NRC·CNRC

NanoCarbon Metrology: Standard Development for Solution Processed Graphene Films

Measurement Science and Standards Portfolio

National Research Council Canada

For ASTM E56 Meeting May 8-9 Toronto, Ontario

Background:

Quality of commercial graphene related materials is highly variable. There are many challenges in sample preparation, i.e., deposition method and substrates can affect measured parameters. The National Research Council of Canada (NRC), Measurement Science and Standards (MSS) has formed a Special Interest Group (SIG) made up of Canadian graphene companies to facilitate the development of standards for graphene made by exfoliation methods.

This is initiated from the Nanocarbon Metrology project in MSS, which has focused on the development of new capabilities to characterize a range of graphene related materials by using atomic force microscopy (AFM), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS).

It is also an excellent opportunity for graphene producers to work collaboratively with NRC in determining the optimal techniques to properly characterize graphene, develop standardized methods for use in confidently comparing materials, and strengthening the graphene industry as a whole.

Background:

- There are currently many concerns in the emerging graphene industry about whether material being sold as ‘graphene’, is really graphene.

The accurate measurement of the material is therefore key:
?? Is the material you have actually the type of material you require?
?? Are the properties adequate for the targeted application?

- Development of the metrology underpinning these questions are necessary, in order for the vast amount of different ‘graphene’ materials now available in the market to be accurately compared.

- The measurement of properties such as the number of layers, lateral dimensions, the level of disorder, and the chemical composition, are to be determined before using the material or the results obtained (whether good or bad).

Metrology research will lead to standardised measurement protocols and address this barrier to commercialisation, as well as form the foundation for future high-throughput and validated quality control (QC) processes.

- There are many techniques that may provide insight into the structural and chemical properties of graphene - a big part of what we want to develop at NRC-MSS and with our external collaborators is the simple (hopefully optimal) way to use these techniques so that the results can be compared.

It is important to look at how a set of complementary techniques can be used to determine the many different properties required, whilst minimising the cost for industry.

Typical techniques used to determine the structural properties are optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), **atomic force microscopy (AFM), scanning tunnelling microscopy (STM)** and **Raman spectroscopy/mapping**.

Meanwhile X-ray photoelectron microscopy (XPS), Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), X-ray diffraction and inductively coupled plasma mass spectrometry (ICP-MS) are common techniques used for chemical and composition characterisation.

WK56764

Sponsoring Subcommittee: E56.02

Target Ballot Date: 12/2017

Target Completion Date: 6 - 12 Months 5/30/2017 to 11/30/2017

Standard Type: Guide For

Proposed Title: Characterization of Graphene Flakes Produced by Exfoliation

Proposed Scope: This standard will cover the measurement approaches for assessment of lateral flake size, average flake thickness, Raman intensity ratio of the D to G bands, and carbon/oxygen ratio for graphene and related products made of exfoliation. The techniques used are atomic force microscopy, Raman spectroscopy and X-ray photoelectron spectroscopy methods. Examples will be given for each measurement.

Rationale: To be generated by NRC Canada as a need to standardize materials and manufacturers in the grapheme area.

Existing Standards: Need for the international community. ISO TC229 has a bunch of TSs and TRs in this area, but this will be a full guide and standard.

Notify Other Committee: E29, E42, E13.08, ISO/TC229

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Collaboration Area

Collaboration on WK56764

New Standard Characterization of Graphene Flakes Produced by Exfoliation

Created: 2016-11-30 Target Date: 2017-12-01 Technical Contact : Shan Zou

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Work Item Description:

To be generated by NRC Canada as a need to standardize materials and manufacturers in the grapheme area.

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Draft Standard

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- **Draft 1** (no content yet) - Received **Thursday, December 1 2016 14:49:13** from Shan Zou

Add Comment or File View All Comments (1)

Well done, Shan! Looks like you've worked through the system with ease.

Received Thursday, December 1 2016 14:56:51 from Alan Rawle

What's New?

New Comment
by Alan Rawle, Thursday, December 1 2016 2:56:51

New Draft (1)
Thursday, December 1 2016 2:49:13

New File
by Shan Zou,Thursday, December 1 2016 2:46:26

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Project/Assignments Timeline

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New Draft (1)
Thursday, December 1 2016 2:49:13

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Related Links

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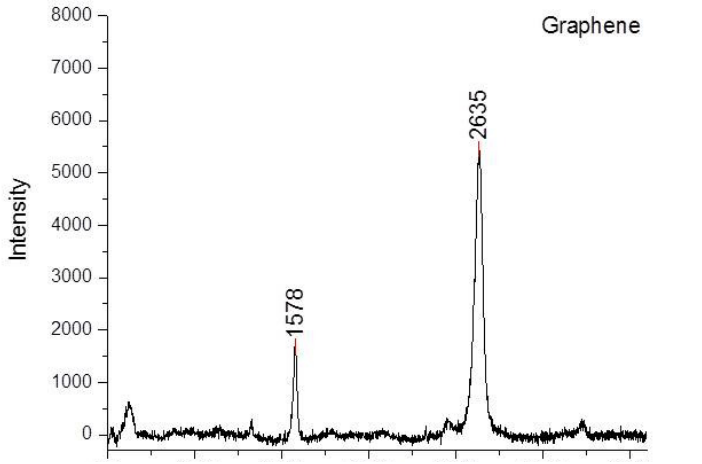
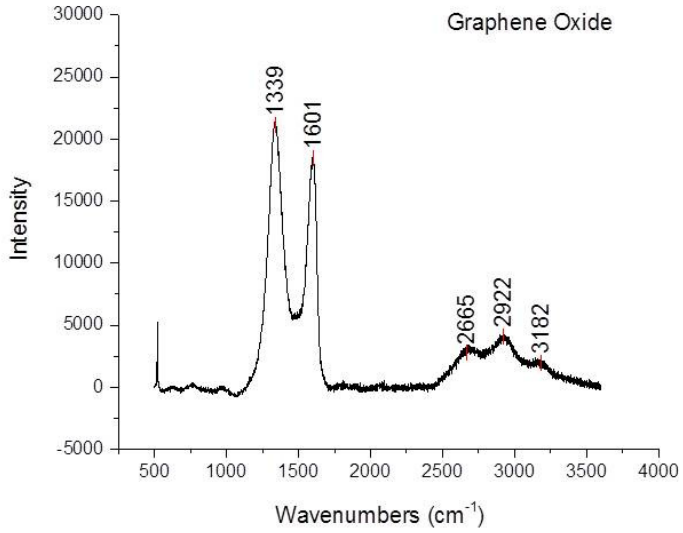
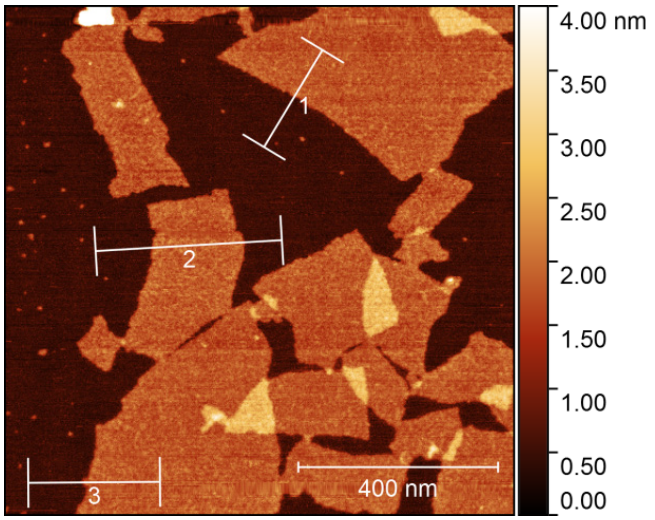
- Submit Item For Ballot
- Schedule Online Mtg/Conf. Call
- Collaboration Video Demo

Raman

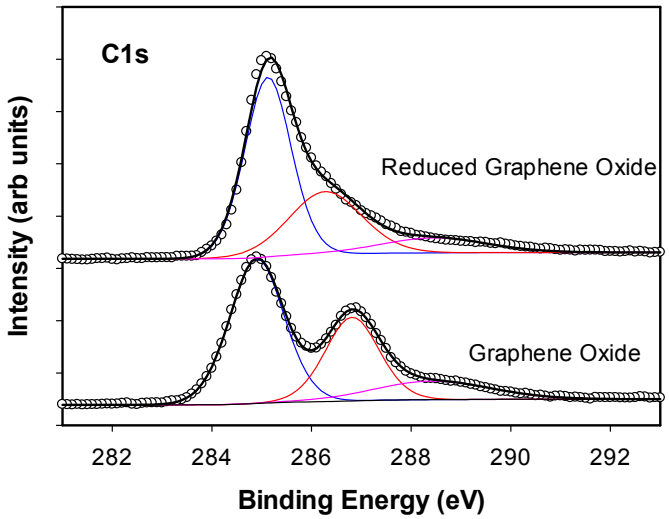




AFM

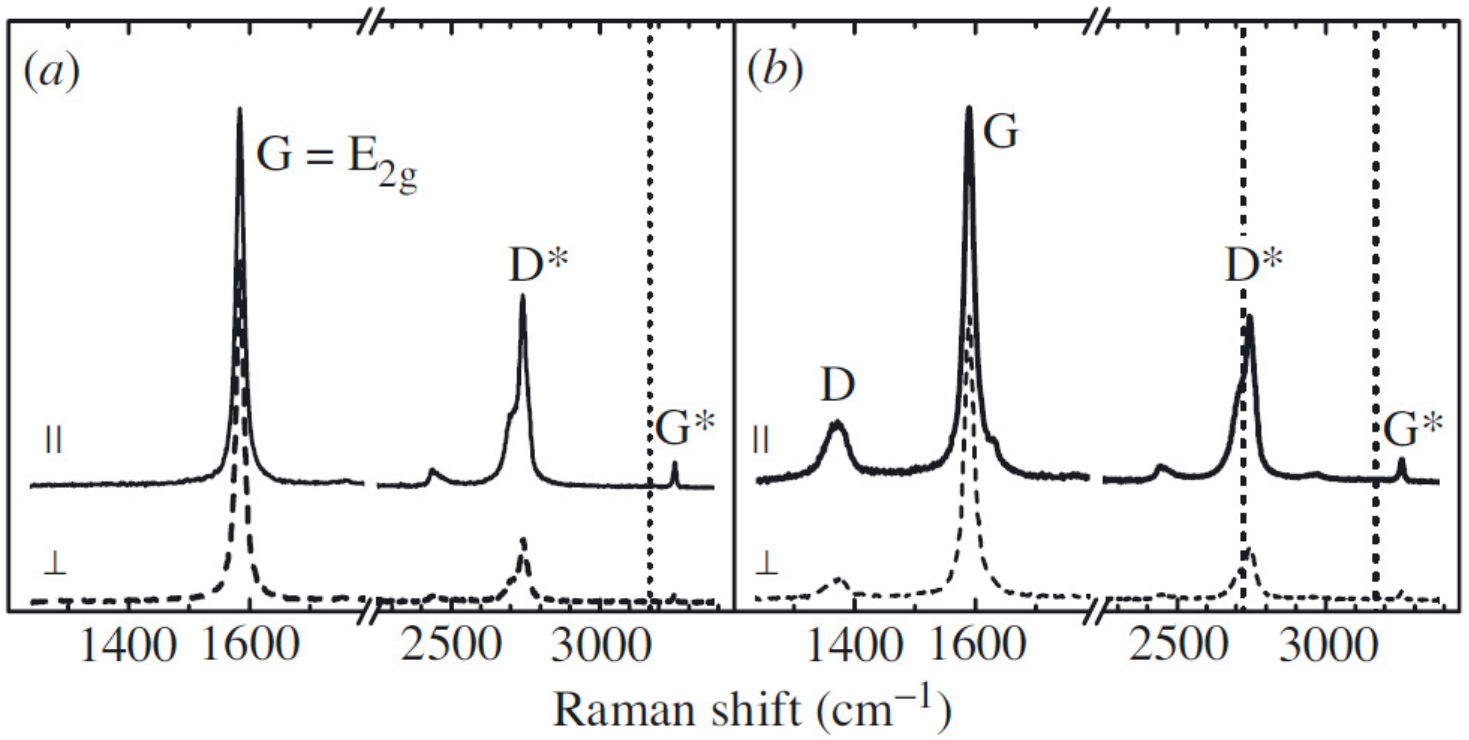


XPS

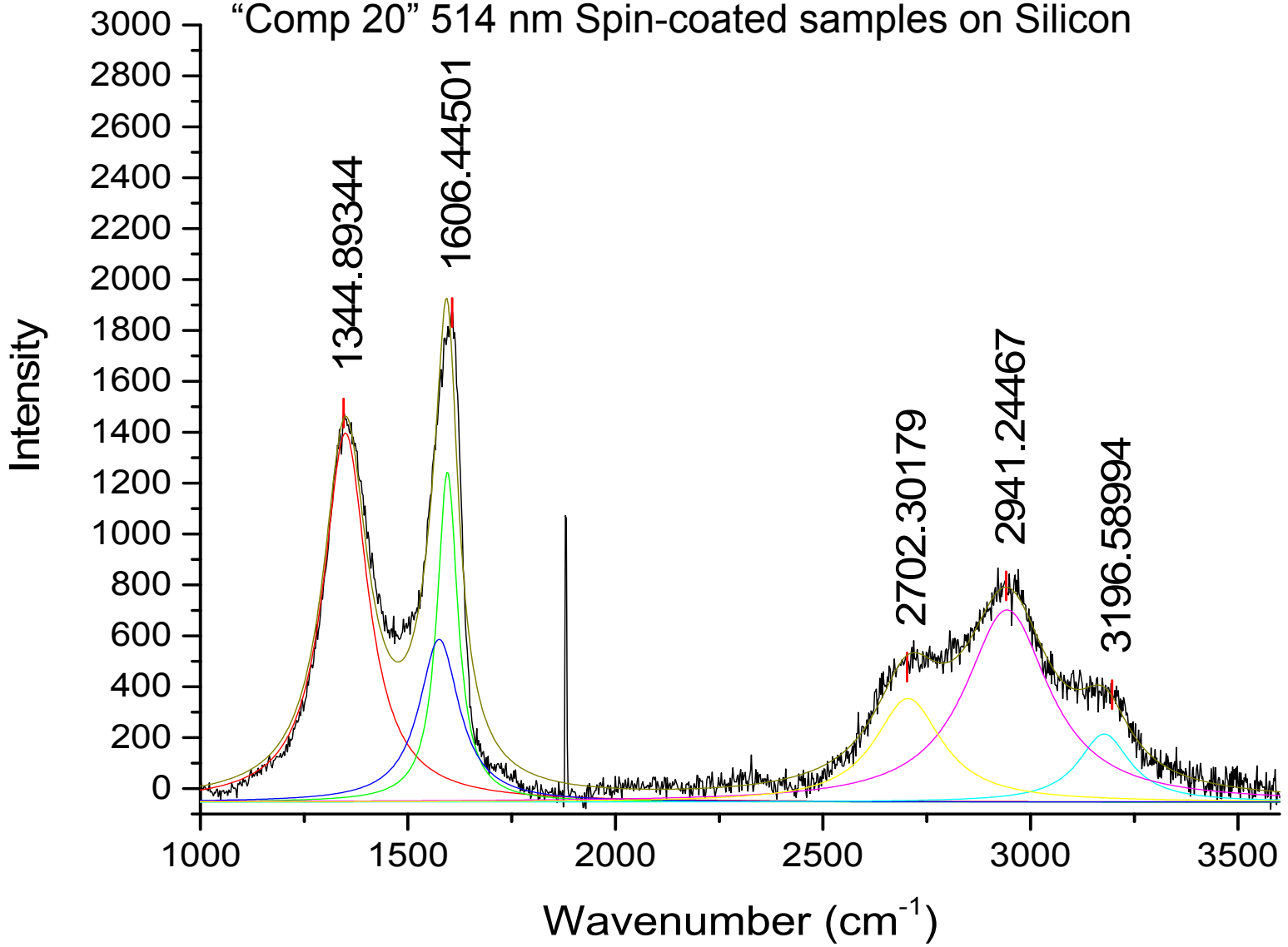


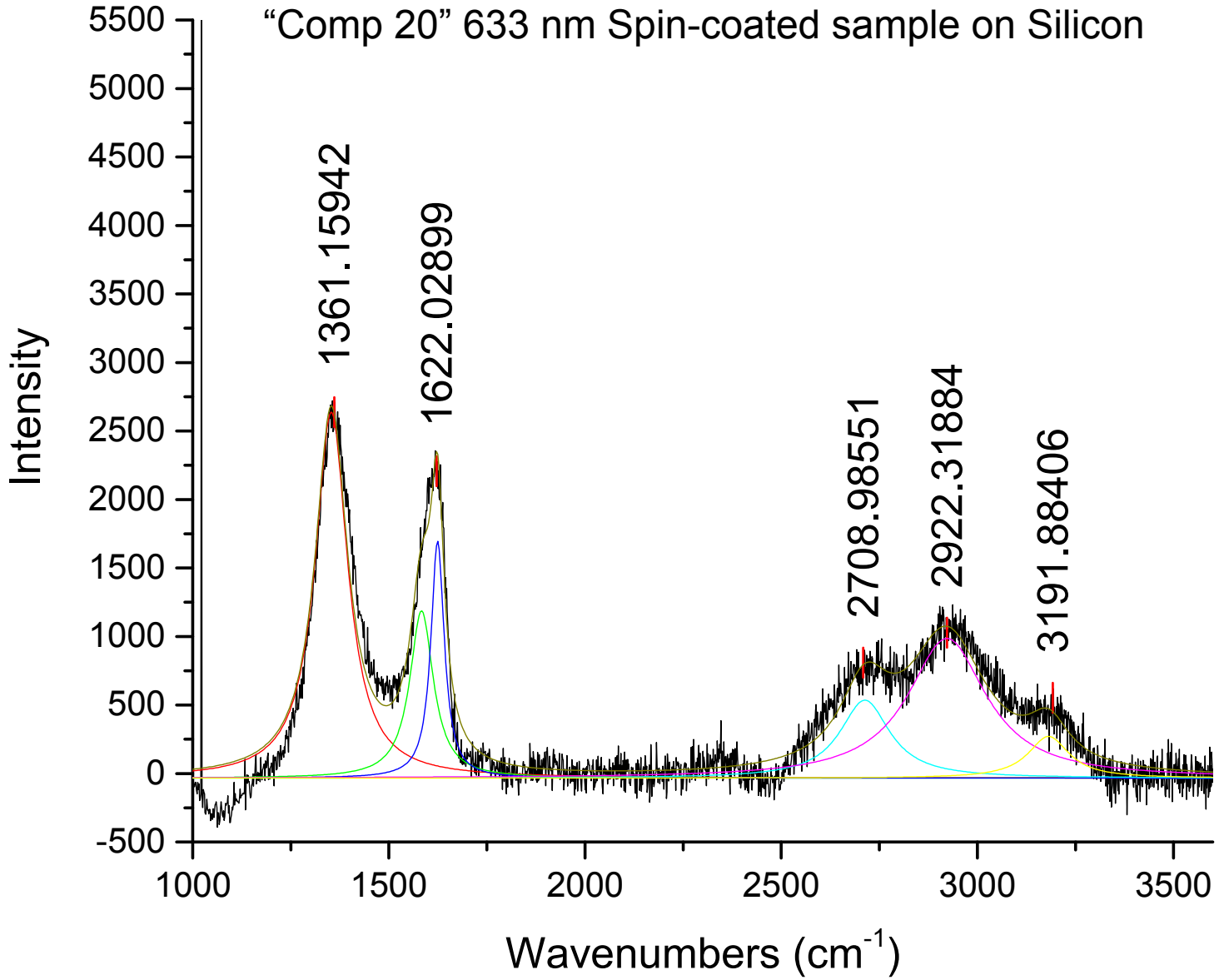
EN: http://www.nrc-cnrc.gc.ca/eng/stories/2017/graphene_standards.html
FR: http://www.nrc-cnrc.gc.ca/fra/vedette/2017/normes_graphene.html

Raman spectroscopy of graphite



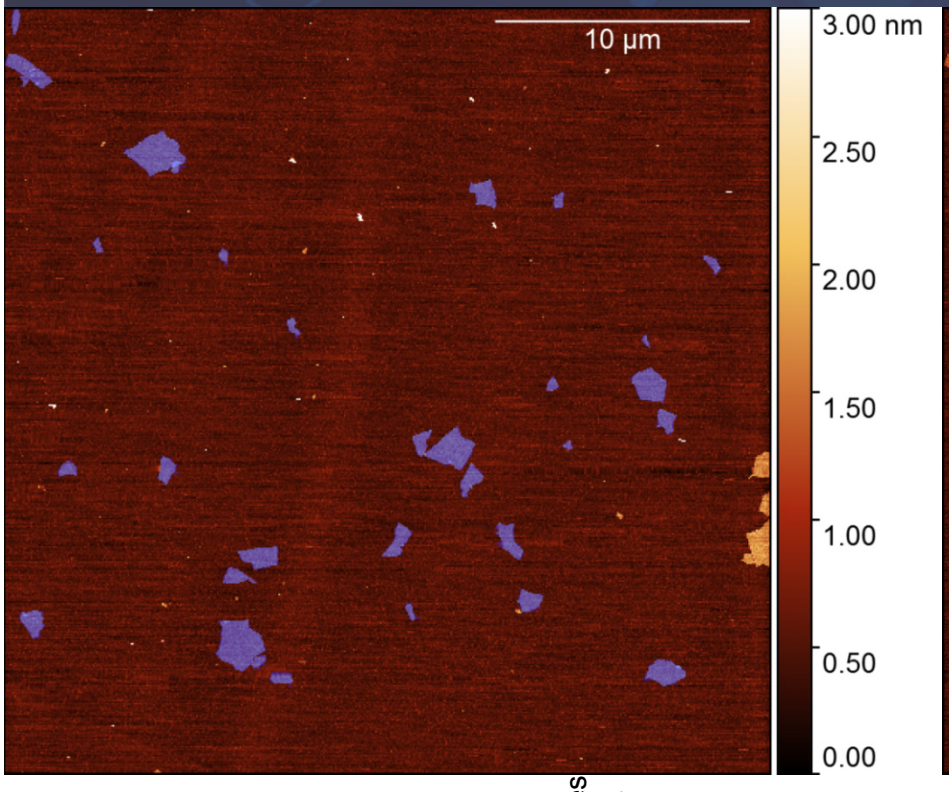
(a) First- and second-order Raman spectrum of a perfect crystallite in the sample. The first-order spectrum shows a single line at 1583 cm−1.
(*b*) Raman spectrum of graphite in the presence of disorder in the focal spot of the laser. An additional line at 1370 cm−1 and a high-energy shoulder at the E2g line are observed.
The dotted lines are positioned at twice the frequency of the fundamentals of the D and G modes.

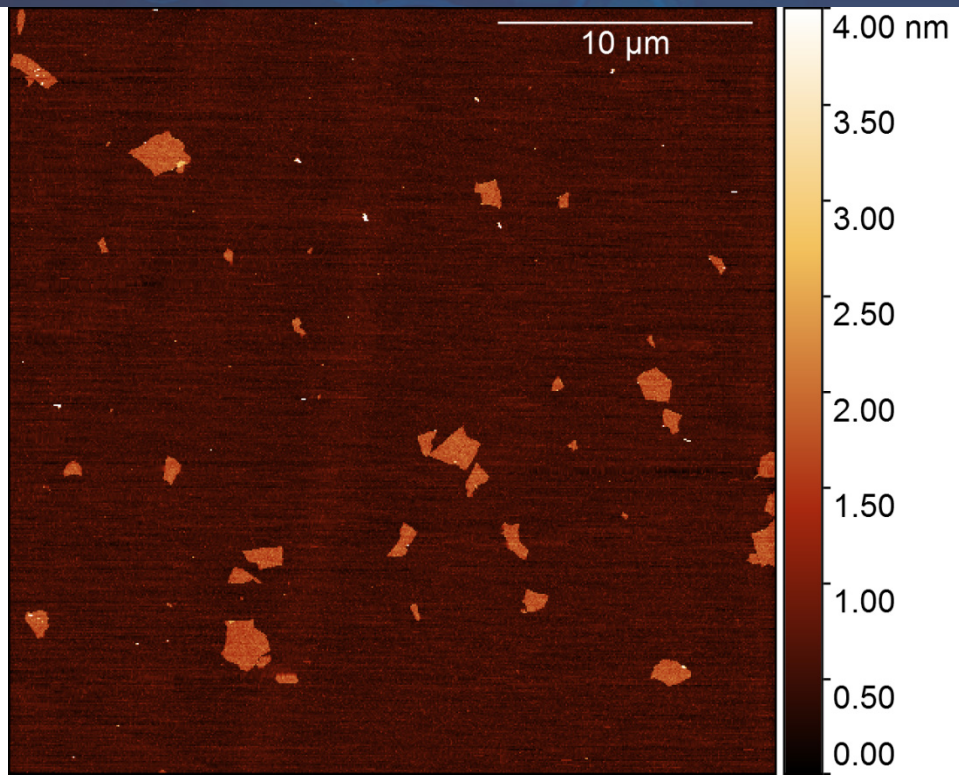

"Comp 20" 514 nm Spin-coated samples on Silicon
Intensity
Wavenumber (cm-1)
1344.89344
1606.44501
2702.30179
2941.24467
3196.58994
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
2800
3000
1000
1500
2000
2500
3000
3500

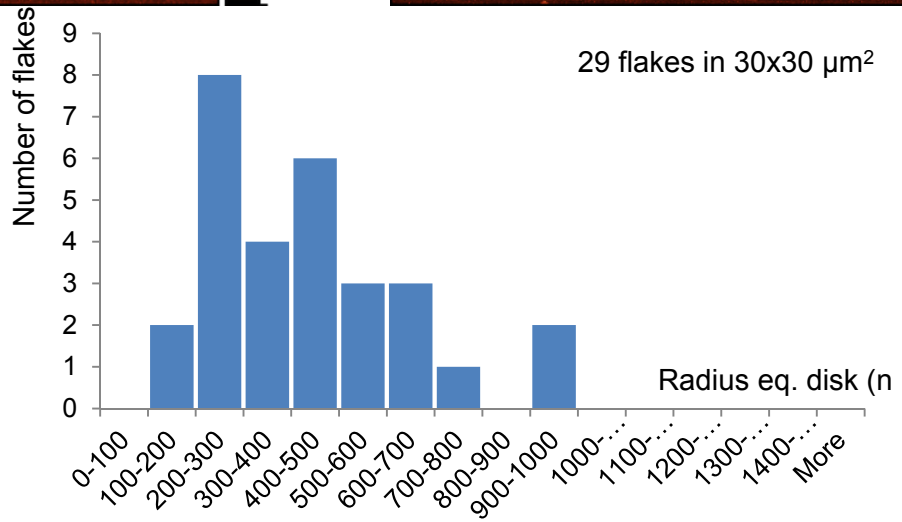

"Comp 20" 633 nm Spin-coated sample on Silicon
Intensity
Wavenumbers (cm-1)
1361.15942
1622.02899
2708.98551
2922.31884
3191.88406
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
1000
1500
2000
2500
3000
3500

Sample Name	Laser Wavelength (nm)	D (cm^{-1})	G_{app} (cm^{-1})	2D (cm-1)	D+D* (cm-1)	2D' (cm-1)
“Comp 20”	514	1348.41	1605.21739	2700.29	2943.76812	3166.3768
“Comp 20”	633	1361.16	1622.02899	2708.986	2922.31884	3191.8841

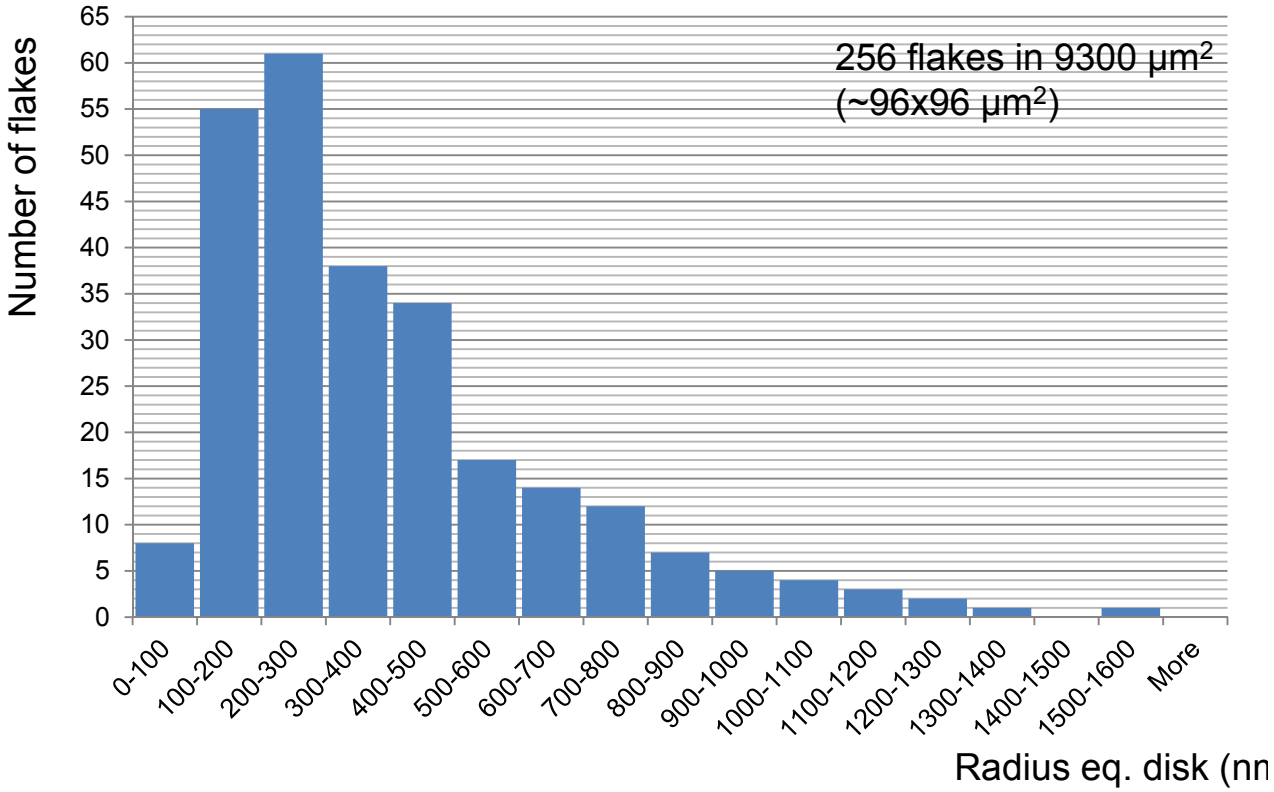
“Comp 20” spincoated on mica (2x 30ul @5000rpm for 45s each) 004







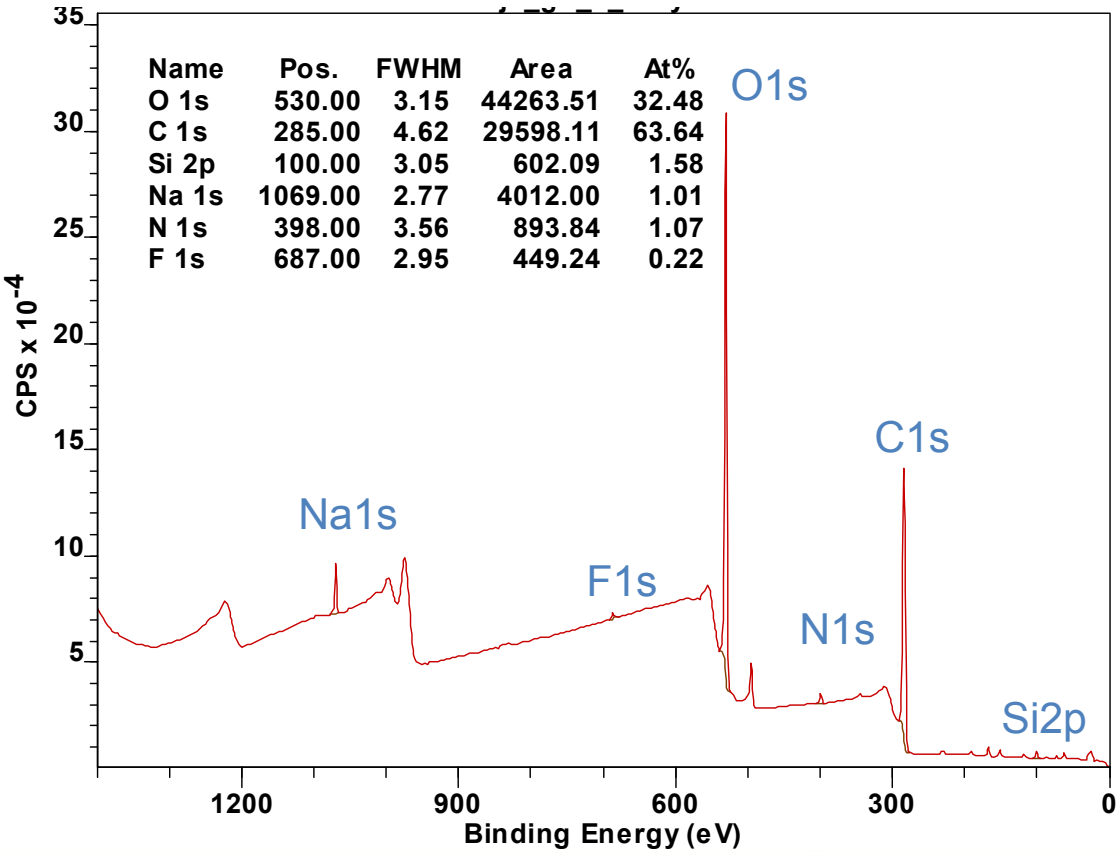
“Comp 20” spin-coated on mica (@3000 & @5000 rpm)

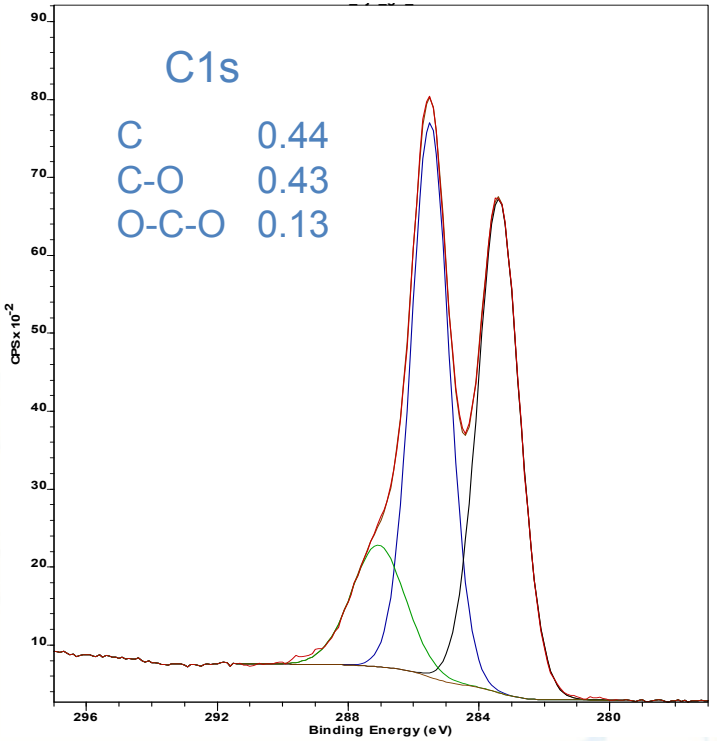


Conclusions:

- All the images that were used to compile this histogram are shown below. Samples were somewhat inhomogeneous, often with clusters of flakes together. I’ve tried spin coating with 2000, 3000 or 5000 rpm, always depositing either one or two 30 μL droplet. The 2000 rpm sample did not give me any good areas. The other four samples were used to make the histogram.
- Concerning the size, there is a reasonable amount of flakes in the 1 to 2 μm diameter range, none that are bigger than 3 μm, and a lot of small flakes at ~.5 μm diameter. Few 0-100 nm radius flakes could just be due to me eliminating them in the analysis process (I used “large” 30 x 30 μm images with 512 x 512 pixels, up to 50 x 50 μm with 1024 x 1024 pixels, and eliminated single pixel spikes as noise, but they could have been small 0-100 nm flakes).

XPS Analysis of "Comp 20" sample- deposited on silicon (native oxide)





- Small but measureable amount of N (1%), Na (1%) and F contamination.
- C/O ratio ~2 as expected for GO.
- C1s region characteristic of GO- no evidence for carboxyl functionality.