Electron Irradiation and Raman Characterization of Reduced Graphene Oxide Film

UNT
HONORS COLLEGE
McNair Scholars Program

Avin Gupta

Texas Academy of Math and Science

APS Texas Section

Texas Christian University

2025

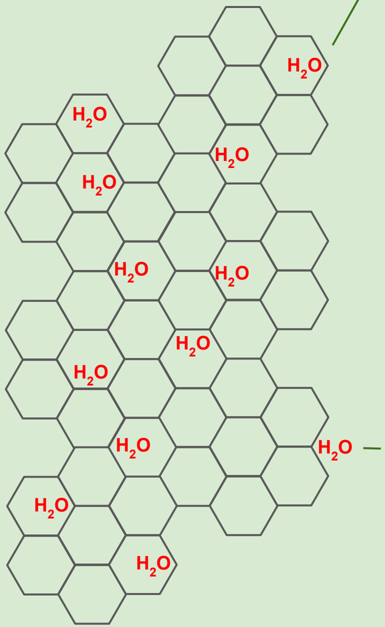
NSF

Supported by NSF Grant No. DMR-2312436

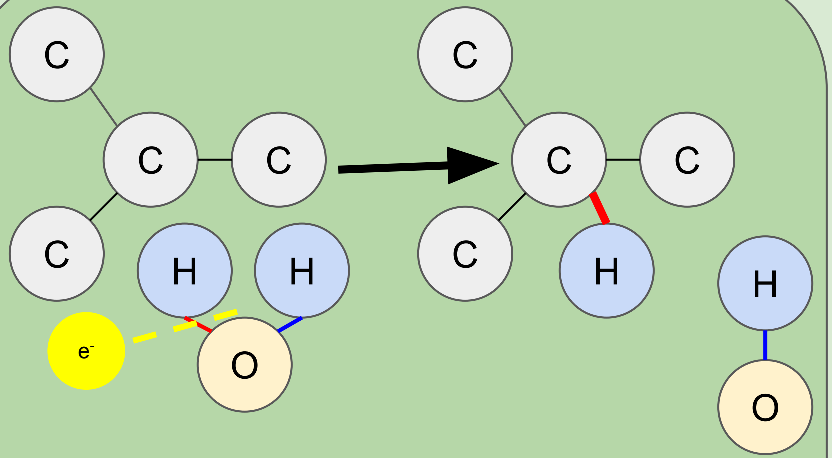
Outline

Motivation: Hydrogenation of Graphene

- Graphene has low weight and high surface area → ideal for chemisorption
- Hydrogenation creates sp^3 type defects
- Possible hydrogen adsorption through electron irradiation



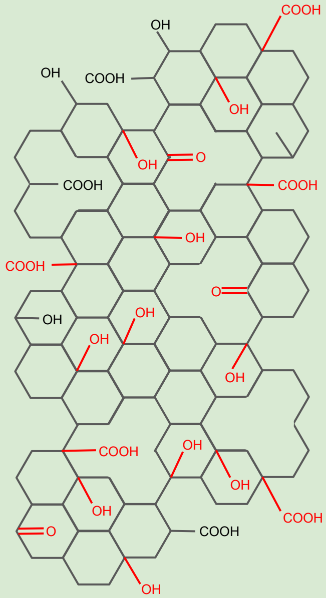
Layer of water can form from hydration or exposure to air



Irradiation breaks bonds, possibly causes chemisorption

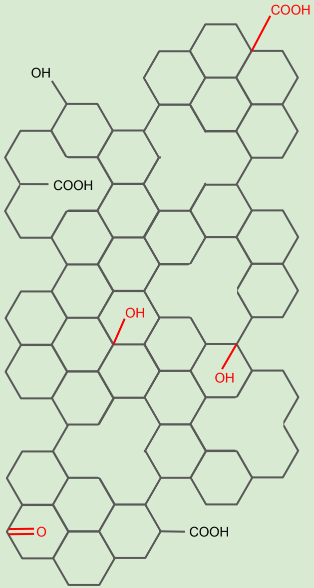
Knowledge Gap: Reduced Graphene Oxide

Graphene Oxide



Oxygen-containing functional groups create sp^3 defects

Reduced Graphene Oxide



Less functional groups from reduction

Functional groups on rGO → more versatility for different forms of storage

rGO powder can be produced from bulk graphite → lower production costs, more scalable

Lack of low-energy irradiation of rGO

Goal: apply group’s previous findings on irradiation of graphene to more industrially relevant rGO

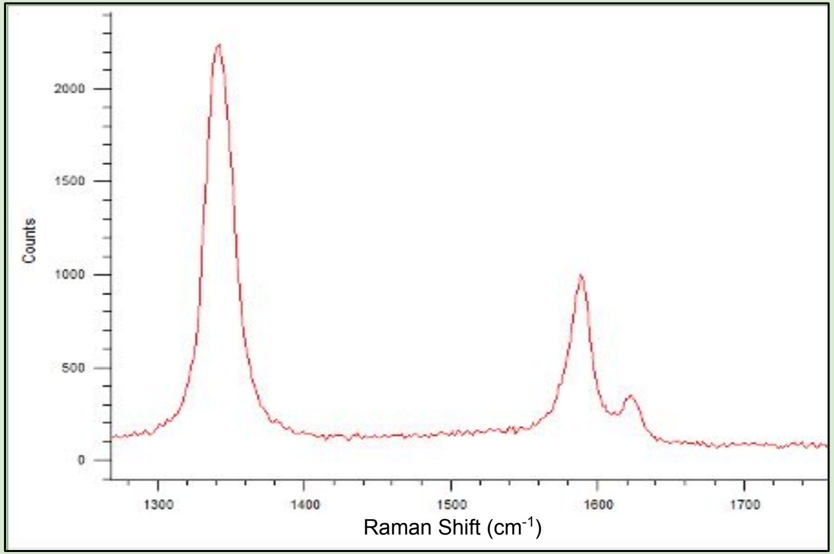
Raman Spectroscopy

Raman Spectroscopy characterizes bonds by showing the energy loss of light

Useful for characterizing graphene and its derivatives due to how properties depend on bonds

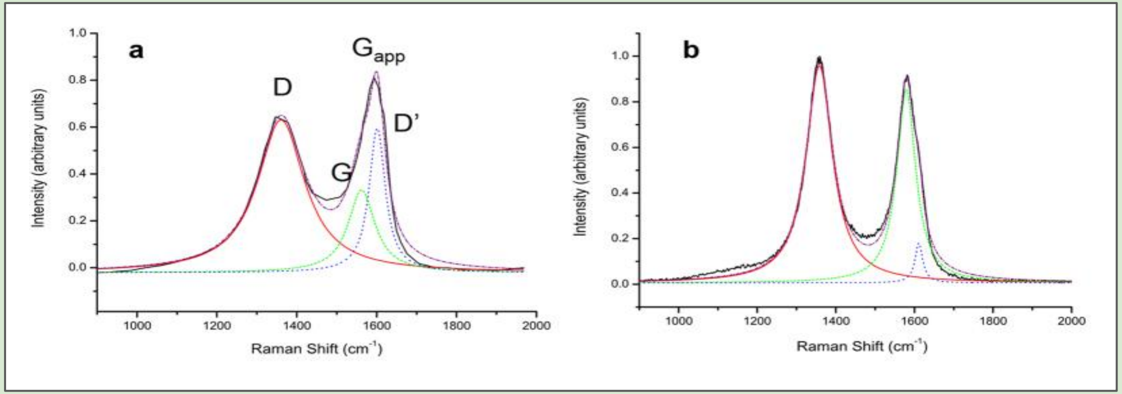
Gives peaks that can be extracted and analyzed

Raman Spectra of Defected Graphene



J. Hardin, et al. "*Electron Irradiation of Chemical Vapor Deposition Grown Graphene in Ultra High Vacuum and X-Ray Photoelectron Characterization*", Fall 2024 Joint Meeting of the Texas Section of the APS

Raman Metrics in rGO



A. King, et al. "*A New Raman Metric for the Characterisation of Graphene oxide and its Derivatives*", Scientific Reports (2015)

G Peak: Always present in graphene samples

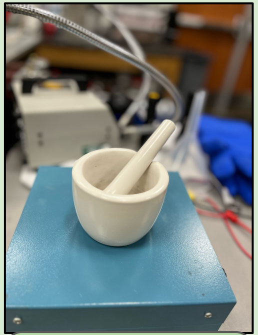
D Peak and D' Peak: Defect-activated

Because of extreme defect density (even with rGO), D' blends with G to form observed single peak G_{app}

Sample Preparation and Irradiation

rGO Powder

Hydration

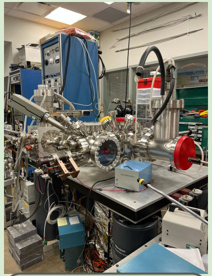


Mortar and Pestle

Hydration

SiO_2 Wafers

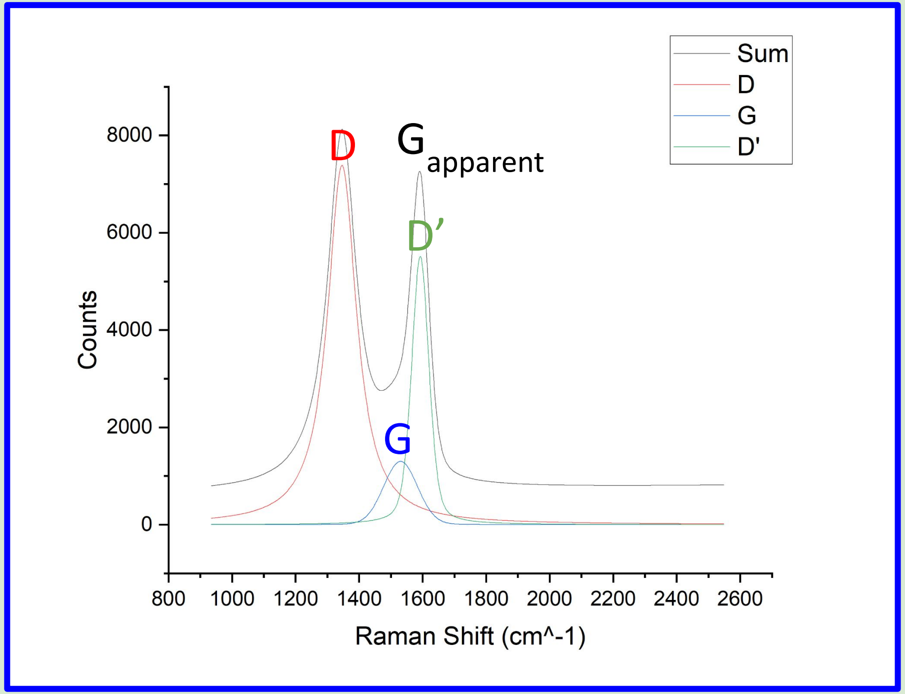
Pre Irradiation Raman Spectroscopy



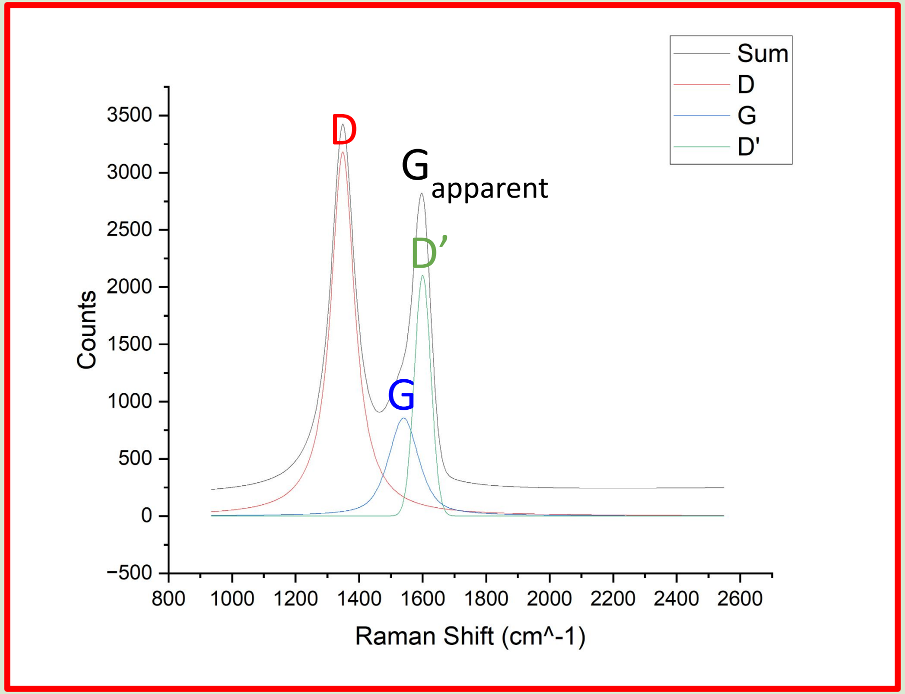
UHV Irradiation

Post Irradiation Raman Spectroscopy

Results: Raman Spectra

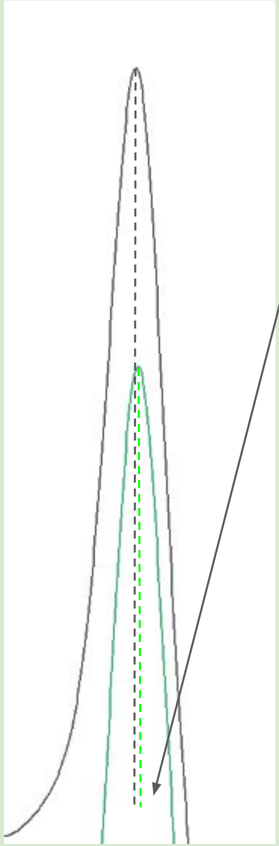


Pre-irradiation deconvolved Raman Spectra



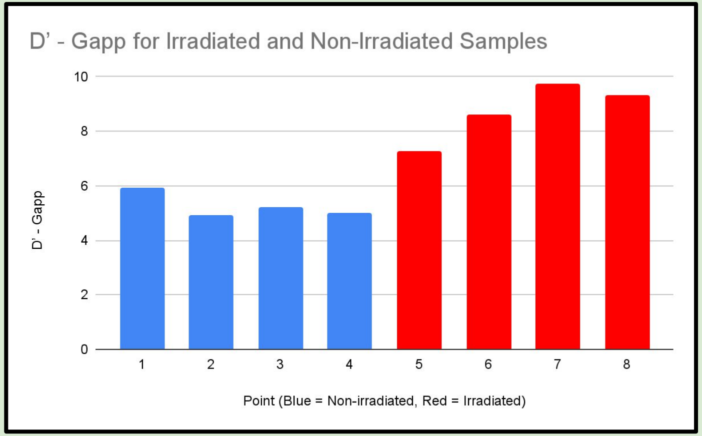
Post-irradiation deconvolved Raman Spectra

Results: D’ - G_{app}



Difference between peak centers is denoted by D’ - G_{app}

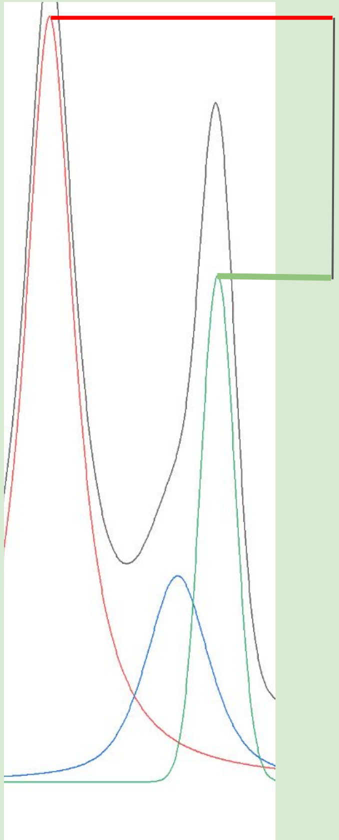
Shown to increase with increasing reduction / removal of functional groups on rGO



D’ - G_{app} shown to increase after irradiation: Indicates that irradiation remove functional groups from the lattice

Consistent with previously observed C-O bond scission caused by irradiation

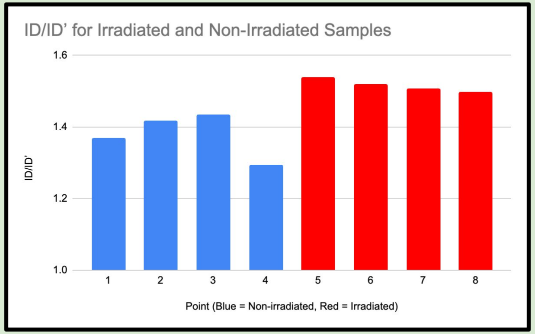
Results: $I_D/I_{D'}$ and $A_D/A_{D'}$

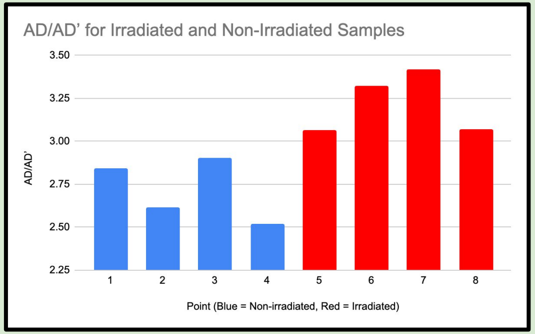


Ratio between peak heights is denoted by $I_D/I_{D'}$

Indicates defect type - high values correlate with adsorbed molecules, lower values correlate with vacancies or edges

Corroborated by area ratio $A_D/A_{D'}$





Increases in $I_D/I_{D'}$ and $A_D/A_{D'}$ due to irradiation: irradiation also results in the addition of new adsorbates bonded to the lattice

Conclusions

Contradiction: irradiation causes removal of functional groups, but overall addition of new atoms bonded to the lattice

Proposition: Irradiation results in the removal of functional groups, but addition of new type of adsorbate: most likely hydrogen atoms due to splitting of water

Implications and Future Work

Demonstrates plausible irradiation-induced hydrogenation of reduced graphene oxide

Promising for rGO’s viability as a low-cost, efficient method of industrial hydrogen storage

Limited by Raman Spectroscopy being unable to directly confirm elemental identity

Presence of hydrogen can be confirmed through annealing studies combined with thermogravimetric analysis or mass spectrometry to confirm identity

References

[1] A. Tararan, A. Zobelli, A. M. Benito, W. K. Maser, and Odile Stéphan, *Revisiting Graphene Oxide Chemistry via Spatially-Resolved Electron Energy Loss Spectroscopy*, Chemistry of Materials **28**, 3741 (2016).

[2] Atsushi Sutoh, Y. Okada, S. Ohta, and M. Kawabe, *Cracking Efficiency of Hydrogen with Tungsten Filament in Molecular Beam Epitaxy*, Japanese Journal of Applied Physics **34**, (1995).

[3] A. Eckmann, A. Felten, Artem Mishchenko, L. Britnell, R. Krupke, K. S. Novoselov, and Cinzia Casiraghi, *Probing the Nature of Defects in Graphene by Raman Spectroscopy*, Nano Letters **12**, 3925 (2012).

[4] A. Augusto, Santos, Filipe, Odilon Souza Leite-Barbosa, L. Altoé, and Junior, *Chemical and Structural Analysis of Graphene Oxide Reduced with Naringenin: A Natural Product-Based Alternative*, Journal of Materials Research and Technology (2025).

[5] I. Ojo, E. Hathaway, J. Li, R. Gonzalez, Y. Jiang, J. Cui, and J. Perez, *Effects of Electron Irradiation on Graphene Drums*, Journal of Vacuum Science & Technology a Vacuum Surfaces and Films **42**, (2023).

[6] D. C. Elias et al., *Control of Graphene's Properties by Reversible Hydrogenation: Evidence for Graphane*, Science **323**, 610 (2009).

[7] E. Jin, J. He, K. Sheng, Z. Zhang, G. Shi, and Q. Zheng, *Electron-Irradiation-Induced Reinforcement of Reduced Graphene Oxide Papers*, Acta Materialia **61**, 6466 (2013).

[8] L. Chen, Z. Xu, J. Li, C. Min, L. Liu, X. Song, G. Chen, and X. Meng, *Reduction and Disorder in Graphene Oxide Induced by Electron-Beam Irradiation*, Materials Letters **65**, 1229 (2011).

[9] R. Muzyka, S. Drewniak, Tadeusz Pustelny, Maciej Chrubasik, and Grażyna Gryglewicz, *Characterization of Graphite Oxide and Reduced Graphene Oxide Obtained from Different Graphite Precursors and Oxidized by Different Methods Using Raman Spectroscopy*, Materials **11**, 1050 (2018).

[10] A. A. K. King, B. R. Davies, N. Noorbehesht, P. Newman, T. L. Church, A. T. Harris, J. M. Razal, and A. I. Minett, *A New Raman Metric for the Characterisation of Graphene Oxide and Its Derivatives*, Scientific Reports **6**, (2016).

[11] Y. Yang, L. Chen, D.-Y. Li, R.-B. Yi, J.-W. Mo, M.-H. Wu, and G. Xu, *Controllable Reduction of Graphene Oxide by Electron-Beam Irradiation*, RSC Advances **9**, 3597 (2019).

[12] H. Zare, M. A. Hosseini, and Shahryar Malekie, *Evaluation of 10 MeV Electron Irradiation-Induced Defects in Graphene Oxide and Multi-Walled Carbon Nanotube Using a Multi-Analytical Approach*, Nuclear Instruments and Methods in Physics Research Section B Beam Interactions with Materials and Atoms **543**, 165089 (2023).

[13] Y. Fei, S. Fang, and Y. H. Hu, *Synthesis, Properties and Potential Applications of Hydrogenated Graphene*, Chemical Engineering Journal **397**, 125408 (2020).

[14] J. R. Morse, D. A. Zugell, E. Patterson, J. W. Baldwin, and H. D. Willauer, *Hydrogenated Graphene: Important Material Properties Regarding Its Application for Hydrogen Storage*, Journal of Power Sources **494**, 229734 (2021).

[15] V. Tozzini and V. Pellegrini, *Prospects for Hydrogen Storage in Graphene*, Phys. Chem. Chem. Phys. **15**, 80 (2013).

[16] A.-M. Chirosca, E. Rusu, and V. Minzu, *Green Hydrogen—Production and Storage Methods: Current Status and Future Directions*, Energies **17**, 5820 (2024).

[17] A. S. Mekonnin, K. Wacławiak, M. Humayun, S. Zhang, and H. Ullah, *Hydrogen Storage Technology, and Its Challenges: A Review*, Catalysts **15**, 260 (2025).

[18] M. Hossain and Z. Siddique, *Hydrogen as an Alternative Fuel: A Comprehensive Review of Challenges and Opportunities in Production, Storage, and Transportation*, International Journal of Hydrogen Energy **102**, 1026 (2025).

[19] W. Liu and G. Speranza, Tuning the Oxygen Content of Reduced Graphene Oxide and Effects on Its Properties, ACS Omega 6, 6195 (2021).

[20] S Bidmeshkipour, M Alidoosti, A. Hosseinzadeh, S M S Seyyedi, M. Elahi, M Pourfath, and S Mohajerzadeh, Hydrogenated Graphene Oxide (H-G-SiO2) Janus Structure: Experimental and Computational Study of Strong Piezo-Electricity Response, Journal of Physics D Applied Physics 53, 175303 (2020).

Thank you!

Avin Gupta

Dr. Jose Perez

HONORS COLLEGE
McNair Scholars
Program

Supported by NSF
Grant No.
DMR-2312436

Questions Welcome!