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Russian Science Foundation

Crystallography and Crystal Chemistry VIII International School-Conference of Young Scientists 2023

Methods and approaches for the investigation of disorder or hard carbon materials

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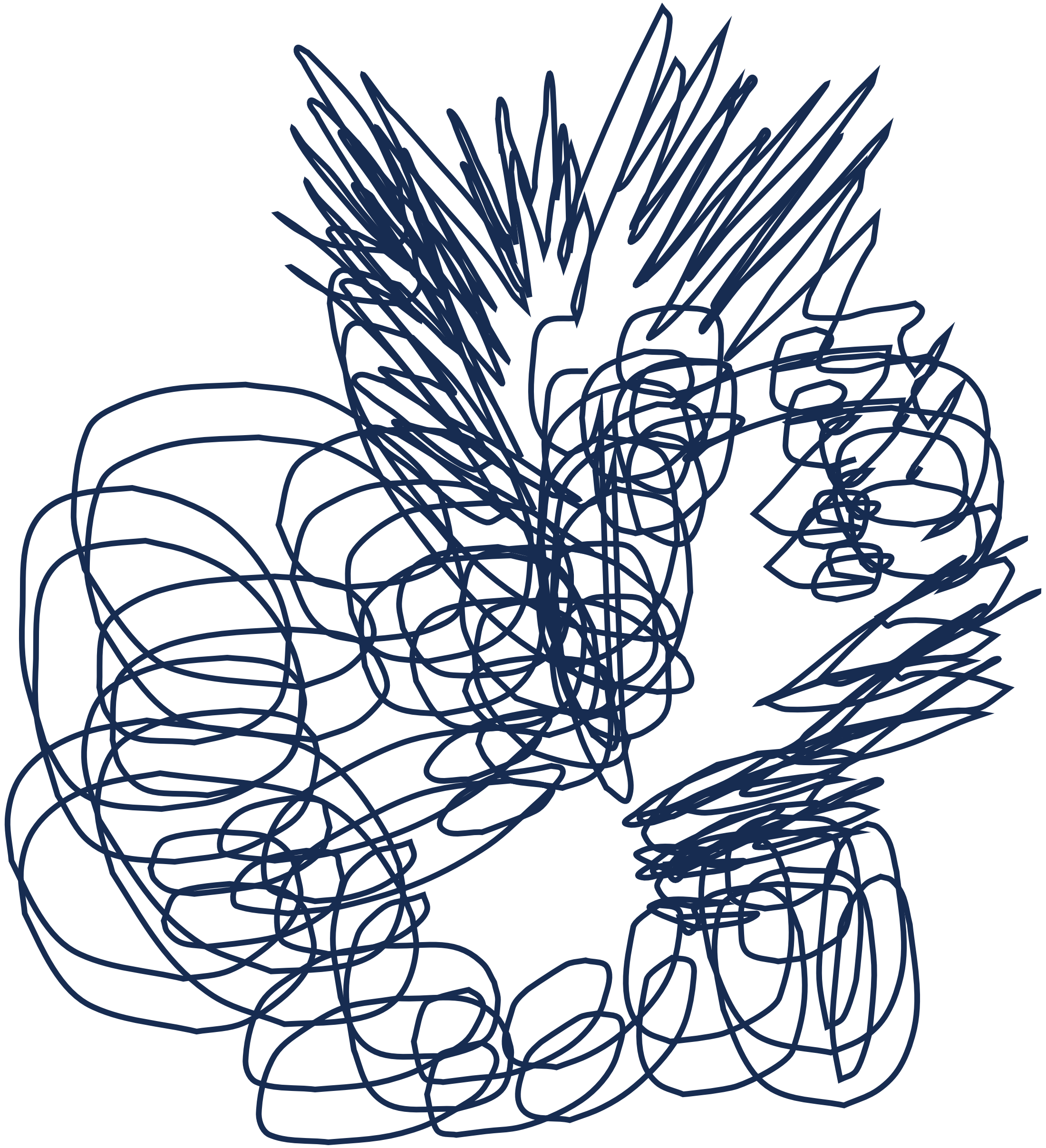
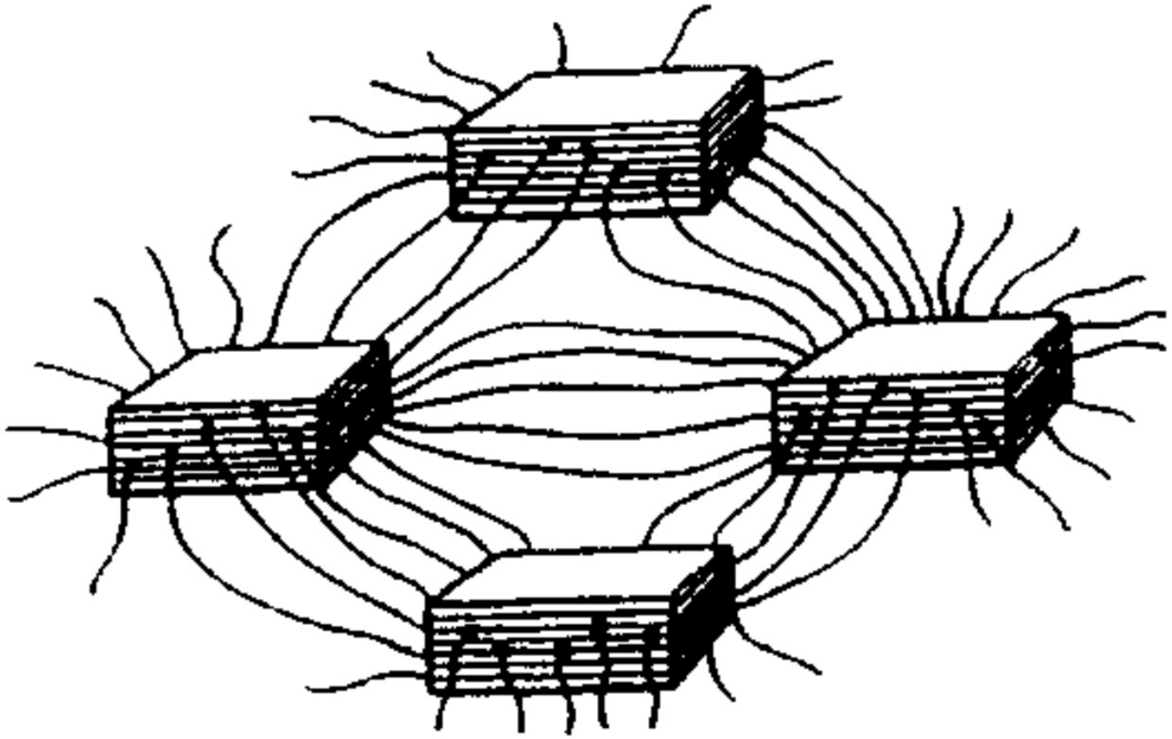
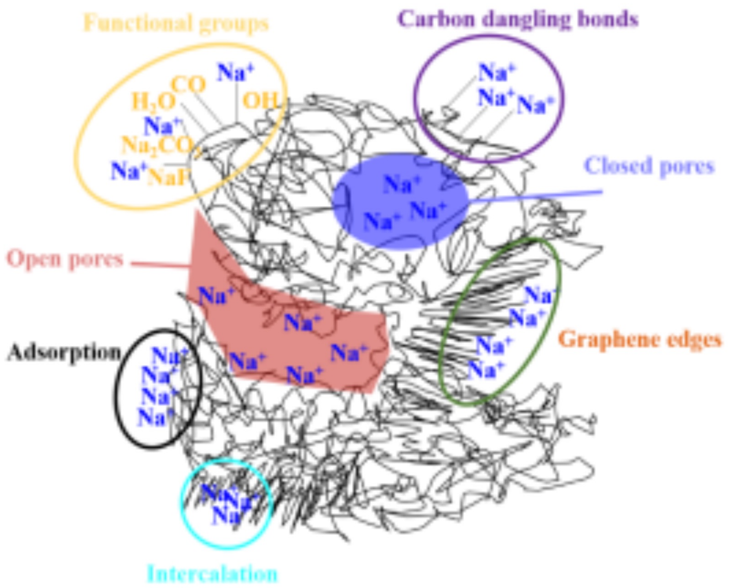
November 10th, 2023



70 years…!?



Pachechno-bahromchataya model
Kasatochkin group
1950



Not a model
FARADION group
2022

Rosalind Franklin's work on coal, carbon, and graphite

TABLE 1. VALUES OF THE NUMBER OF LAYERS PER PARALLEL GROUP (M) AND THE LAYER DIAMETER (L) FOR NON-GRAPHITIZING AND GRAPHITIZING CARBONS HEATED TO DIFFERENT TEMPERATURES (T)

substance	T (°C)
	non-graphitizing carbons
polyvinylidenechloride (commercial product 'Saran')	1000
	2000
	2140 (2 hr.)
	2160
	2700
	3000
sugar charcoal	1000
	2160
hexachlorobenzene	1000
coal, 82·4 % carbon (Northumberland)	2160
	3000
coal, 83·1 % carbon (Yorkshire)	2850
	graphitizing carbons
polyvinylchloride	1000 (2 hr.)
	1000 (13 hr.)
	1220
	1480
	1720
petroleum coke	1000
	1220
	1480
	1720
pitch coke	1220
	1480
Welsh coking coal	1460

Franklin, R. E. (1951). Crystallite growth in graphitizing and non-graphitizing carbons. Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences, 209(1097), 196-218.

The first representation of carbon's microstructure

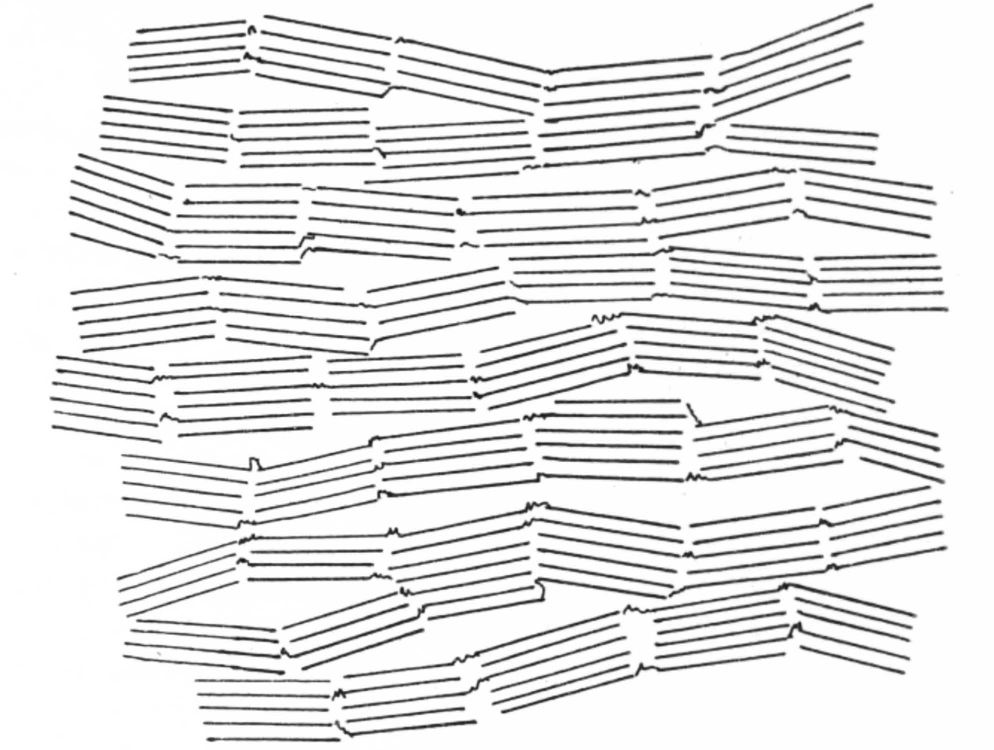


FIGURE 7. Schematic representation of the structure of a graphitizing (but non-graphitic) carbon.

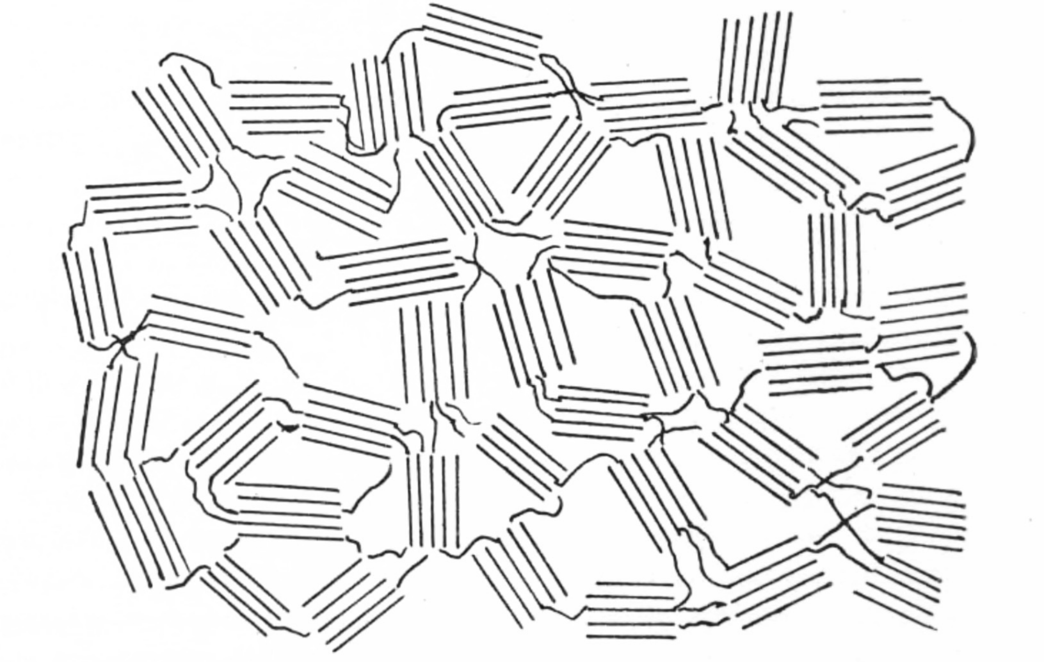
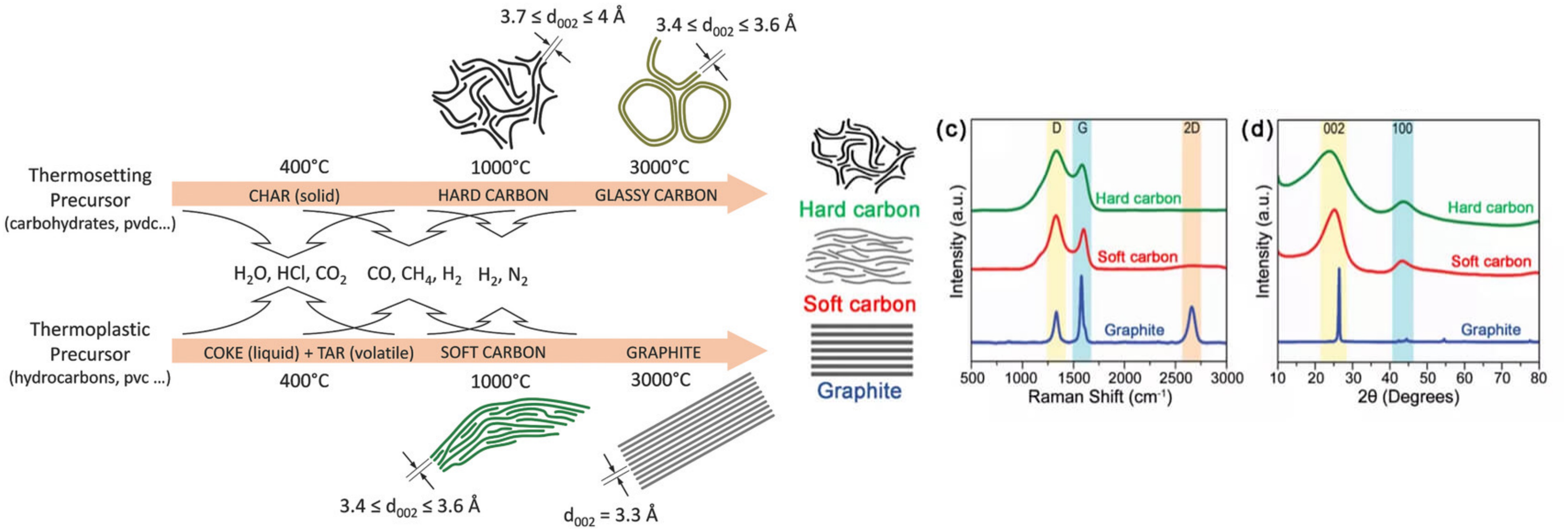


FIGURE 8. Schematic representation of the structure of a non-graphitizing carbon.

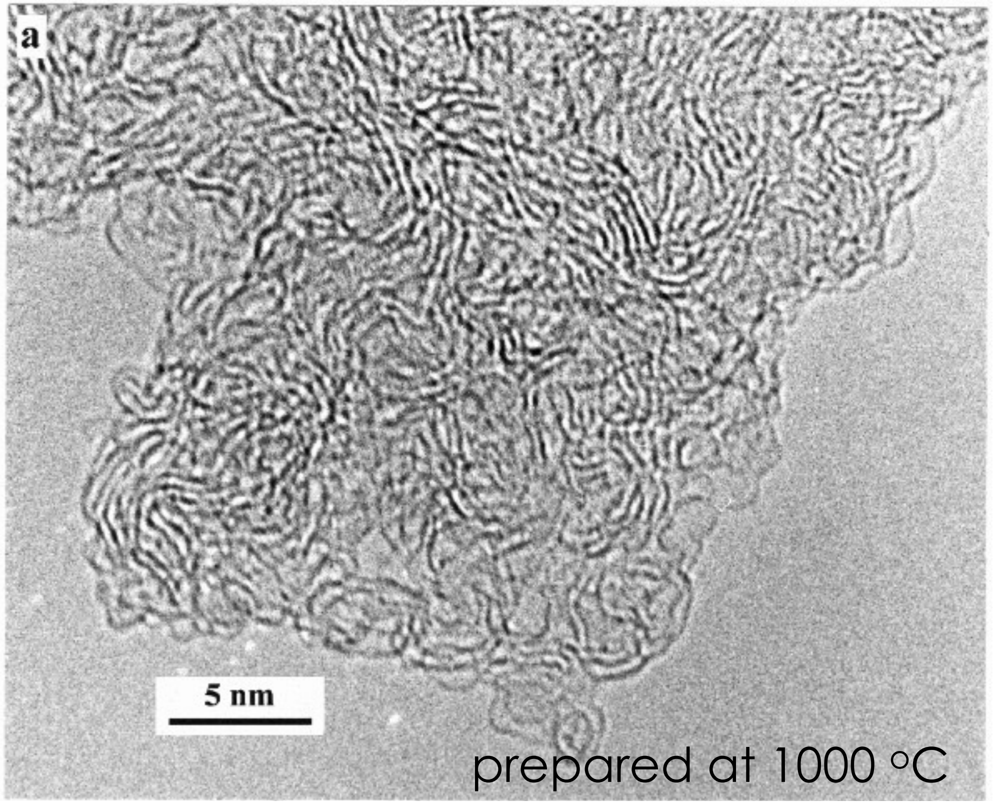
Franklin, R. E. (1951). Crystallite growth in graphitizing and non-graphitizing carbons. Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences, 209(1097), 196-218.

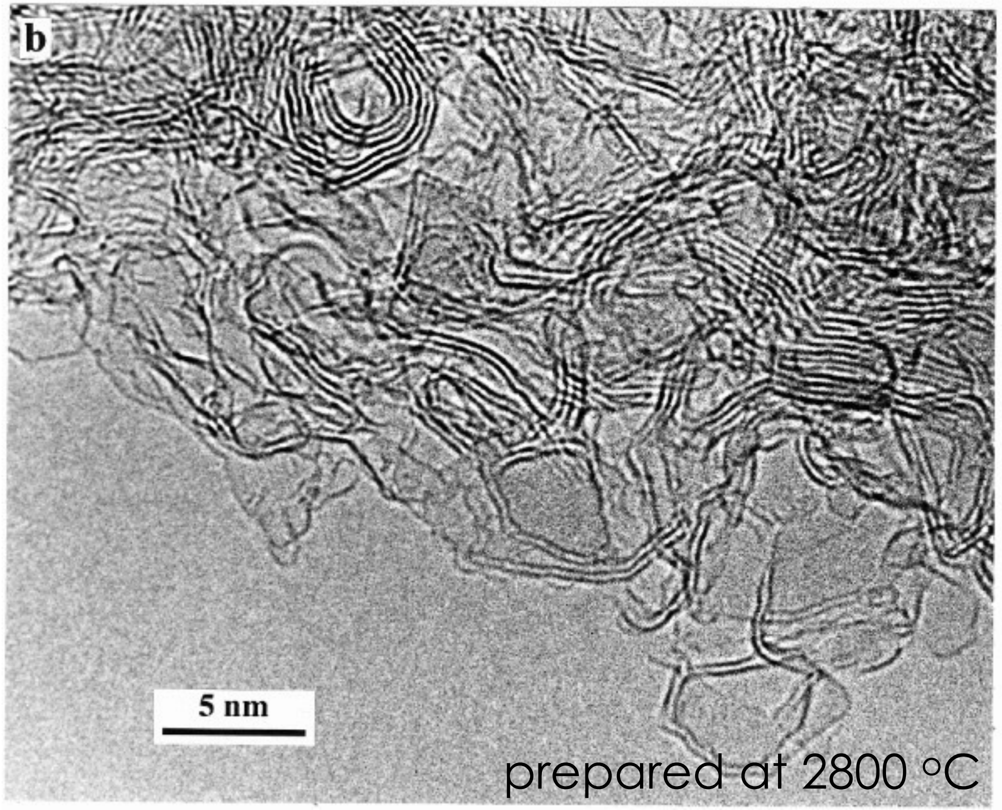
The pyrolysis of thermosetting and thermoplastic organic precursors



Saurel, D. (2018). *Advanced Energy Materials*, *8*(17), 1703268.

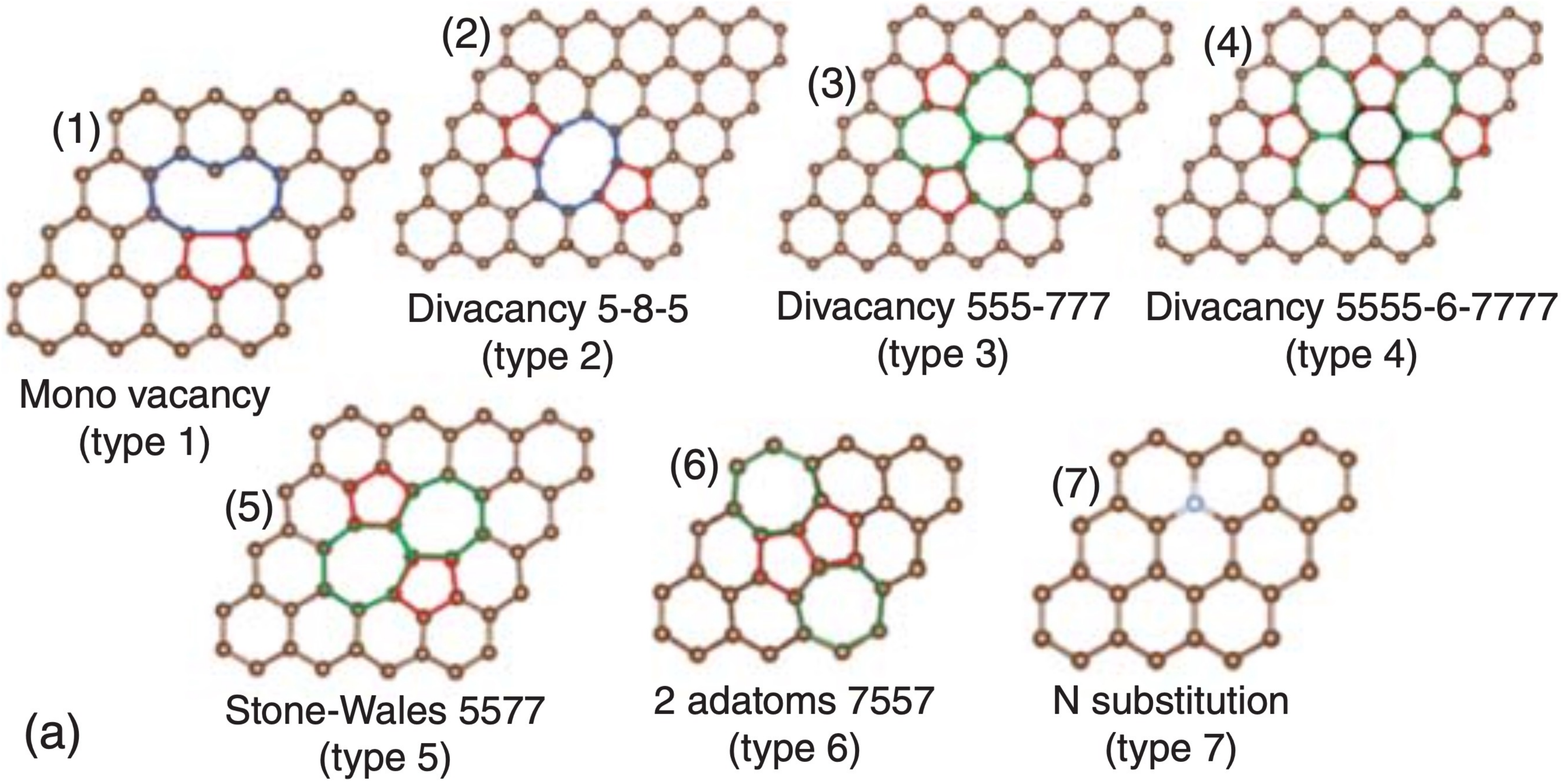
TEM images of ‘low-temperature’ and ‘high-temperature’ glassy carbons





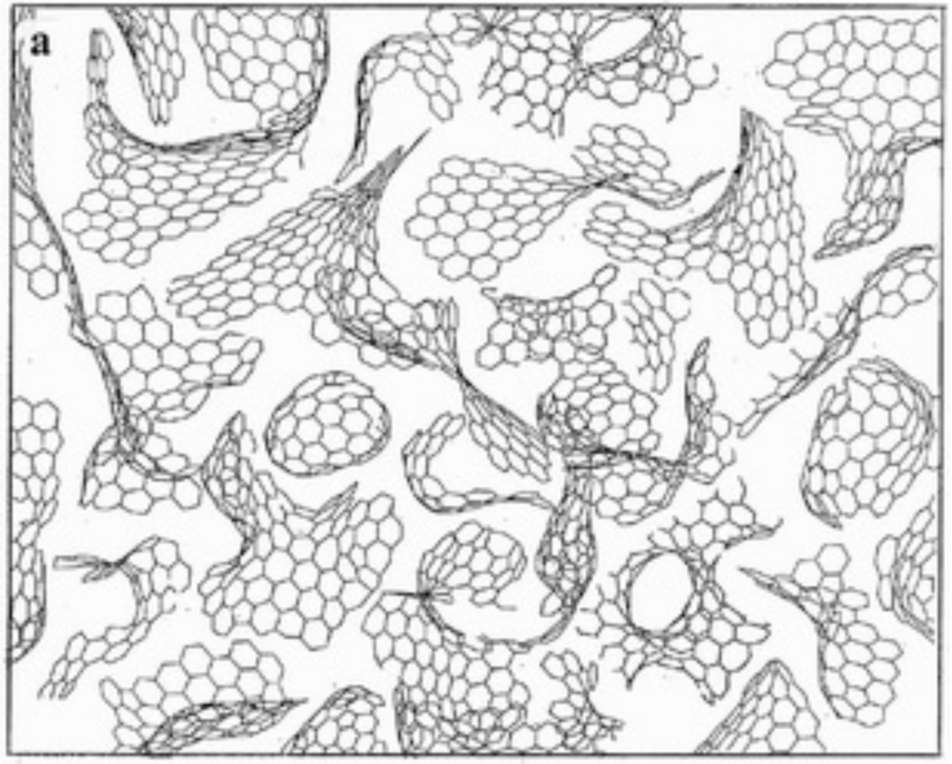
Harris, P. J. F. (2004). Fullerene-related structure of commercial glassy carbons. *Philosophical Magazine*, *84*(29), 3159-3167.

Where are the defects that create curvature?

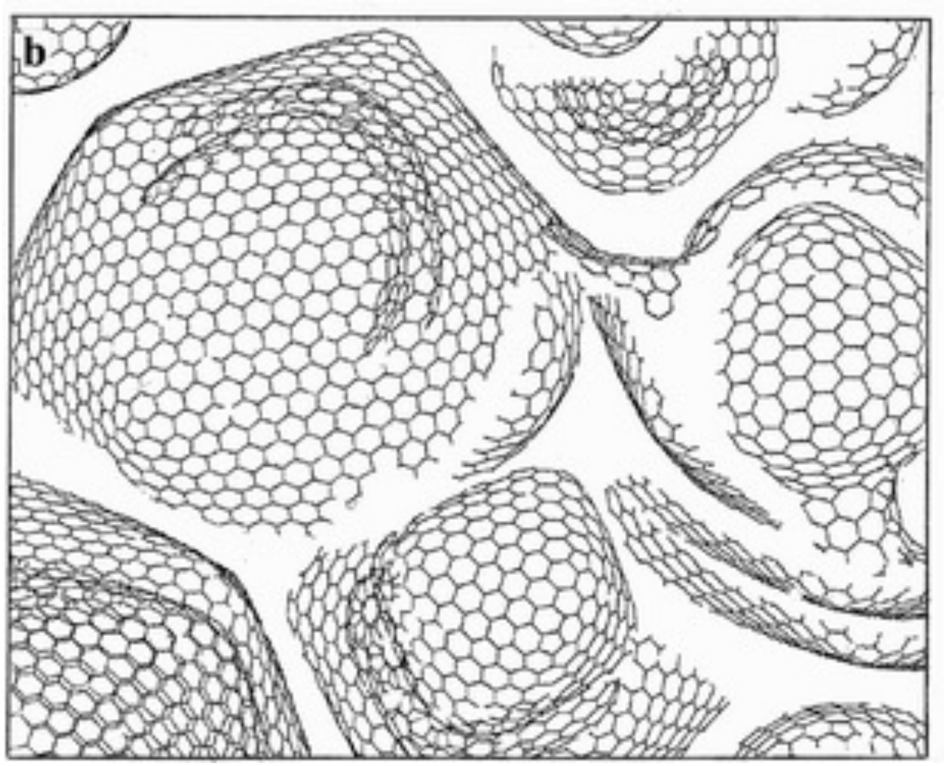


Xie, F. (2022). Hard Carbon Anodes for Na-Ion Batteries. Sodium-Ion Batteries: Materials, Characterization, and Technology, 1, 27-59.

We need pentagons and heptagons!



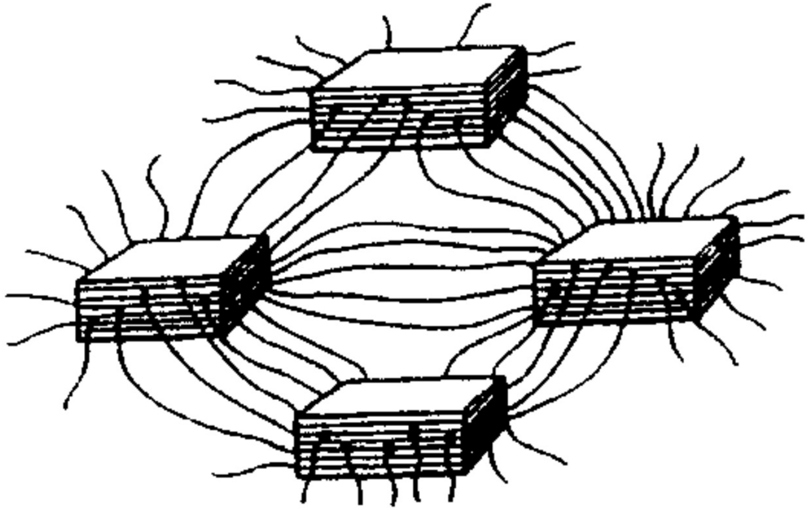
prepared at 1000 $^{\circ}$C



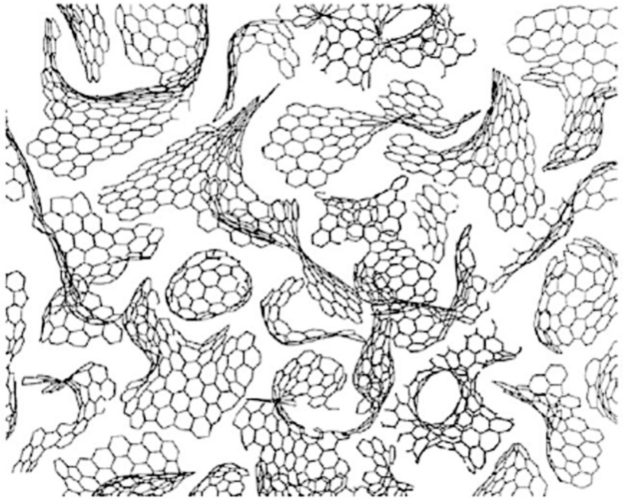
prepared at 2800 $^{\circ}$C

Harris, P. J. F. (2004). Fullerene-related structure of commercial glassy carbons. *Philosophical Magazine*, *84*(29), 3159-3167.

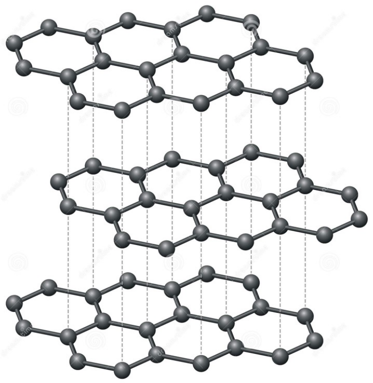
From the 1950s to the 2000s



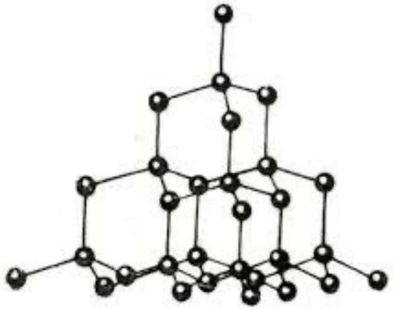
Franklin model
Kasatochkin model



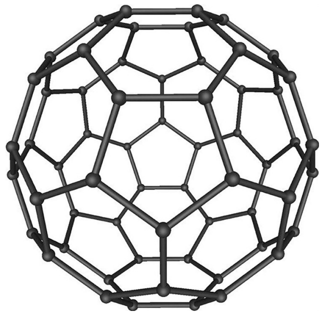
Harris model



Graphite

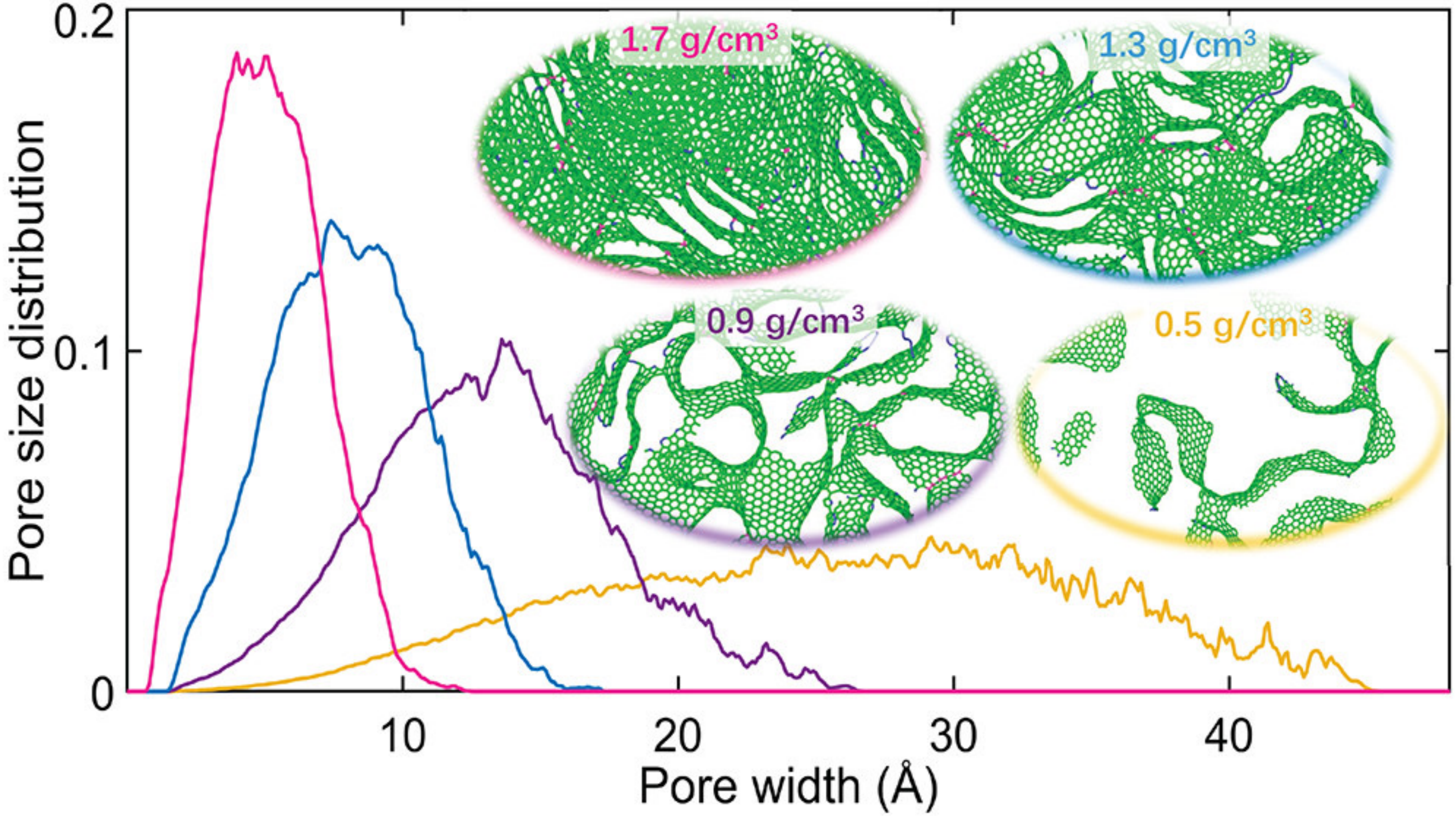


Diamond



Fullerene

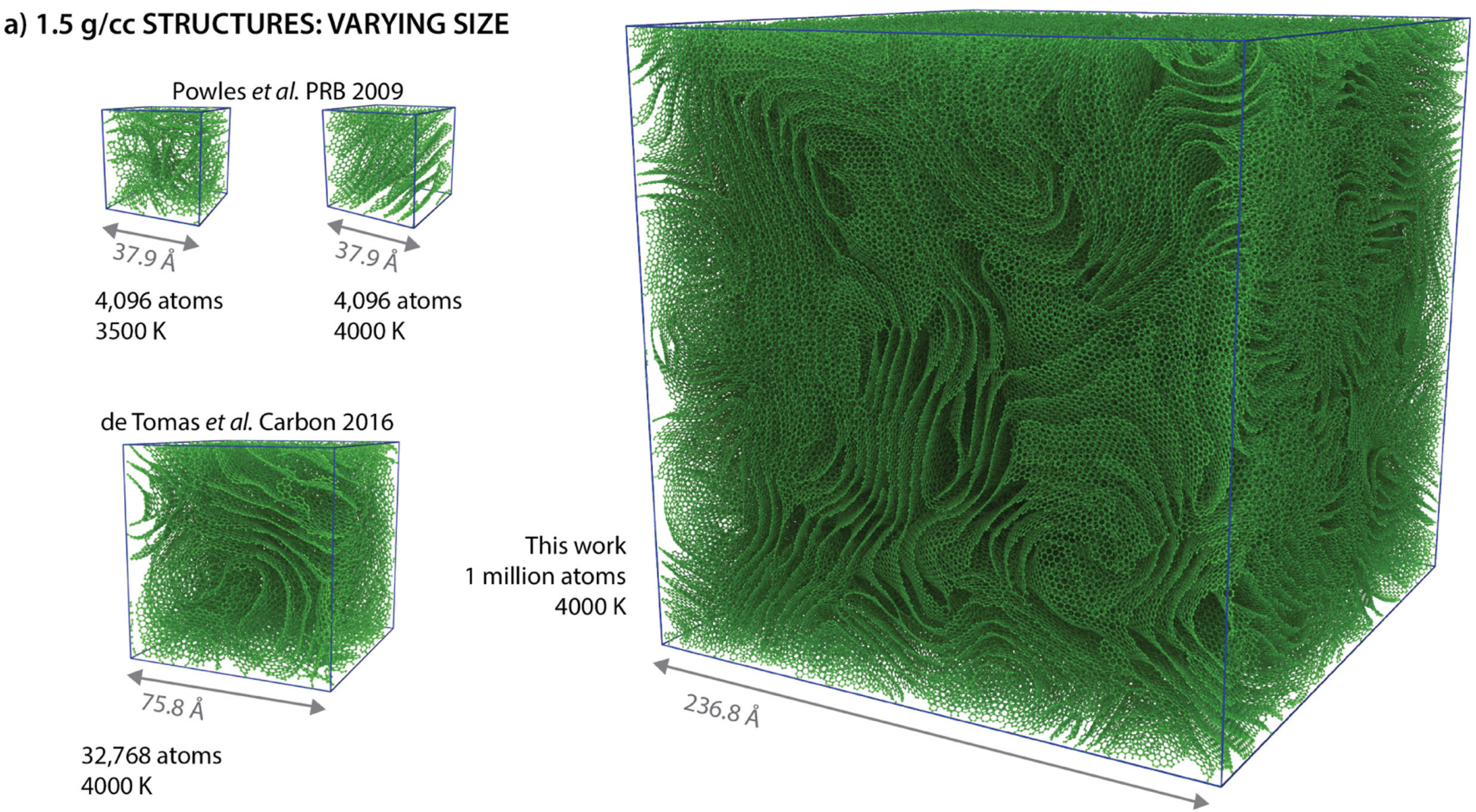
Current state



Extensive atomistic ML driven MD simulations

Wang, Y., Fan, Z., Qian, P., Ala-Nissila, T., & Caro, M. A. (2022). Structure and pore size distribution in nanoporous carbon. *Chemistry of Materials*, *34*(2), 617-628.

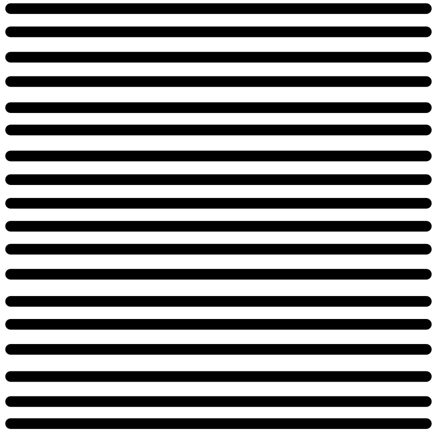
Let's take 1,000,000 atoms



Putman, K. J. (2023) *Carbon*, *209*, 117965.

“How to make disorder carbon” the recipe

graphite

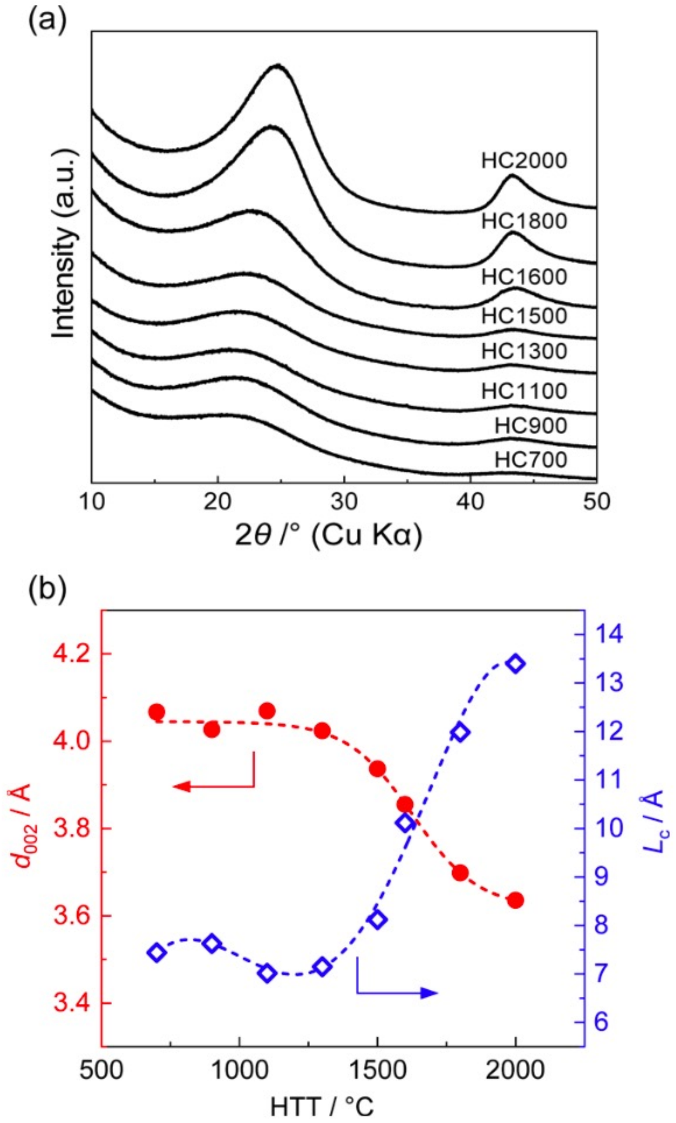


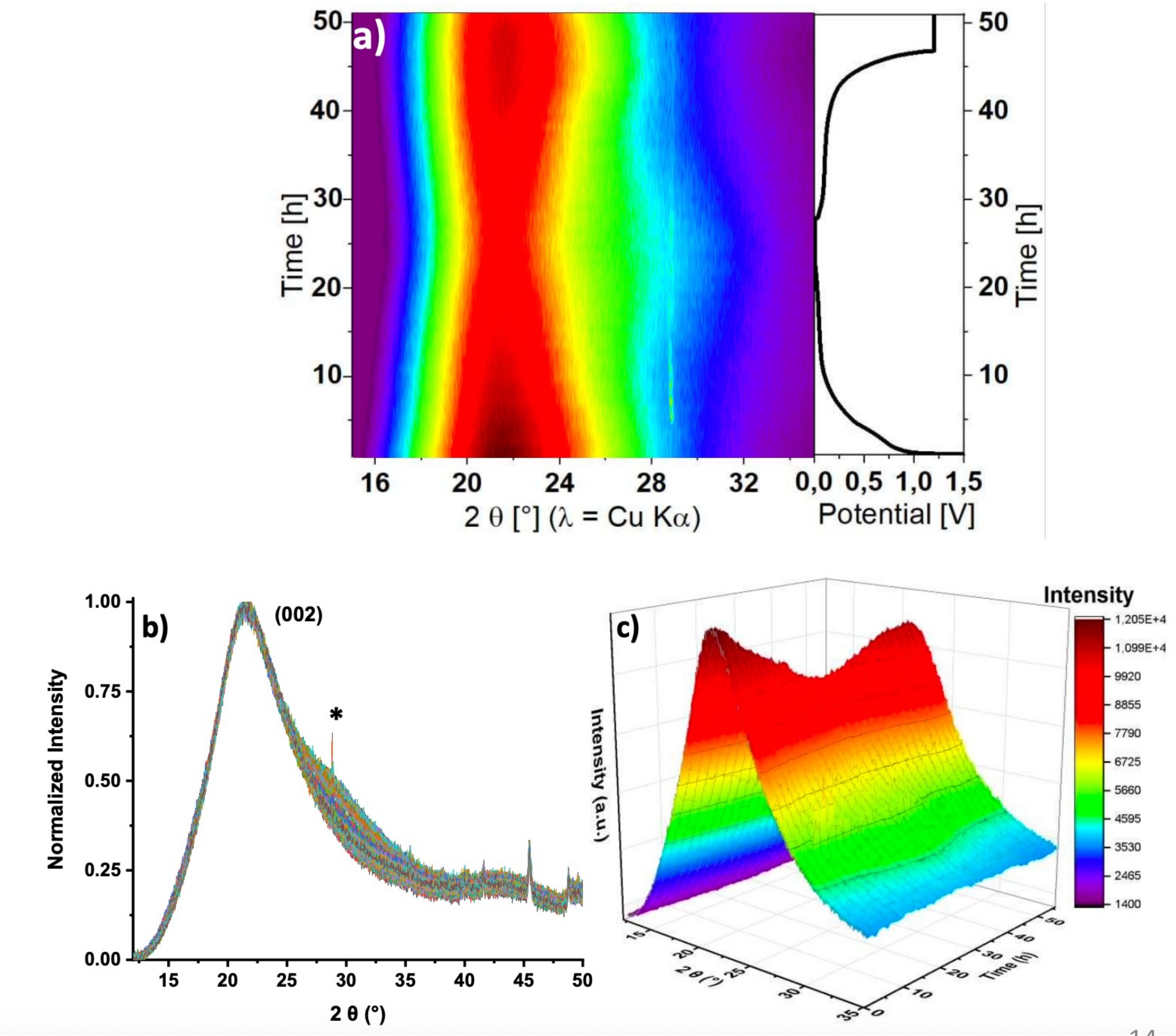
hard carbon

Thermosetting precursors
High temperature pyrolysis (> 1000 °C, inert atmosphere)

Curved graphene-like layers (pentagons and heptagons)
Short graphite-like domains (sp^3-bonded carbons)
Heteroatoms
Defects
Pores

Method 1. Powder X-Ray Diffraction (PXRD)

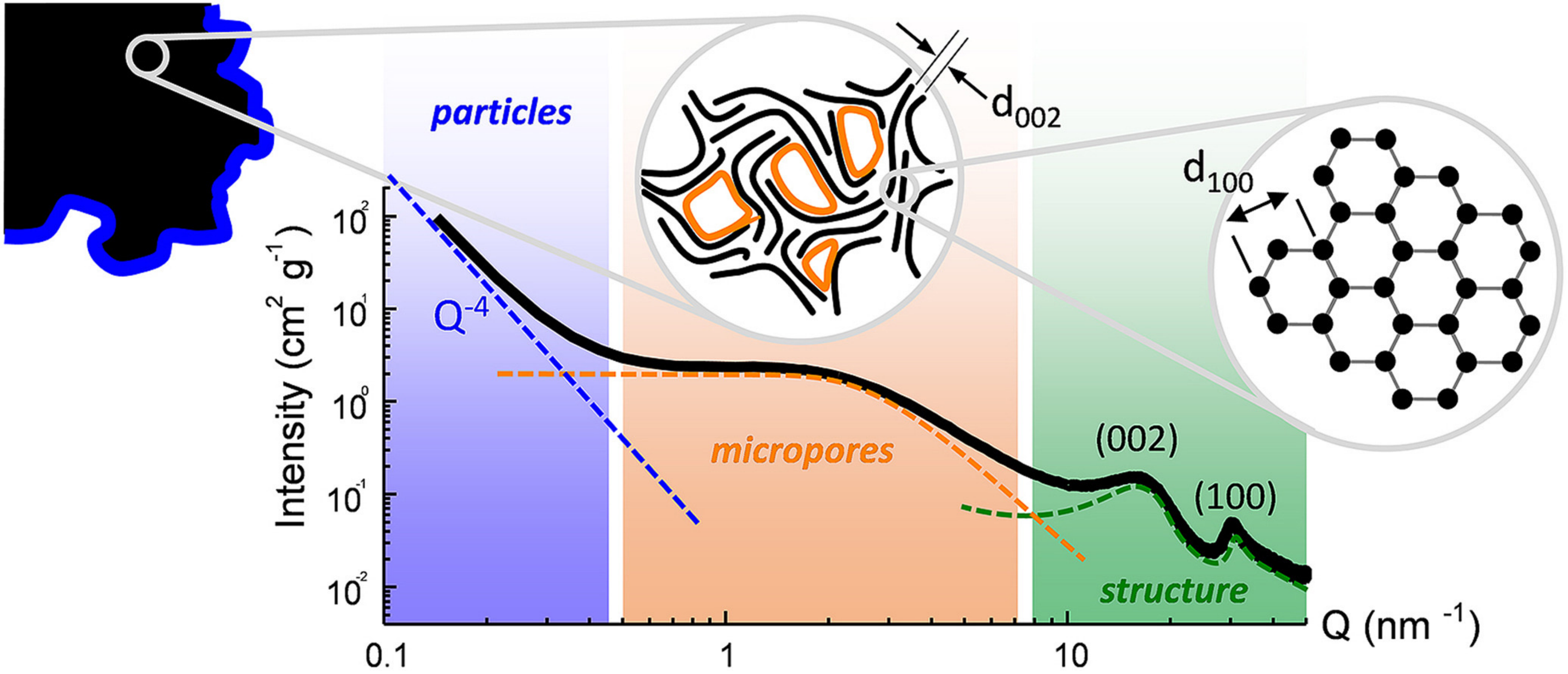




Kubota, K *Chemistry of Materials*, 32(7), 2961-2977.

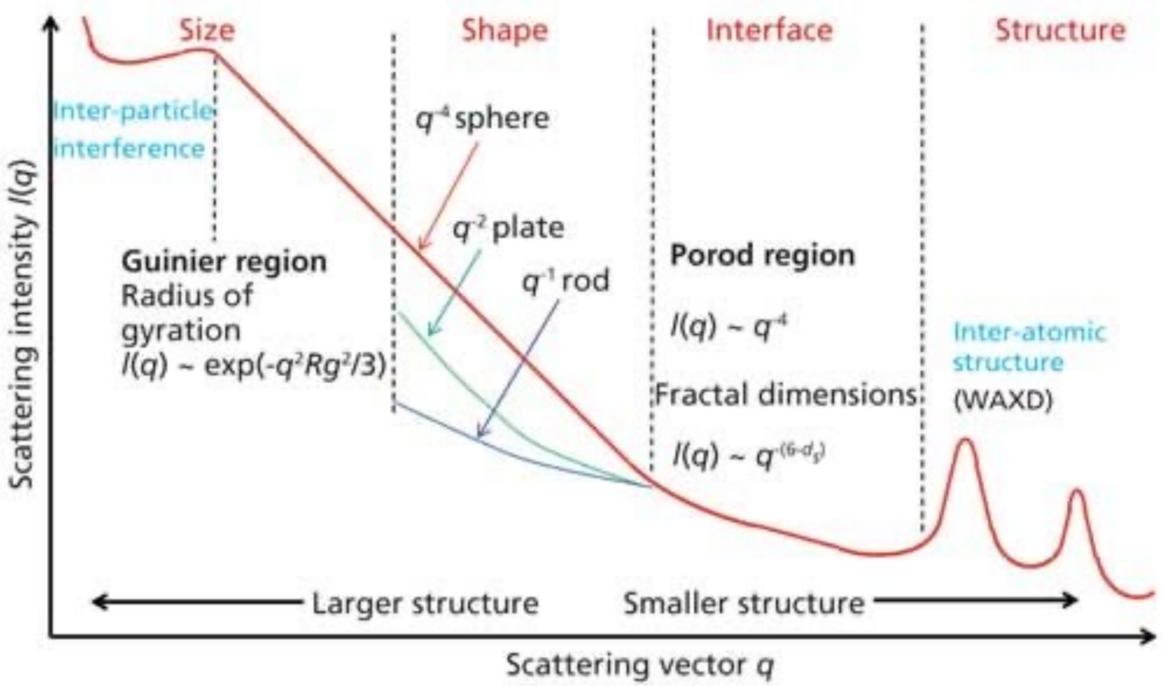
Beda, A. *Journal of Materials Chemistry A*, 8(11), 5558-5571.

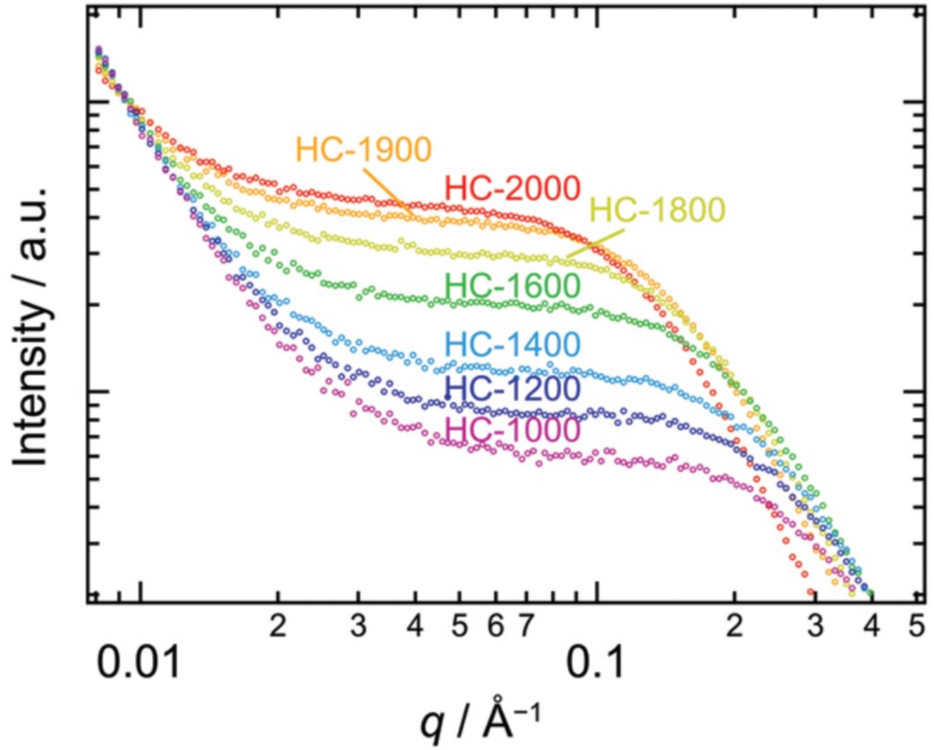
Method 2. Small Angle X-ray Scattering (SAXS)



Saurel, D., Segalini, J., Jauregui, M., Pendashteh, A., Daffos, B., Simon, P., & Casas-Cabanas, M. (2019). A SAXS outlook on disordered carbonaceous materials for electrochemical energy storage. *Energy Storage Materials*, *21*, 162-173.

Method 2. The fitting of SAXS curves

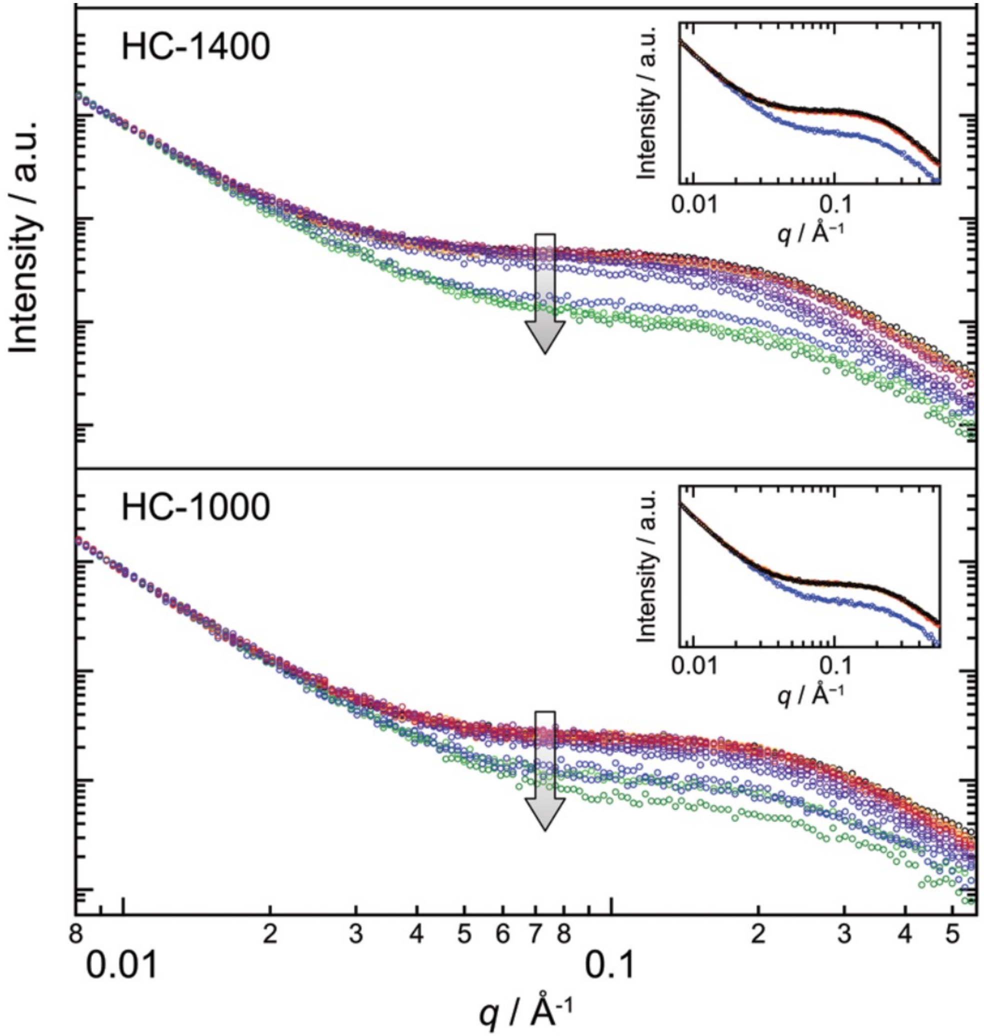


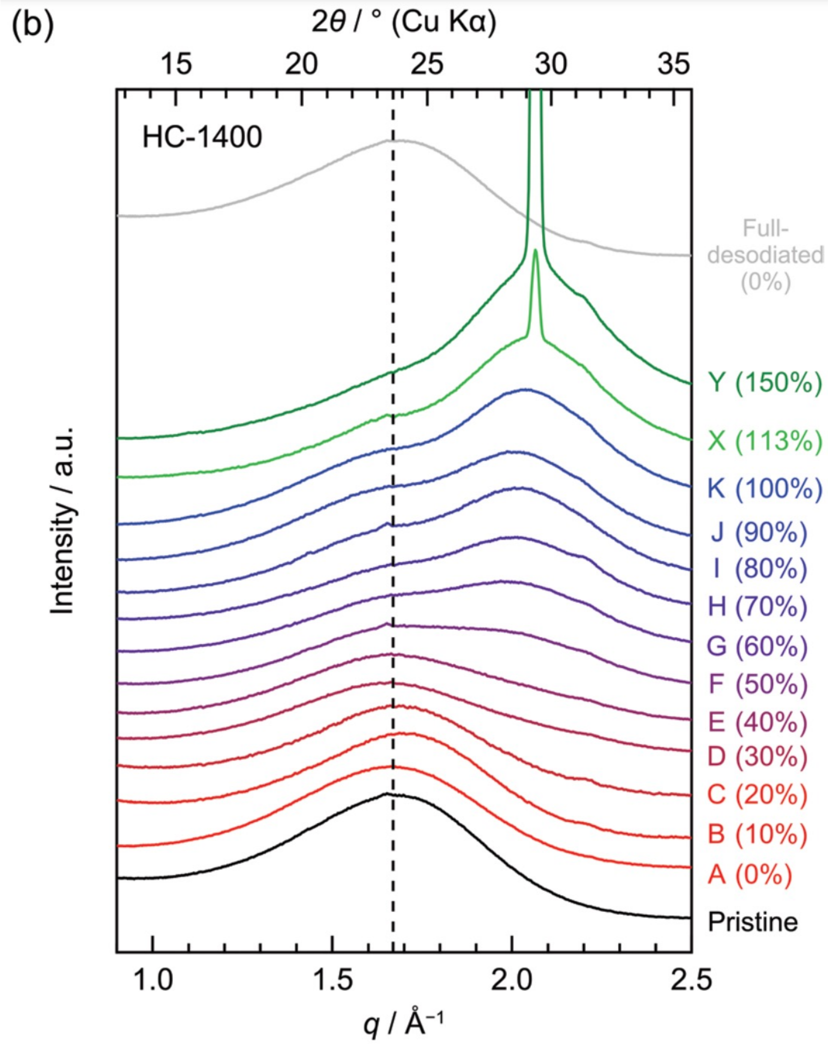


https://www.spectroscopyonline.com/view/recent-developments-small-angle-x-ray-scattering

Kubota, K *Chemistry of Materials*, *32*(7), 2961-2977.

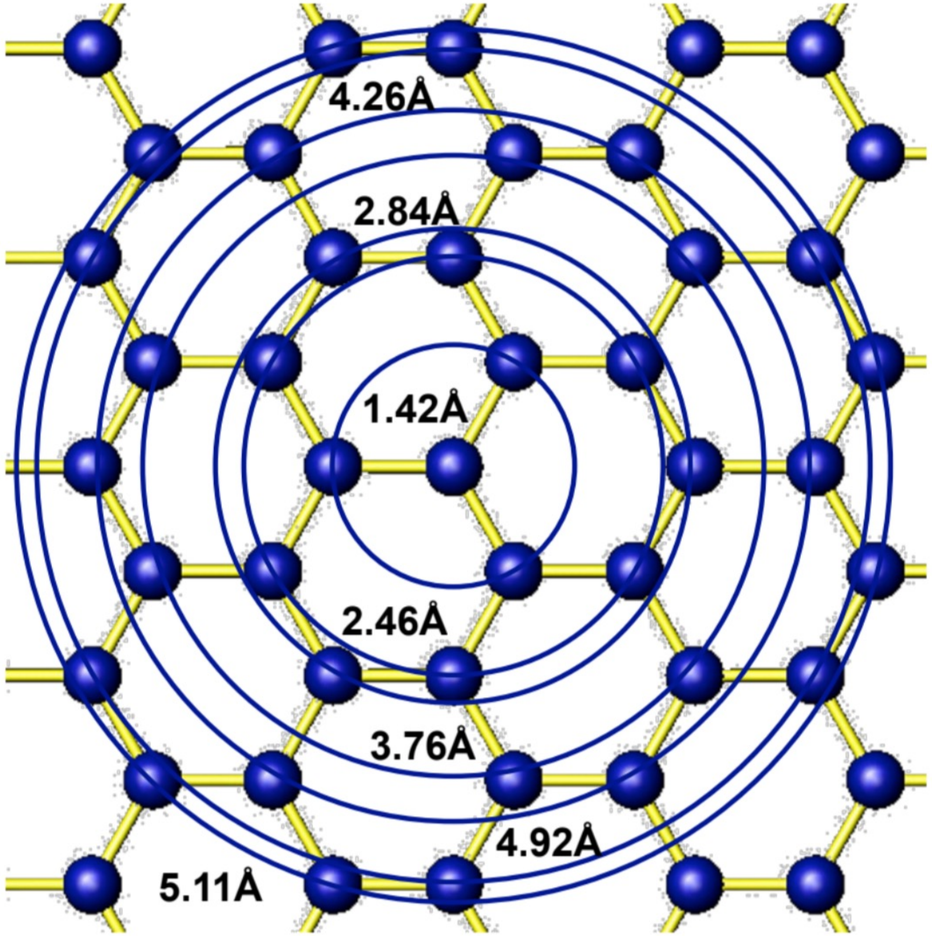
Method 2. The pores filling was revealed by ex *situ* SAXS



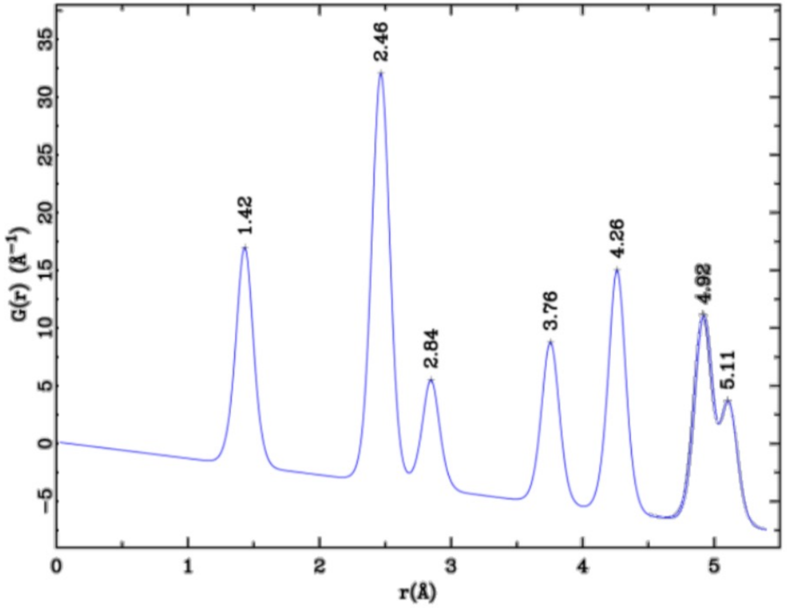


Morikawa, Y. *Advanced Energy Materials*, *10*(3), 1903176.

Method 3. Pair distribution function (PDF)



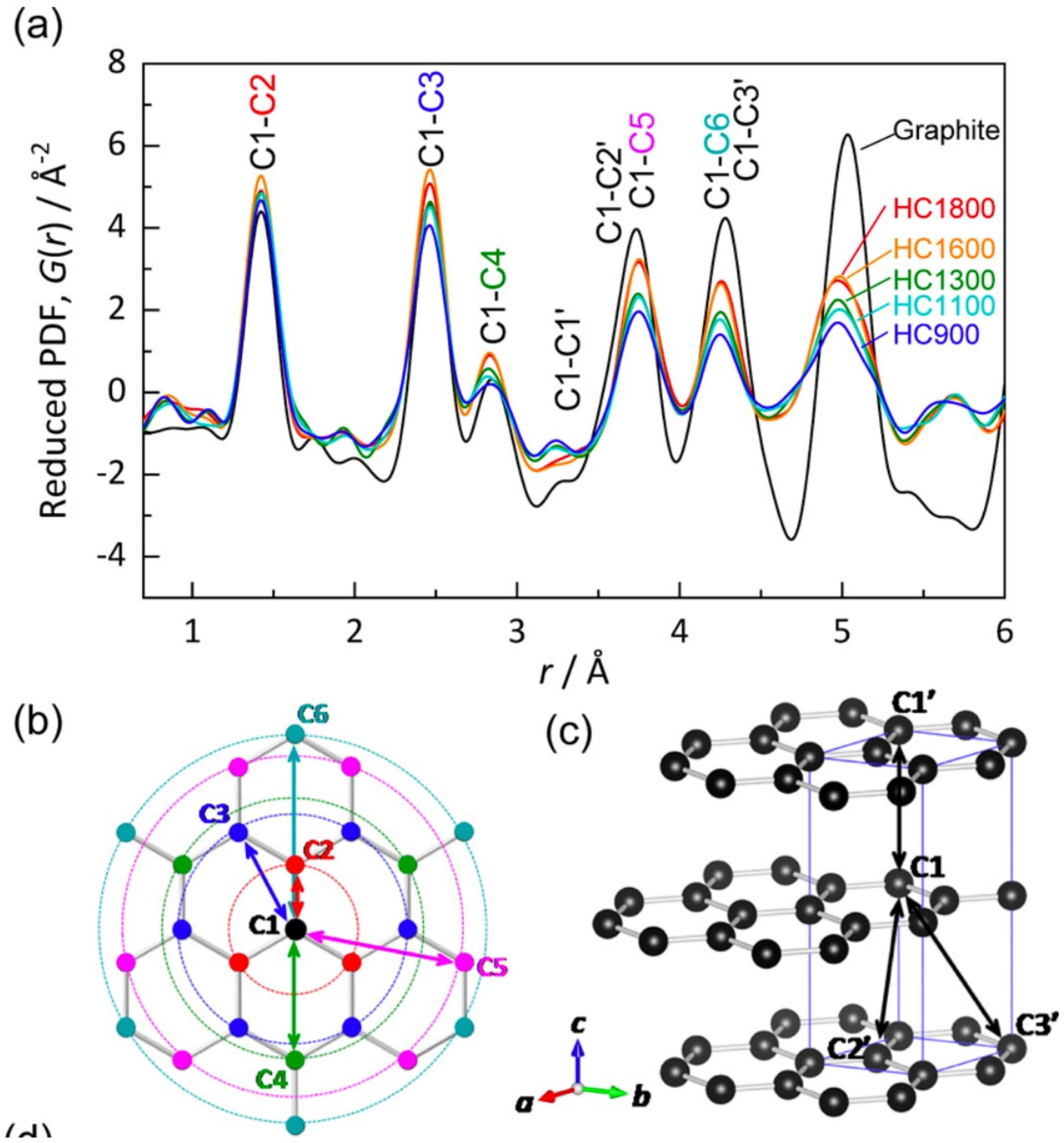
Pair distribution function (PDF) gives the probability of finding an atom at a distance "r" from a given atom.



Thomas Proffen: "Total Scattering. The Key to Understanding disordered, nano-crystalline and amorphous materials"
Tutorial 9th Canadian Powder Diffraction Workshop

Elena Willinger: "Analysis of Local Structure by Atomic Pair Distribution Function"
Lecture series: Modern Methods in Heterogeneous Catalysis Research

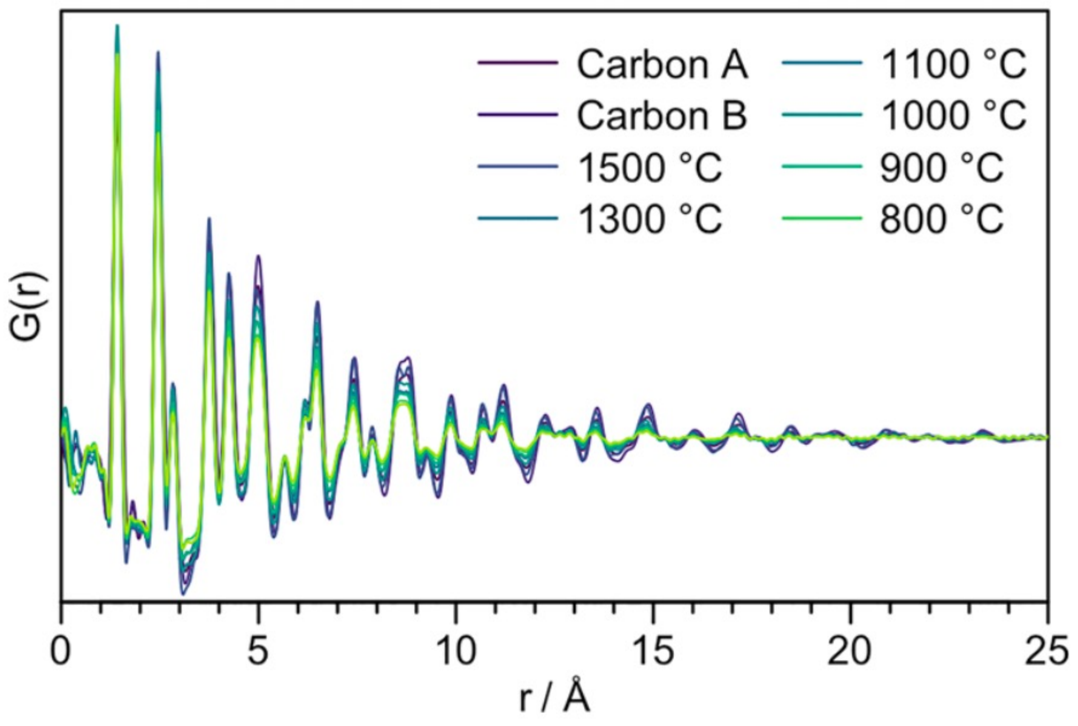
Method 3. PDF for hard carbons

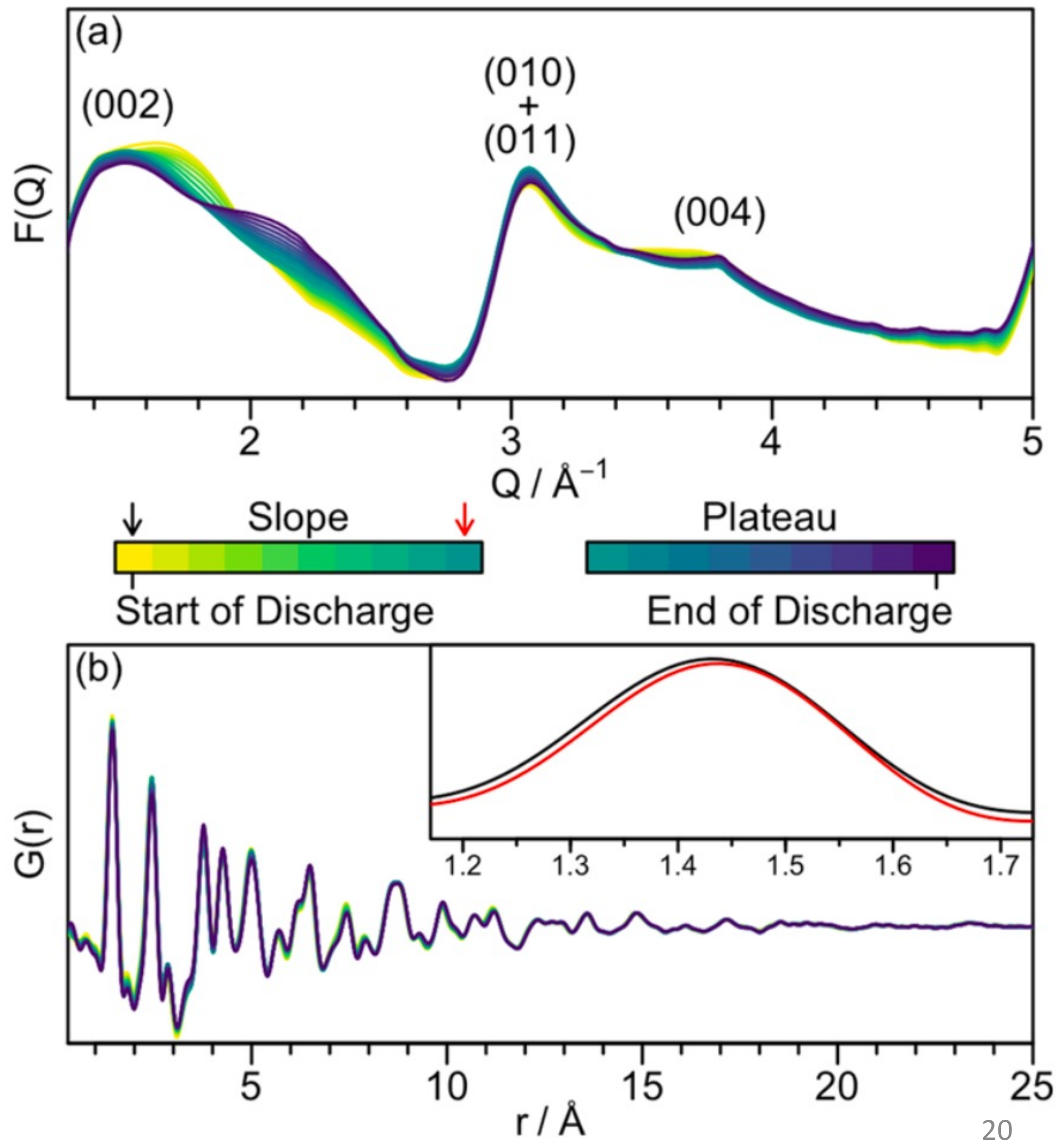


sample	interlayer distance (Å)	density (g cm^{-3})
HC900	4.02(17)	1.92(6)
HC1100	4.02(14)	1.92(5)
HC1300	3.97(13)	1.94(5)
HC1600	3.85(10)	2.00(4)
HC1800	3.75(10)	2.05(4)
graphite	3.349(2)	2.2699(12)

Kubota, K *Chemistry of Materials*, *32*(7), 2961-2977.

Method 3. *Operando* PDF





Stratford, J. M. *Journal of the American Chemical Society*, *143*(35), 14274-14286.

Thx!