

# Instrumentation and Analysis for Characterization of New Graphene-Based Soft Materials

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ASHLEY ROBERTS

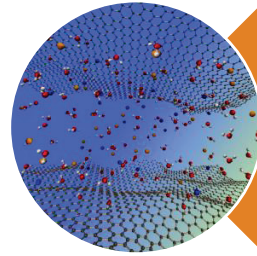
PHD CANDIDATE IN MATERIALS ENGINEERING

MONASH UNIVERSITY, AINSE PGRA

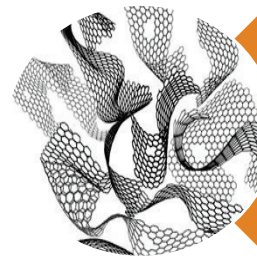


# Presentation Overview

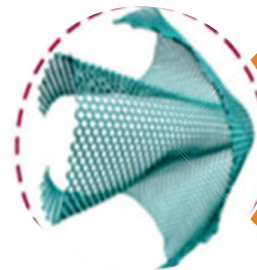
Graphene-based materials consisting of chemically converted graphene (CCG), graphene oxide (GO), or partially reduced GO sheets can be functionalized to exhibit responsive behavior and also formed into **membranes, gels, or sponges**.



Processing Soft Materials from Solvated Nanocarbons



Current Research to Characterize Graphene Structures



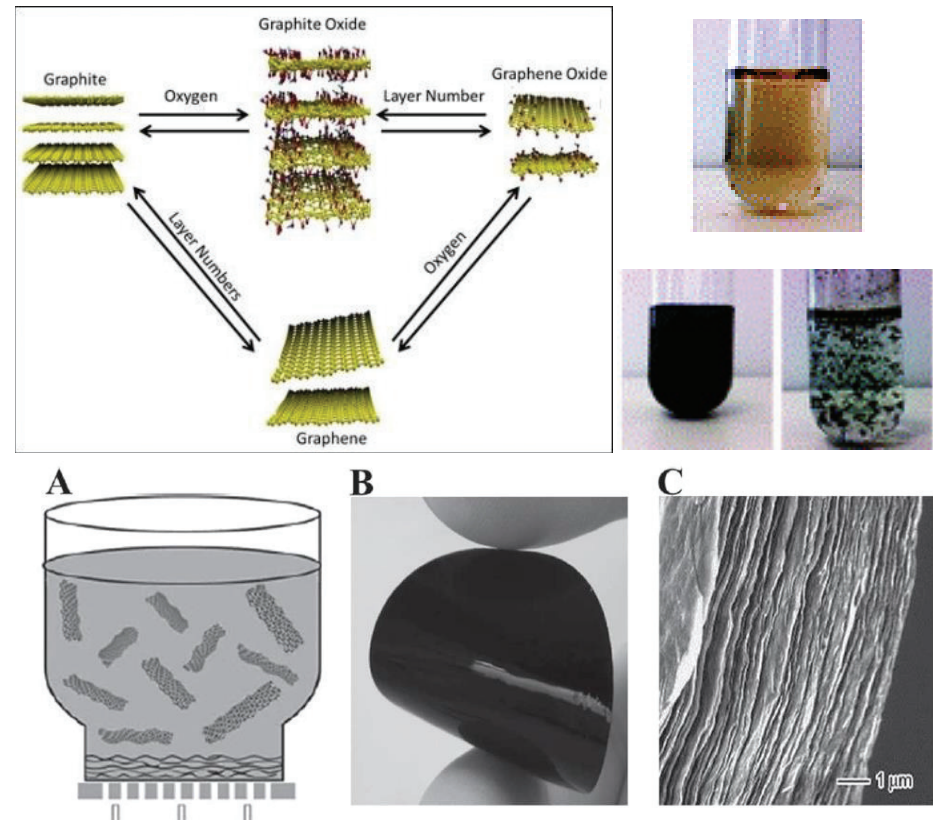
Interpretations of Scattering Results

# Colloid Assembly for Scalable Fabrication of Graphene Materials

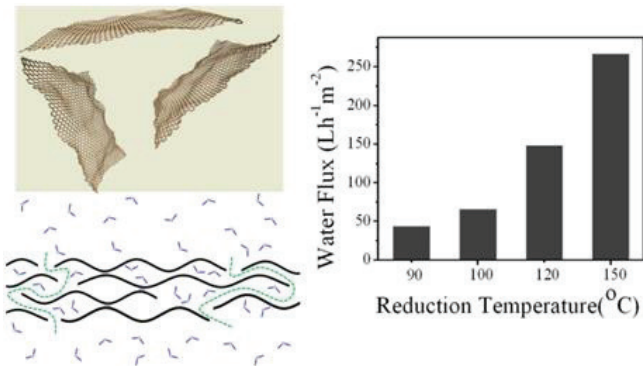
Stable, **aqueous graphene dispersions** can be readily prepared by chemical conversion of inexpensive, natural graphite flakes, without the need for any foreign dispersants. (*Nature Nanotechnology* 3, 101-105, 2008)

This success enables the use of **low-cost, solution processing techniques** to combine individual graphene sheets into a range of macroscopic, practical and useable forms. (*Science* 320, 1170-1171, 2008)

CCG can self-gel at the liquid-solid interface in a face-to-face manner to form an oriented, **conductive hydrogel film** during filtration.

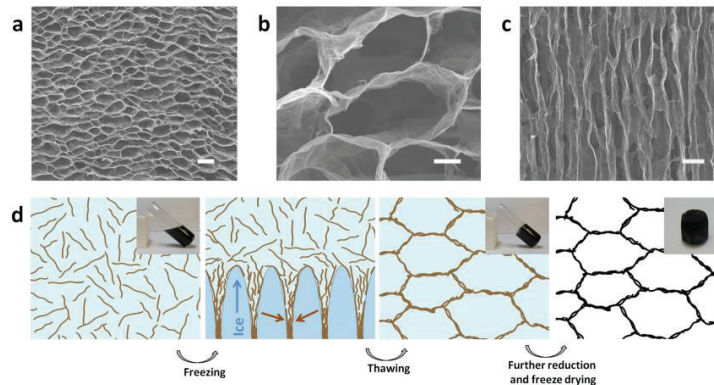


# Separation and Nanofluidics, Sponge Elastomer, and Functional Materials



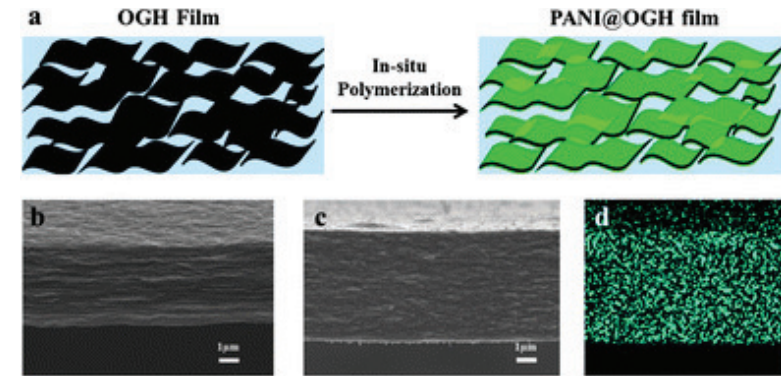
Corrugated CCG sheets stacking face-to-face, the membrane is thus endowed with an interconnected nanochannel network with a slit-shape channel scaling from 0.5 to 10 nm acting as a **multi-channel fluidic device**.

(*Chemical Communications* 47, 5810-5812, 2011)



A self-supporting, structurally adaptive, and **3D macroscopic CCG sponge** is ultralight and superelastic. The unique biomimetic hierarchical structure also provides this **new class of elastomers** with exceptionally high-energy absorption capability and good electrical conductivity.

(*Nature Communications* 3, Article number: 1241, 2014)



Through nanostructure engineering, many **composite graphene-based materials** enhance performance.

- **Polyaniline composite** for high capacitance (*Energy & Env Science* 6, 477-481, 2013)
- Hierarchically structured **carbon nanohybrids** (*Chemistry: A EU J.* 16, 10653-10658, 2010).
- Solution-dispersible **nanoparticle assemblies** (*Chemistry: A EU J.* 17, 5958-5964, 2011)

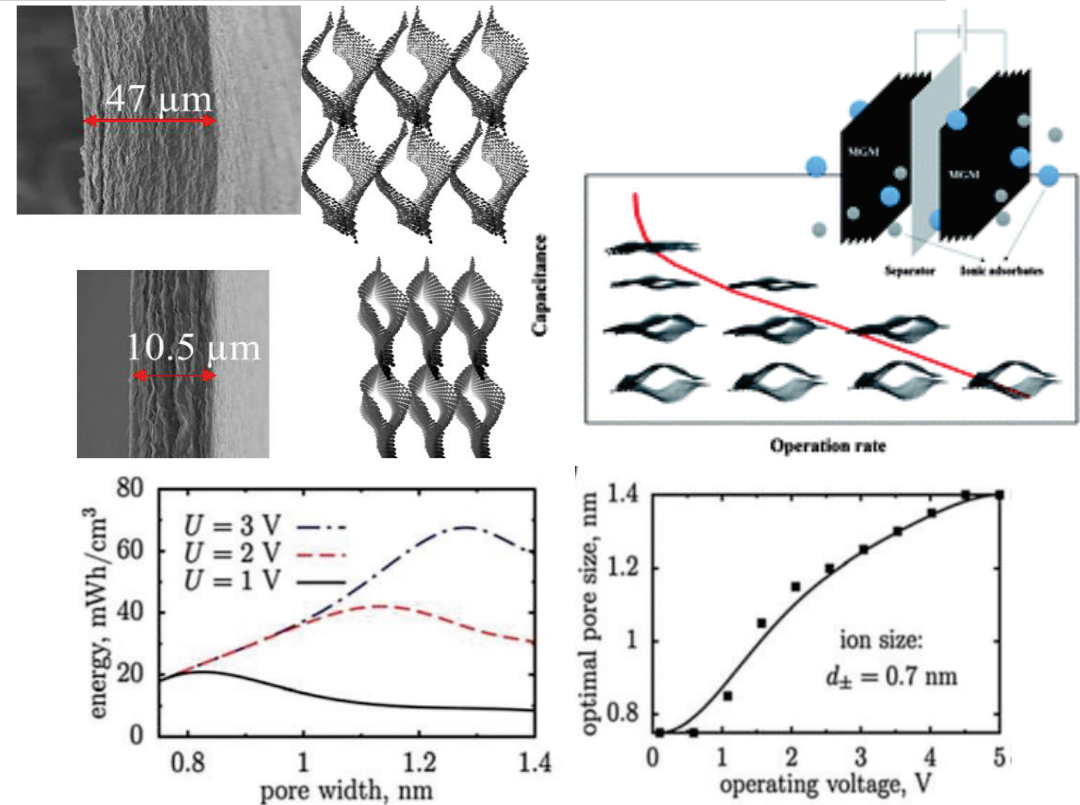
# Relevance in the Field: Porous Carbons

Engineered membranes that are selectively ion, gas, or liquid permeable are key aspects of emerging technology especially in the fields of gas separation, water purification, and energy storage.

In an electrochemical supercapacitor, there is an optimal micropore size that correlates with a specific electrolyte system within a given voltage window.

- A **relationship** between pore size, energy density, and voltage is shown here for an ion with diameter of 0.7nm.
- Uniformity of the pore sizes, described as the **pore size distribution** (PSD), as well as the way the pores are interconnected has a large impact on capacitor performance.

**The size and structure of the pore network will determine the material performance.**



J. Mater. Chem. A, 2013, 1, 9332; Phys. Chem. Chem. Phys., 2011, 13, 15384

# Background on Common Terms: What are we characterizing?

**Defects:** holes, bonds, functional groups, edge effects

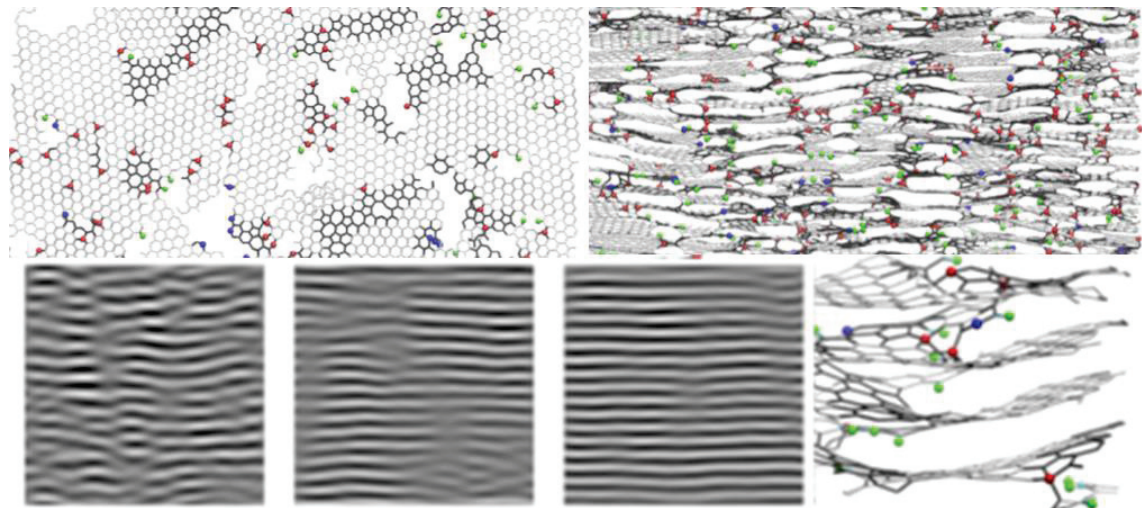
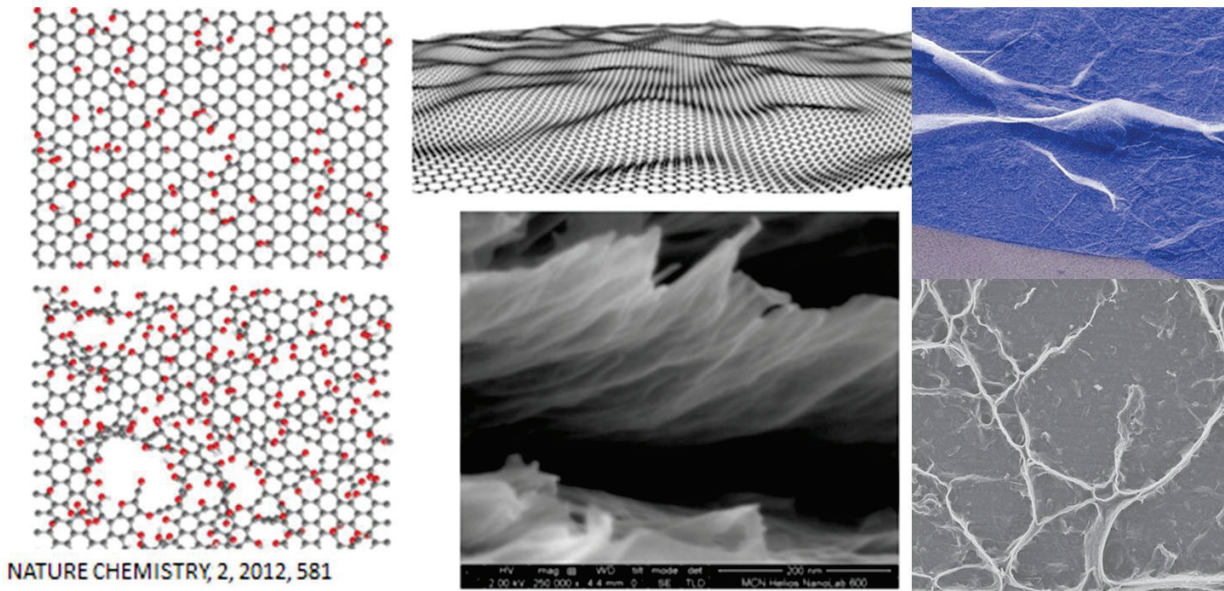
**Corrugation:** in-plane fluctuation,

**Other in-plane fluctuations:** wrinkles, folds, curling

**In-plane Pores vs Inter-sheet pores:** defects vs lamellar space

**Disorder:** evaluate the degree of misalignment from crystal

**Restacked Regions:** areas of material that return to graphite 002 d-spacing



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# Characterizing Pore Structure across a Broad Range of Length Scales

**Micropore** region (0-2 nm), especially sub-nm, is main determinant for:

- Ions size to optimize energy storage capabilities
- Molecule kinetic radius determines permeation
- Fluid structure when confined inside specific size pores

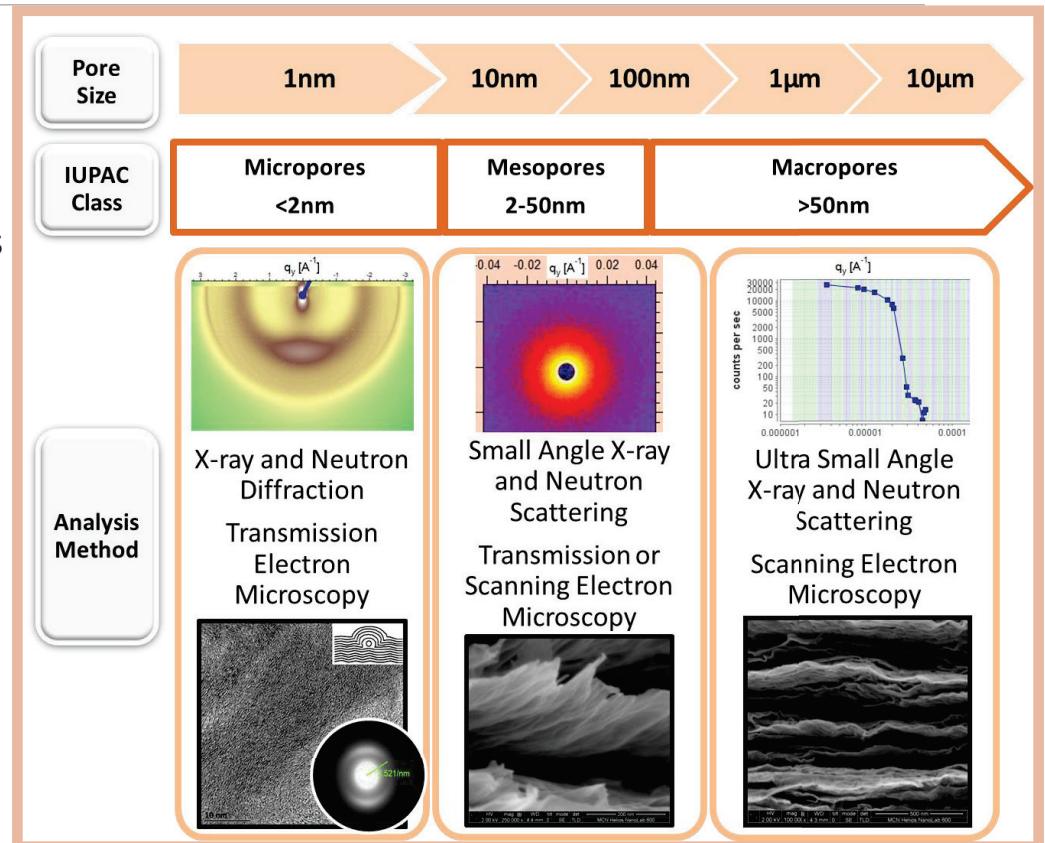
**Mesopore** region (2-50 nm) and Pore Network also play large role

- Pore size distribution (PSD) will impact properties of material
- Pore network describes how pores are organized (can be directionally dependent: isotropic or anisotropic)

**Macropore** region (>50 nm)

- Graphene **sheet length** can range into micron region

Existing models for other porous carbons (Pyrocarbons, Activated Carbons, Coal) can be adapted for graphene assemblies.



# Why Use Neutrons?

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## Advantages

- Contrast matching to resolve accessible vs closed porosity
- Can obtain total scattering surface (gas adsorption not possible with hydrated systems)
- Resolution for light elements (Hydrogen, Lithium, Carbon, Oxygen)
- Water transport
- Magnetism
  
- Limitations of other systems
  - Overlap of electronic structure in small pores of carbon systems limits x-ray
  - *In-situ* testing is severely limited with vacuum requirements

## Challenges

- Very large q-range necessary for full characterization
- Relatively featureless curves
- Not a powder, but needs orientation measurements at intermediate q-range sub-nm to 10nm

## Requirements

- Sample environments!
  - Humidity controls
  - Ion transport
  - Magnetic field
  - Mechanical testing
- A lot of accumulated beam time for so much q and sample carbon sample with small mass...



# Extended q-Range of Porous Carbons

## Space-Filling Fractal Networks of Carbon Nanopores

Fractal channels of pores create a “negative image” of mass fractals and can be used to model confined processes.

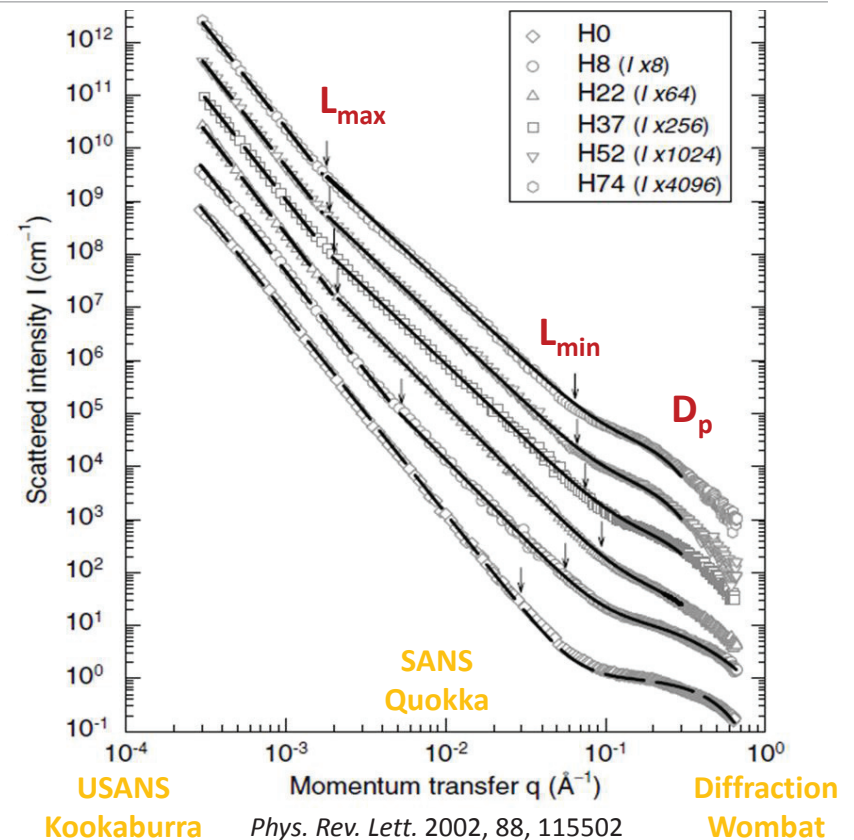
Scattering curves can be fitted with as little as three parameters and span a scaling regime comparable to the most extended regimes to date.

High q gives dimension of the pore,  $D_p$

Fractal network extends from a minimum size just above  $D_p$  ( $L_{min}$ ) along a linear (Porod) region to  $L_{max}$

When networks touch, they are fractal below  $L_{max}$  and uniform at scales above  $L_{max}$

**CCG pore networks extend orders of magnitude farther than those reported here.**



# Defining Lamellar Carbon Structures

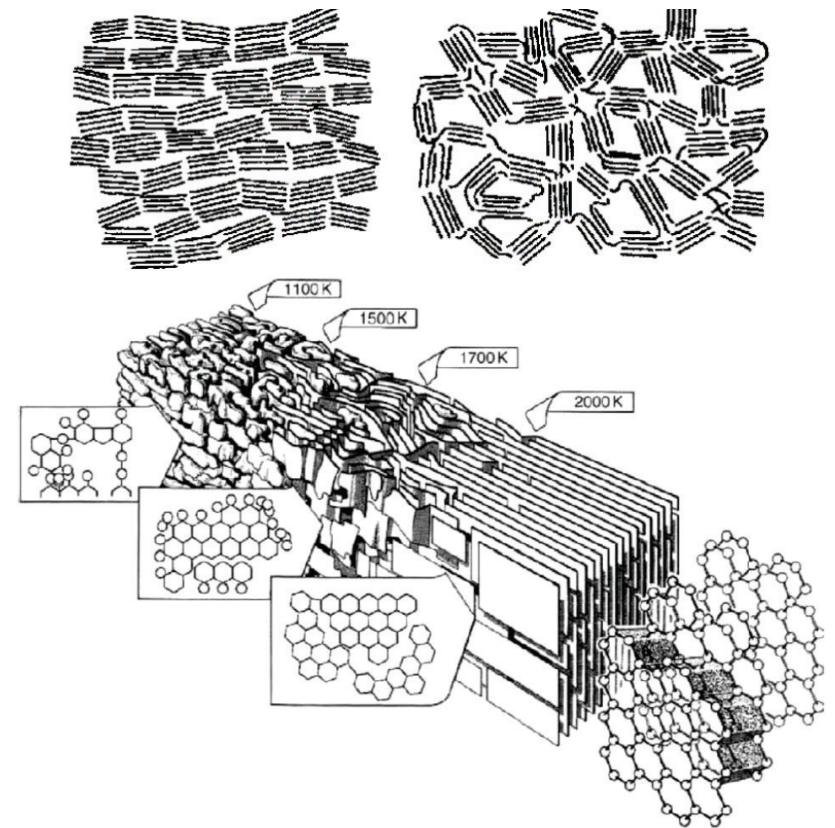
Two main categories of **graphitizable** (a) and **non-graphitizable** (b) described by Franklin in 1950.

XRD is commonly used to describe the distance between graphene planes (002 plane).

XRD line-broadening can be explained, for non-graphitic carbons as resulting from structures made up of **roughly parallel, quite defective** associations of carbon planes – termed **defective micro-graphene layers**.

- Small crystallite size dictated by graphene layers in the stack
- Strain within the lattice, causing an interlayer distance to vary – as in curvature

Visual representation by Marsh (1991) shows the structural changes that occur during heat treatment of a graphitizable carbon from 1000-3300 K.



# Micropores on the Nanoscale: XRD Impact of Oxidation Level and Drying

GO sheets remain rigid due to attached oxygen groups, creating a more defined XRD peak from the orderly system.

When the oxygen-containing functional groups are removed, the carbon sheets become quite corrugated with defects and residual functional groups.

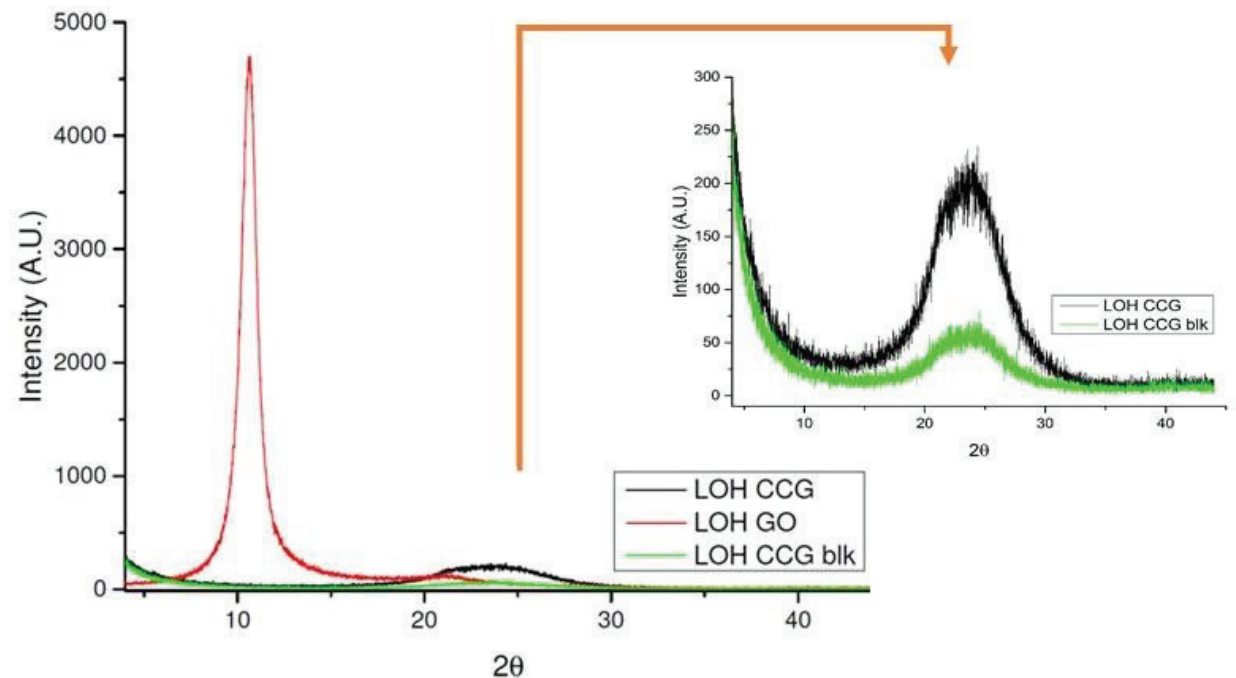
Soft matter methods must be applied to interpret the disorder in the CCG lamellar system.

Graphite peak is  $26.2 = 3.4\text{\AA}$

GO peak at  $10.5 = 8.3\text{\AA}$

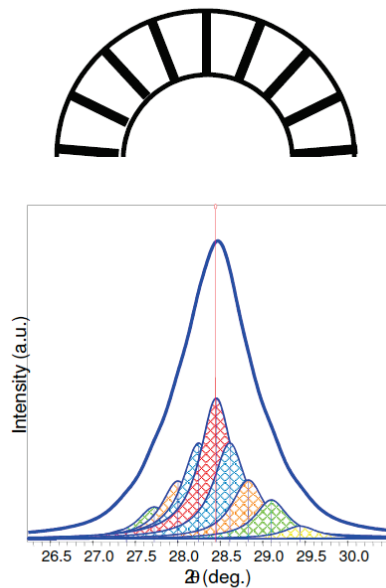
CCG peak at  $23.5 = 3.9\text{\AA}$

Drying on pump (with pressure) or drying in air (no pressure) influences peak intensity, but not position.



# Micropores on the Nanoscale: XRD Results to Characterize Peak Broadening

## NON-UNIFORM LATTICE DISTORTIONS

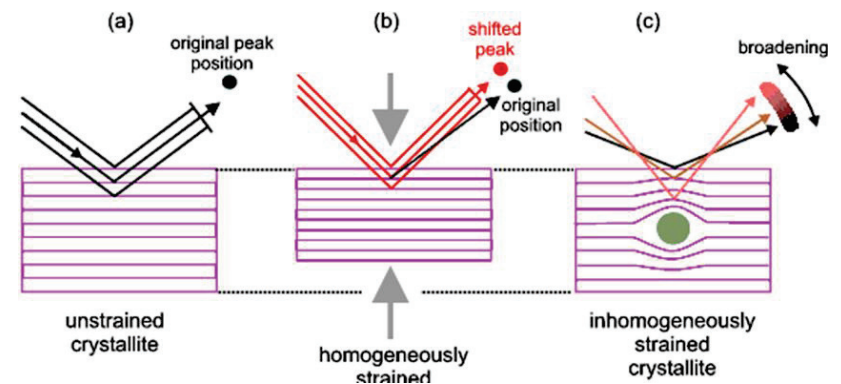


Rather than a single d-spacing, the crystallographic plane has a distribution of d-spaces

## CRYSTALLITE SIZE AND STRAIN

$$\beta_L = K \lambda L \cos\theta$$
$$\beta_e = C \varepsilon \tan\theta$$

Scherrer Formula



# Micropores on the Nanoscale: XRD Results to Characterize Peak Broadening

Without higher order peaks, we cannot use the line profile alone to distinguish between the broadening from strain vs crystallite size.

We know the CCG sheets are wrinkled, buckled, curved, and corrugated - we attribute the shift in lamellar spacing (d002 peak) to wrinkling and distributed bonding.

**This is strain within the lattice: thus, both strain and crystallite size should be incorporated into the interpretation of peak broadening**

Rough estimation for strain broadening:

$$\text{Thus microstrain, } \varepsilon = \frac{\Delta d_{002}}{d_{002}} \approx 0.085$$

And strain broadening,  $\beta = 4\varepsilon \tan \theta \approx 4^\circ$

**This maximum strain is 60% of total broadening**

*Other carbon materials report values  $\approx$  10%-20%*

*Use of other techniques to support conclusions is needed (Raman)*

# But can we even use the term 'crystallite' for these CCG materials?

There is debate in this area, and overall, the term is misused with porous carbons.

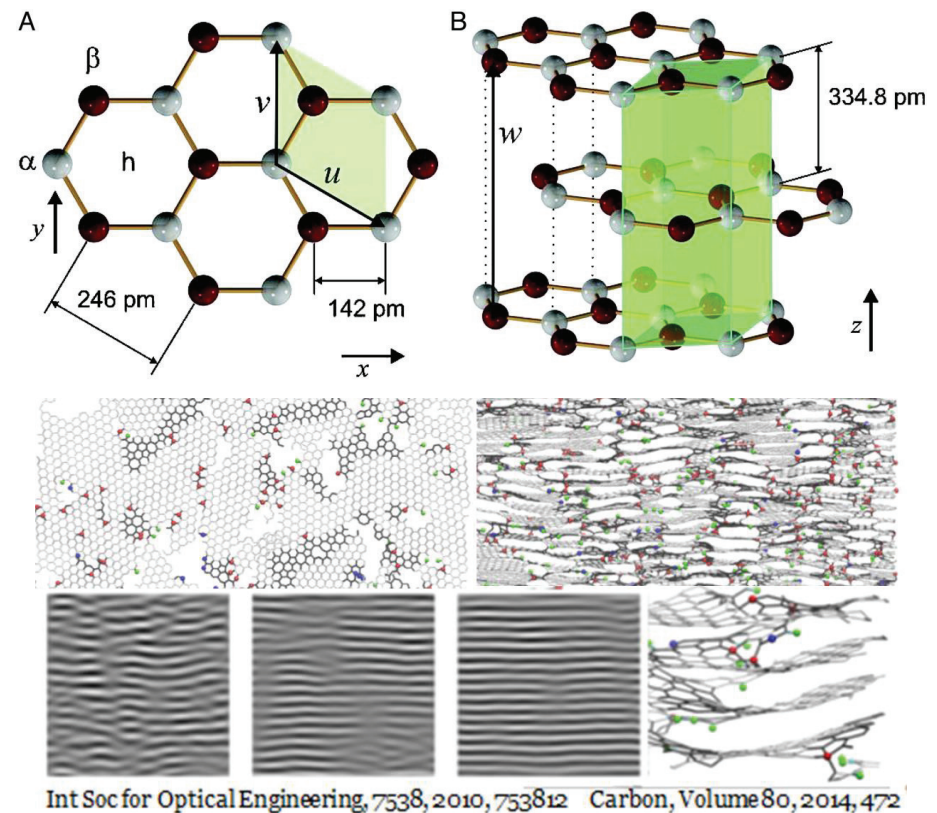
Some highly ordered systems apply (pyrocarbons, HOPG, etc.), but most systems do not (even turbostratic carbon).

Layers arranged parallel, relative equal distances, but with rotation and translation.

Lamellar reflections of  $(00l)$

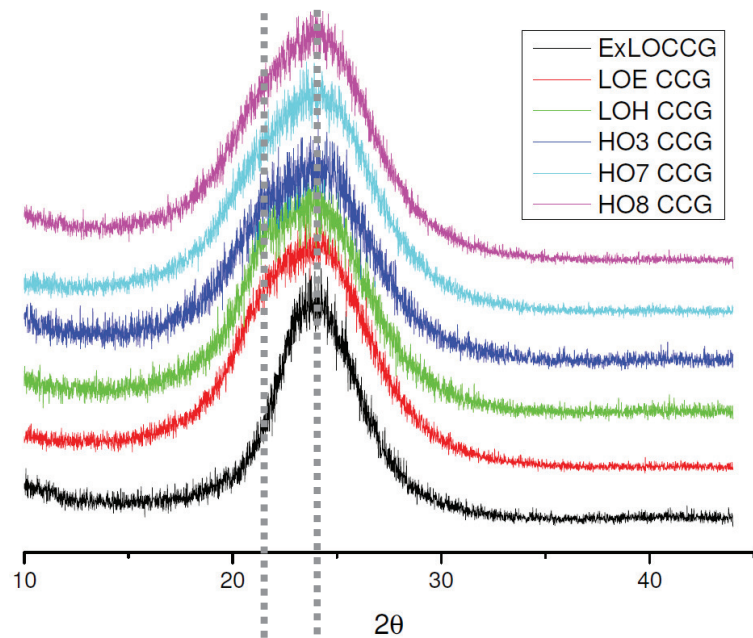
2D reflections of  $(hk)$

No general reflections of  $(hkl)$  the  $(00l)$  and  $(hk)$  are **not related** in these porous carbons



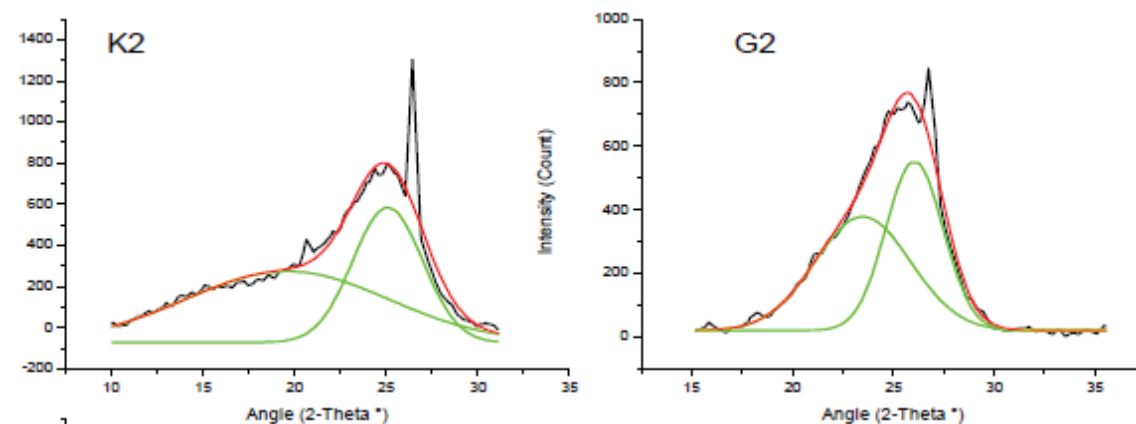
# Micropores on the Nanoscale: XRD Results to Characterize Peak Broadening

CCG SAMPLES NORMALIZED TO PEAK HEIGHT



CCG peak at  $23.5^\circ = 3.9\text{\AA}$   
Peak skew to left, second phase at  $21^\circ = 4.2\text{\AA}$

XRD CHARACTERIZATION FOR COAL: TWO BANDS



Two peaks from different bond types in the  $d_{002}$  lattice:

The  $20^\circ$   $\pi$ -band (002) spacing of aromatic ring layer,  
while  $26^\circ$   $\gamma$ -band reflects the packing distance of saturated  
structures (aliphatic carbon).

(sharp peaks at  $26.6^\circ$  from graphite domains)

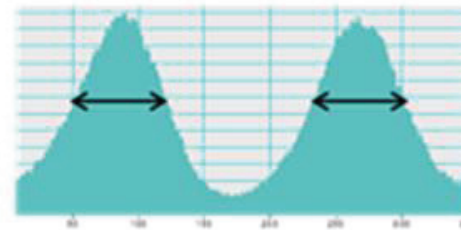
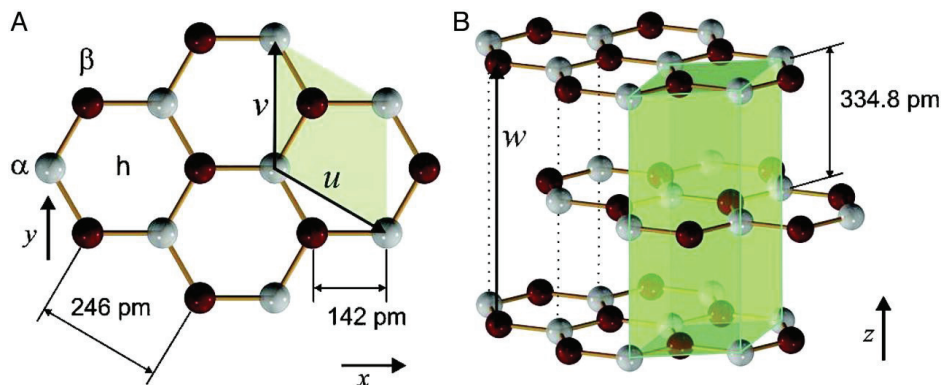
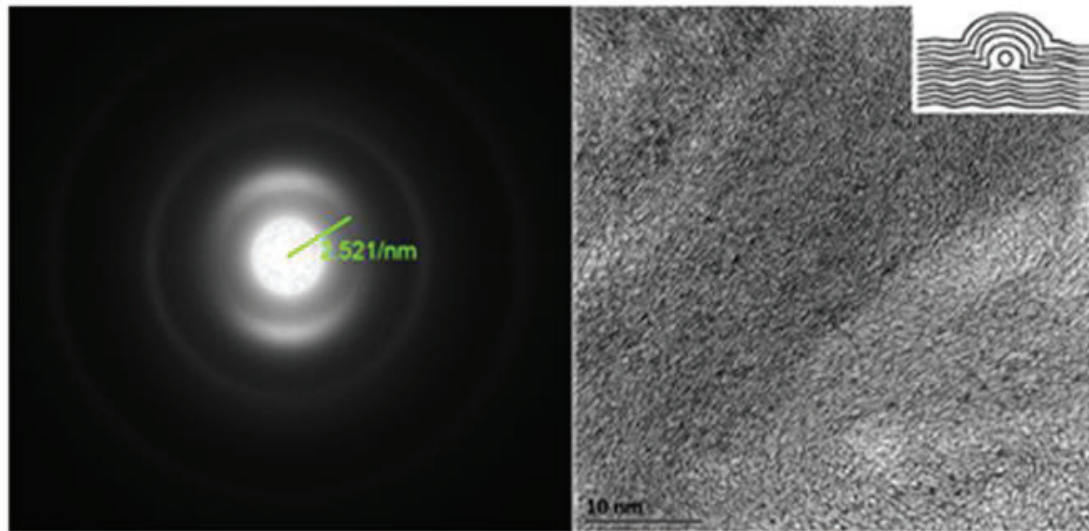
B. Manoj and A.G. Kunjomana, 2012. *Trends in Applied Sciences Research*, 7: 434-444.

# Micropores on the Nanoscale: SAED for Intrashheet Bonding

SAED image to classify **intersheet order** and **intrashheet bonding**

- Resolves higher order peaks (c-c bond)
- Shows spatial distribution in d002 plane
- Compareable with other lamellar carbon materials

*Cons: Requires extensive sample preparation methods, localized area, and **dry samples only**.*



$d_{002}$	OA	Classification for Texture
3.9Å	71.5°	Medium-Low

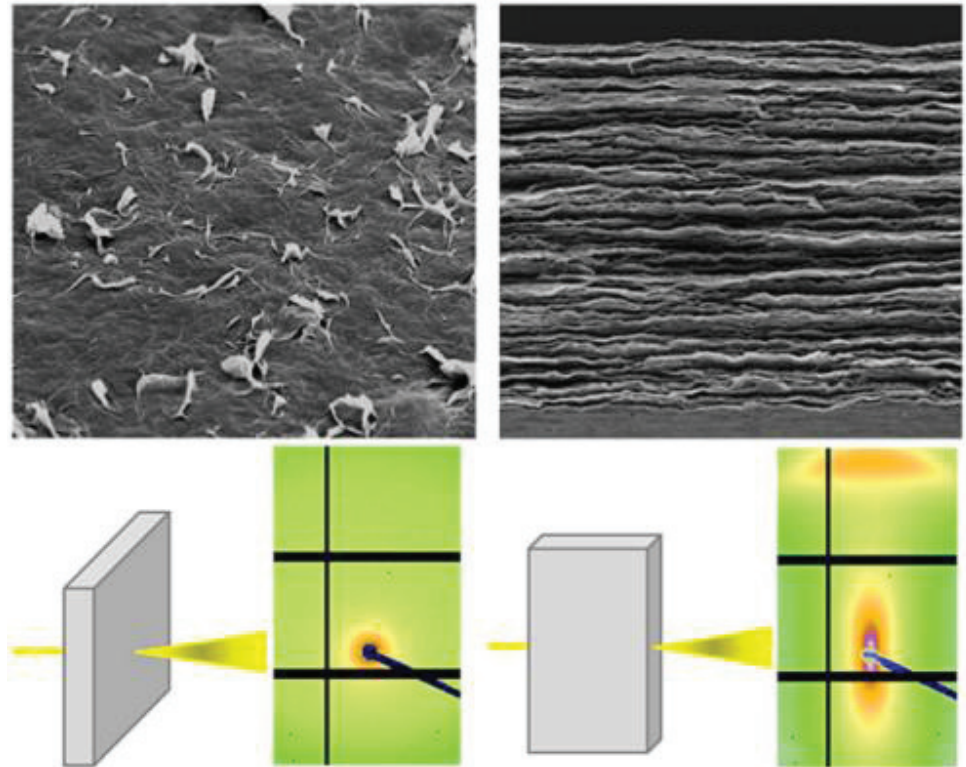


# Anisotropic Geometry of Graphene-Based Membrane Assemblies

Anisotropic structure yields scattering patterns with geometric dependence.

Scattering **through the sheets** shows Bragg spacing and pore network along the sheet.

Scattering **through the edge** shows alignment of sheets and the degree of disorder of inter-sheet pores.



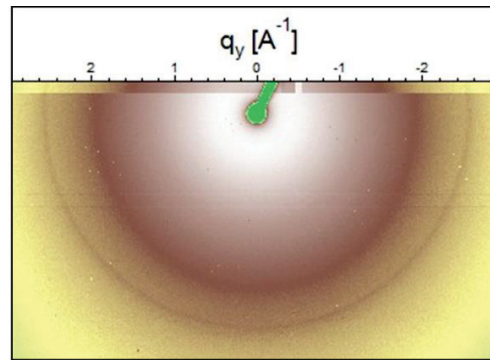
# Anisotropic Geometry of Graphene-Based Membrane Assemblies

The diffraction peaks show clear orientation in the membranes

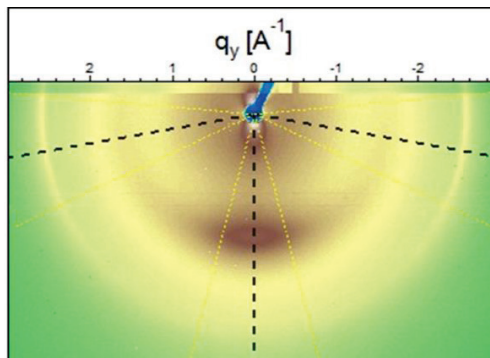
- $\pi$ - $\pi$  bonding between CCG sheets (002)
- C-C bonding along the sheets (100)

Lamellar spacing is expanded in the  $\parallel$  sheet direction from that of pure graphite (3.354 Å)

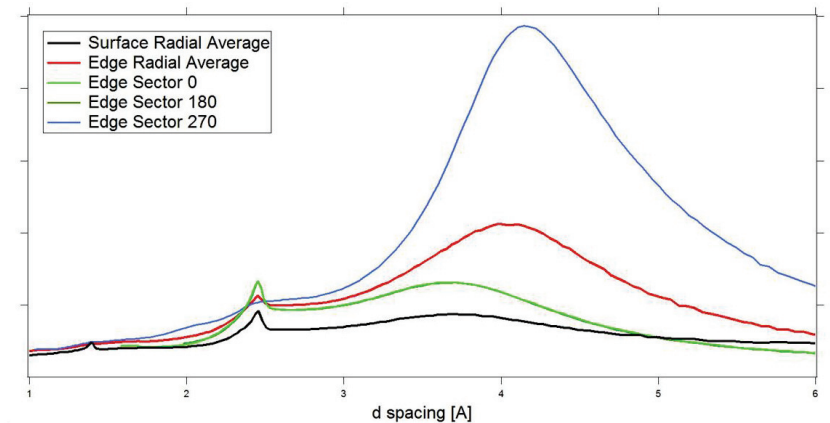
Orientated scattering patterns indicate elongated disk-like stacking of these regions



Through the Surface

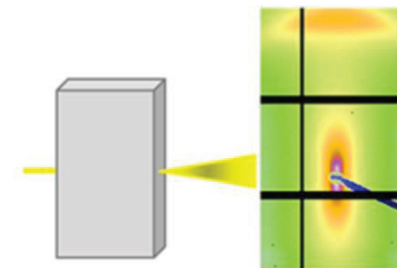


Through the Edge



Diffraction Peak	002 (Å)	FWHM	100 (Å)
Surface Radial	3.69	0.68	2.45
Edge Radial	4.04	0.88	2.45
Edge $\parallel$ Sheet	4.18	0.84	N/A
Edge $\perp$ Sheet	3.65	1.00	2.45

# Mesopores and Pore Networks: Through the Edges and Slits

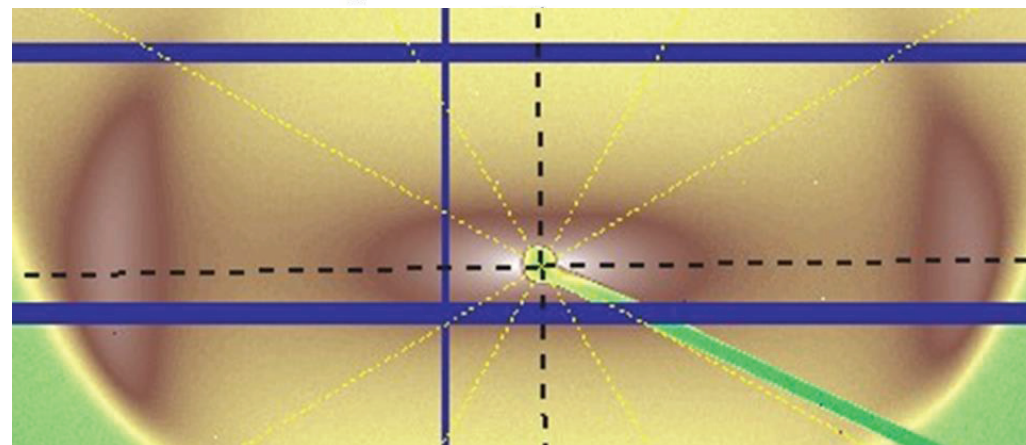
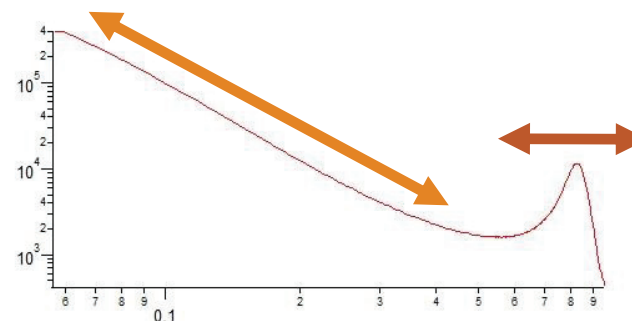


Scattering through the edge shows **scattering along the graphene sheets** (small angles) is well ordered with OA of  $<15^\circ$  and extends down to nm scale.

Disorder is more pronounced at wider angles, describing **the inter-sheet 002 spacing** ranging from  $3.7\text{\AA} - 4.2\text{\AA}$  depending on orientation with  $4.2\text{\AA}$  peak OA close to  $30^\circ$



$$4.2\text{\AA} \cos(30^\circ) = 3.6\text{\AA}$$



Jan Ilavsky, "Nika - software for 2D data reduction", J. Appl. Cryst. (2012), vol. 45, pp. 324-328.

# Acknowledgements

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