Characterization of Low-Energy Electron-Irradiated Reduced Graphene Oxide using Raman Spectroscopy and Desorption Analysis

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Outline

Motivation and Background

Prior Studies on Hydrogenation/Irradiation of Graphene Drums and CVD Graphene

Materials and Procedure

Single-Walled Carbon Nanotubes and Reduced Graphene Oxide

Results and Analysis

Raman of Reduced Graphene Oxide and SWCNT, Temperature-Programmed Desorption of SWCNT

Conclusions and Future Work

Summary, Future Work, and Thank you!

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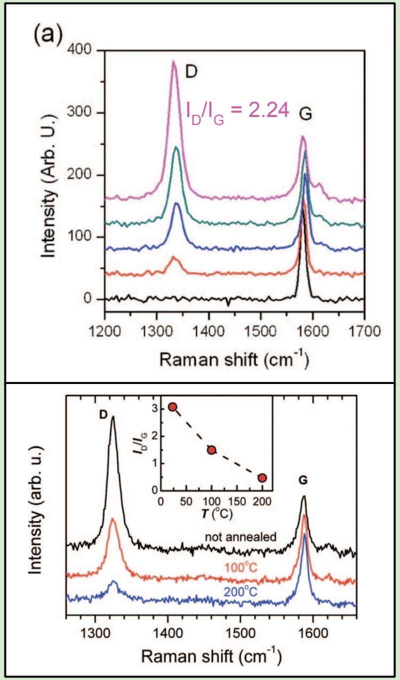
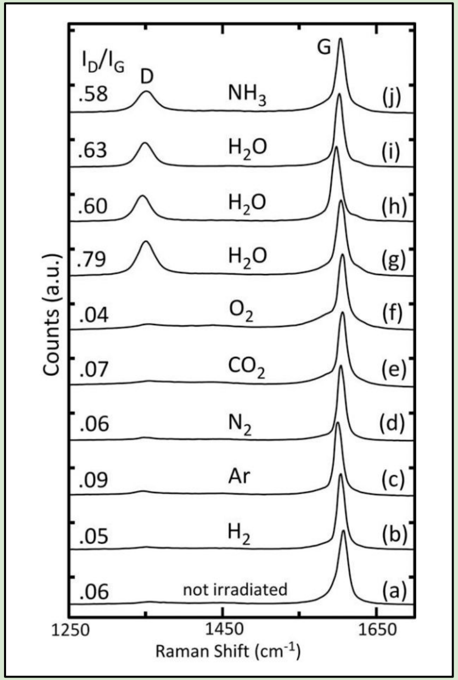
Previous Reports of Electron Irradiation-Induced Hydrogenation in Graphene

Previous reports on in-vacuum electron irradiation of CVD-grown graphene shows evidence that defects produced may be **hydrogen adsorbates**.

Ryu, S., Han, M. Y., Maultzsch, J., Heinz, T. F., Kim, P., Steigerwald, M. L., & Brus, L. E. (2008), “Reversible Basal Plane Hydrogenation of Graphene”, Nano Letters, 8(12), 4597–4602.



Jones, J. D., Mahajan, K. K., Williams, W. H., Ecton, P. A., Mo, Y., & Perez, J. M. (2010), “Formation of graphane and partially hydrogenated graphene by electron irradiation of adsorbates on graphene”, Carbon, 48(8), 2335–2340.



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Electron Irradiation of Graphene Drums

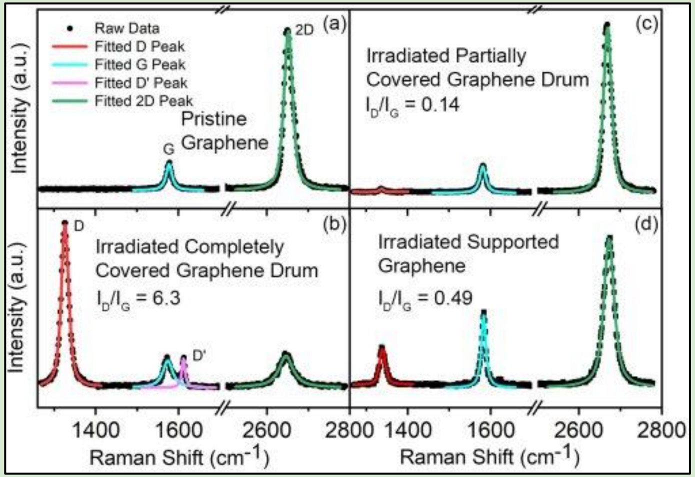
Irradiated using SEM

15 keV

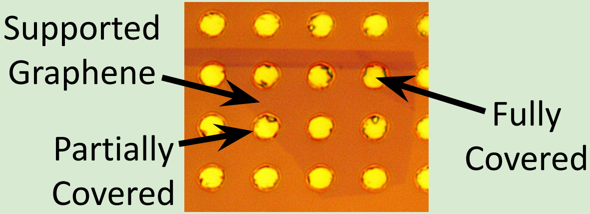
1×10^{17} e^{-}/cm^{2}

↑ I_D/I_G for covered drums

Raman of Different Locations



Optical Image of Graphene Drum



If hydrogen adsorbates are also produced when irradiating graphene at near-atmospheric pressure, then the observed high defect densities may imply high hydrogen coverages that **meet or exceed the Department of Energy's 4.5 weight % for hydrogen storage**

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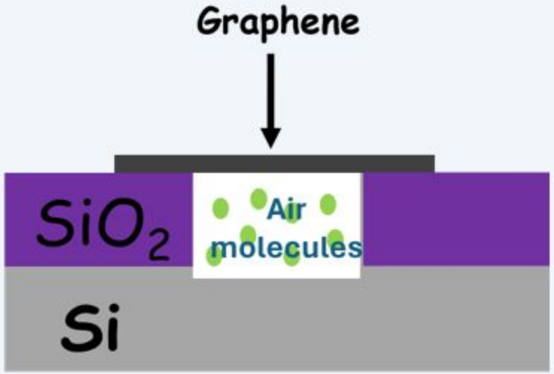
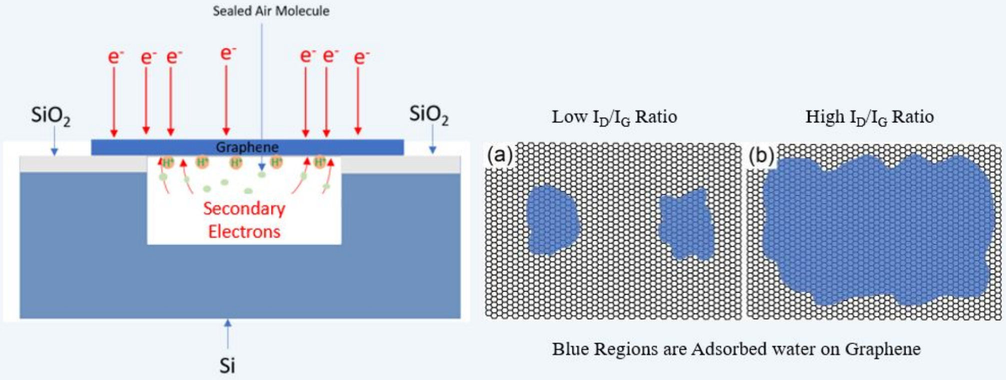
Mechanism for Irradiation of Graphene Drums



- Hole Diameter: 4.6 µm
- Hole Depth: 500 nm
- Density of Air at S.T.P: 2.7 X 10^{19} molecules/cm^3
- Leakage rate of air in graphene drum: 2 X 10^3 Atoms/s
- 0.96 atm of air in graphene drum after placement in a vacuum chamber for 1 hour

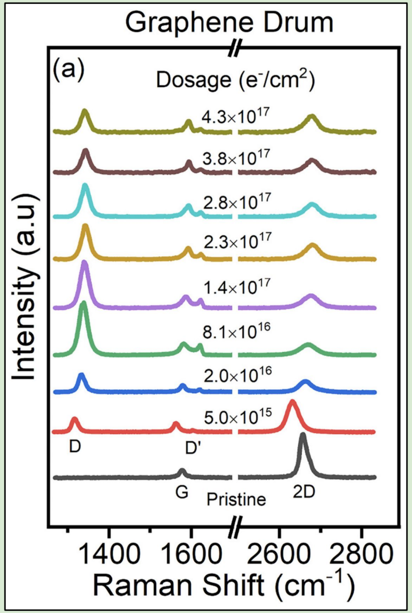


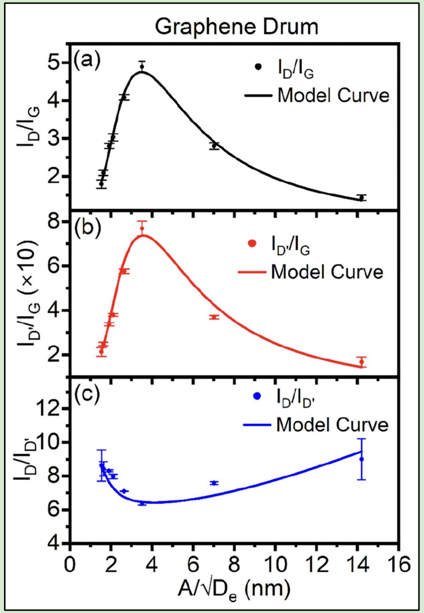
Blue Regions are Adsorbed water on Graphene

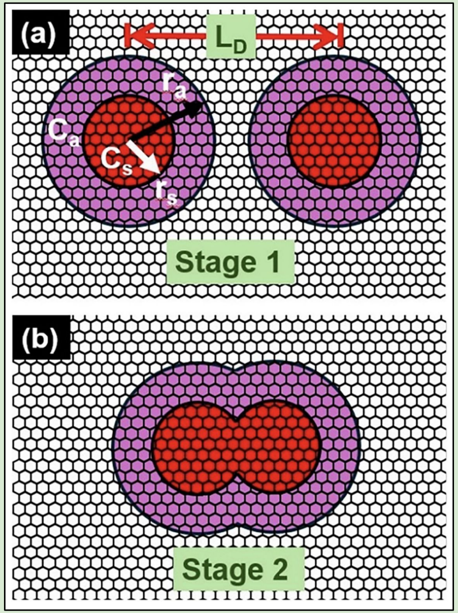
Bunch, J. S., Verbridge, S. S., Alden, J. S., van der Zande, A. M., Parpia, J. M., Craighead, H. G., & McEuen, P. L. (2008). Impermeable Atomic Membranes from Graphene Sheets. Nano Letters, 8(8), 2458–2462.

Modeling Irradiation of Graphene Drums

$$\frac{I_D}{I_G} = C_a \frac{r_a^2 - r_s^2}{r_a^2 - 2r_s^2}\left[e^{\frac{-\pi r_s^2}{L_D^2}} - e^{\frac{-\pi\left(r_a^2 - r_s^2\right)}{L_D^2}}\right] + C_s\left[1 - e^{\frac{-\pi r_s^2}{L_D^2}}\right]$$







Ojo, I., Thineth Bandara Jayamaha Hitihamilage, Hardin, J., Anil Pudasaini, Gonzalez, R., Yan, J., Cui, J., & Perez, J. (2024). Modeling the effects of electron irradiation on graphene drums using the local activation model. Journal of Vacuum Science & Technology a Vacuum Surfaces and Films, 43(1)

Changes in Raman Spectra of graphene drums can be modeled using the Local Activation Model[1]

[1]Lucchese, Márcia Maria, F. Stavale, EH Martins Ferreira, Cecılia Vilani, MV de O. Moutinho, Rodrigo B. Capaz, Carlos Alberto Achete, and A. Jorio. "Quantifying ion-induced defects and Raman relaxation length in graphene." Carbon 48, no. 5 (2010): 1592-1597.

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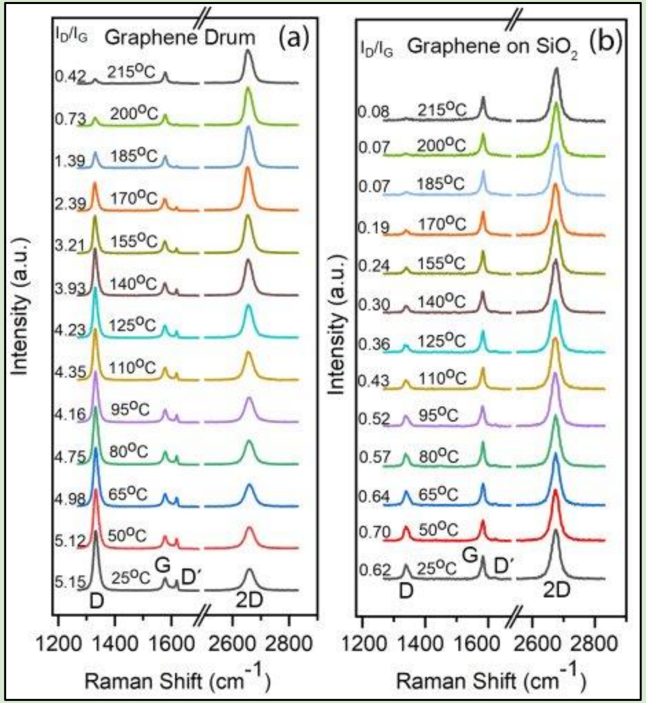
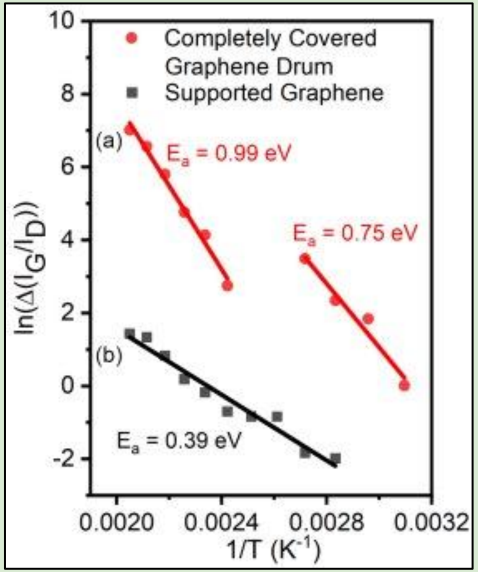
Annealing Studies on Graphene Drums

I_D/I_G decreases with annealing temperature

Activation energies in-line with H and OH related desorption processes



Arrhenius Plot



Migration Barriers*:

Hydrogen:
0.3eV – 1.0eV

Hydroxyl group:
0.5eV – 1.0eV

Hydroxyl group with attached H_2O:
0.6eV – 0.7eV

*Boukhvalov, D. W. (2010). Physical Chemistry Chemical Physics, 12(47), 15367-15371.

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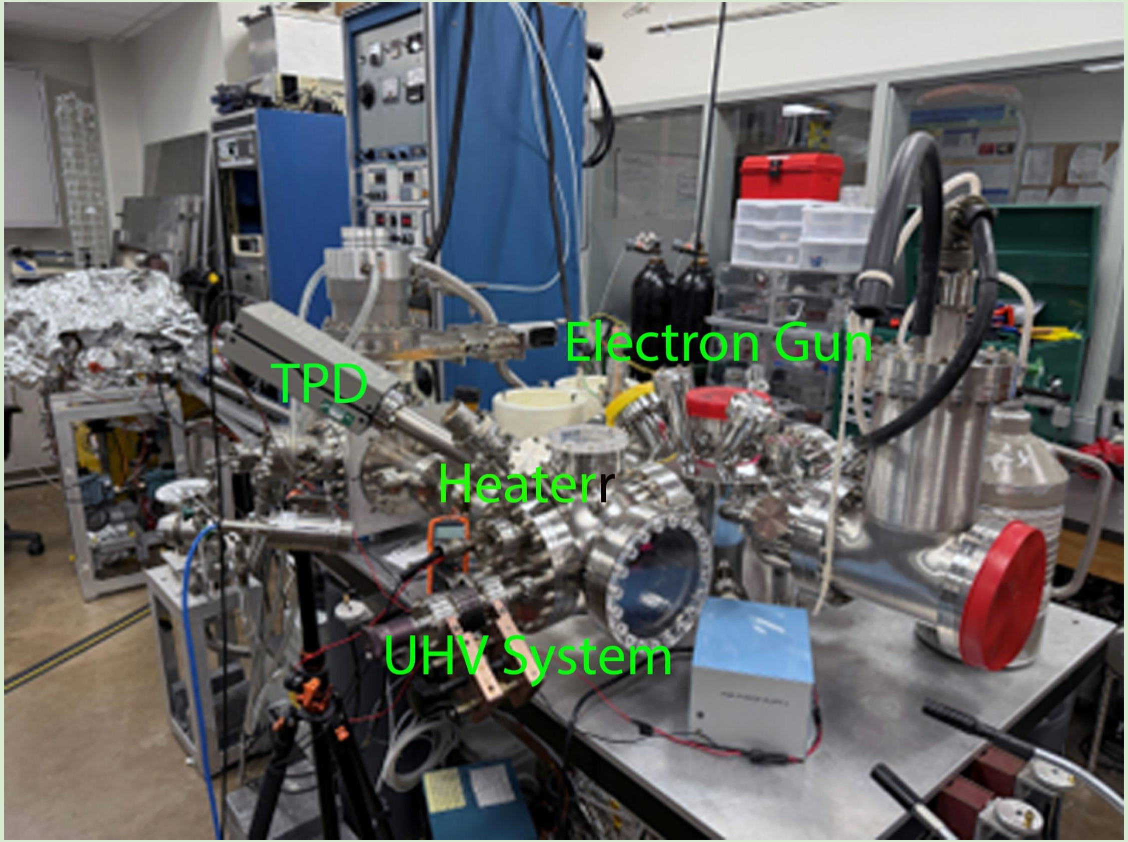
Ultra-High-Vacuum Irradiation System

CVD Irradiated in UHV to avoid carbonaceous contamination from SEM breakup of hydrocarbons

For use in XPS and TPD analysis



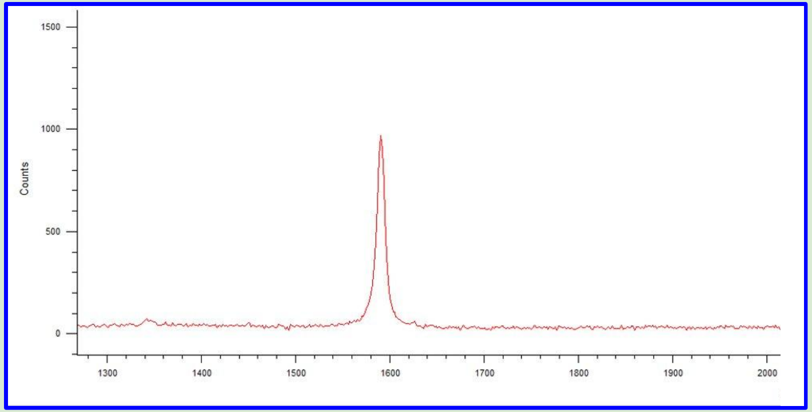
Raman of CVD Graphene

Irradiated in UHV to avoid carbonaceous contamination from SEM breakup of hydrocarbons

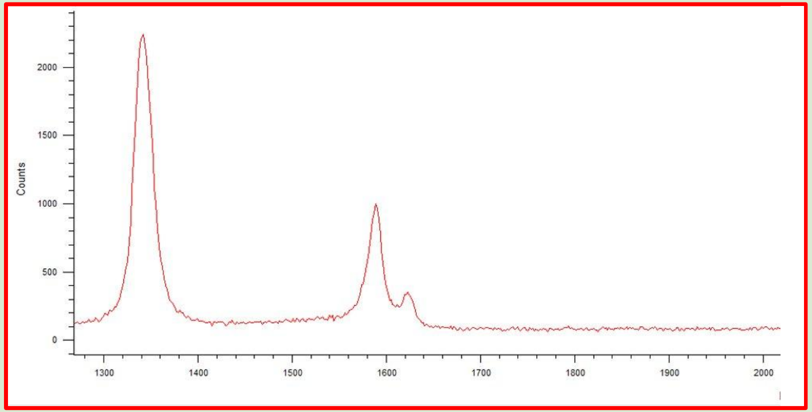
Irradiated $I_D/I_G = 2.5$ indicates high defect density

Irradiated $I_D/I_{D'} = 11.4$, from 8 - 13 indicates sp^3 type defects

Purchased from Graphenea, Inc



Before UHV Electron Irradiation

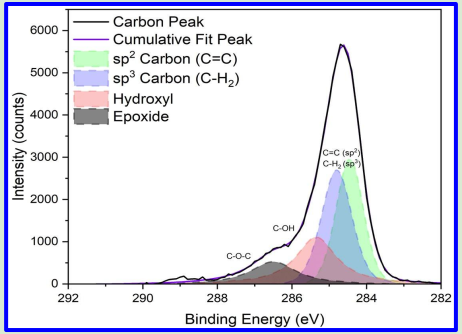


After UHV Electron Irradiation

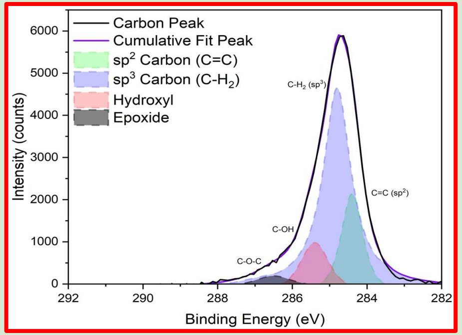
XPS of CVD Graphene

Large-Area CVD Graphene irradiated at 1.5 keV and $1*10^{17}$ e^{-}/cm^{2}, annealed at 270 °C for 10 min, re-irradiated with same parameters

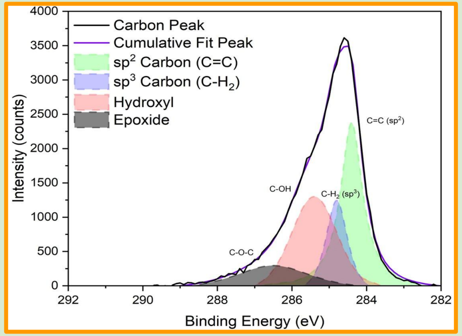
Purchased from Graphenea, Inc



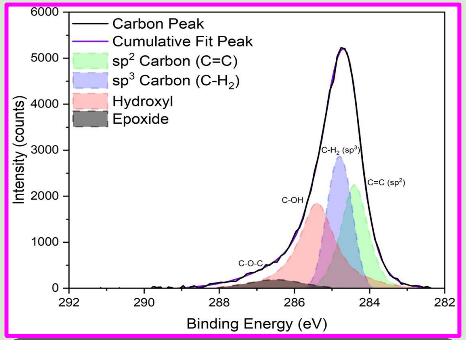
XPS C1s Spectrum Before UHV Irradiation



XPS C1s Spectrum After UHV Irradiation



XPS C1s Spectrum After Annealing



XPS C1s Spectrum After Re-Irradiation

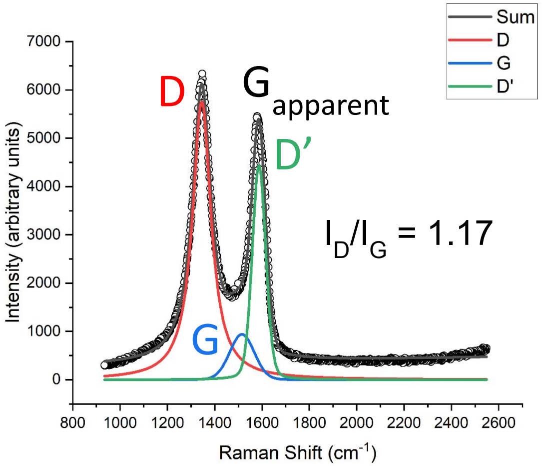
C1s spectrum for pristine graphene (↑ sp^2 carbon) has asymmetric tail towards higher binding energy

C1s spectrum for sample with ↑ sp^3 carbon is symmetric and shifted to higher binding energy

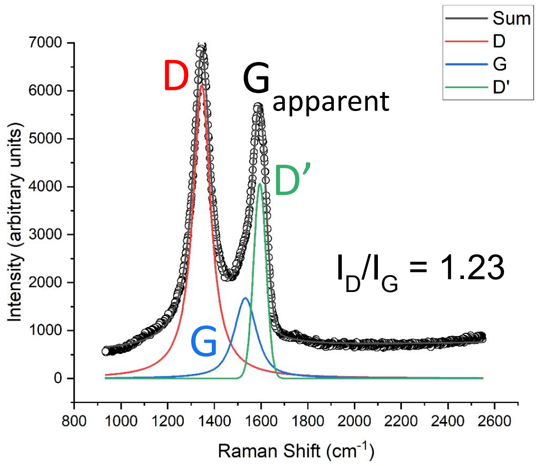
Annealing as low as 250 °C is expected to remove hydrogen from graphene

Raman of Reduced Graphene Oxide

Before UHV Electron Irradiation



After Electron Irradiation



Deconvolution into D peak, and G + D' Peaks that form $G_{apparent}$[1]

No change in D-peak

Possibly due to edge defects in powder

I_D/I_G increased, but heavily dependent on fitting

Also performed XPS showing no increase in sp^3, but a decrease in OH. Presented by Park et al. tomorrow

[1]King, A. A. K., Davies, B. R., Noorbehesht, N., Newman, P., Church, T. L., Harris, A. T., Razal, J. M., & Minett, A. I. (2016). A New Raman Metric for the Characterisation of Graphene oxide and its Derivatives. Scientific Reports, 6(1). https://doi.org/10.1038/srep19491

Single-Walled Carbon Nanotubes

Carbon nanotubes maintain carbon lattice without oxygen defects

Studied Purified HiPCo-grown SWCNTS and unpurified tubes that contain Fe catalysts + amorphous carbon

Dispersed in DMF, deposited onto SiO2

Irradiated in UHV at 10^{-10} Torr, 2 nA, $2.55 * 10^{15}$ e^{-}/cm^{2} at 1.5 keV

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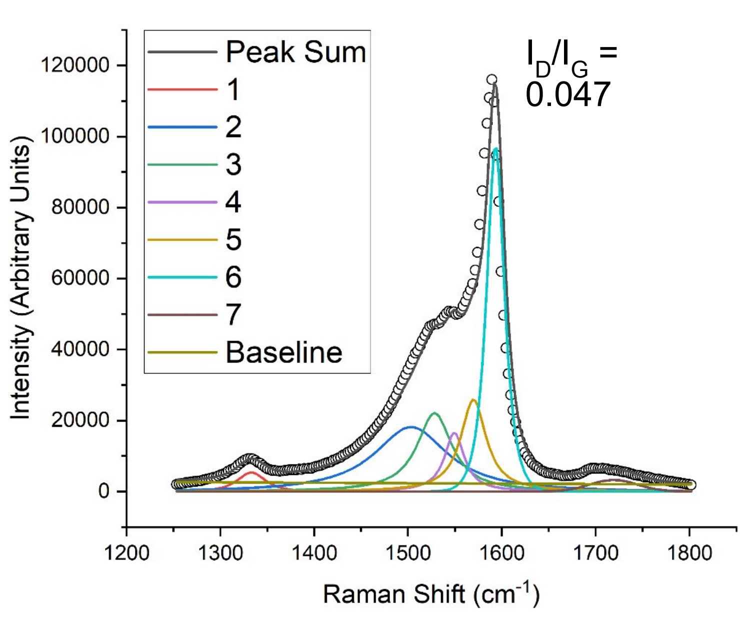
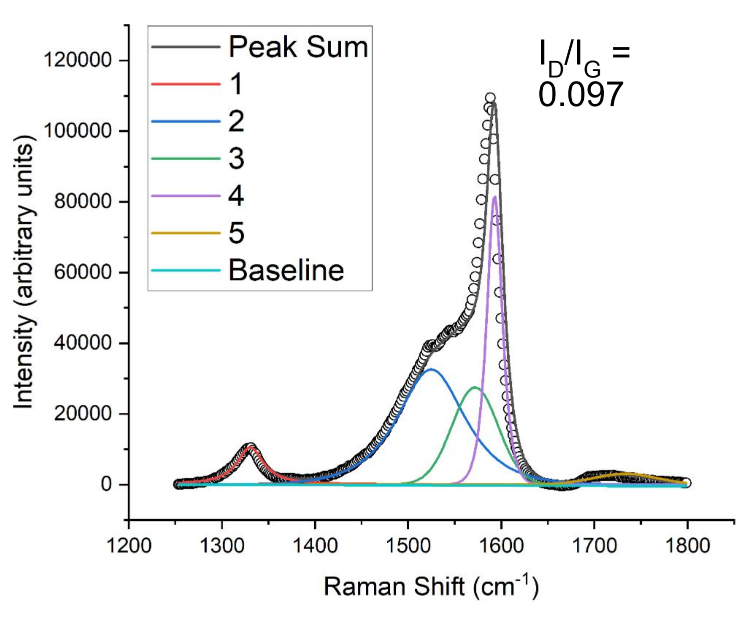
Results: Raman of Unpurified HiPCO SWCNT

Pre-Irradiation Raman Spectra of Unpurified HiPCO-Grown SWCNT Pre-TPD



Post-Irradiation Raman Spectra of Unpurified HiPCO-Grown SWCNT Pre-TPD



Irradiation induces increase in D-peak

Changes in substructure of G-Peak

More noticeable increase in I_D/I_G, but still dependent on fitting complex peaks

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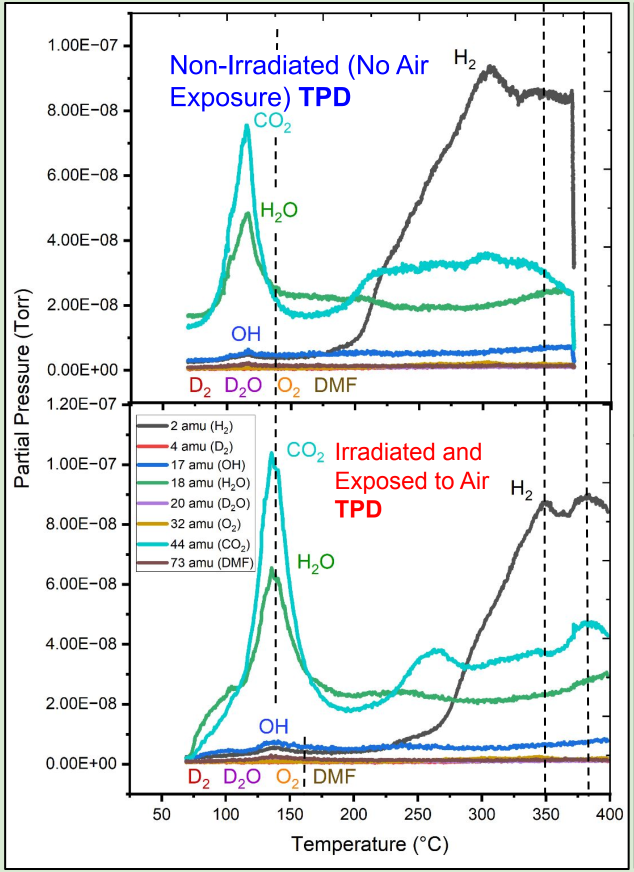
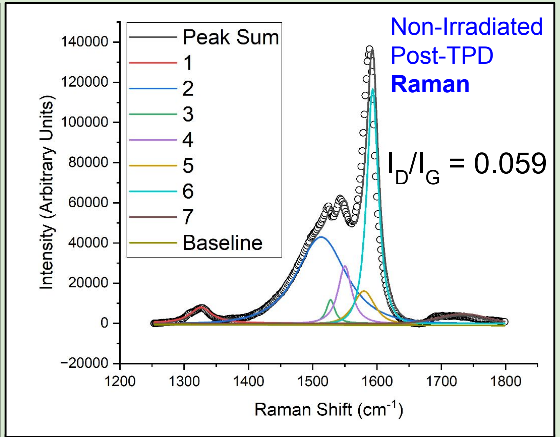
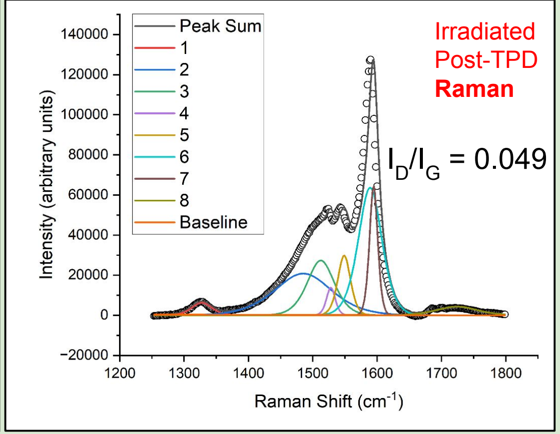
Results: Temperature-Programmed Desorption of Unpurified HiPCO SWCNT

Unpurified HiPCO SWNT

Low-temperature H_2 peak disappears, higher temperature peak appears - indicates irradiation possibly produced hydrogen species with higher binding energy







Raman overall shows ↑ I_D/I_G after irradiation, ↓ after thermal desorption

Summary

- We found that powdered forms of graphene such as Reduced Graphene Oxide do not show the same Raman clear properties of exfoliated and CVD graphene when irradiated with electrons. We believe that this is due to residual oxidation or edge defects.
- We therefore investigated carbon nanotubes that can be produced in large quantities, but do not have edge defects.
- In carbon nanotubes, we observed the similar effects of irradiation in Raman spectra as observed in exfoliated and CVD graphene.
- Detailed TPD studies of electron-irradiated Reduced Graphene Oxide and SWCNT are currently being carried out.
- There is a talk tomorrow by my colleague Jian Park et al. about the TPD of Reduced Graphene Oxide.

Thank you!

Questions Welcome!

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References

[1] 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).

[2] D. W. Boukhvalov, “Modeling of hydrogen and hydroxyl group migration on graphene,” Physical Chemistry Chemical Physics, vol. 12, no. 47, pp. 15367–15367, Jan. 2010, doi: https://doi.org/10.1039/c0cp01009j.

[3] Bunch, J. S., Verbridge, S. S., Alden, J. S., van der Zande, A. M., Parpia, J. M., Craighead, H. G., & McEuen, P. L. (2008). Impermeable Atomic Membranes from Graphene Sheets. Nano Letters, 8(8), 2458–2462. https://doi.org/10.1021/nl801457b

[4] 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).

[5] 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).

[6] 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).

[7] 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).

[8] 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).

[9] 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)

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