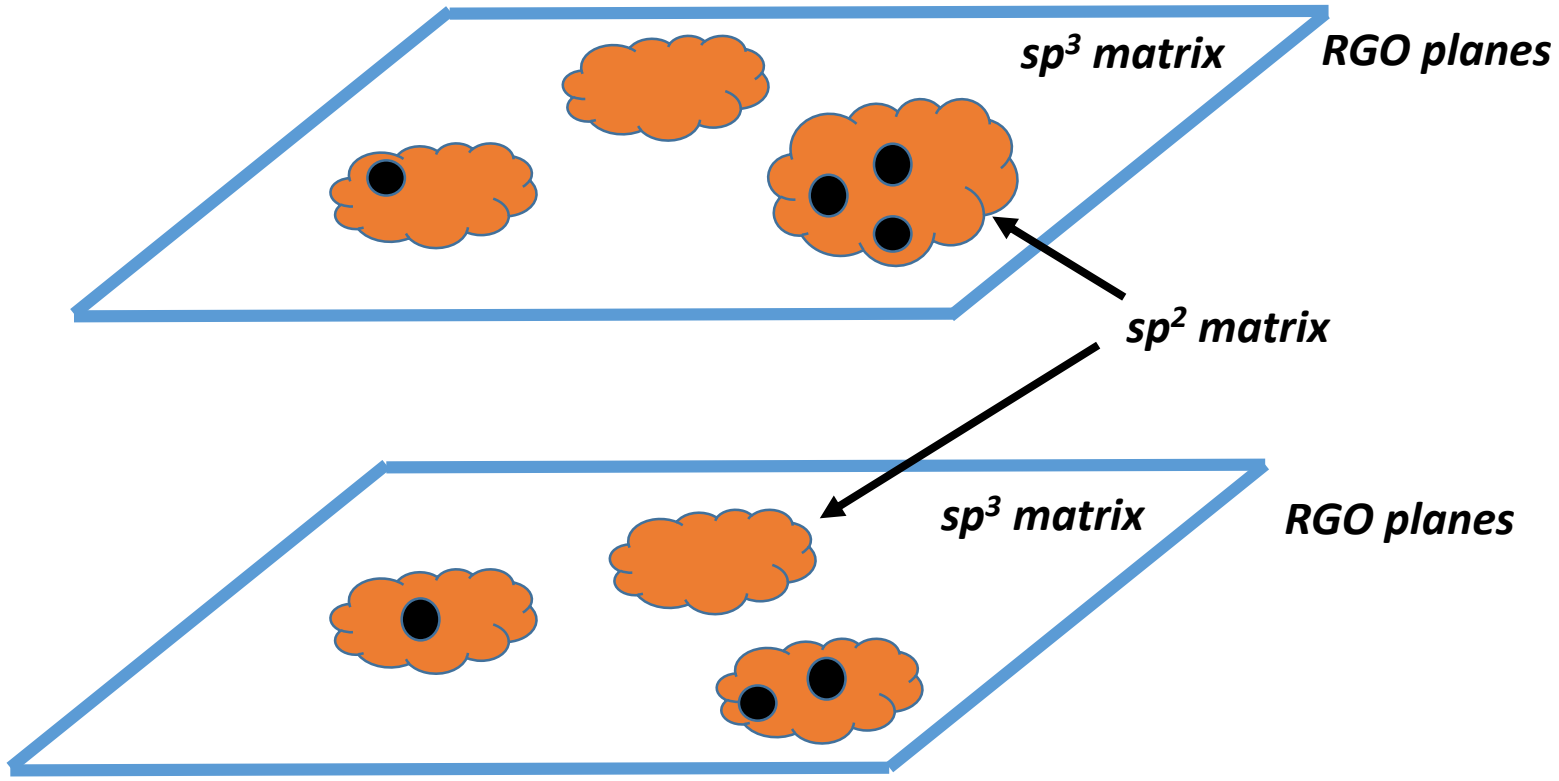


C.Mattevi,G.Fanchini et.al, Adv.Funct.Mater.2009,19,2577



G. Venugopal et al. / Materials Chemistry and Physics 132 (2012) 29– 33.

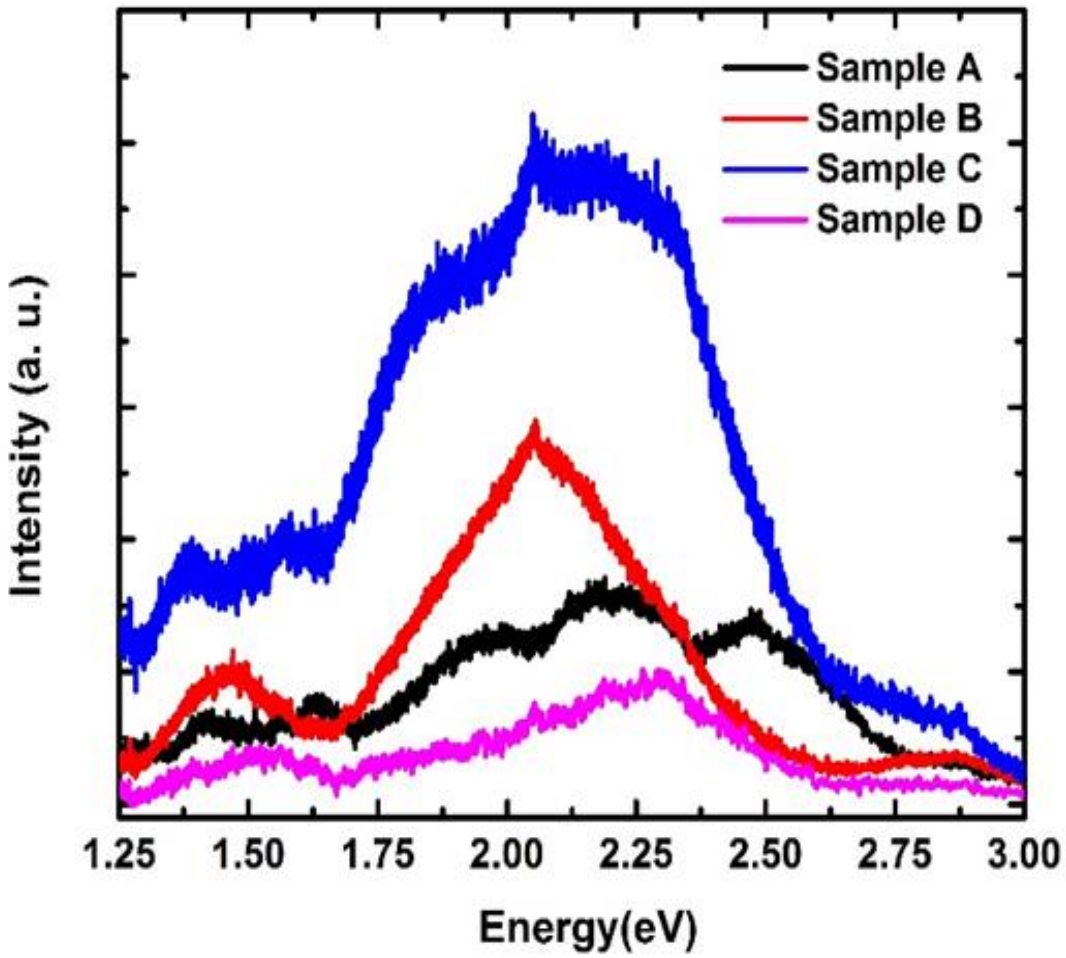
Charge carrier hopping in Sample D



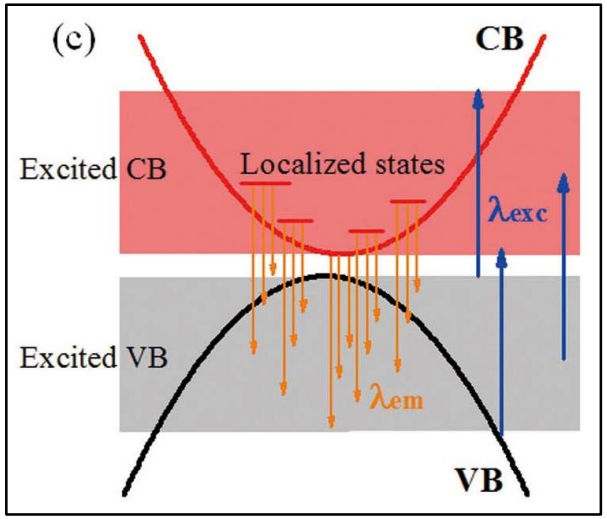
2D Material-Graphene

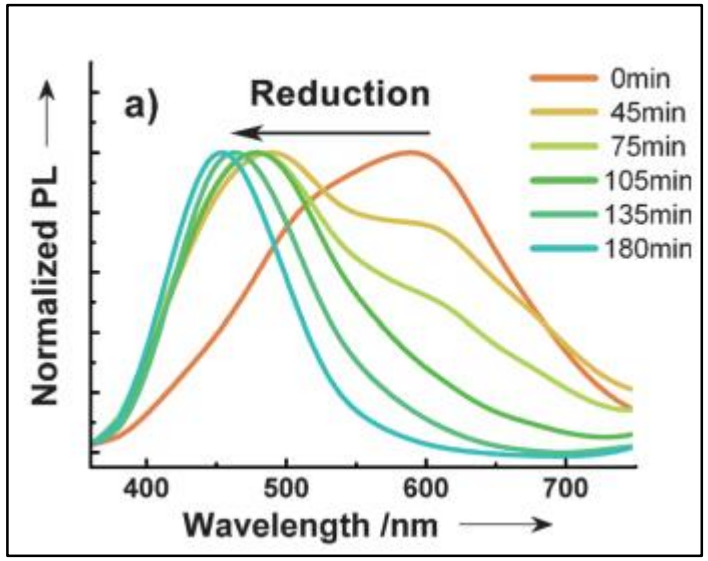
Sample Name	Localization Length (nm)	Activation Energy (meV)	Hopping Energy (meV)
Sample A	916	4.7	4.2
Sample B	4	42.1	17.7
Sample C	1401	3.4	3.9
Sample D	4227	2.3	3.7

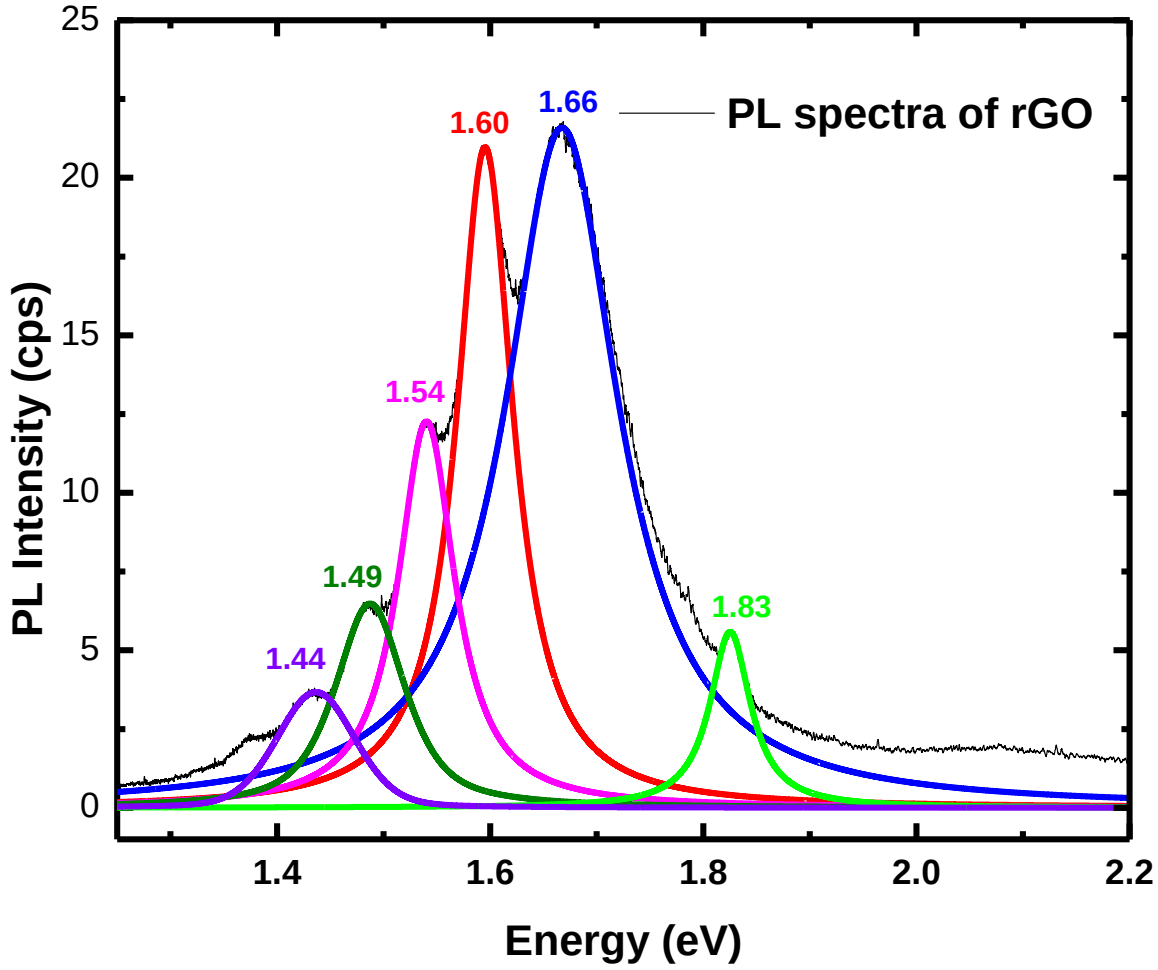
PL Spectroscopy of RGO



Photoluminescence Spectroscopy

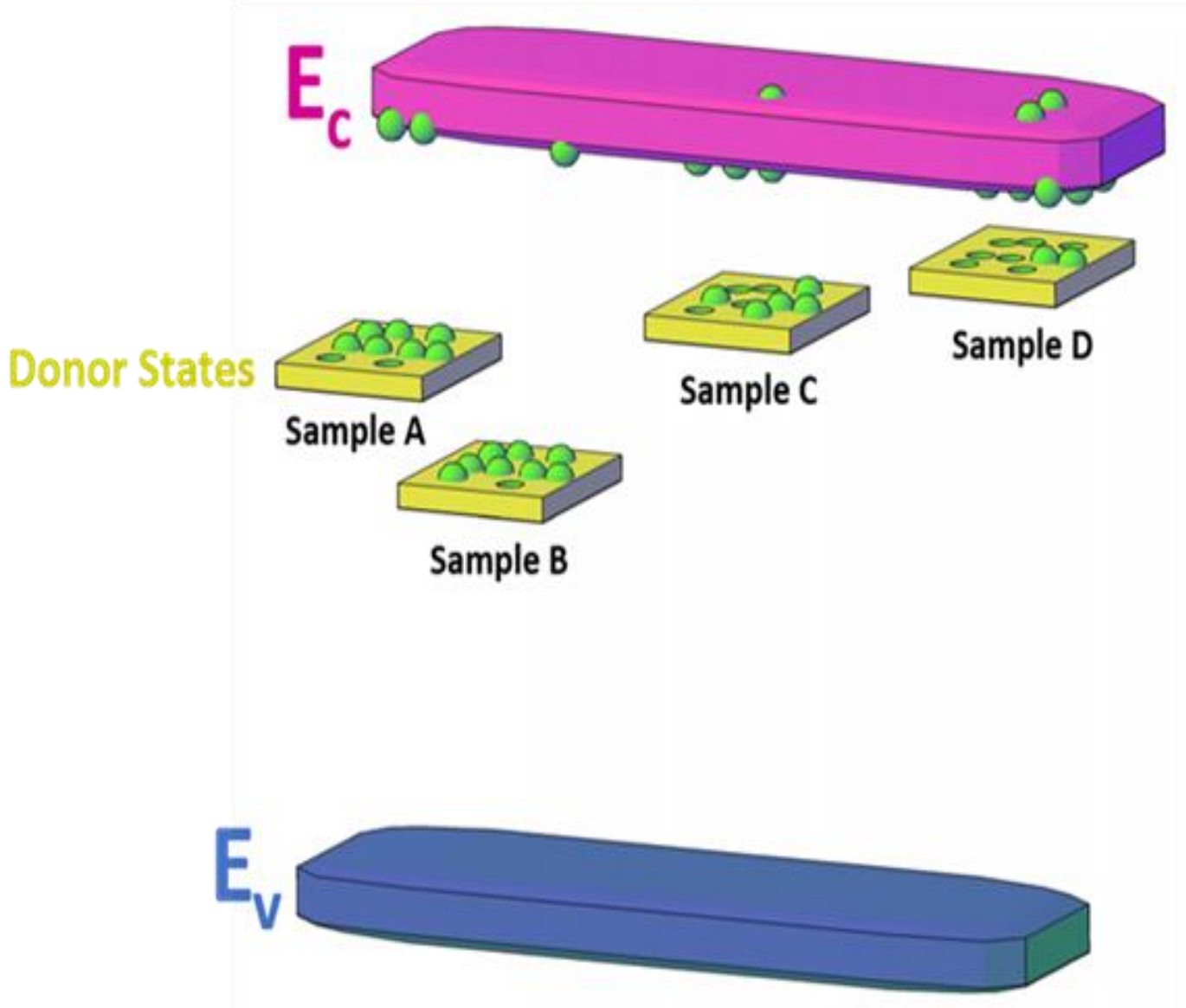




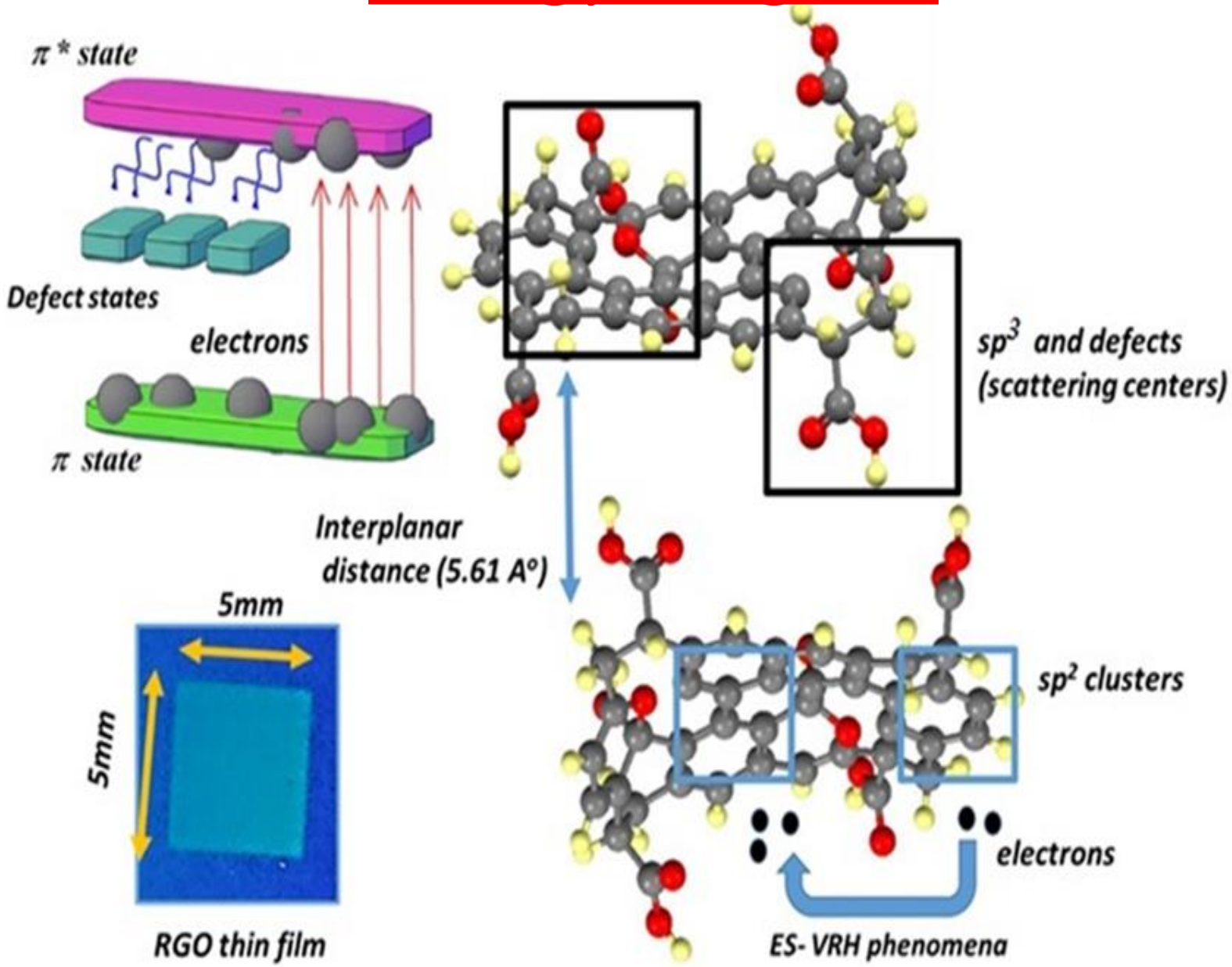


Angew. Chem. Int. Ed. 2012, 51, 6662 –6666

Energy Diagram

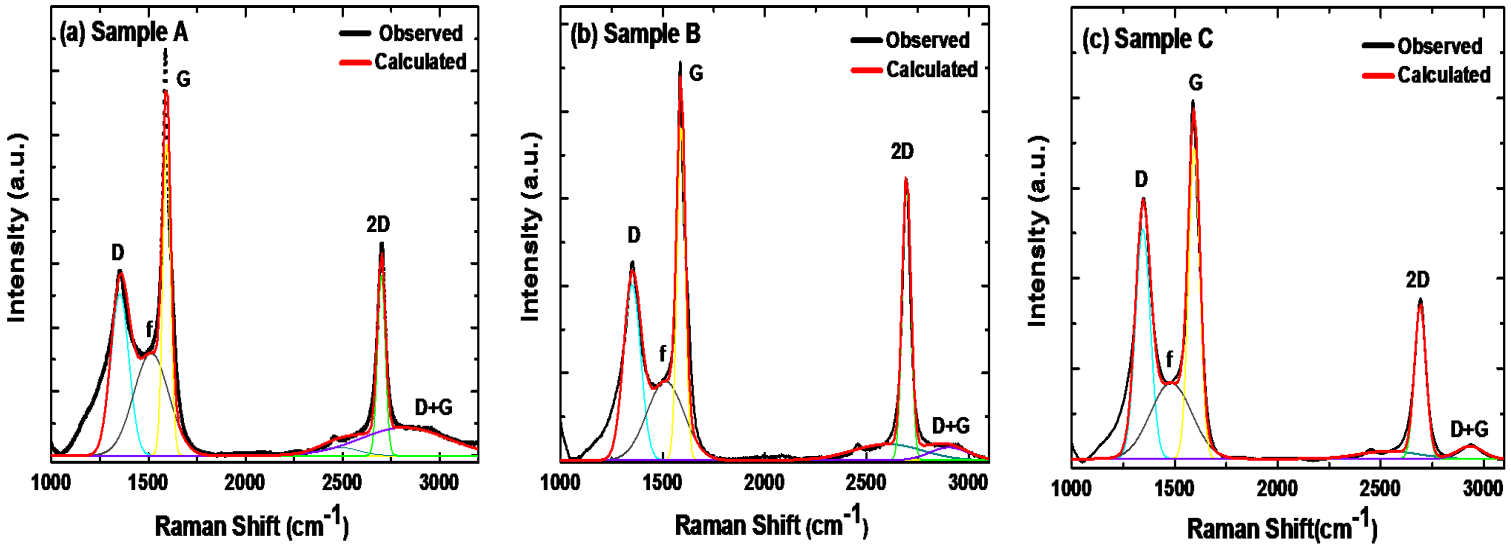


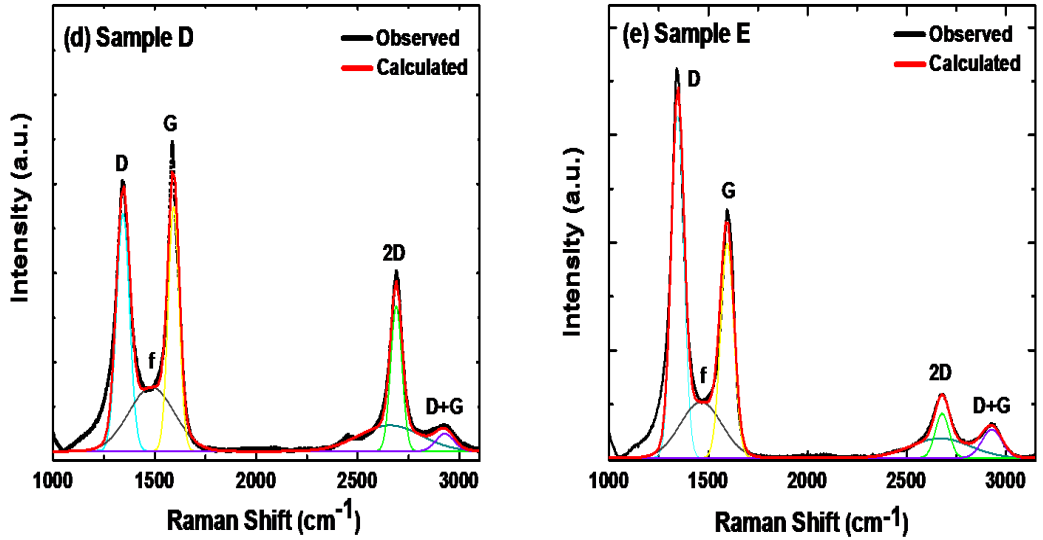
Energy Diagram



Sample ID	Number of shots SLG
A	300
B	2000
C	5000
D	10000
E	20000

Raman Spectroscopy





λ_L = the wavelength in nm (532 nm) of the laser excitation.

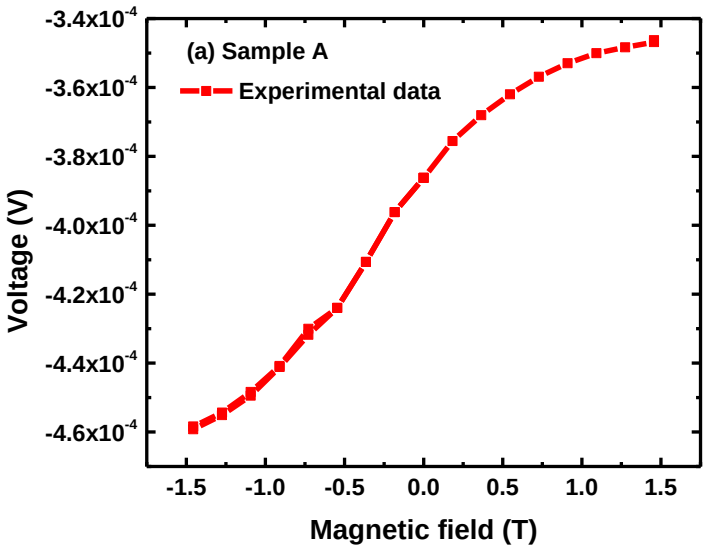
Raman Analysis

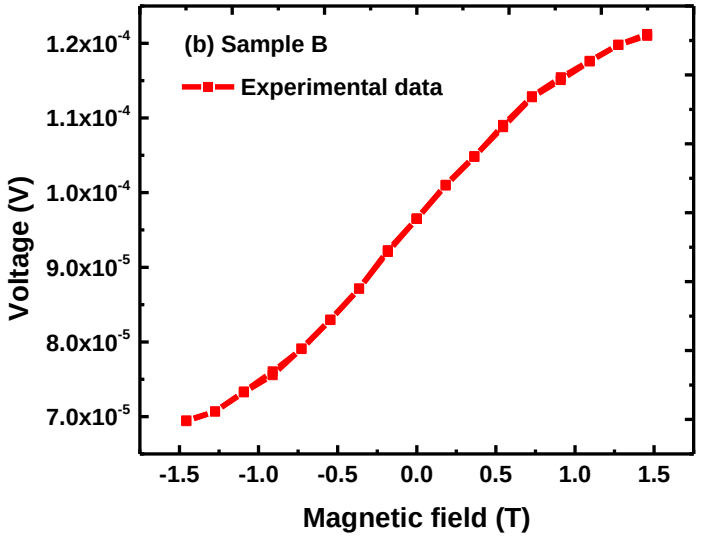
Sample	Shots	D (cm^{-1})	G (cm^{-1})	2D (cm^{-1})	I_D/I_G	A_{2D}/A_G	I_{2D}/I_{D+G}	L_D (nm)	n_D (cm^{-2})
A	200	1353	1594	2700	0.52	0.57	6.42	18.98	$8.98*10^{10}$
B	2000	1347	1590	2694	0.40	0.74	21.6	16.65	$1.16*10^{11}$
C	5000	1346	1593	2692	0.59	0.48	10.77	15.63	$1.32*10^{11}$
D	10000	1343	1591	2689	0.79	0.61	9.03	13.50	$1.77*10^{11}$
E	20000	1343	1598	2677	1.31	0.41	2.00	10.49	$2.94*10^{11}$

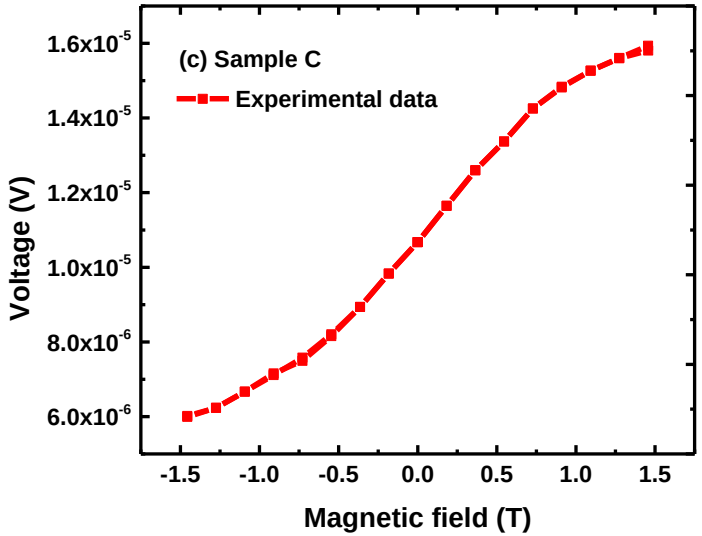
$$L_D^2(nm^2) = (1.8 * 10^{-9})\,\lambda_L^4\,\left(\frac{I_D}{I_G}\right)^{-1}$$

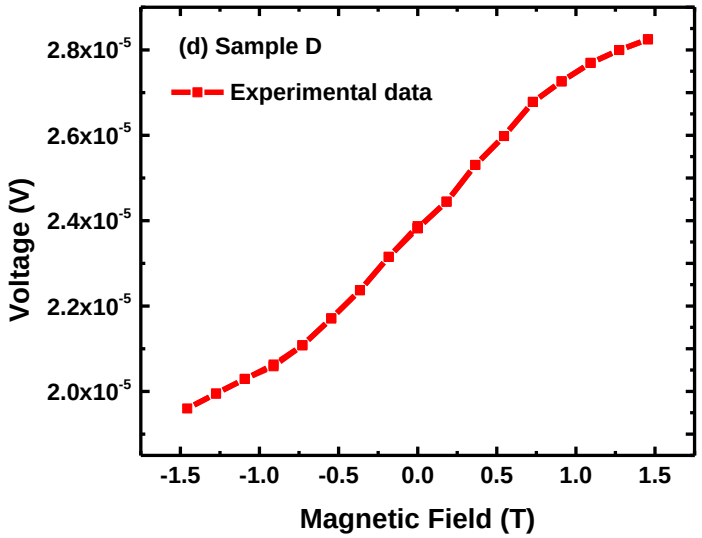
$$n_D\,(cm^{-2}) = \left(\frac{1.8 * 10^{22}}{\lambda_L^4}\right)\left(\frac{I_D}{I_G}\right)$$

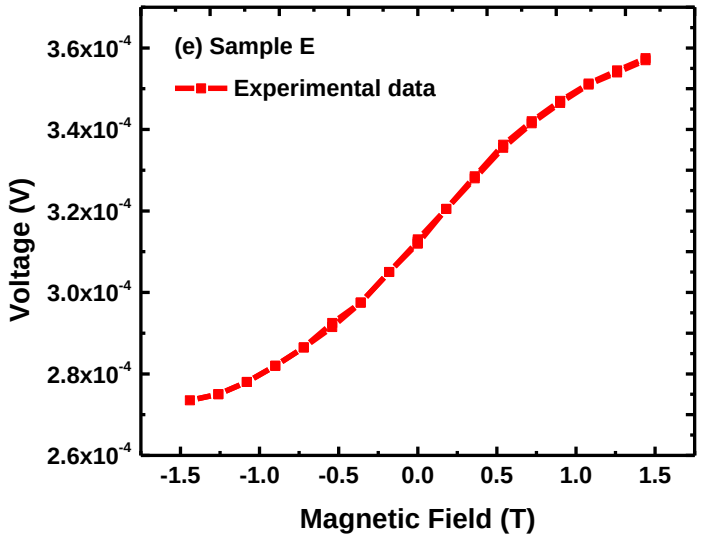
Hall Effect







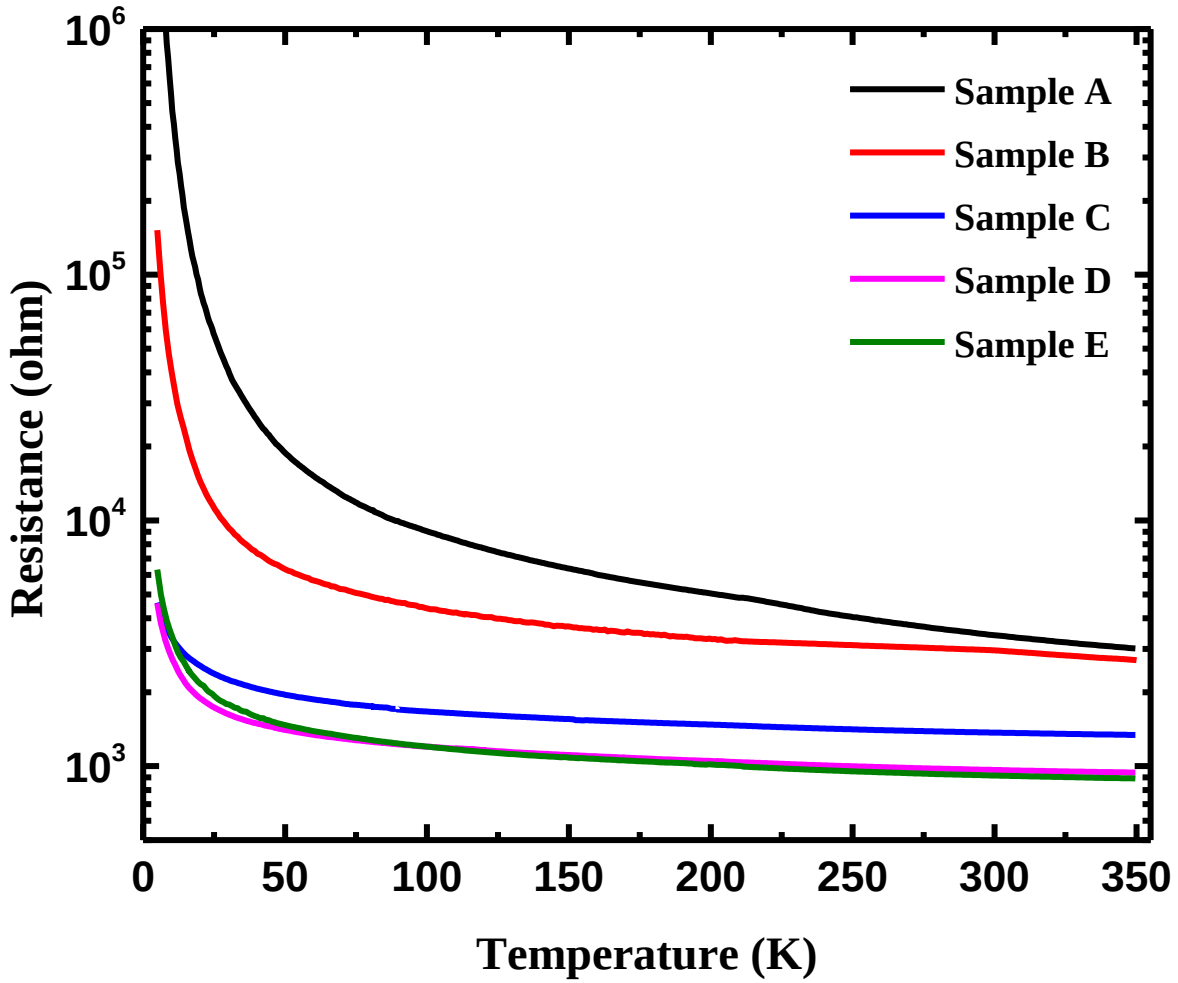




$$n = \frac{1}{R_H}$$

$$\mu = \frac{1}{e\rho_s n}$$

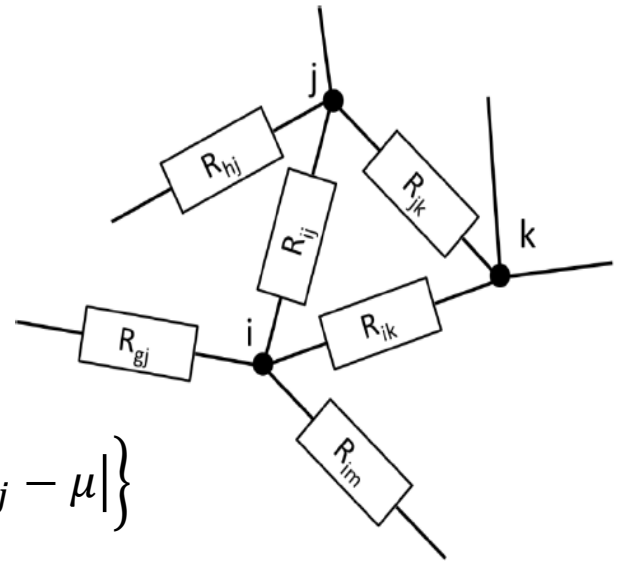
Temperature Dependent Resistivity



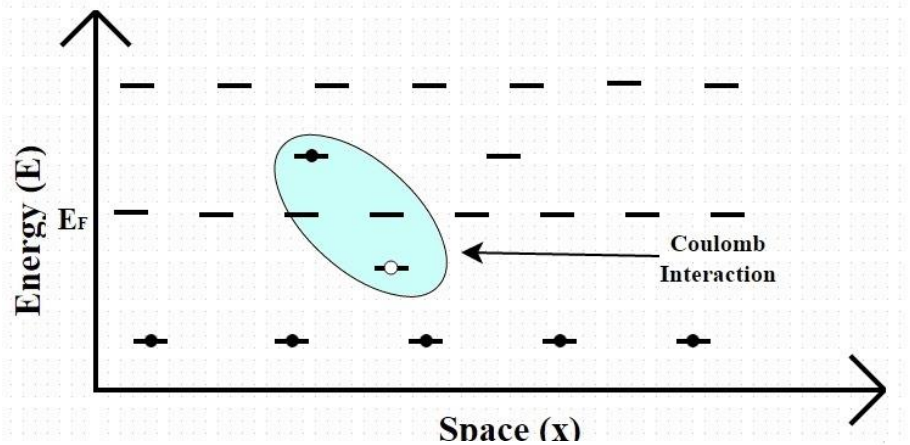
Hopping mechanism

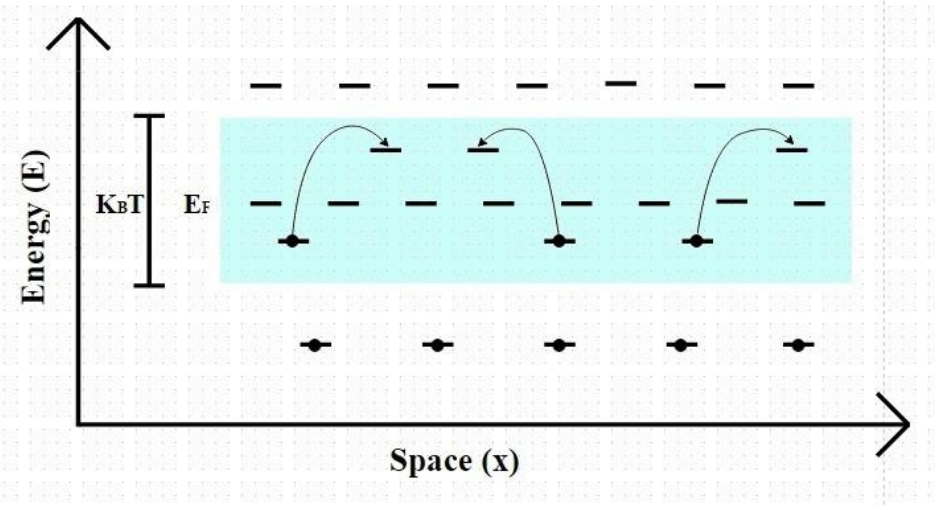
$$R(T) = R_0\, e^{\left(\frac{T_0}{T}\right)^p} \qquad R(T) = R_0 \exp\left(\frac{E_0}{K_b T}\right)$$

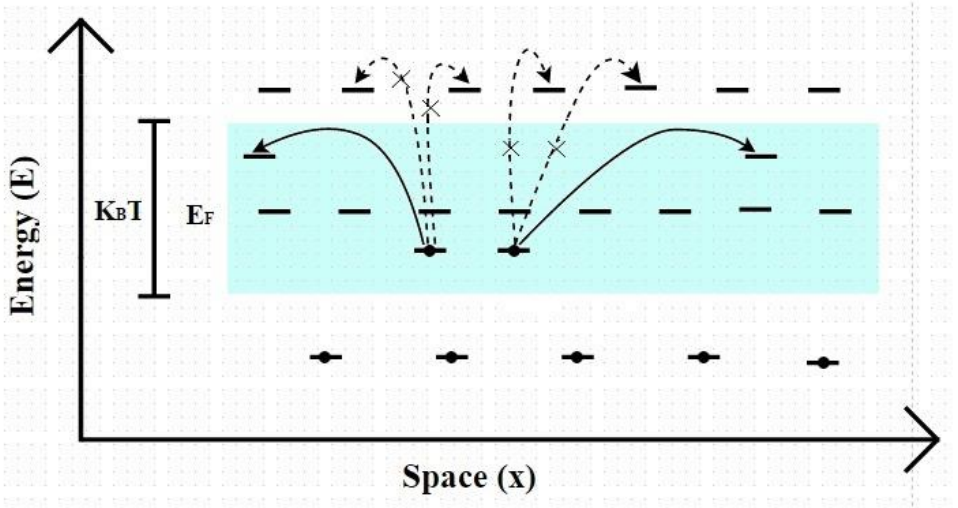
$$R_{ij} = R_{ij}^0 \exp\left\{\frac{2r_{ij}}{a}\right\} \exp\left\{\frac{\epsilon_{ij}}{K_B T}\right\}$$



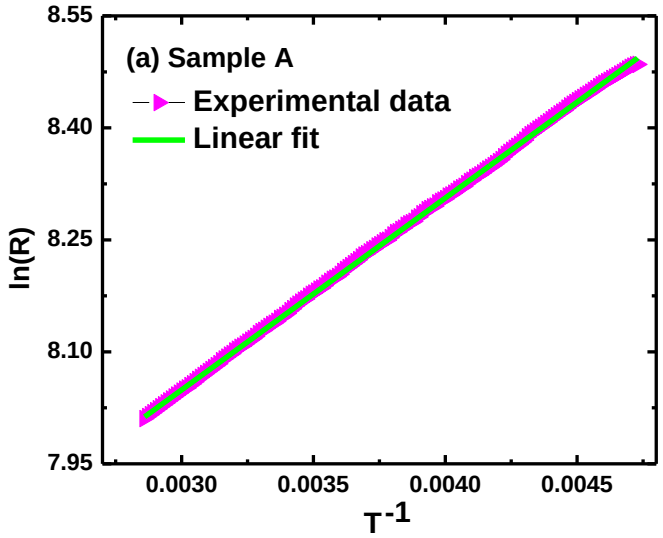
$$\epsilon_{ij} = \frac{1}{2}\left\{\left|\epsilon_i - \epsilon_j\right| + \left|\epsilon_i - \mu\right| + \left|\epsilon_j - \mu\right|\right\}$$

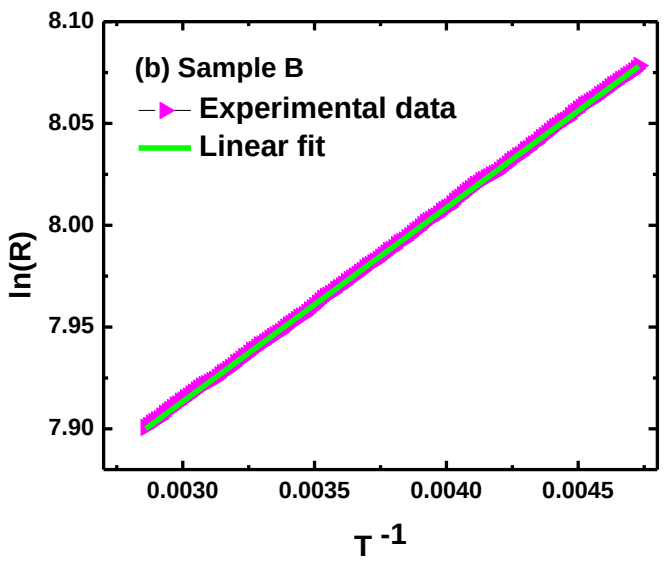


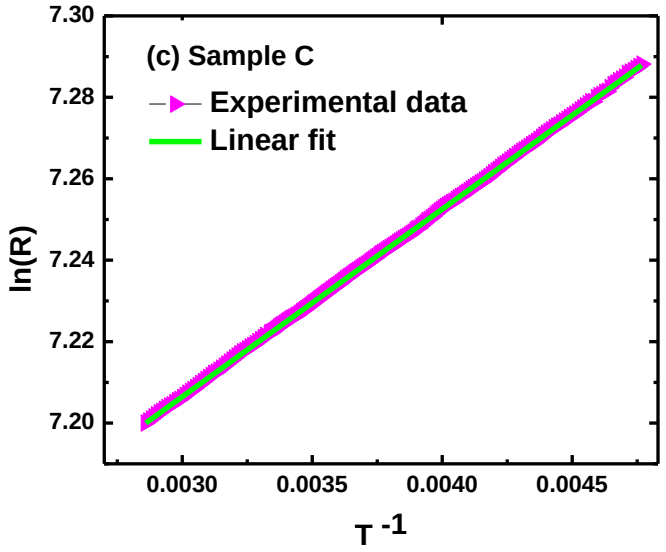


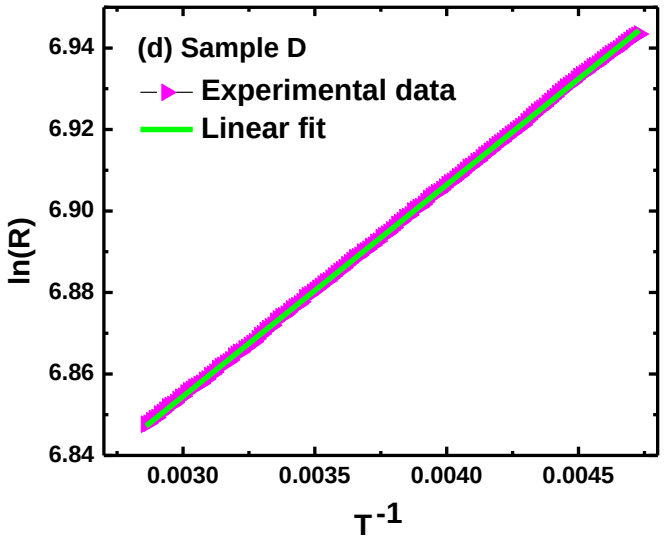


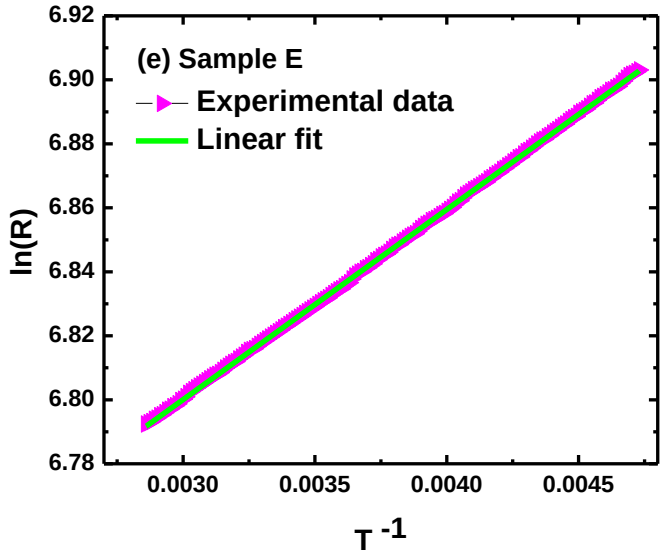
Arrhenius Conduction in graphene oxide thin film (210K to 350K)





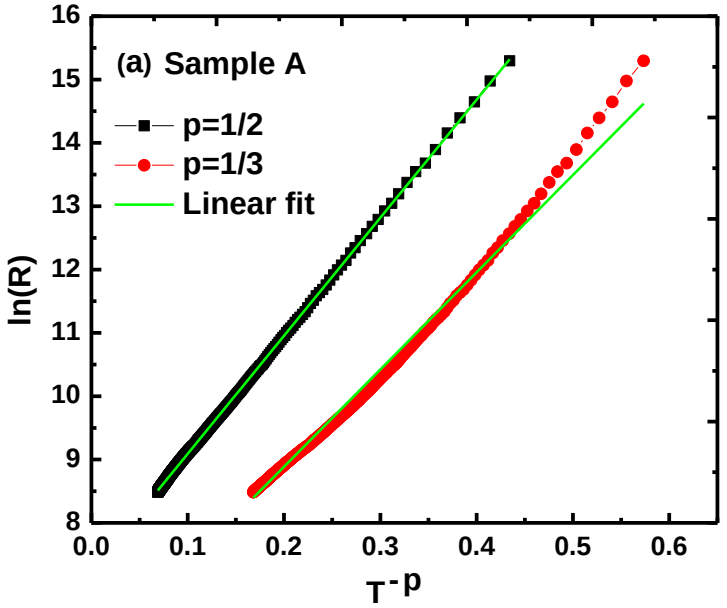


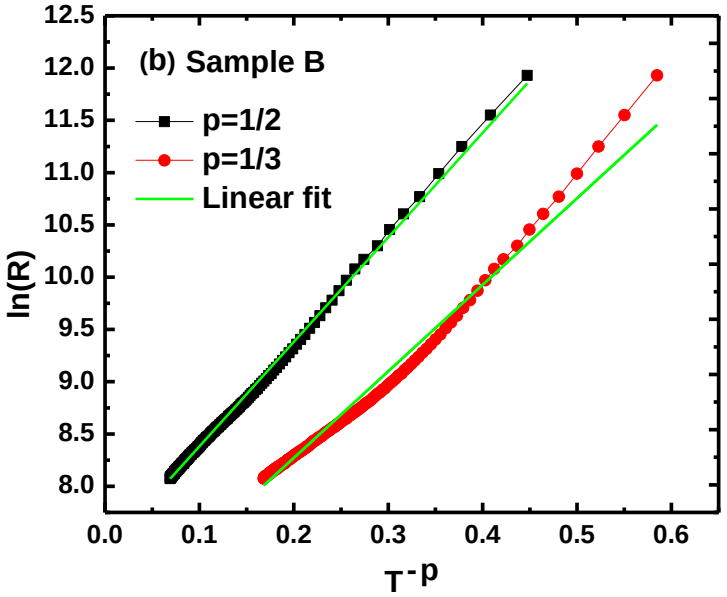


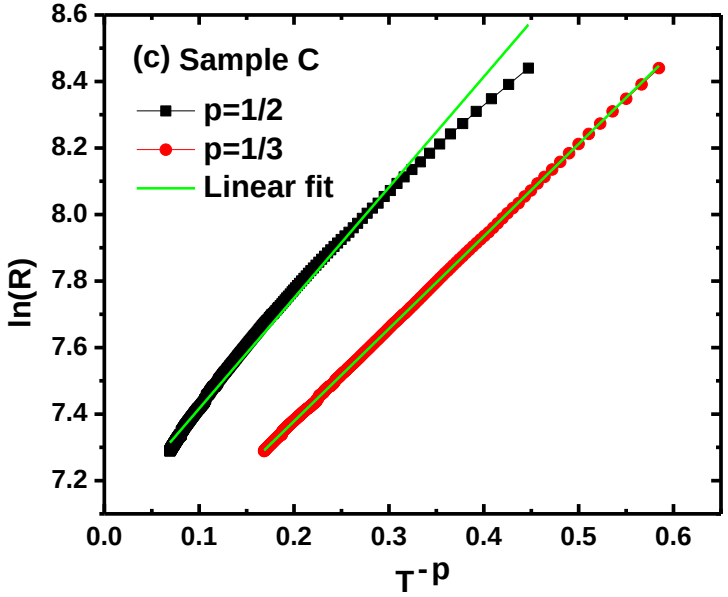


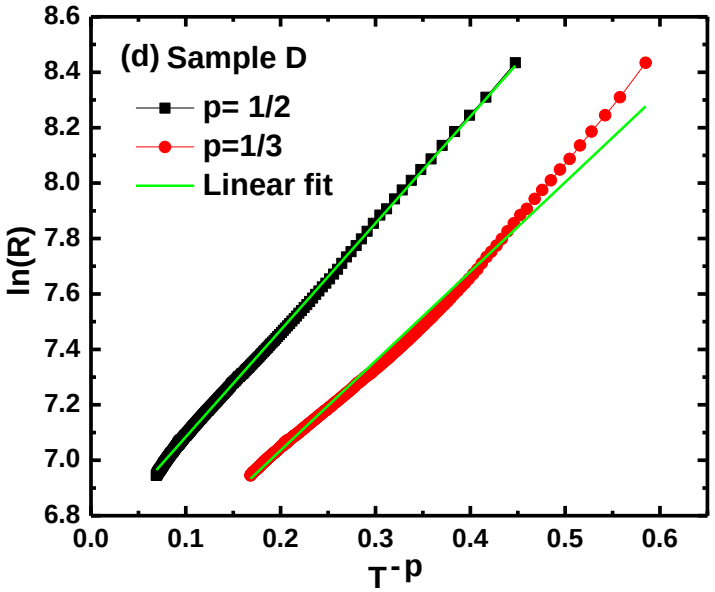
$$R = R_0\, e^{\frac{E_g}{k_B T}}$$

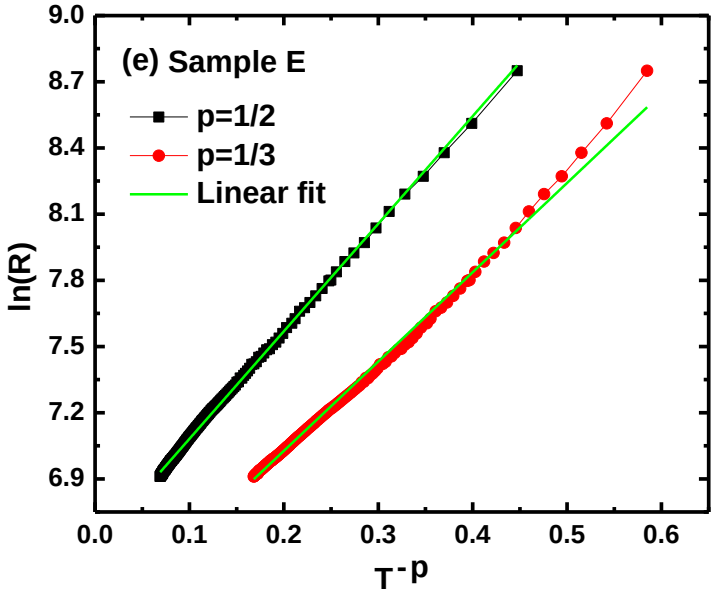
Variable Range Hopping in graphene oxide thin film (5K to 210K)











$$R = R_0\, e^{\left(\frac{T_0}{T}\right)^p}$$

$$T_0 = T_{ES} = \frac{2.8\, e^2}{4\pi\epsilon\epsilon_0 k_B \xi}$$

Calculation of Electronic Parameters.

$$R = R_0\, e^{\left(\frac{T_0}{T}\right)^p}$$

$$T_0 = T_{ES} = \frac{2.8\, e^2}{4\pi\epsilon\epsilon_0 k_B \xi}$$

$$E_{hop} = \frac{1}{2} T_{ES}^{\frac{1}{2}} T^{\frac{1}{2}}$$

$$R_{hop} = \frac{\xi}{4}\left(\frac{T_{ES}}{T}\right)^{\frac{1}{2}}$$

$$E_g = \frac{\hbar \nu_F}{\xi}$$

$$E_{CG} = \frac{T_{ES}}{\beta\sqrt{(4\pi)}}$$

Electronic Parameters from ES-VRH

Sample	Mobility ($cm^2v^{-1}s^{-1}$)	Localization Length, ξ (nm)	E_A (meV)	R_{hopp} (nm)	E_{hopp} (meV)	E_{CG} (meV)	E_g (meV)
A	249	38.4	22.14	56.56	29.46	35	17.2
B	906	133.4	8.46	105	15.803	10	4.94
C	1596	1414	3.98	343	4.856	0.95	0.47
D	612	898	4.48	273.6	6.094	1.5	0.74
E	464	561	5.26	216	7.706	2.4	1.18

Calculation of Electronic Parameters.

$$R = R_0 \, e^{\left(\frac{T_0}{T}\right)^p}$$

$$T_0 = T_M = \frac{3}{K_B N(E_F) \xi^2}$$

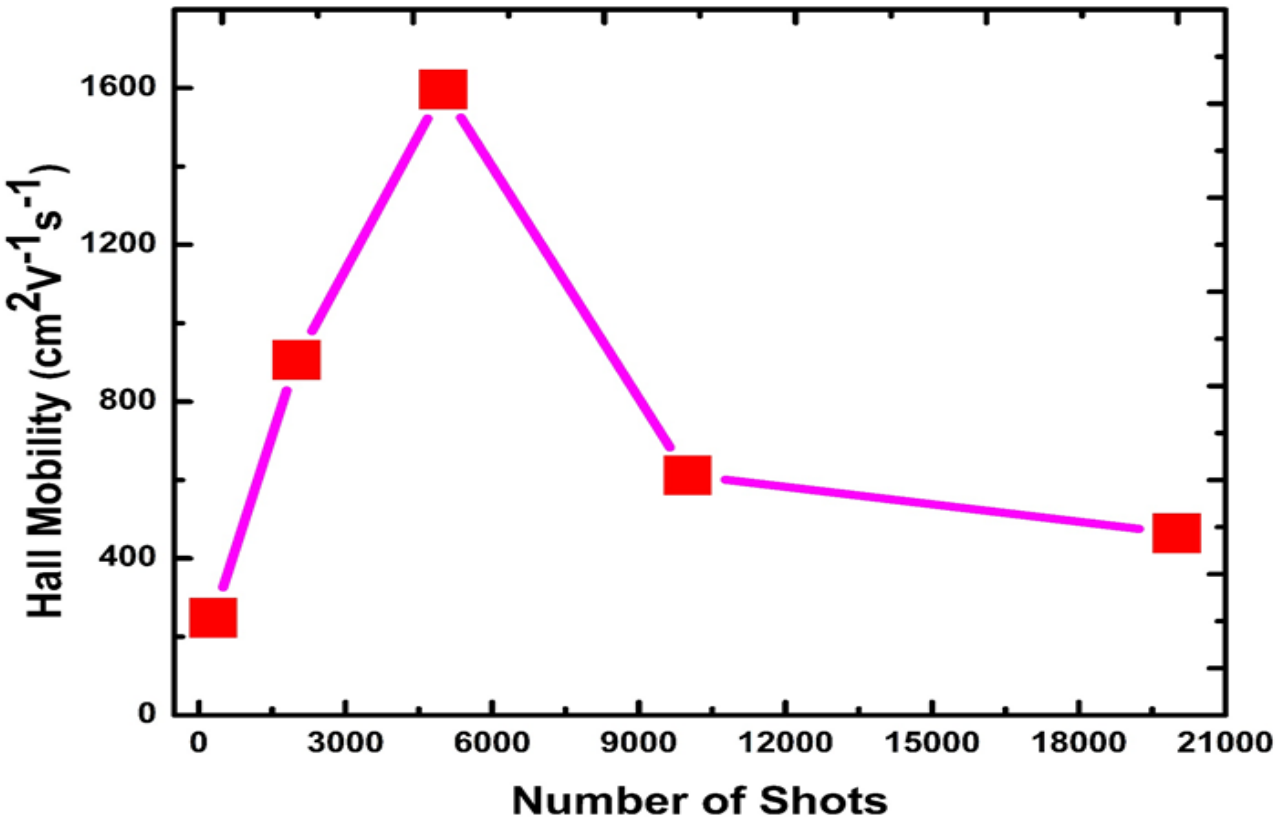
$$E_{hop} = \frac{1}{3} T_M^{\frac{2}{3}} T^{\frac{1}{3}}$$

$$R_{hop} = \frac{\xi}{3} \left(\frac{T_M}{T}\right)^{\frac{1}{3}}$$

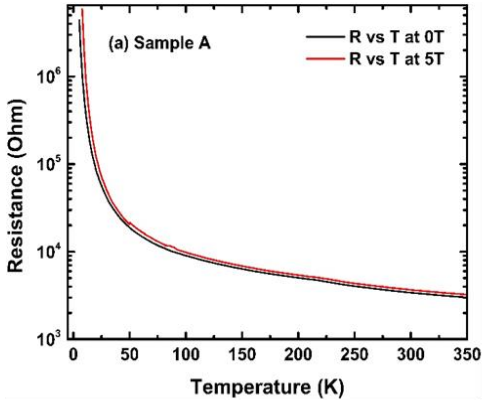
Electronic Parameters from Mott-VRH

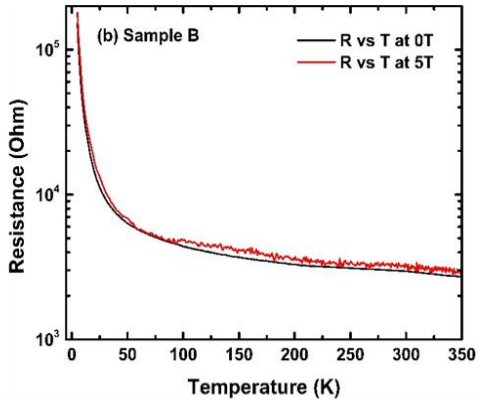
Sample	Carrier concentration n (cm^{-2})	DOS ($cm^{-2}ev^{-1}$)	R_{hopp} (nm)	E_{hopp} (meV)	R_{hop} / ξ
A	$1.72x10^{12}$	6.53×10^{15}	62	169.21	1.618
B	$2.83x10^{12}$	3.45×10^{15}	107	49.2	1.28
C	$4.03x10^{12}$	8.19×10^{14}	606	5.51	0.428
D	$1.61x10^{13}$	1.29×10^{15}	448	7.47	0.4988
E	$1.84x10^{12}$	1.67×10^{15}	351	11.76	0.626

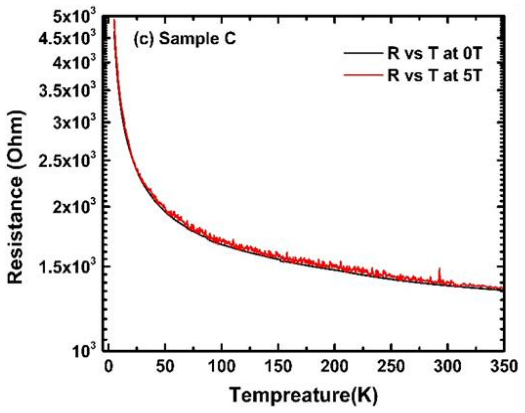
Hall mobility

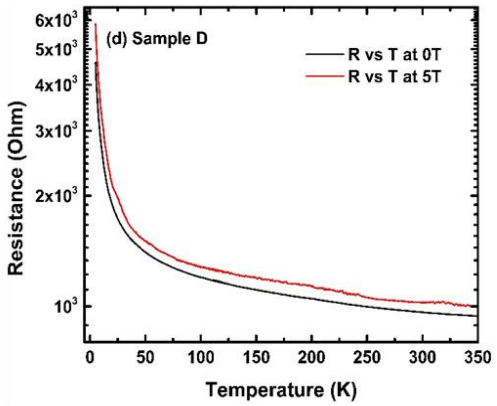


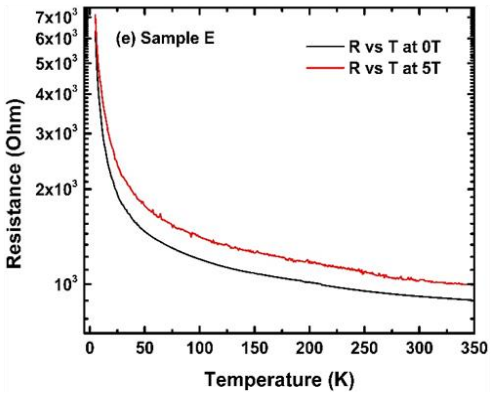
Magneto-resistance at Different Temperatures





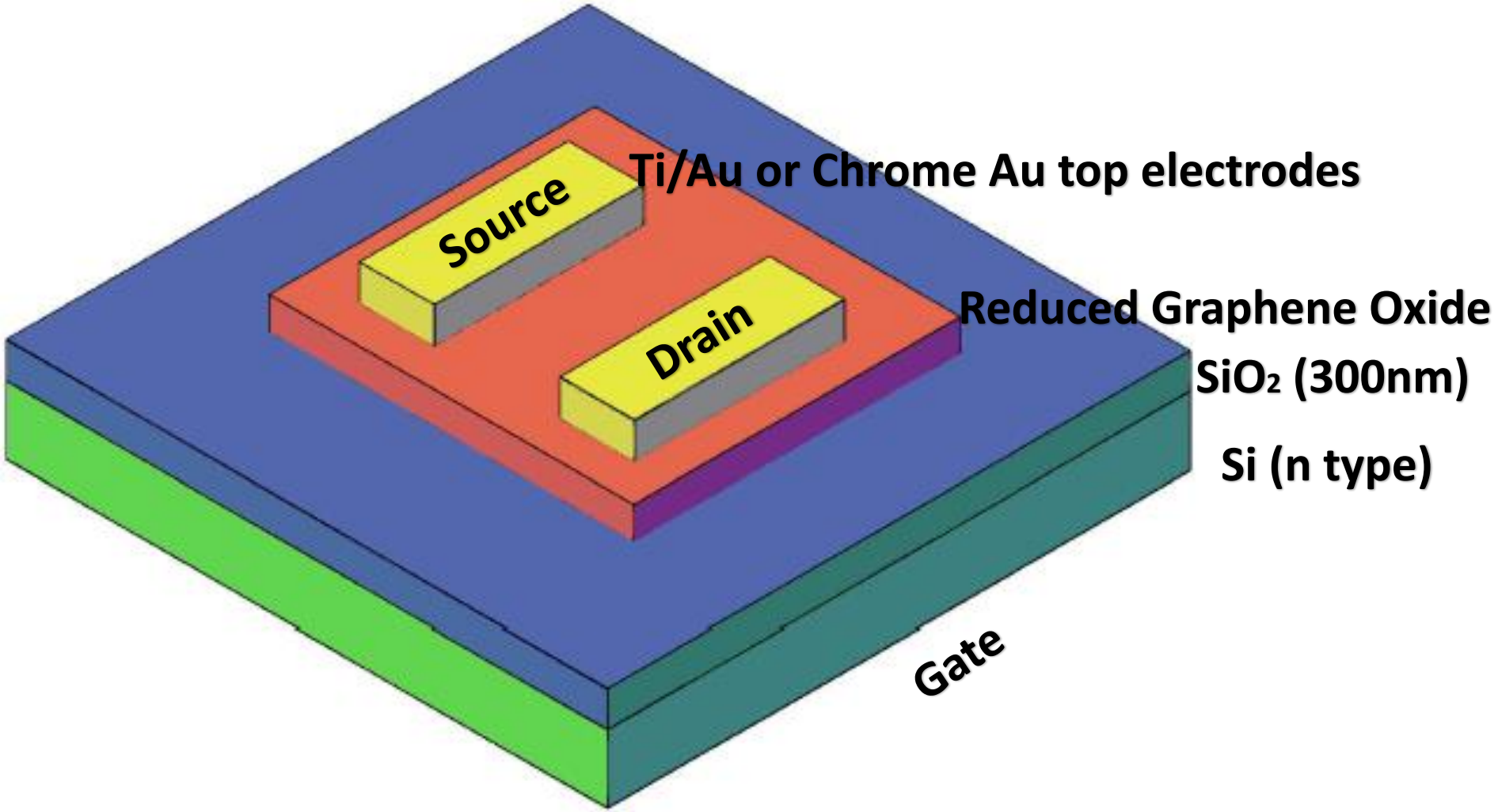






Sample	% of MR at 25K	% of MR at 300K	% of MR at 350K
Sample A	26.87	7.5	7.46
Sample B	17.98	7.97	6.67
Sample C	7.15	1.4	0.8
Sample D	13.91	6.22	5.74
Sample E	23.86	12.05	11.78

Schematic arrangement of the FET device (future work)



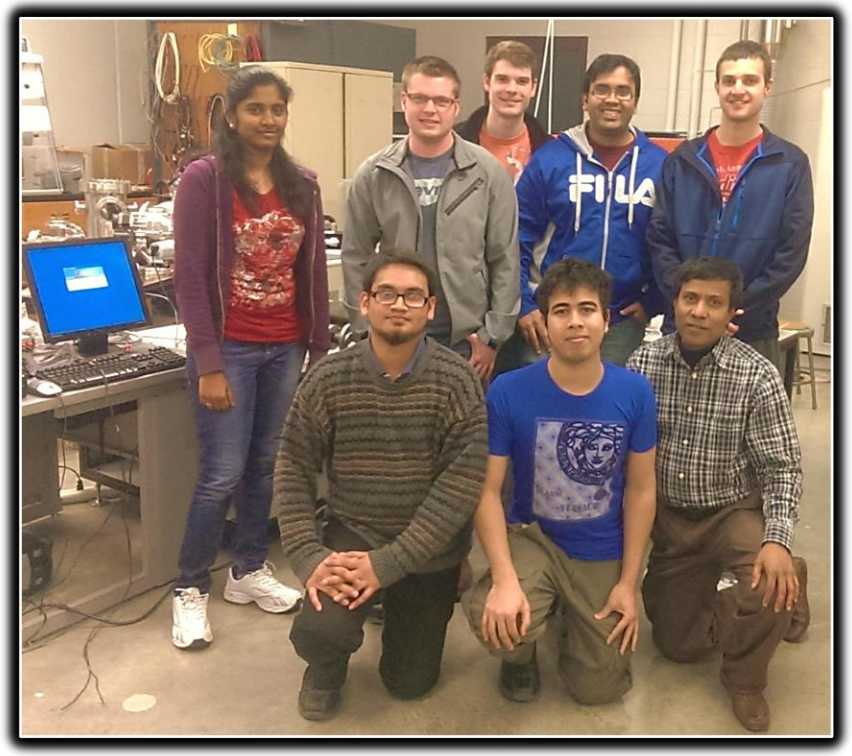
Challenges with Reduced Graphene Oxide thin film grown by PLD technique

- ***Optimization of the rate of reduction.***
- ***Structural integrity of the thin film.***
- ***Precision of cluster size of sp^2 for high mobility electronic devices.***

Conclusions

- Successfully fabricated high mobility reduced graphene oxide
- Correlate the XRD, micro Raman scattering to explain the factors influencing the electrical properties of functionalized graphene
- We can conclude that the electrical properties are governed via three mechanisms:
  - conversion of the sp^2-hybridized state to sp^3
  - intensity of the 2D scattering Raman mode, and
  - low temperature variable range hopping.
- The change in the charge carrier hopping mechanism with temperature is an interesting feature.
- These variable range hopping determination can be beneficial for better low temperature electronic studies in this exciting material.
- The intensity and sharper profile of the second order defect peak plays an important role in the charge carrier mobility.

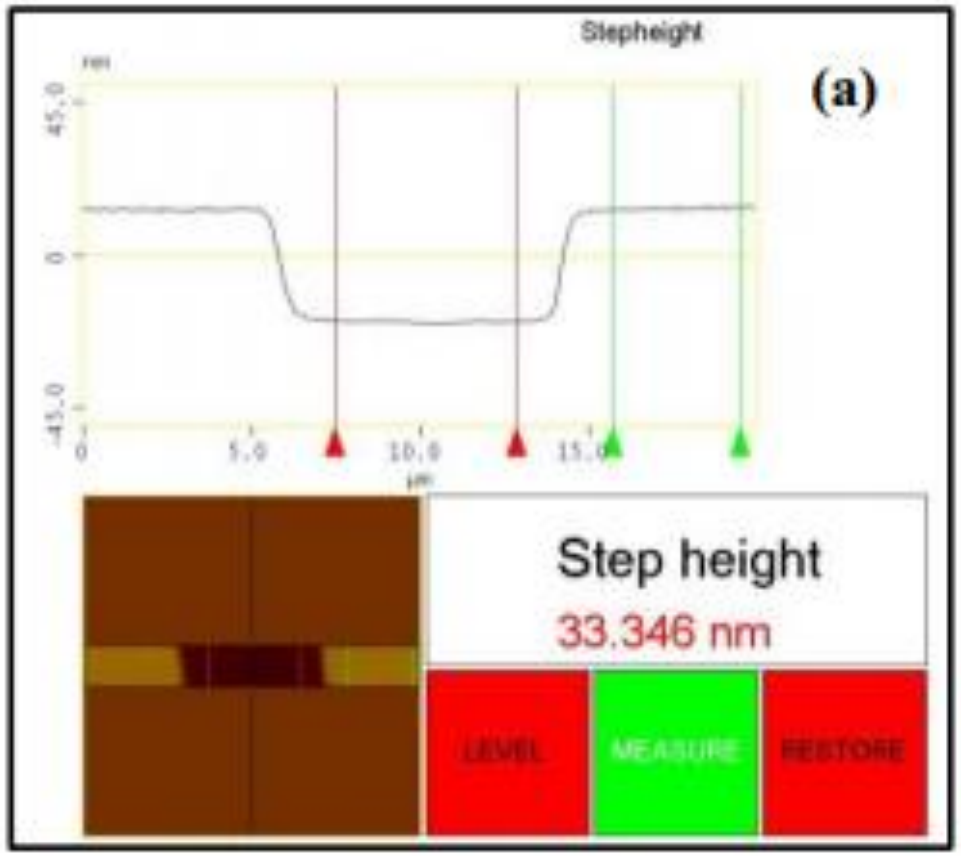
Acknowledgement

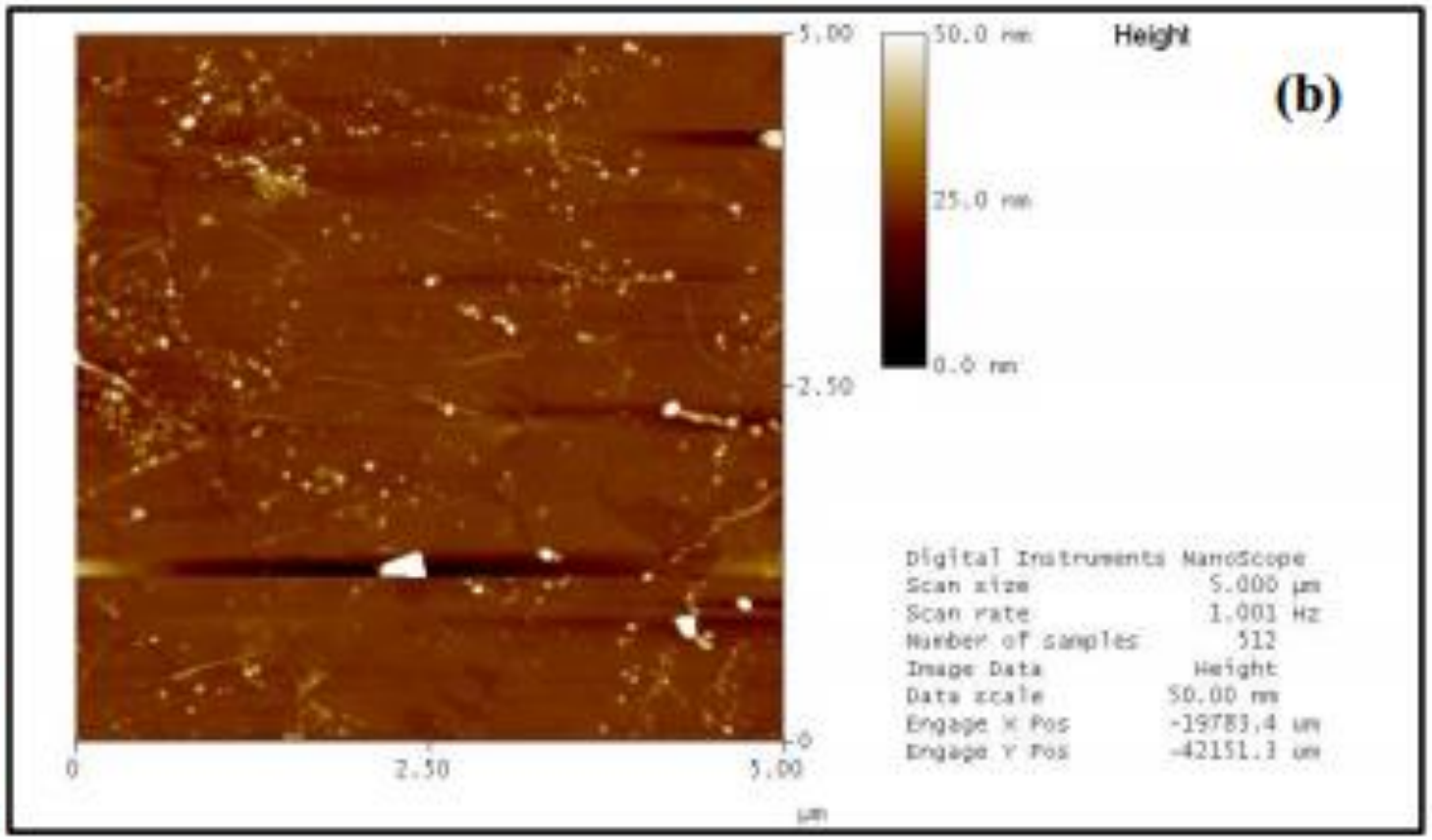


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- Ariful Haque
- Dan Jones
- Priyanka Karnati
- Austin Shearin
- Md. Taufique
- R. Rahaman
- R. Patel

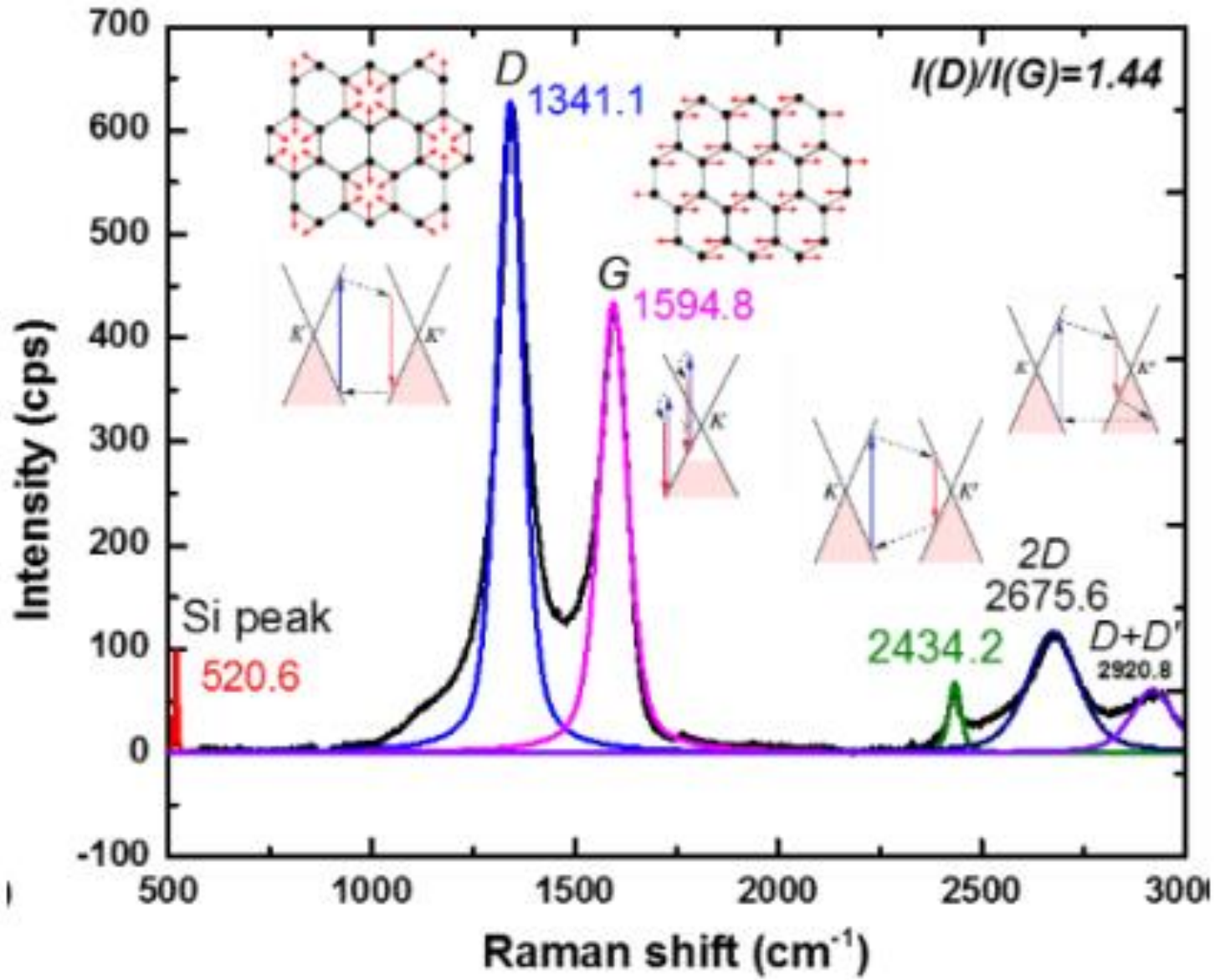
Thank you

AFM Measurements





Raman vibrational modes in rGO thin film



XRD of Reduced Graphene Oxide

