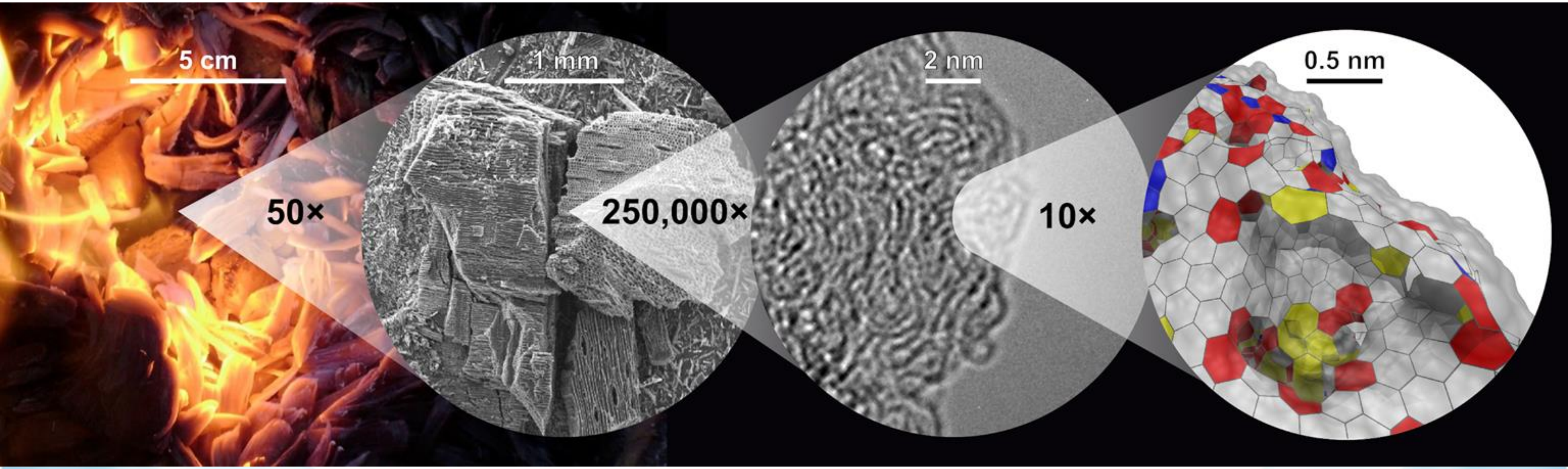
Understanding the lack of fullerenes in fullerene-like carbons



15th Jul 2019 Carbon Conference

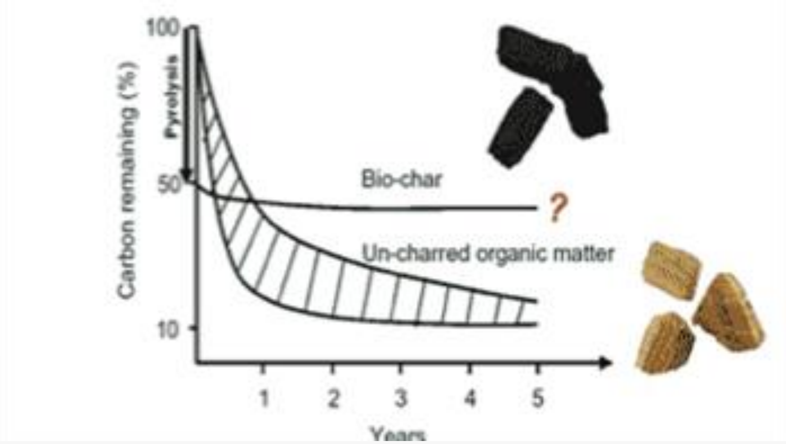
Jacob W. Martin[1], Leonard Nyadong[2], Caterina Ducati[1], Merilyn Manley-Harris[3], Alan Marshall[2], Markus Kraft[1].

[1]University of Cambridge, [2]Florida State University, [3]University of Waikato

Applications

CARBON SEQUESTRATION - BIOCHAR

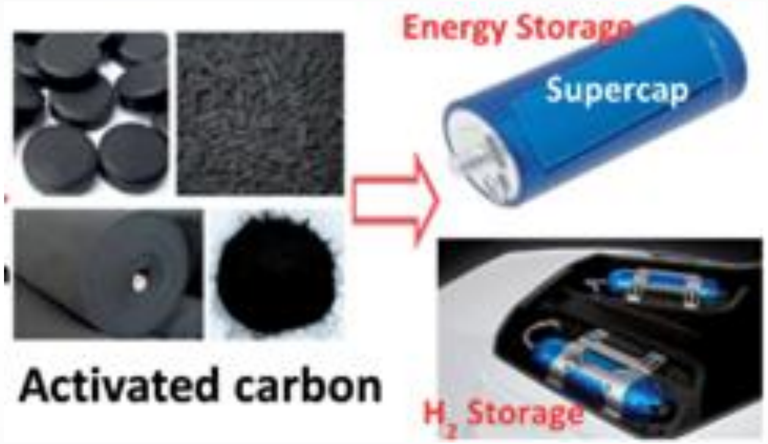
- Why does biochar have such a long life?
- How do we optimise biochar for longevity?
- How does biochar break down?
- How does biochar interact with soil chemistry?
- How do heteroatoms become integrated?



Lehmann et al. 2006, Mitigation and Adaption Strategies for Global Change 11, 403-427

MATERIAL APPLICATIONS

- Sodium-ion batteries (hard/soft carbon electrodes)
- Engineering pores for adsorbents
- Supercapacitors
- Hydrogen storage

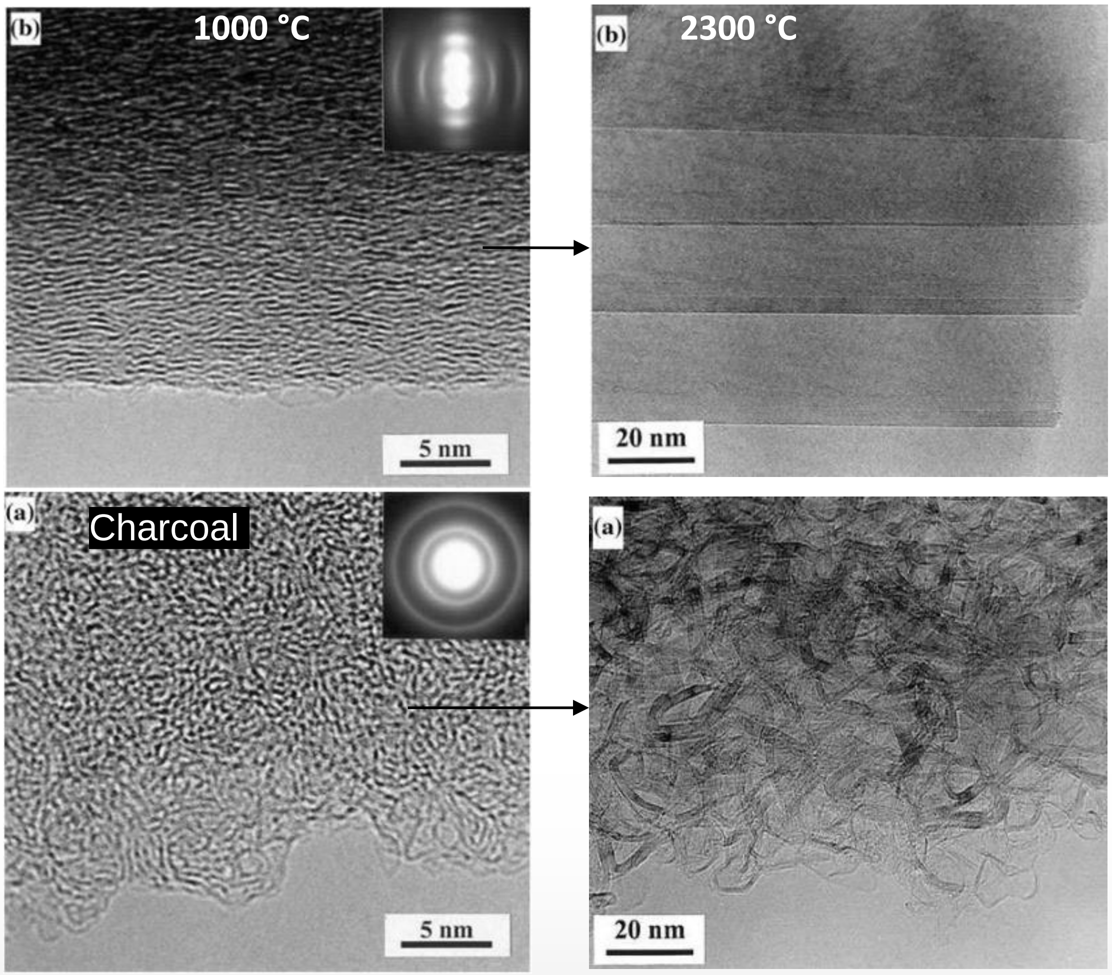


Sevilla, Marta, and Robert Mokaya. "Energy storage applications of activated carbons: supercapacitors and hydrogen storage." Energy & Environmental Science 7.4 (2014): 1250-1280.

Fullerene-like or non-graphitising

anthracene

sucrose



Graphite

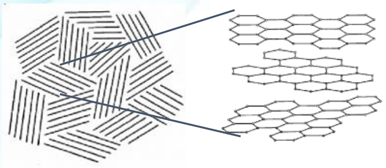
Glassy carbon

Harris, P. J. F. Int. Mater. Rev. Structure of non-graphitising carbons, 1997, 42 (5), 206–218.

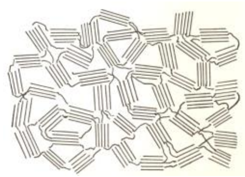
Timeline

Ribbon-like

Fullerene-like

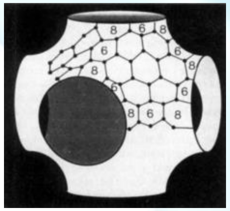


Microcrystalline model
Biscoe and Warren 1942

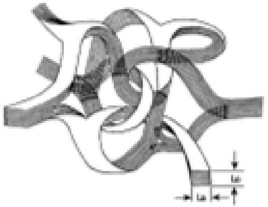


Crosslinked microcrystallite model
Franklin 1951

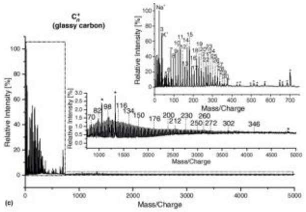
C_{60} discovered
Kroto et al. 1985



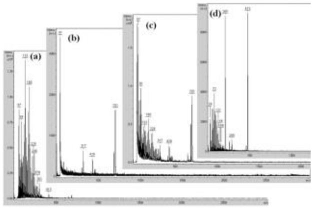
Schwarzite proposed
Mackay and Terrones 1991



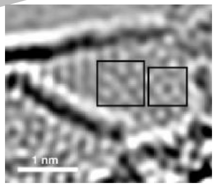
Ribbon model
Jenkins and Kawamura 1971



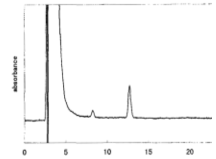
No C_{60} in glassy carbon
Sedo et al. 2006



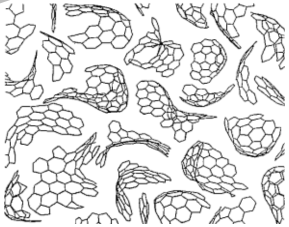
No C_{60} in many charcoals
Bourke et al. 2007



Pentagon imaged
Harris et al. 2008

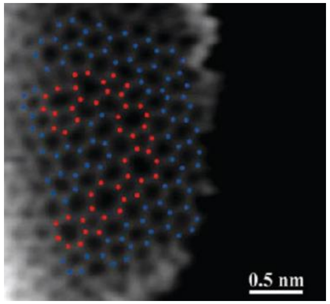


C_{60} in some charcoal
Shibuya 1999

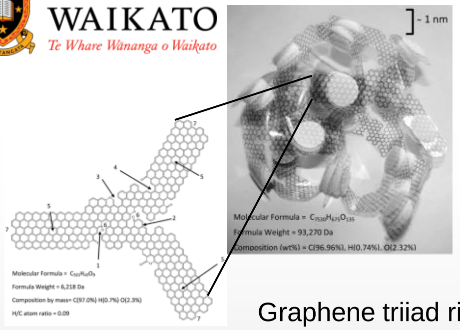


Fullerene-like model
Harris and Tsang 1997

C_{60} extracted from soot
Heymann et al. 1994

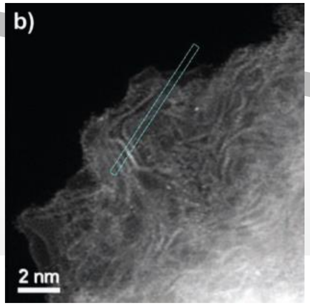


Line dislocation imaged
Guo et al 2012



Graphene triiad ribbon model
McDonald-Wharrey et al. 2015

Where are the C_{60}?
Should we expect to see C_{60}?



Ribbon structures
Guo et al. 2012

THE UNIVERSITY OF WAIKATO
Te Whare Wānanga o Waikato

jwm50@cam.ac.uk

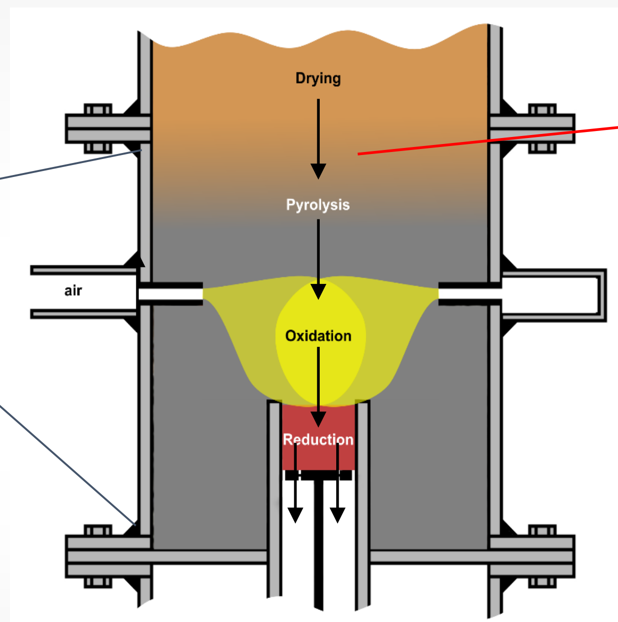
CoMo GROUP

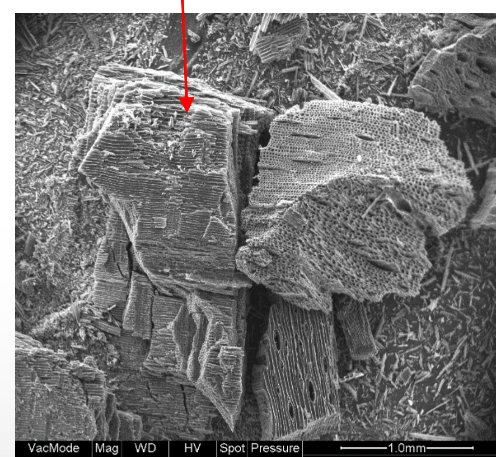
Jacob W. Martin

Where is C_{60} in fullerene-like carbons?

PREPARING SOOT- AND TAR-FREE CHARCOAL

Microlab downdraft gasifier from Fluidyne



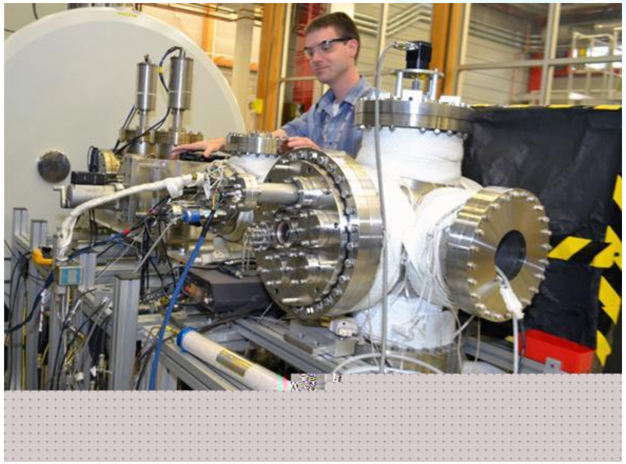


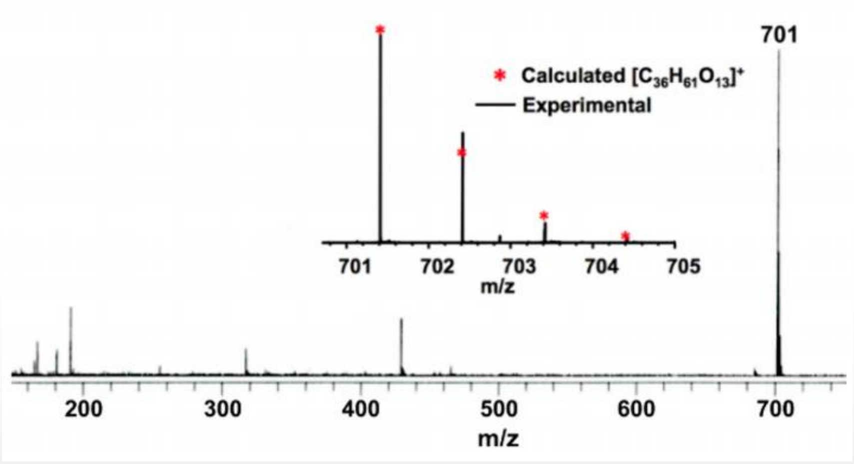
Where is C_{60} in fullerene-like carbons?

autoflex-II LDI-TOF
mass spectrometer

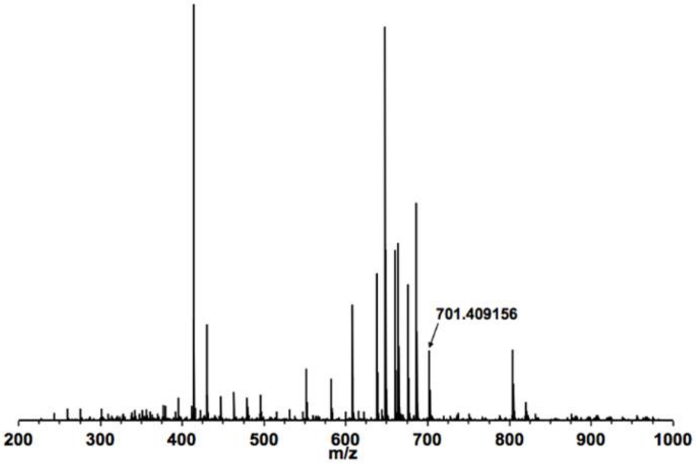
ultrafleXtreme
LDI-TOF

micrOTOF-Q II - ESI-Qq-TOF
mass spectrometer

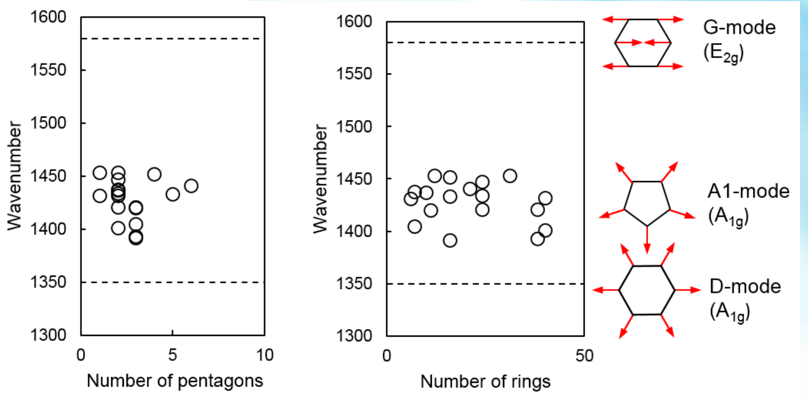




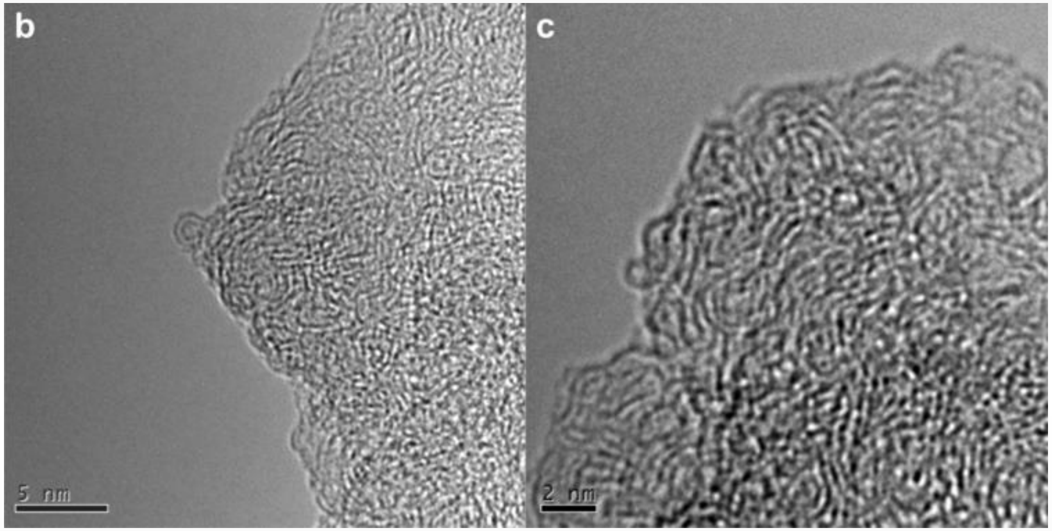
9.4 T FT-ICR-MS



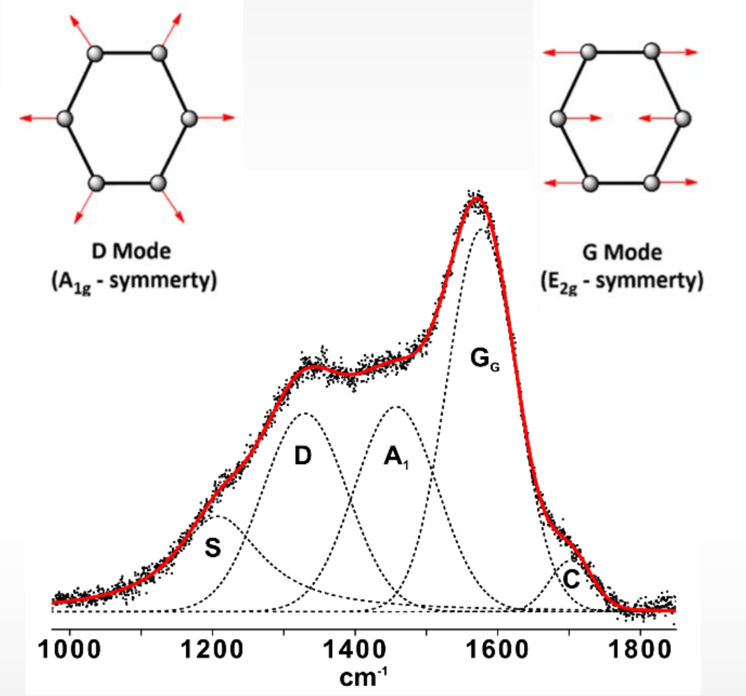
Appears fullerene-like



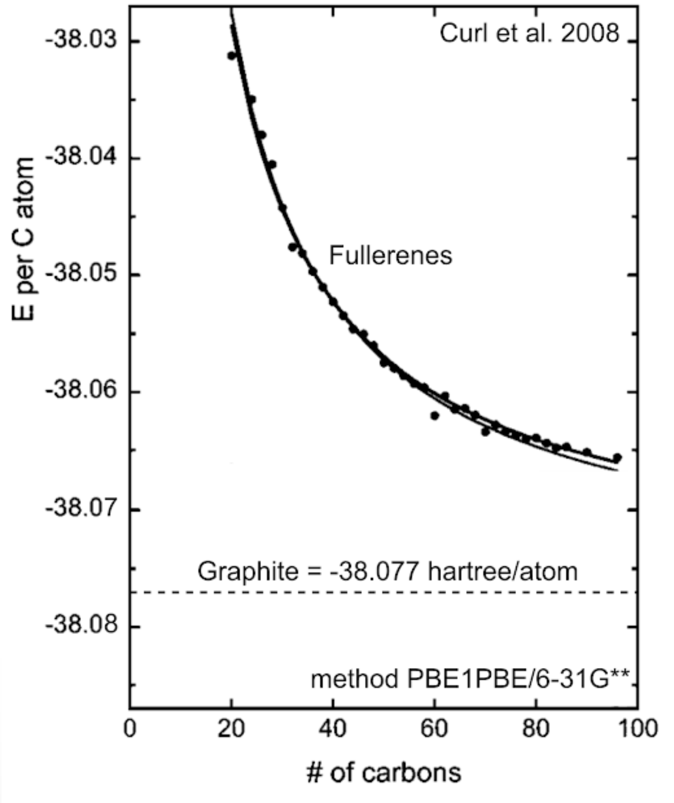
HRTEM and RAMAN SPECTROSCOPY

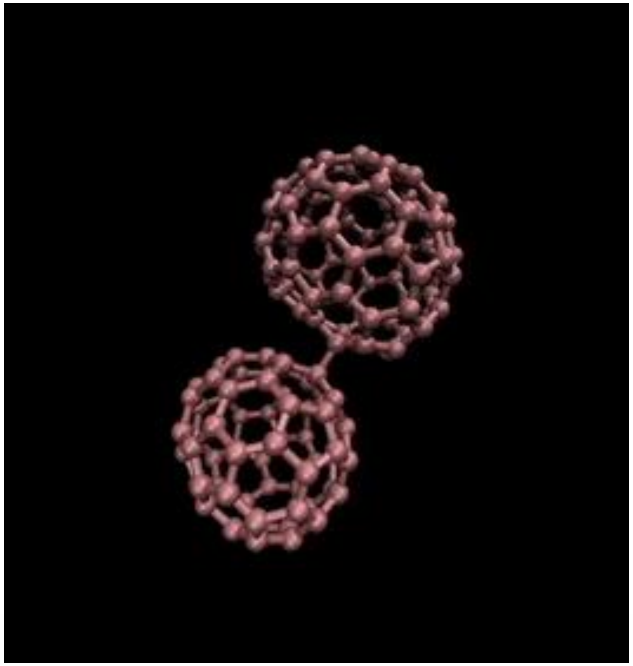


HRTEM 200 kV

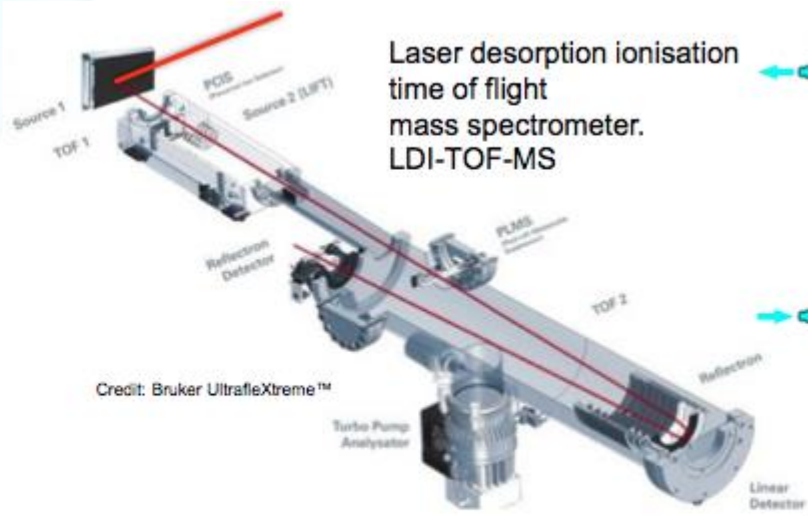


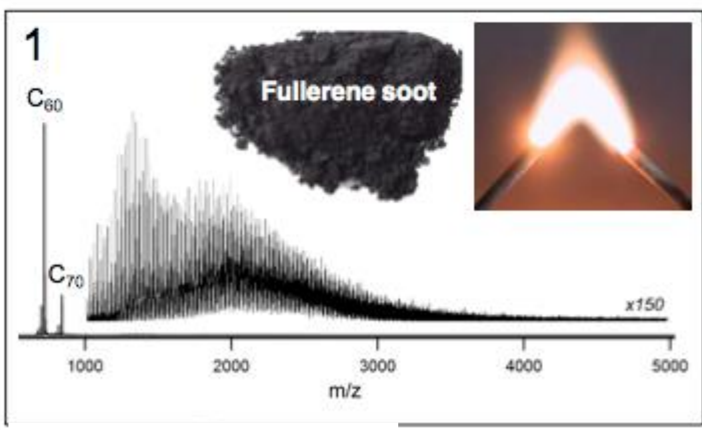
Should we expect to see C_{60} fullerene?

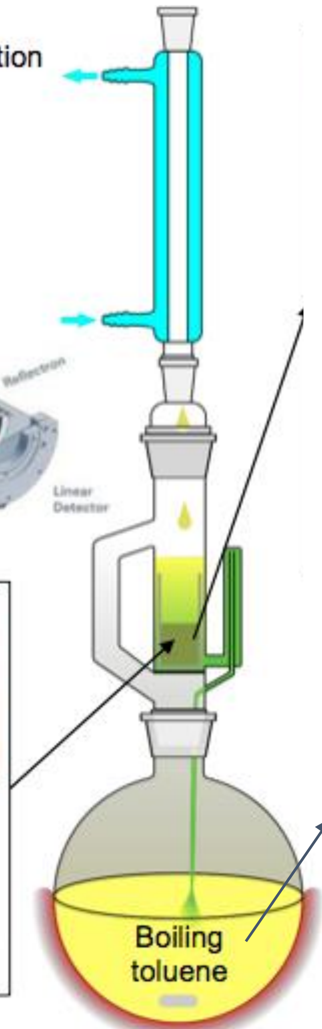


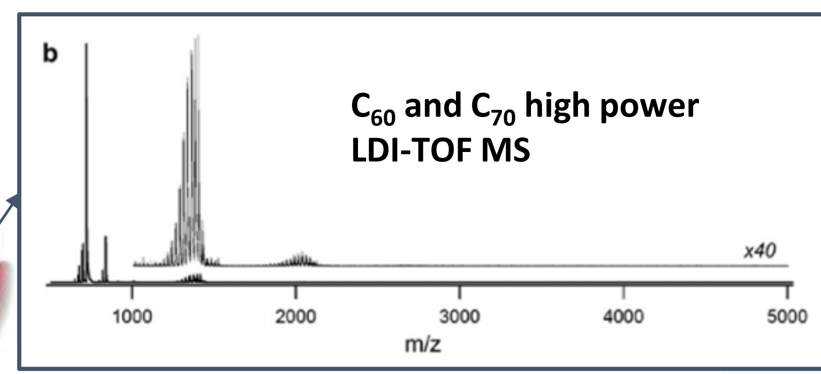


Should we expect to see C_{60} fullerene?



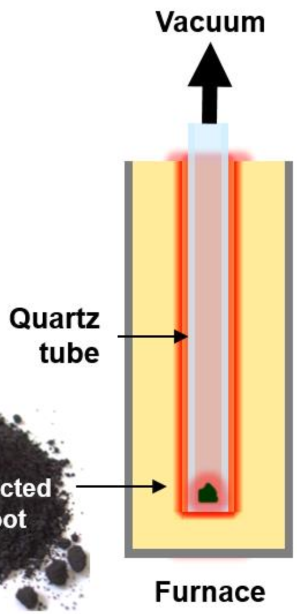


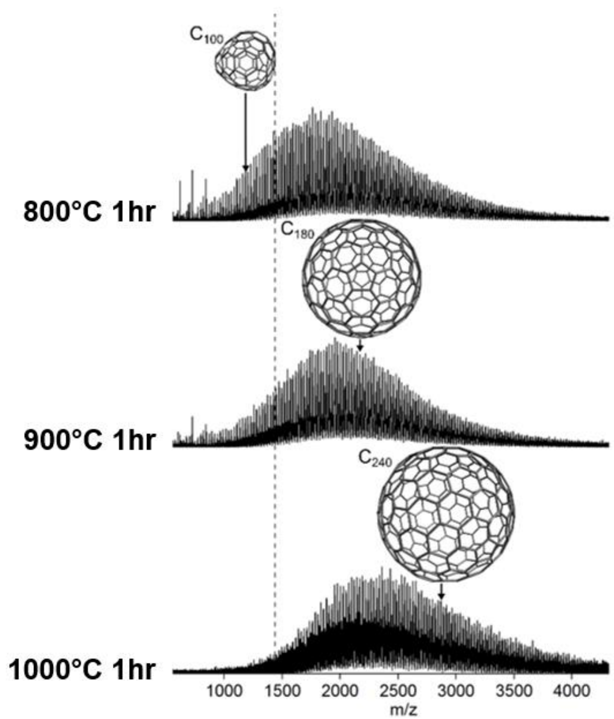


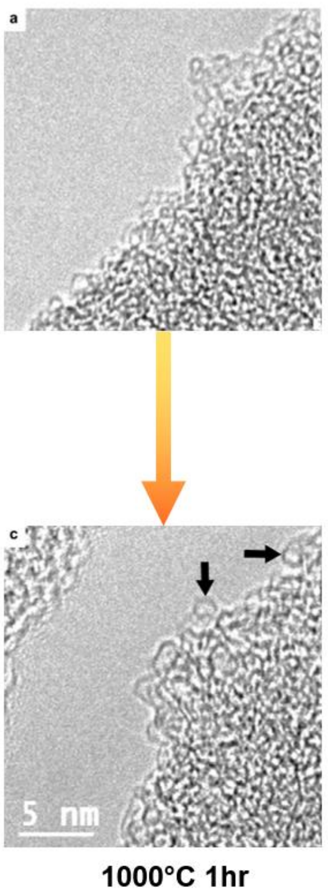


Martin, Jacob W., et al. "**Giant fullerene formation through thermal treatment of fullerene soot.**" *Carbon* 125 (2017): 132-138.

C_{60}/C_{70} consumed through coalescence

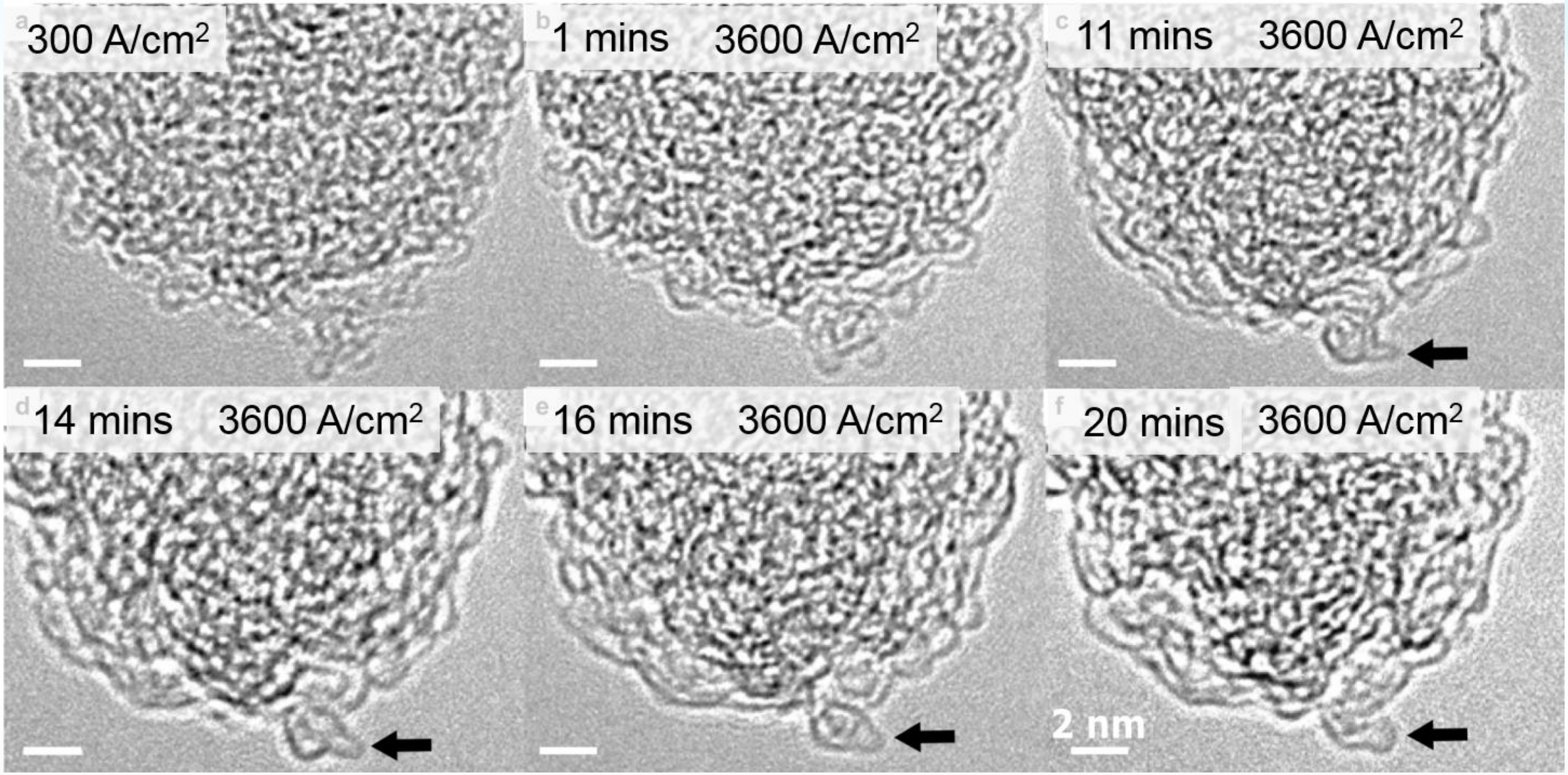






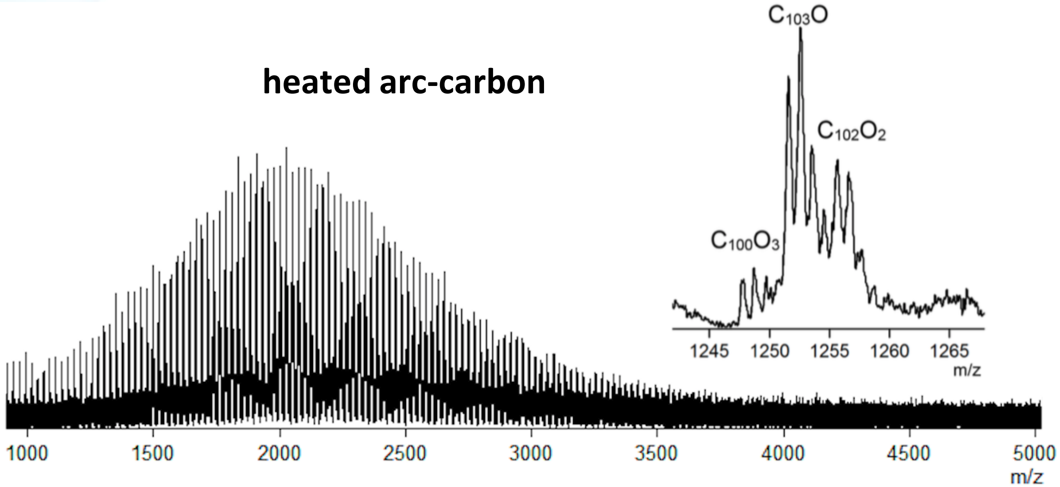
Martin, Jacob W., et al. "**Giant fullerene formation through thermal treatment of fullerene soot.**" *Carbon* 125 (2017): 132-138.

Giant fullerene formation

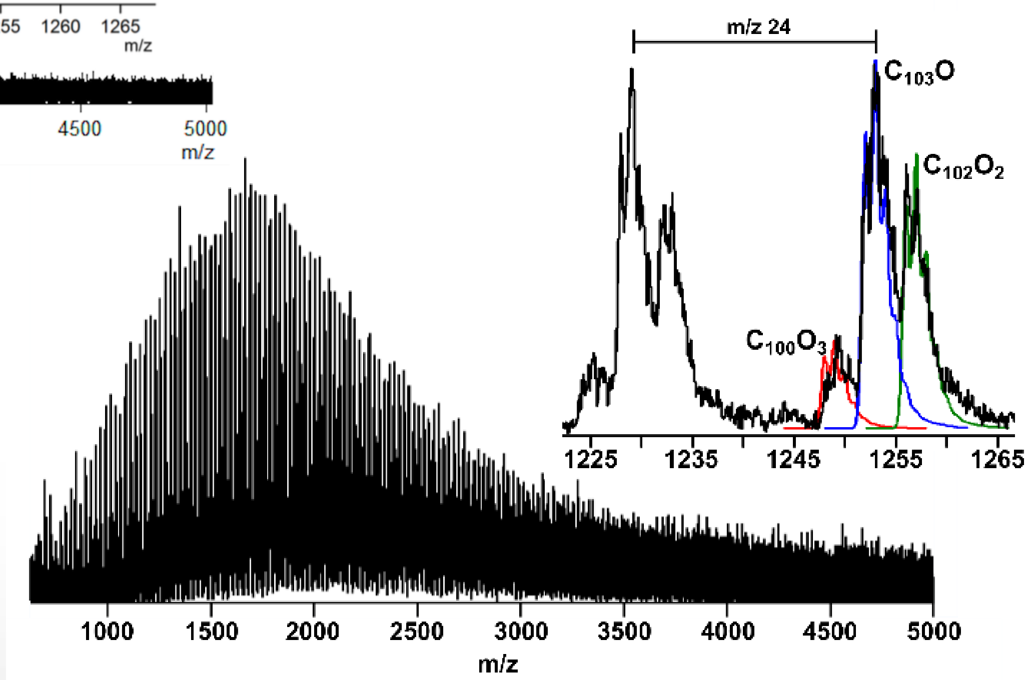


Martin, Jacob W., et al. "**Giant fullerene formation through thermal treatment of fullerene soot.**" *Carbon* 125 (2017): 132-138.

Oxygenated fragments



Non-graphitising carbon
wood charcoal



Environmental Science & Technology

Article

Cite This: Environ. Sci. Technol. XXXX, XXX, XXX−XXX

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Nanostructure of Gasification Charcoal (Biochar)

Jacob W. Martin,[†,‡] Leonard Nyadong,[¶] Caterina Ducati,[§] Merilyn Manley-Harris,[||] Alan G. Marshall,[⊥] and Markus Kraft[*,†,‡,#]

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[‡]Cambridge Centre for Advanced Research and Education in Singapore (CARES), CREATE Tower, 1 Create Way, Singapore 138602

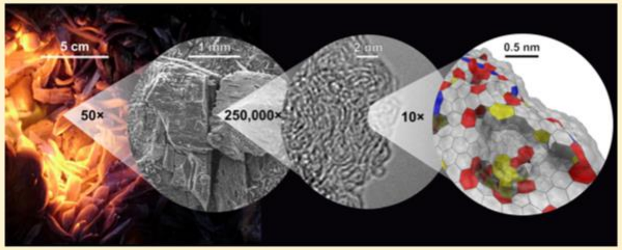
[¶]Phillips 66 Research Center, Highway 60 & 123, Bartlesville, Oklahoma 74003-6607, United States

[§]Department of Materials Science and Metallurgy, University of Cambridge, Philippa Fawcett Drive, West Site, CB3 0FS Cambridge, U.K.

[||]School of Science, University of Waikato, Hillcrest, Hamilton 3216, New Zealand

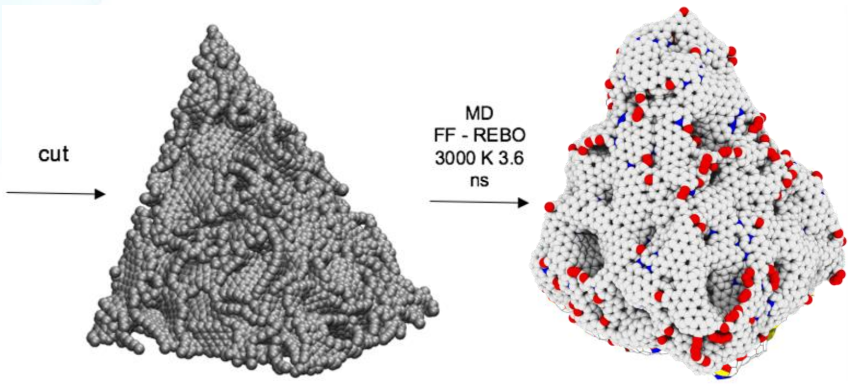
[⊥]National High Magnetic Field Laboratory, Florida State University, 1800 E. Paul Dirac Drive, Tallahassee, Florida 32310-4005, United States

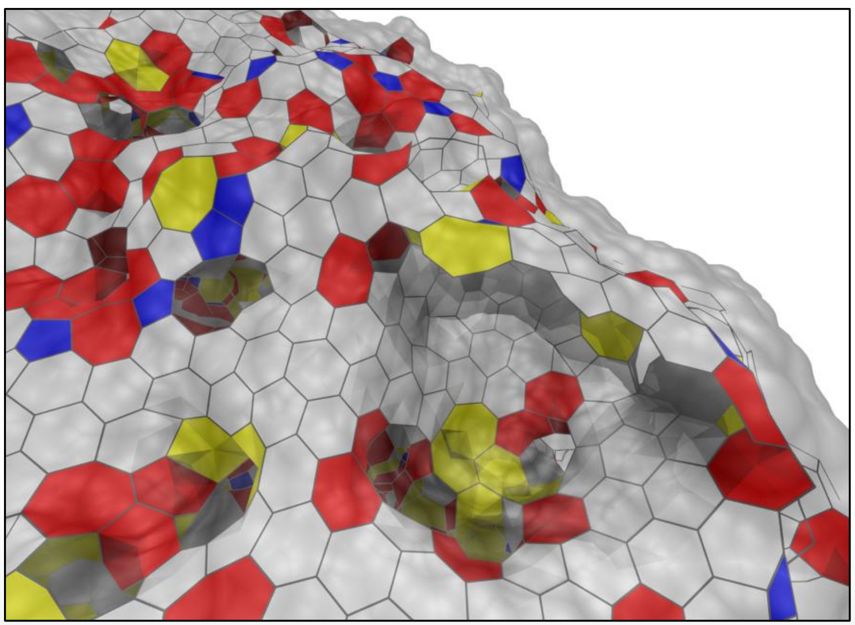
[#]School of Chemical and Biomedical Engineering, Nanyang Technological University, 62 Nanyang Drive, Singapore 637459



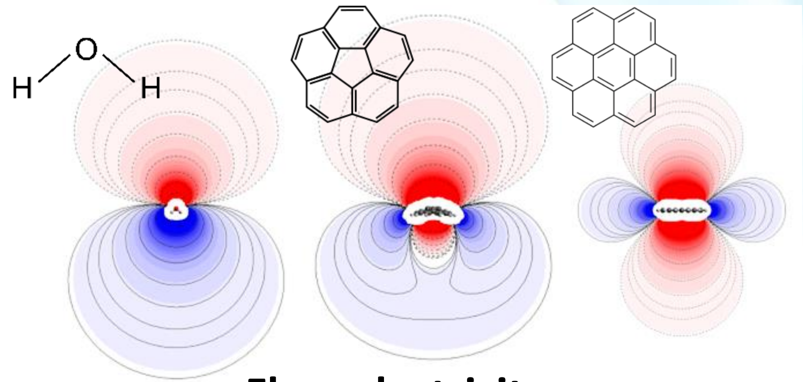
ABSTRACT: In this work, we investigate the molecular composition and nanostructure of gasification charcoal (biochar) by comparing it with heat-treated fullerene arc-soot. Using ultrahigh resolution Fourier transform ion-cyclotron resonance and laser desorption ionization time-of-flight mass spectrometry, Raman spectroscopy, and high resolution transmission electron microscopy we analyzed charcoal of low tar content obtained from gasification. Mass spectrometry revealed no magic number fullerenes such as C_{60} or C_{70} in the charcoal. The positive molecular ion m/z 701, previously considered a graphitic part of the nanostructure, was found to be a breakdown product of pyrolysis and not part of the nanostructure. A higher mass distribution of ions similar to that found in thermally treated fullerene soot indicates that they share a nanostructure. Recent insights into the formation of all carbon fullerenes reveal that conditions in charcoal formation are not optimal for the formation of fullerenes, but instead, curved carbon structures coalesce into *fulleroid-like* structures. Microscopy and spectroscopy support such a *stacked, fulleroid-like* nanostructure, which was explored using reactive molecular dynamics simulations.

Implications for reactivity





Implications for adsorption



Flexoelectricity

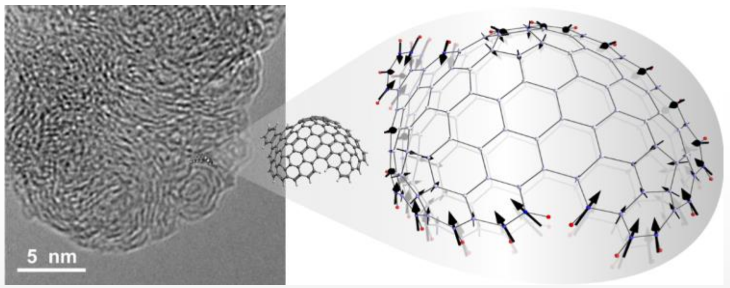
THE JOURNAL OF PHYSICAL CHEMISTRY C
Article
pubs.acs.org/JPCC

The Polarization of Polycyclic Aromatic Hydrocarbons Curved by Pentagon Incorporation: The Role of the Flexoelectric Dipole

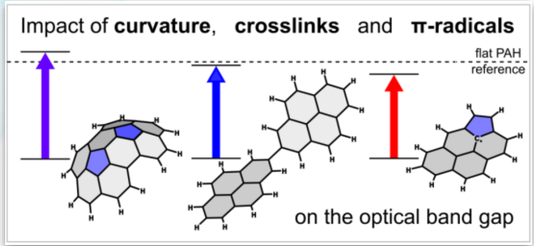
Jacob W. Martin,[†] Radomir I. Slavchov,[†] Edward K. Y. Yapp,[†] Jethro Akroyd,[†] Sebastian Mosbach,[†] and Markus Kraft*[,†,‡,§]

[†]Department of Chemical Engineering and Biotechnology, University of Cambridge, Cambridge CB3 0AS, U.K.
[‡]School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore 637459

Supporting Information

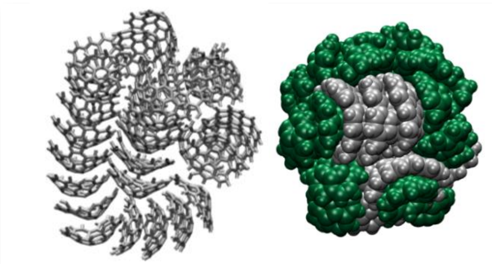


WANT TO SEE MORE!



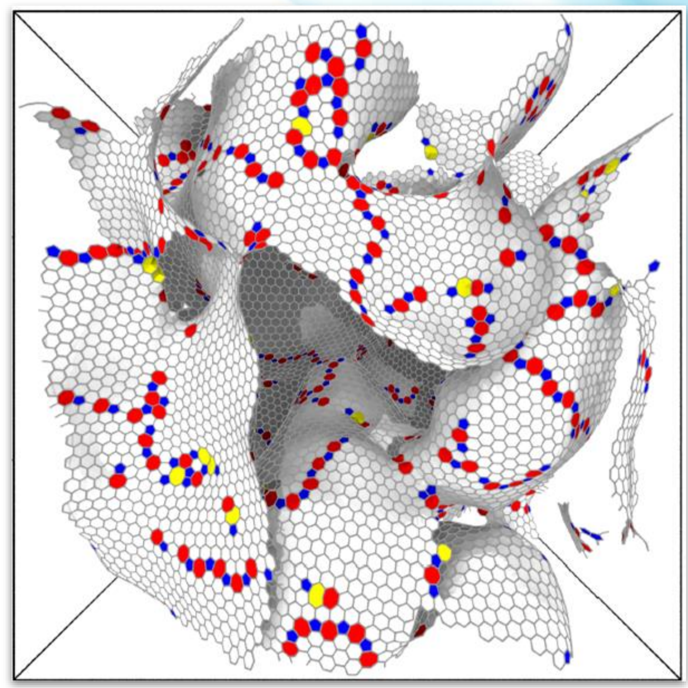
Impact of curved, crosslinks and radicals on the band gap of nanographenes

Menon Thurs. 11:20 am Rm 5



Investigating the self-assembly and structure of nanoparticles containing curved carbons

Bowal Tues. 4:20 pm Rm 2



Topology of disordered carbons

Martin Wed. 3:40 pm Rm. 5

Thanks to the funder

NATIONAL RESEARCH FOUNDATION
PRIME MINISTER'S OFFICE
SINGAPORE

This project is funded by the **National Research Foundation (NRF)**, Prime Minister's Office, Singapore under its Campus for Research Excellence and Technological Enterprise (CREATE) programme.

Thanks to all collaborators

Leonard Nyadong[2], Caterina Ducati[1], Carla DeTomas[4], Irene Suarez-Martinez[4], Merilyn Manley-Harris[3], Alan Marshall[2], Nigel Marks[4], Markus Kraft[1].

[1]University of Cambridge, [2]Florida State University, [3]University of Waikato, [4]Curtin University

Thanks for your attention

jwm50@cam.ac.uk

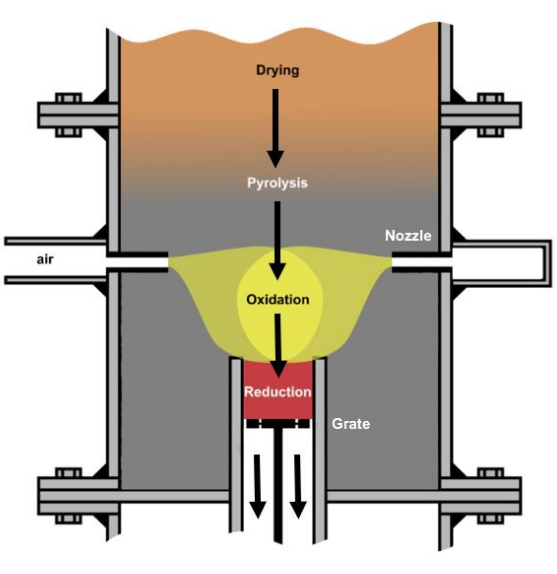
CoMo GROUP

Jacob W. Martin

CAMBRIDGE CARES

Microlab gasifier

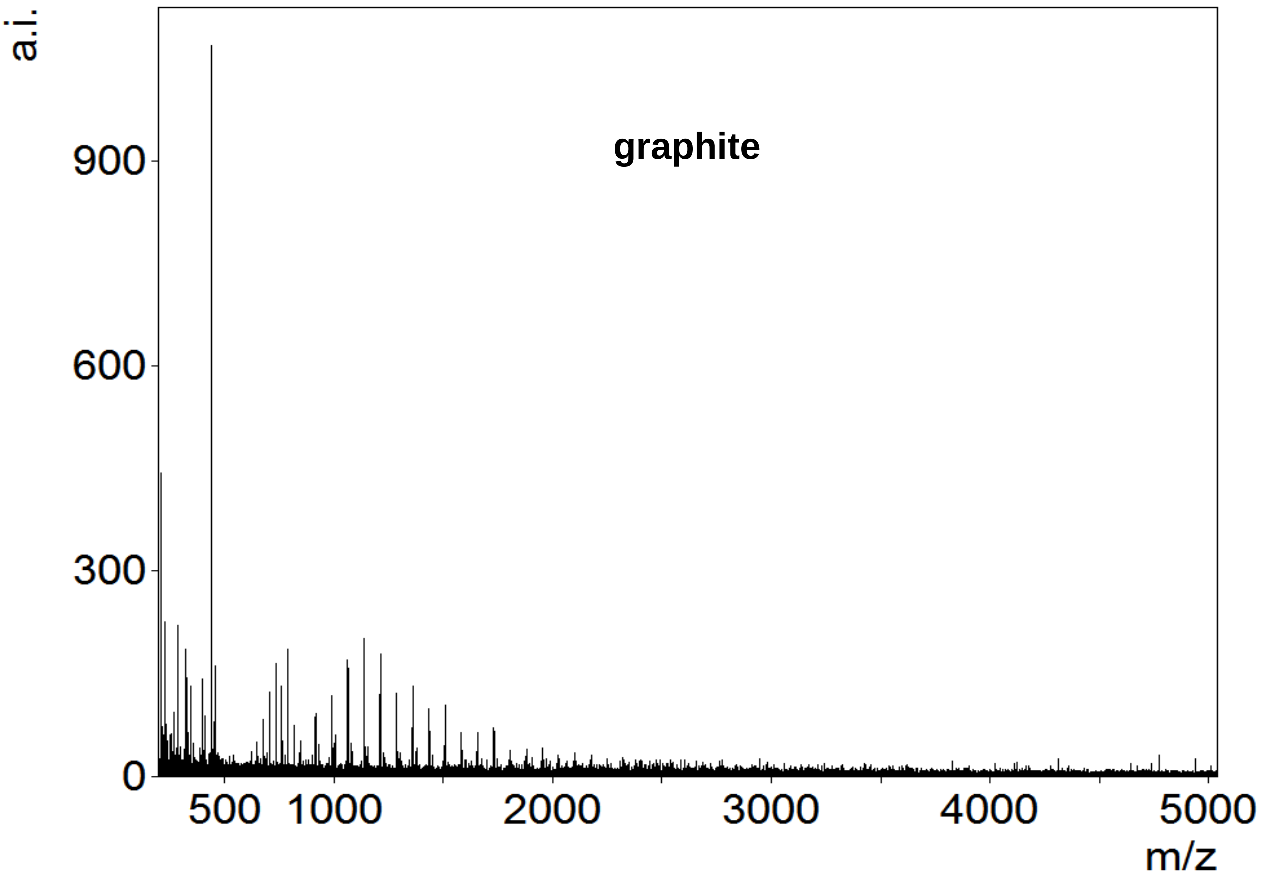
FLUIDYNE GASIFICATION



Experimental downdraft gasifier was developed with Mr. Doug Williams from Fluidyne gasification

Wood block fuel consumption 4.5 kg/hr
Maximum output 9.8 Nm3/hr
Test duration 20 mins
Hopper volume 3 L
Blast tube, cyclone, cooling and sawdust filter

Currently installed at the University of Ulster.


a.i.
graphite
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