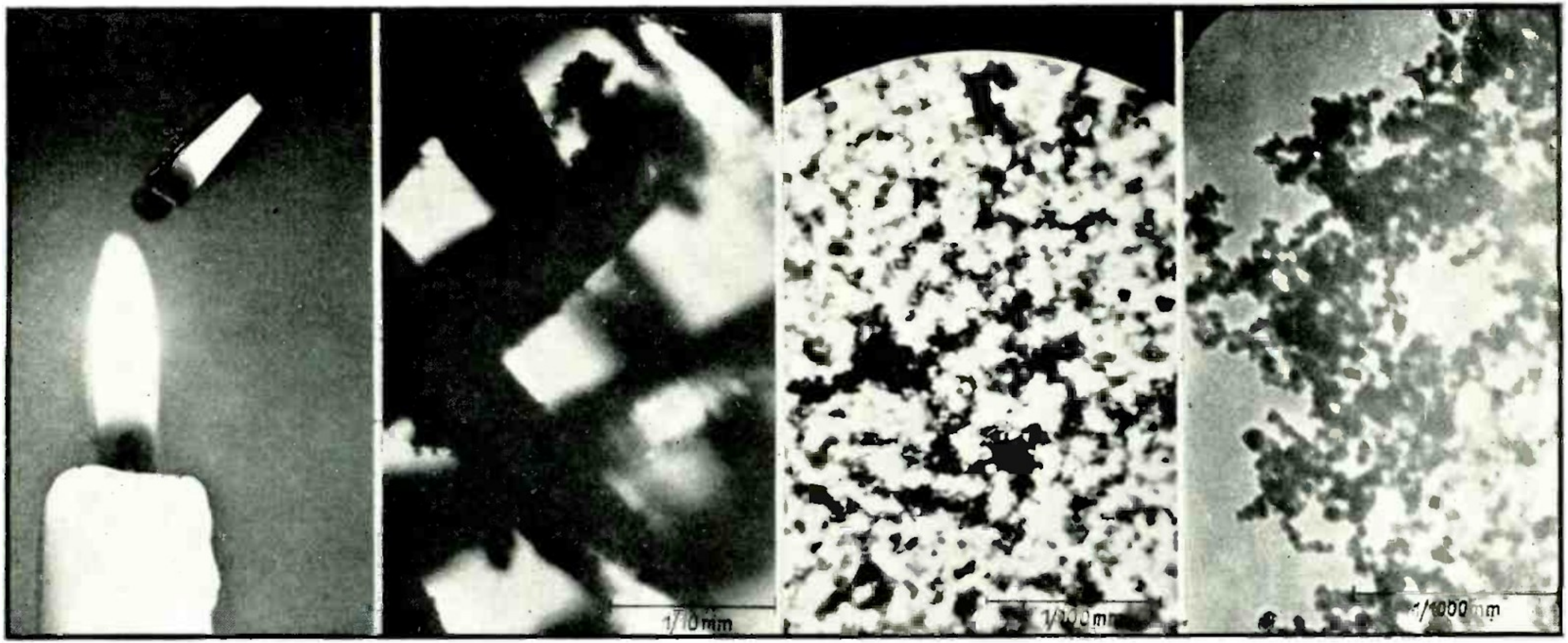
Carbon products without the emissions

Carbonaceous particles formation and structure



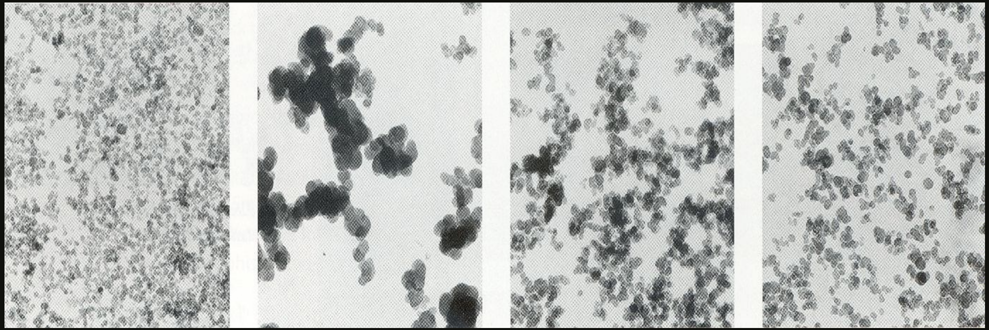
Dr Jacob W. Martin

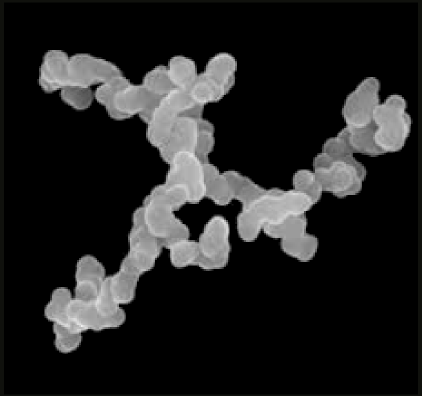
Curtin University

What do carbon blacks and soot look like?

Furnace blacks

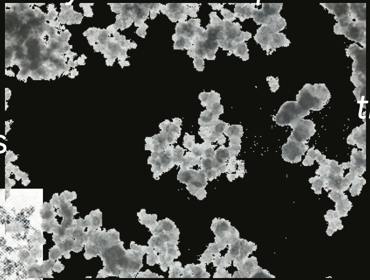
Fine 14 nm | Coarse 50 nm | High structure | Low structure



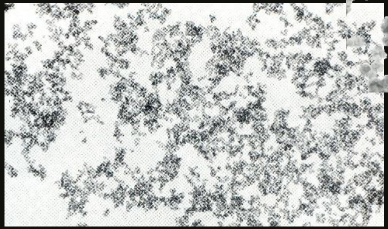


Scanning Electron Micrograph (SEM) of carbon black (Orion)

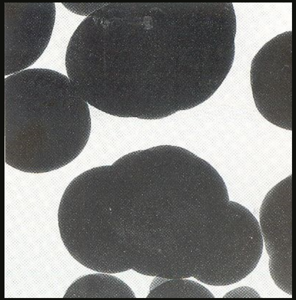
acetylene black particles

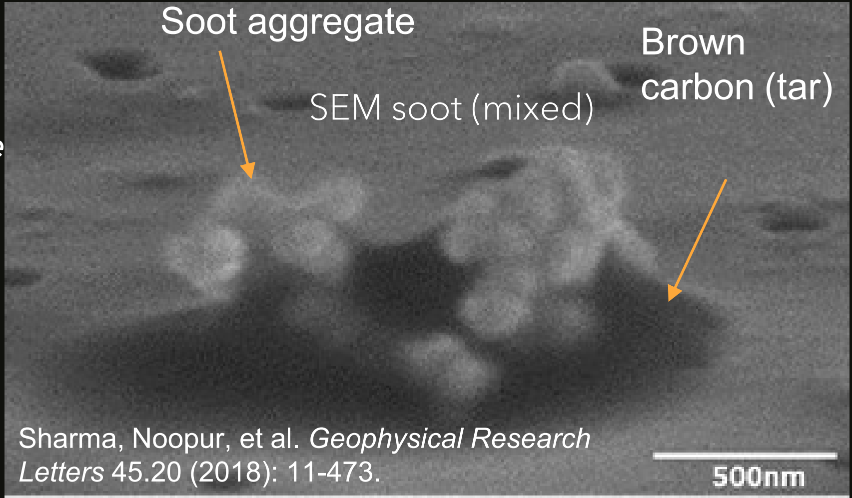


gas black particles



thermal black particle





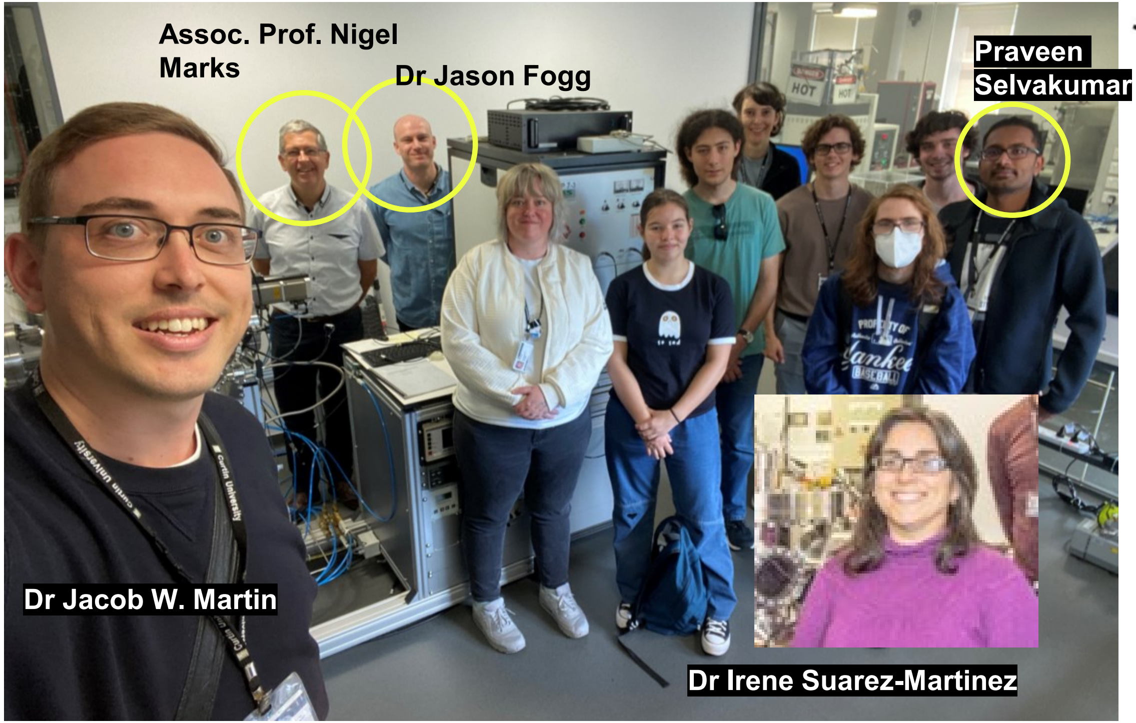
Sharma, Noopur, et al. *Geophysical Research Letters* 45.20 (2018): 11-473.

Curtin Carbon Group

Curtin University
INSTITUTE FOR ENERGY TRANSITION

TRAILBLAZER
RESOURCES TECHNOLOGY & CRITICAL MINERALS

Carbon Materials Scientists in the Department of Physics and Astronomy



John de Laeter Centre

MICROSCOPY AUSTRALIA

FUTURE ENERGY EXPORTS
Cooperative Research Centre

HSRG
Hydrogen Storage Research Group

FUTURE BATTERY INDUSTRIES CRC

ARC Centre of Excellence for
Carbon Science & Innovation

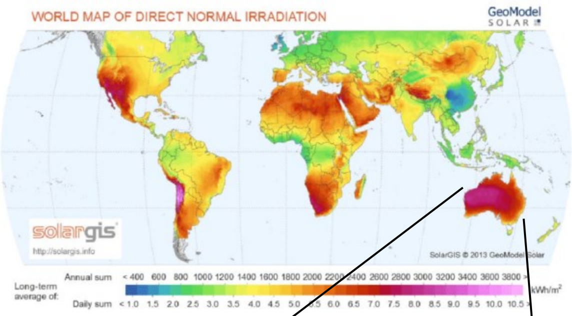
J.W.M. acknowledges the support of the Forrest Research Foundation. I.S.-M. acknowledges the support of the Australian Research Council (No. FT140100191). Characterisation of the samples was undertaken at the John de Laeter Centre, Curtin University.

Computational resources were provided by the Pawsey Centre with funding from the Australian Government and the Government of Western Australia. The authors acknowledge the facilities, and the scientific and technical assistance of Microscopy Australia at the Centre for Microscopy, Characterisation & Analysis, The University of Western Australia, a facility funded by the University, State and Commonwealth Governments.

I would like to acknowledge the Whadjuk People of the Noongar nation on whose land this work was undertaken

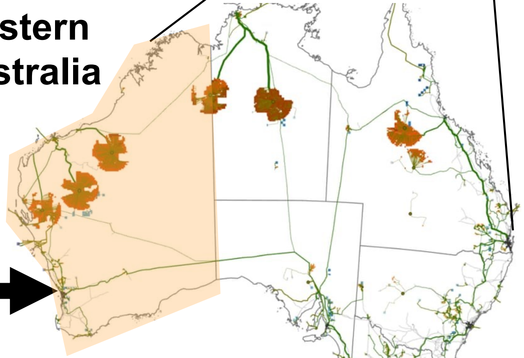
Why Perth?

Renewable energy



Western Australia

Perth



NetZero Australia
solar scenario 2050

Battery minerals

Majority of Lithium
mined in WA

Physics Department

Largest radio telescope.
Supercomputer resources
Materials science

Curtin University

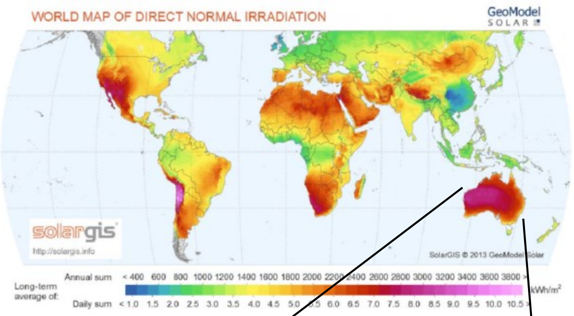
School of mines
leading mining uni

Rottnest Island

Short ferry ride from city

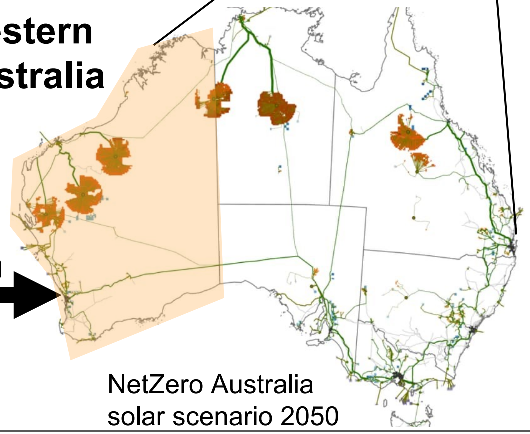
Why Perth?

Renewable energy



Western Australia

Perth



NetZero Australia solar scenario 2050

Battery minerals

Majority of Lithium mined in WA

Curtin Ur

School of mine
leading mining

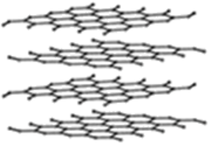
Physics Department

Largest radio telescope.

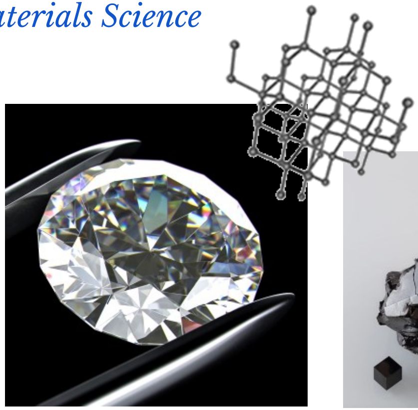
Quokkas on Rottnest Island

Carbon for products not fuels

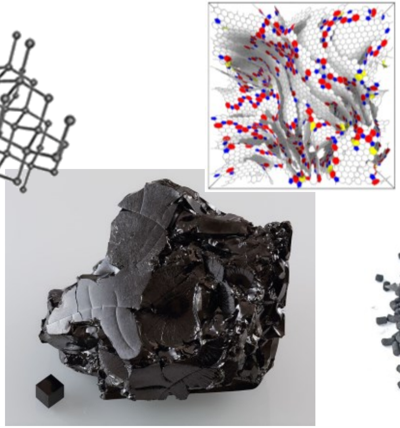
Carbon Materials Science



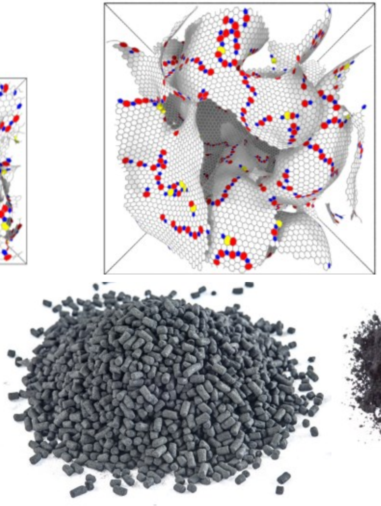
Graphite



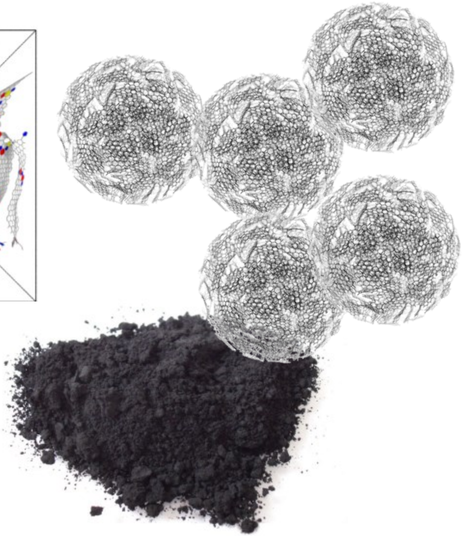
Diamond



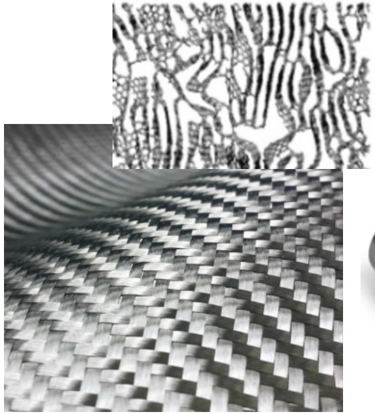
Glassy carbon



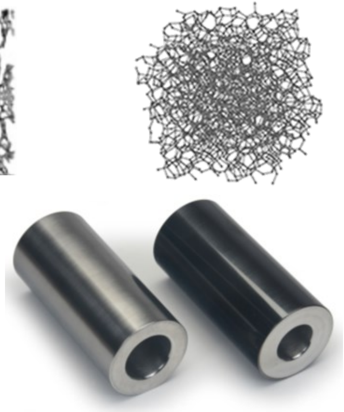
Activated carbon



Carbon black



Carbon fibres



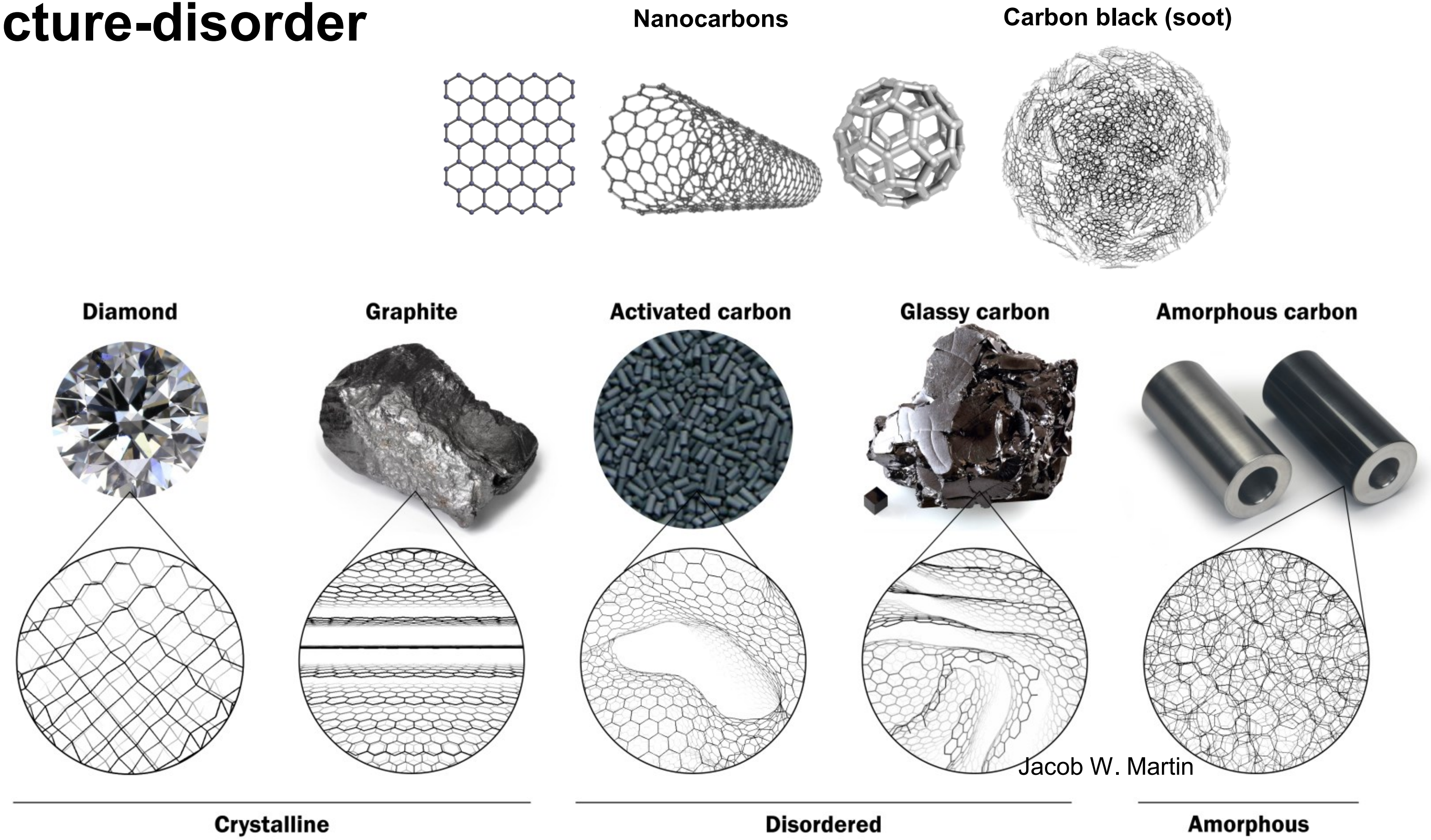
Diamond-like (amorphous) carbon

Fullerenes

Nanotubes

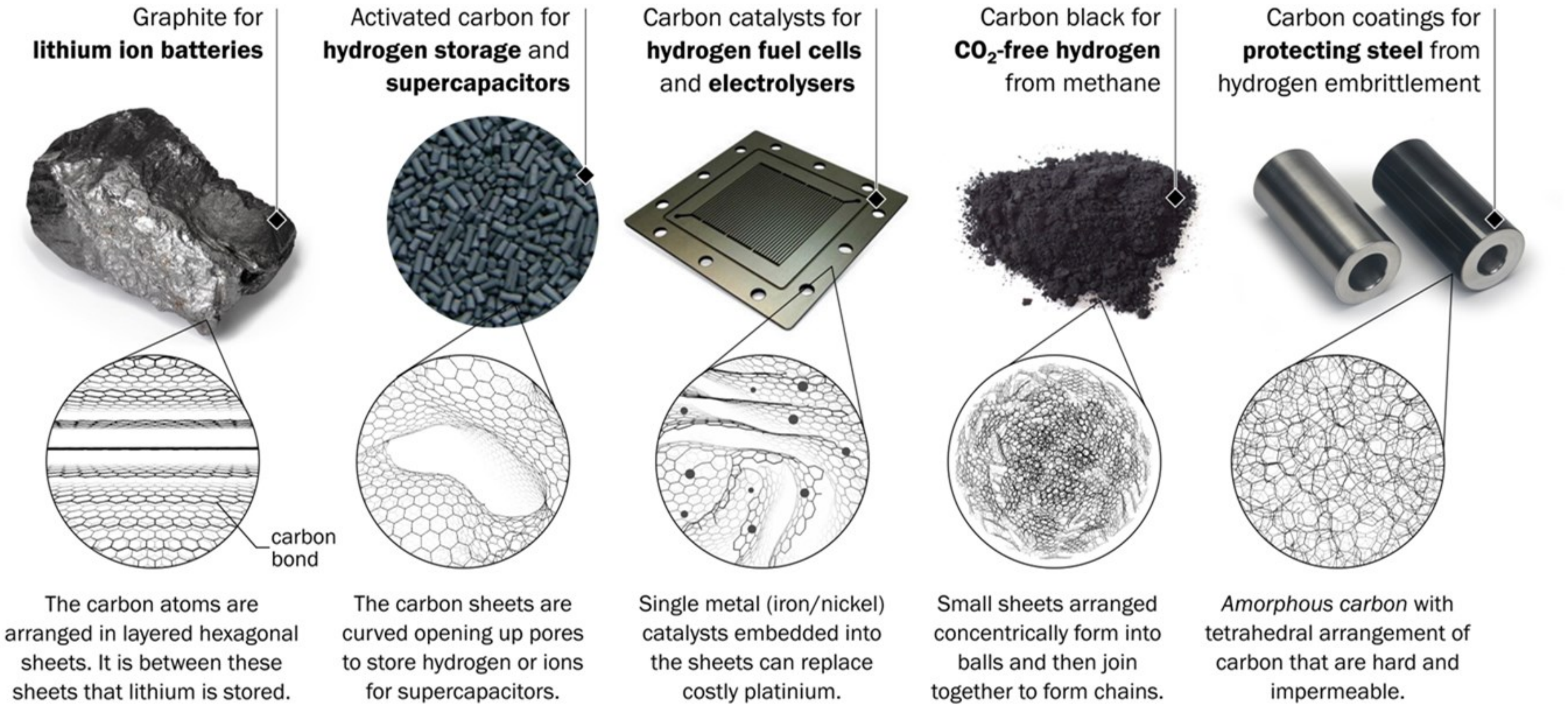
Graphene

Structure-disorder



Carbon materials powering our green technology

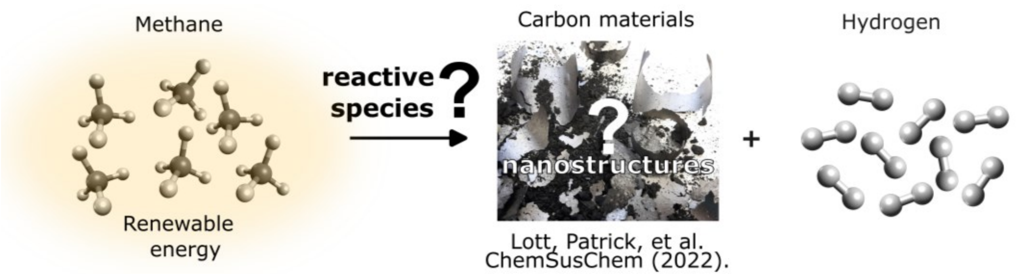
New and improved carbon materials are needed to drive our green transition

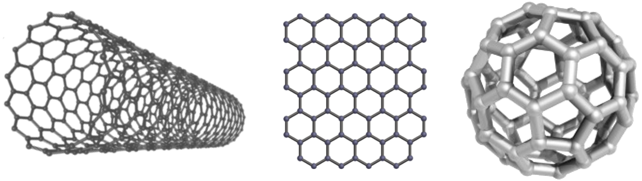


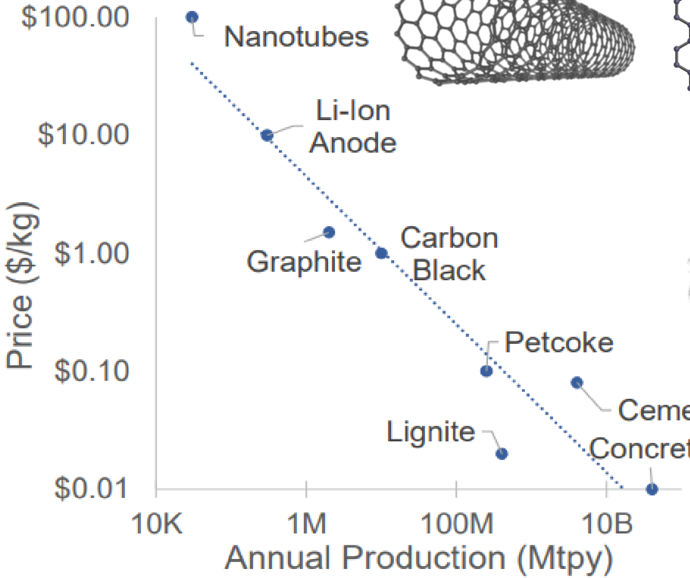
Pyrolysis for products
Challenges and opportunities

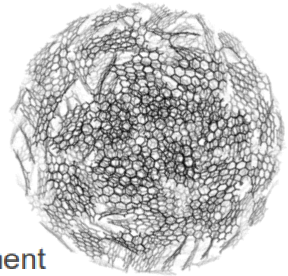
- How can we produce carbon materials without CO_2?
- How can we produce more valuable carbon products?
- How can we increase the efficiency of carbon production?
- How can we stop carbon forming where we don't want it?

1. ***Identify key reactive species***
2. ***Control carbon nanostructures produced in pyrolysis***



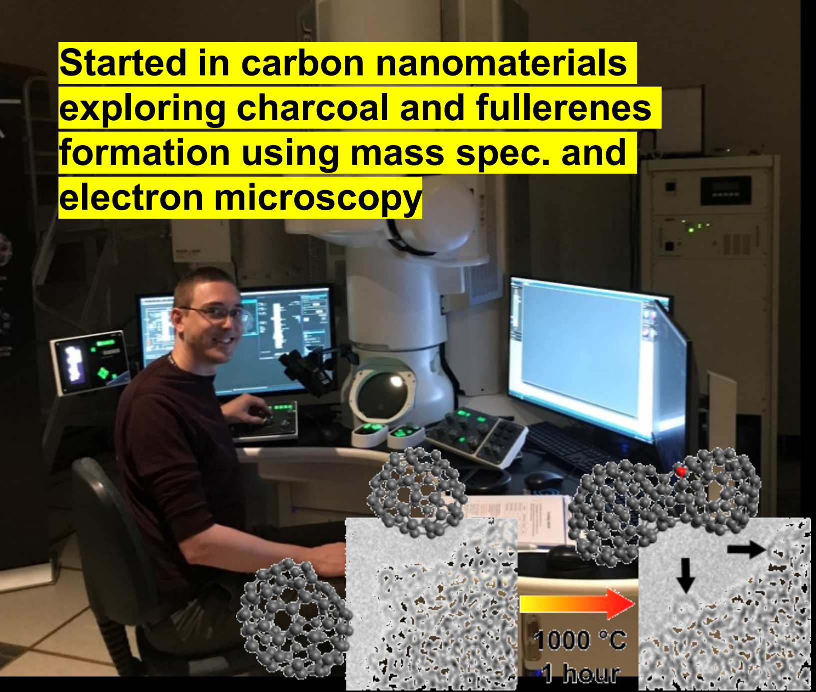




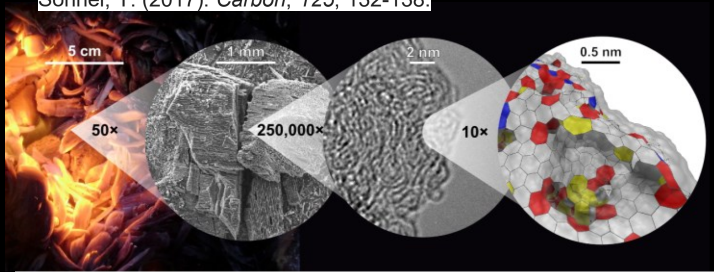


Source: Monolith Commercial scale and Carbon-free: Carbon black and hydrogen

Started in carbon nanomaterials exploring charcoal and fullerenes formation using mass spec. and electron microscopy

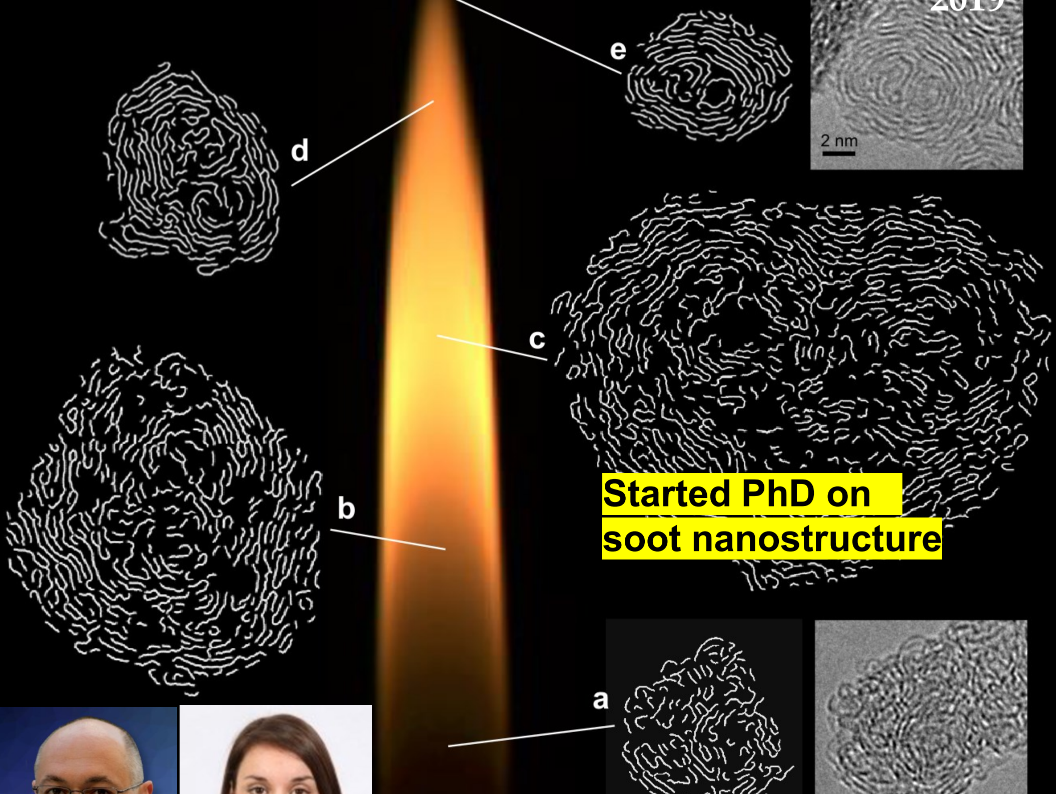


Martin, J. W., McIntosh, G. J., Arul, R., Oosterbeek, R. N., Kraft, M., & Söhnel, T. (2017). *Carbon*, *125*, 132-138.



Martin, J. W., Nyadong, L., Ducati, C., Manley-Harris, M., Marshall, A. G., & Kraft, M. (2019) *Environmental science & technology*, *53*(7), 3538-3546.

Internal structure of soot



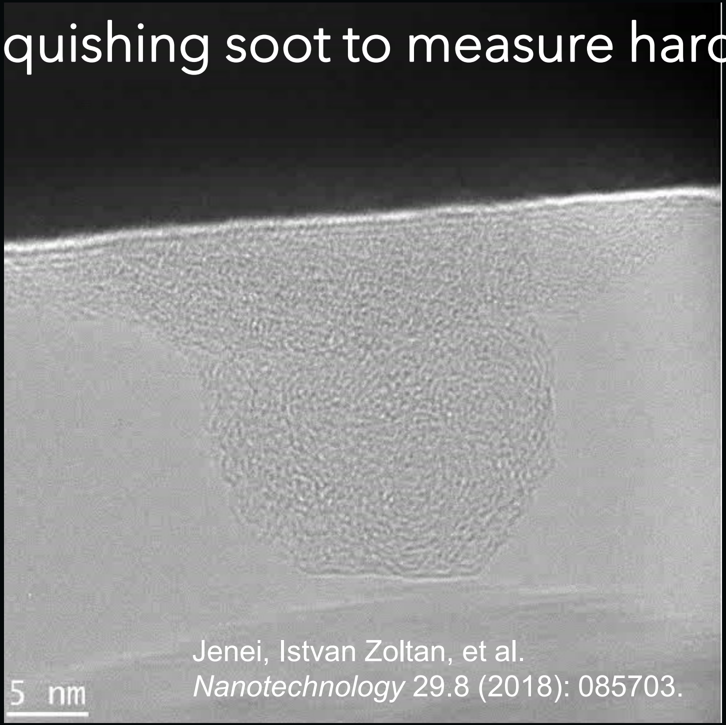
Started PhD on soot nanostructure

Markus Kraft

Maria Botero

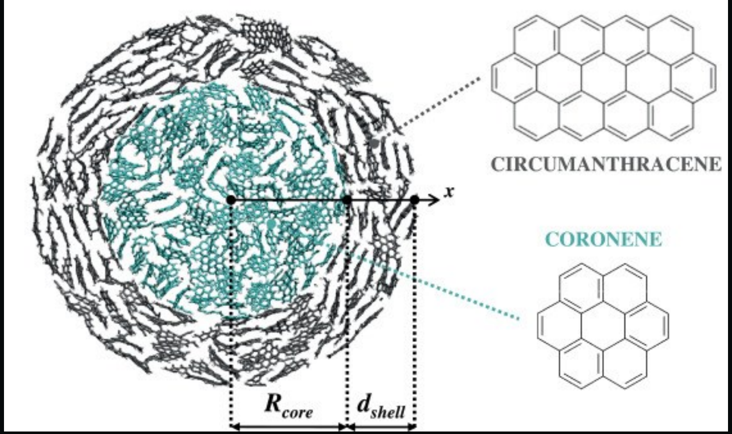
Botero, M. L., Sheng, Y., Akroyd, **J., Martin**, J., Dreyer, J. A., Yang, W., & Kraft, M. (2019). Internal structure of soot particles in a diffusion flame. *Carbon*, *141*, 635-642.

Squishing soot to measure hardness

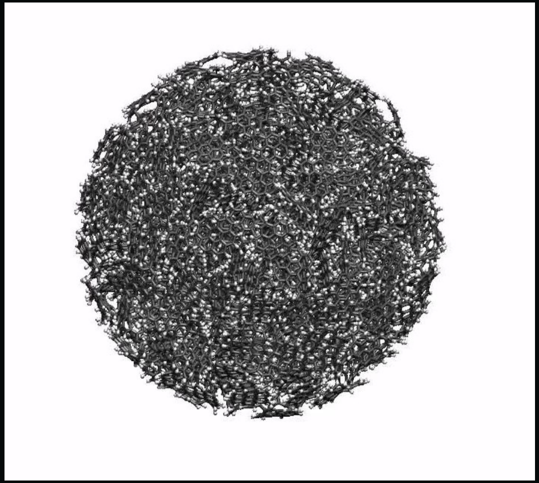


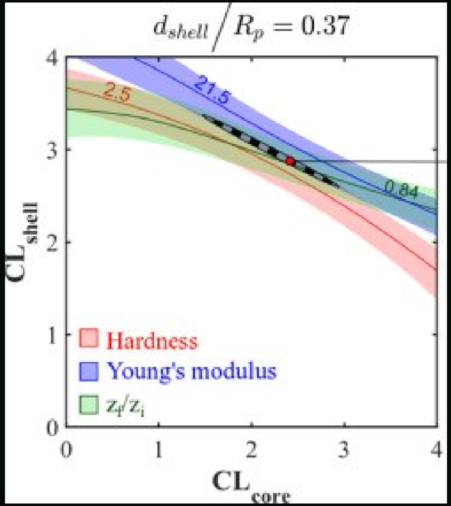
Jenei, Istvan Zoltan, et al. *Nanotechnology* 29.8 (2018): 085703.

Soot is hard like charcoal but has a softer centre

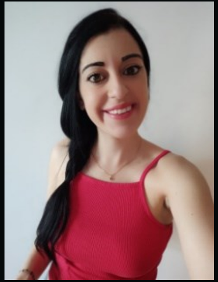


Pascazio, Laura, Martin, Jacob, et al. *Combustion and Flame* 219 (2020): 45-56.





Markus Kraft

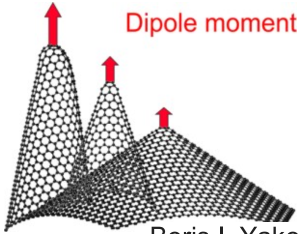


Laura Pascazio

First hypothesis – curved PAH + chemiions

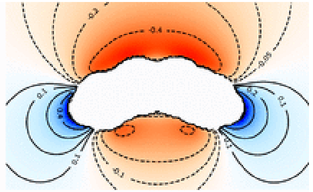
Homann

Kroto

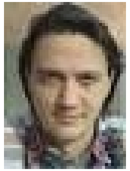


Kvashnin, Alexander G., Pavel B. Sorokin, and **Boris I. Yakobson**. *The journal of physical chemistry letters* 6.14 (2015): 2740-2744.

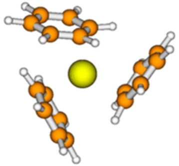
Boris I. Yakobson



Martin, Jacob W., et al. *The Journal of Physical Chemistry C* 121.48 (2017): 27154-27163.



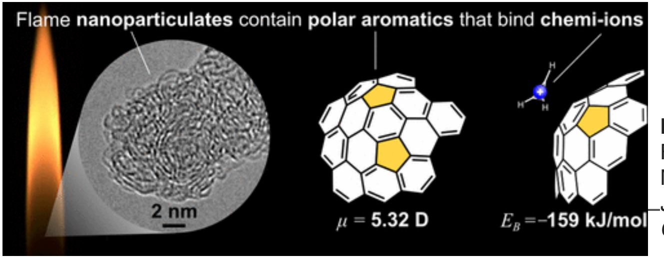
Radomir Slavchov



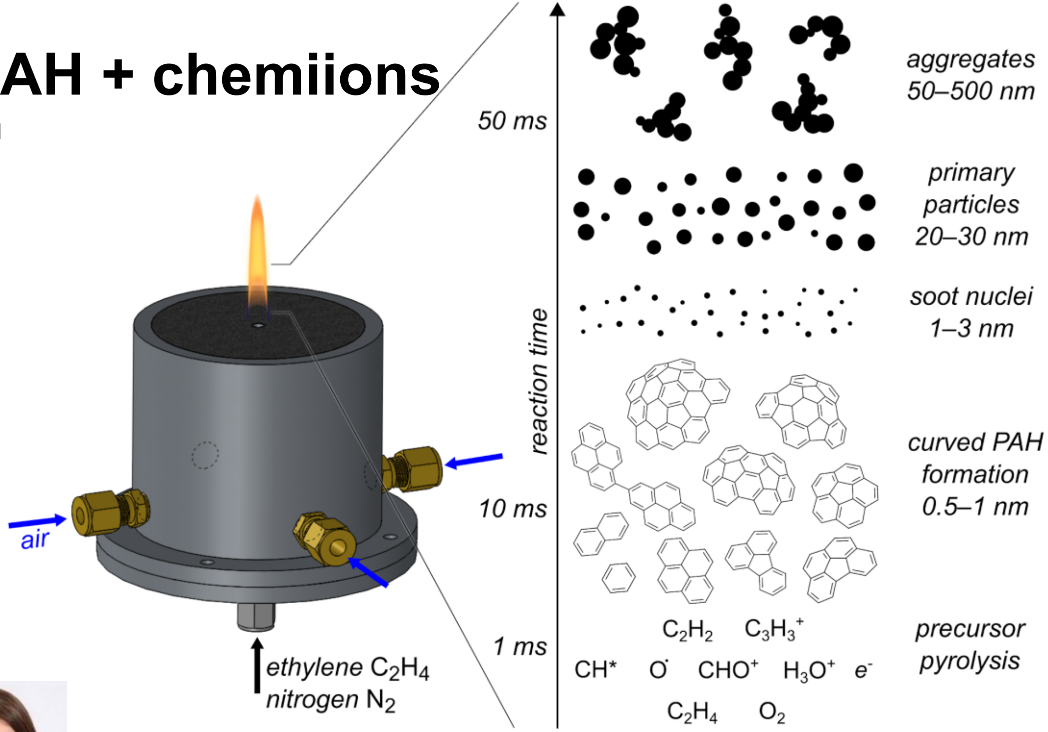
Kolakkandy, S., Pratihar, S., Aquino, A. J., **Wang, H.,** & Hase, W. L. (2014).. The Journal of Physical Chemistry A, 118(40), 9500-9511.

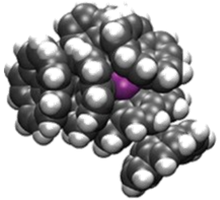
Hai Wang

Maria Botero



Martin, J. W., Botero, M., Slavchov, R. I., Bowal, K., Akroyd, J., Mosbach, S., & Kraft, M. (2018) *The Journal of Physical Chemistry C*, *122*(38), 22210-22215.





Bowal, K., Martin, J. W., Misquitta, A. J., & Kraft, M. (2019*Combustion Science and Technology*, *191*(5-6), 747-765.

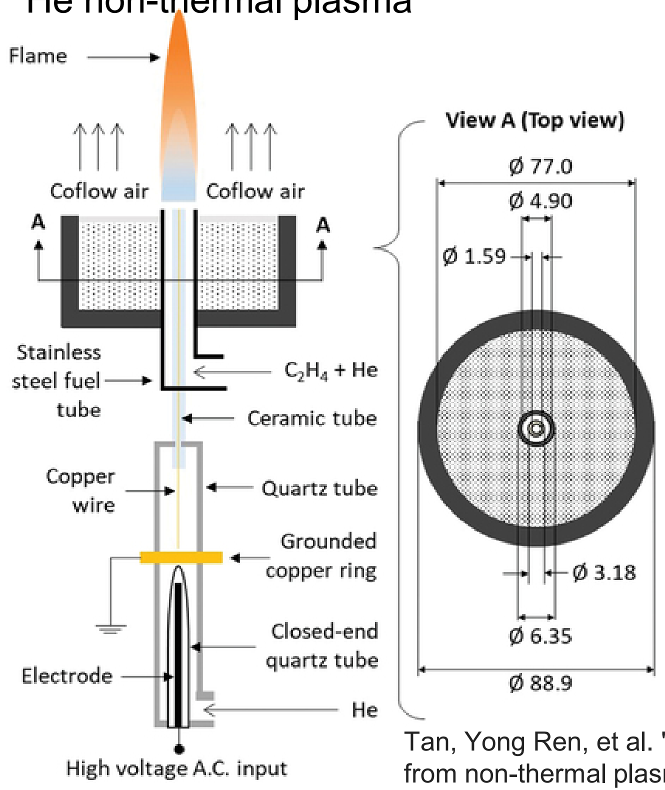
Kimberly Bowal

Alston J. Misquitta

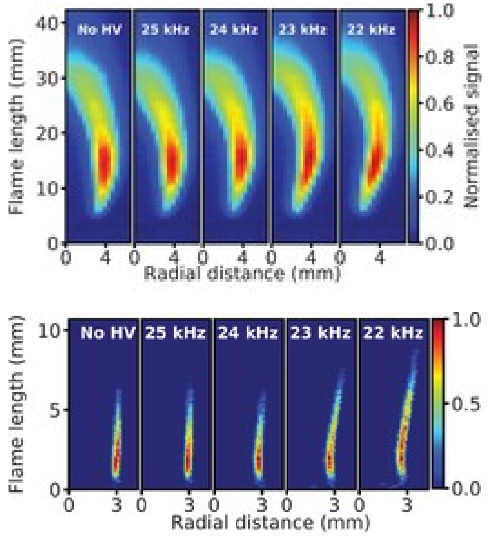
Curtin University

Non-thermal helium plasma injection

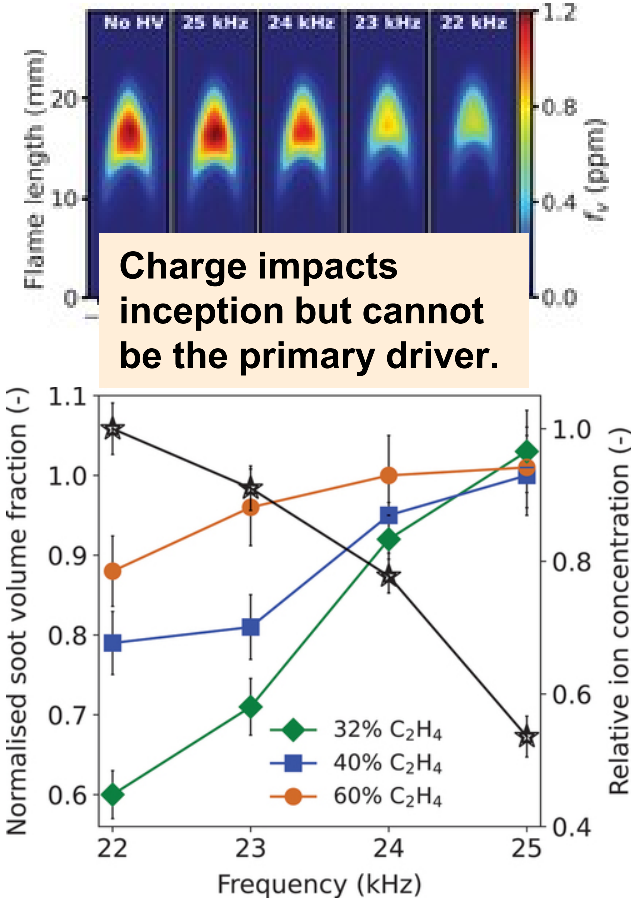
He non-thermal plasma



CH* and OH* not significantly changed



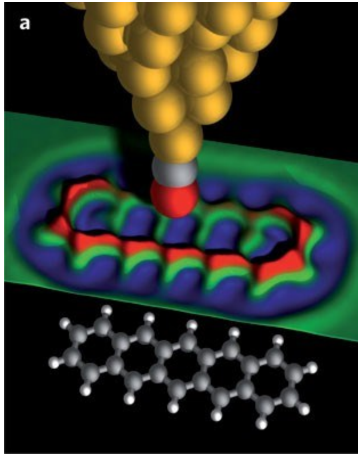
Soot emissions reduced



Charge impacts inception but cannot be the primary driver.

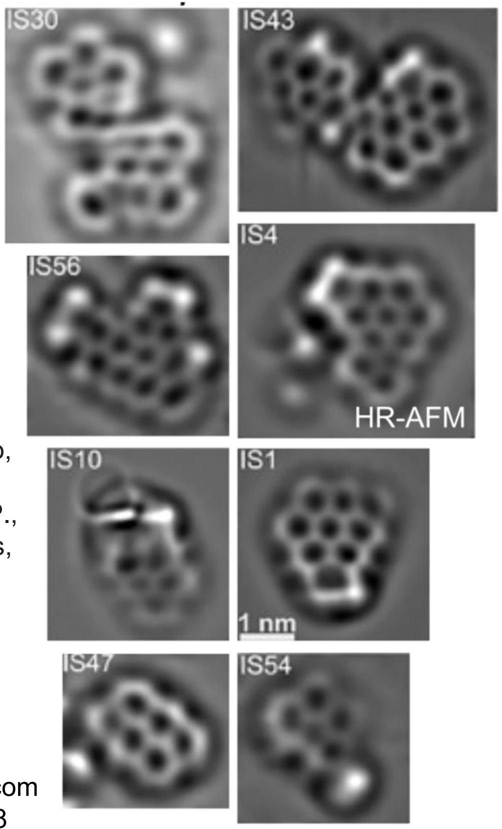
Tan, Yong Ren, et al. "Investigation on the effect of Charge injection from non-thermal plasma on soot formation in Laminar coflow diffusion flame." *Combustion Science and Technology* (2023): 1-22.

Reactive species – Dublin symp.



Schulz, F., Commodo, M., Kaiser, K., De Falco, G., Minutolo, P., Meyer, G., ... & Gross, L. (2019). *Proceedings of the Combustion Institute*, *37*(1), 885-892.

https://www.nature.com/articles/nchem.1008

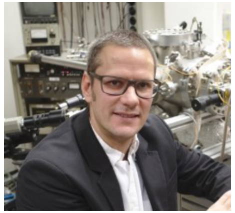


Andrea D'Anna

Mario Commodo

Patrizia Minutolo

Gianluigi De Falco

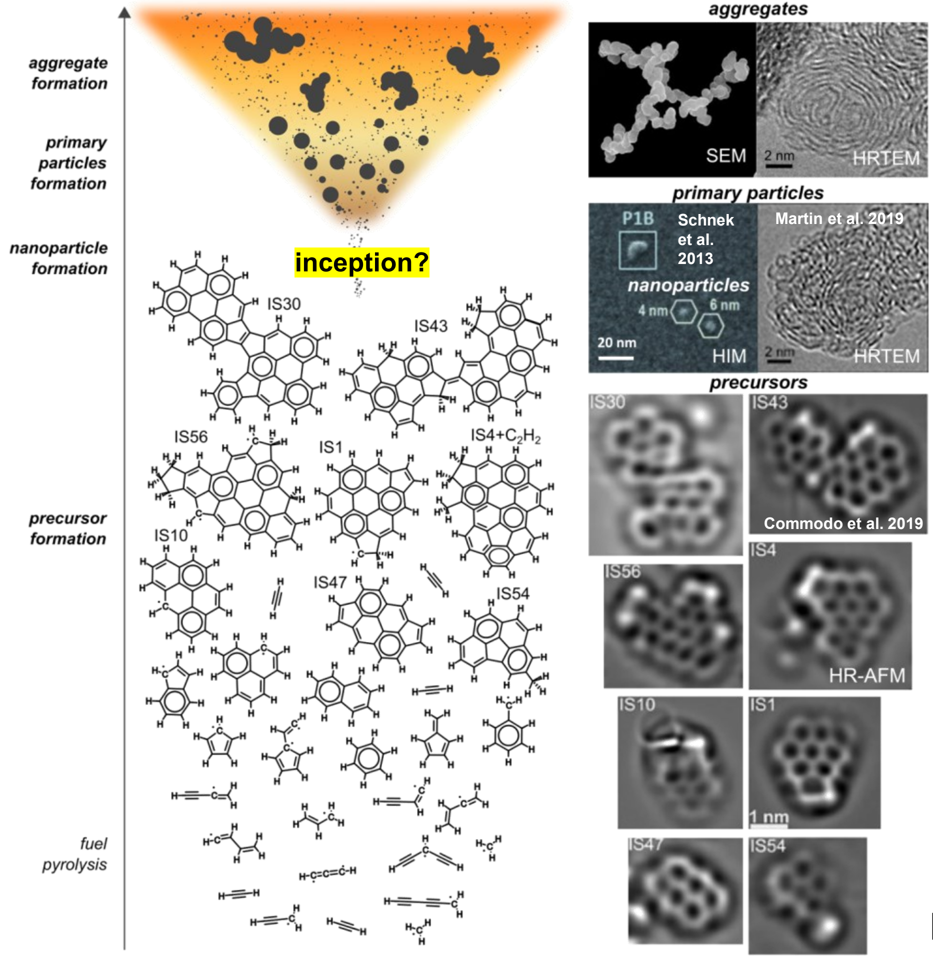


Leo Gross

Gerhard MEYER

Fabian Schulz

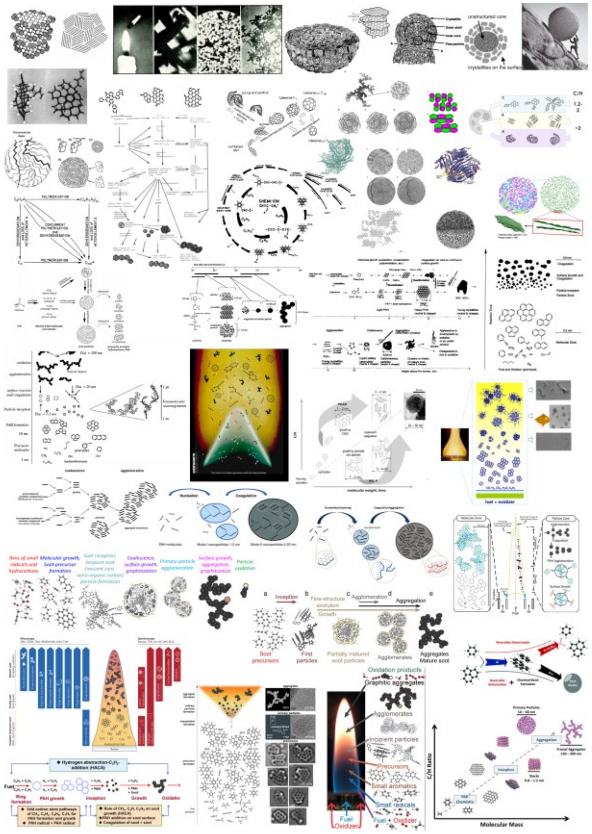
Katharina Kaiser

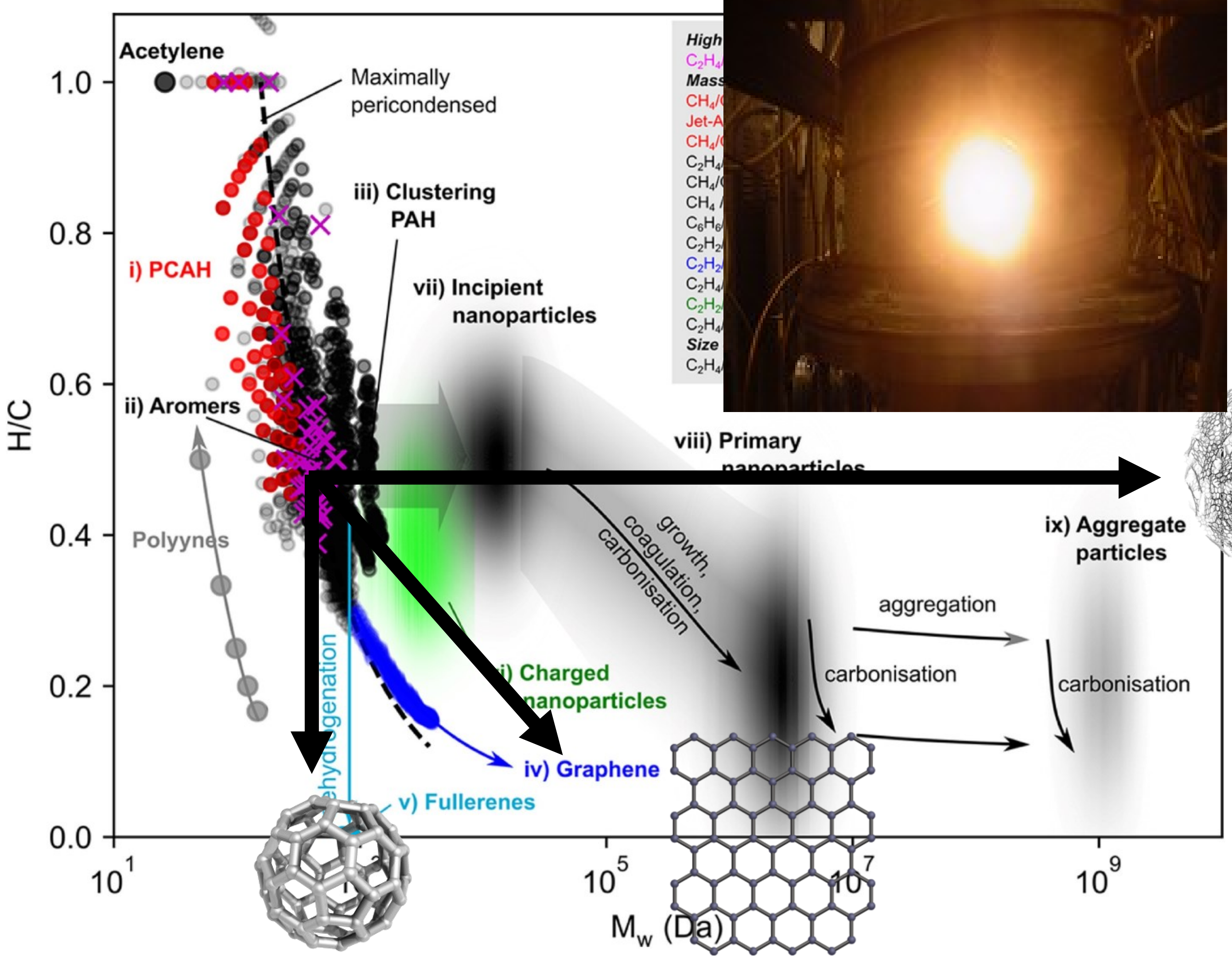


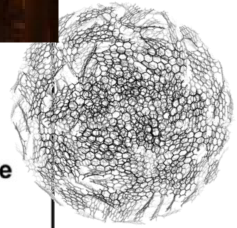
Martin, Jacob W., Maurin Salamanca, and Markus Kraft. "Soot inception: Carbonaceous nanoparticle formation in flames." *Progress in Energy and Combustion Science* 88 (2022): 100956.

Markus Kraft

Maurin Salamanca

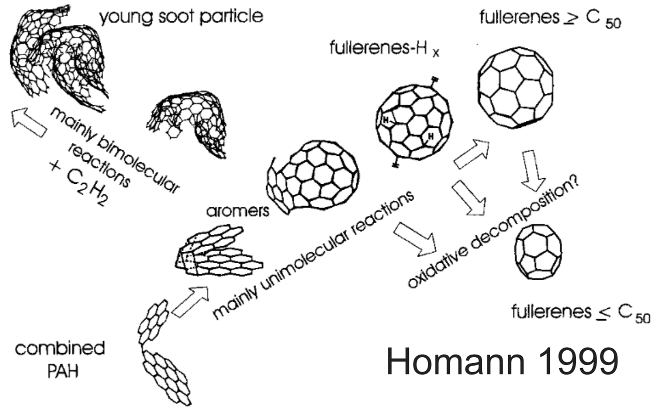




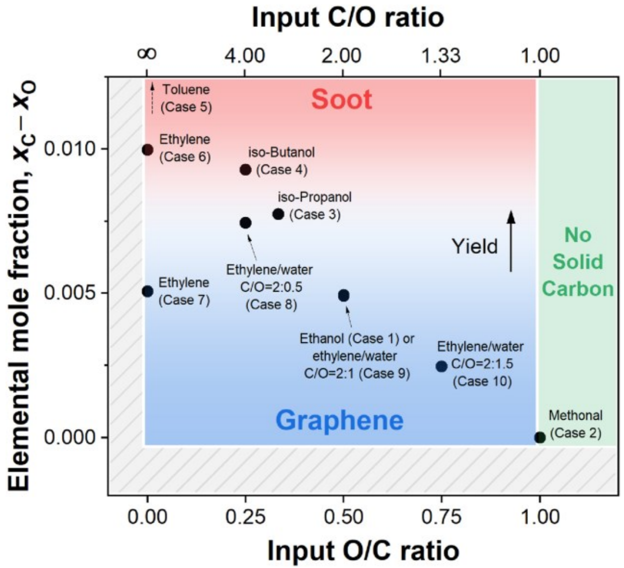


Klaus Homann
Jack Howard low-pressure benzene flame NanoC

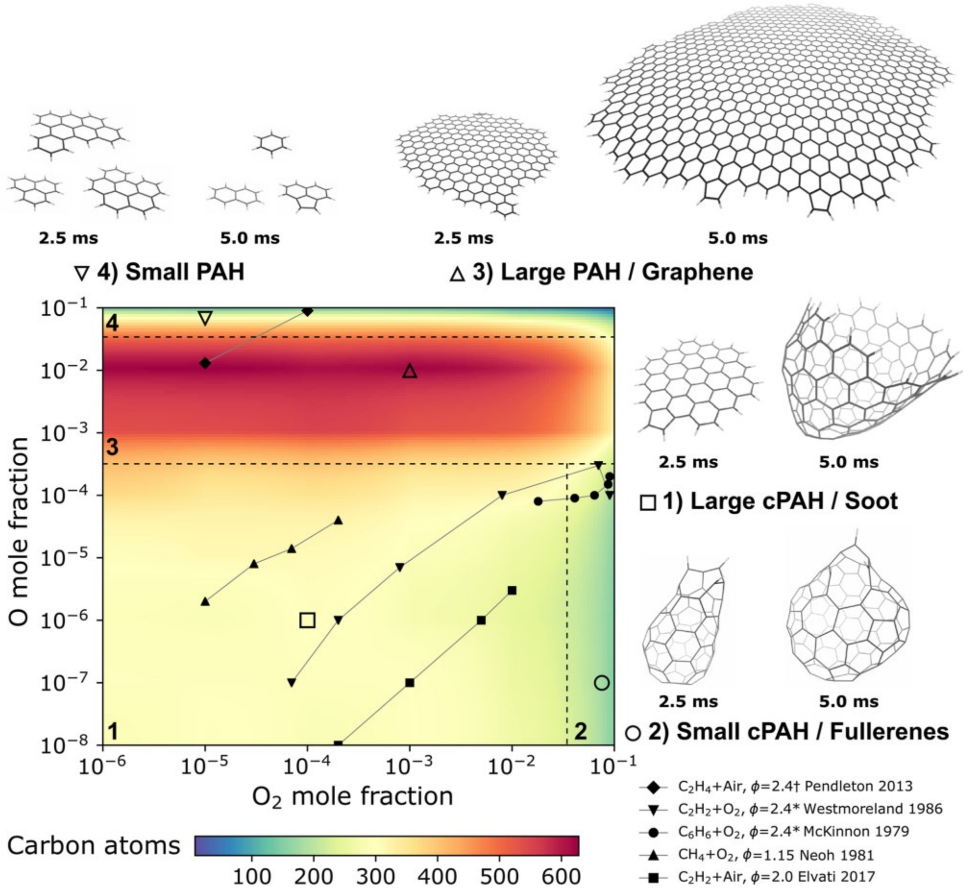
Martin, Jacob W., Maurin Salamanca, and Markus Kraft. "Soot inception: Carbonaceous nanoparticle formation in flames." *Progress in Energy and Combustion Science* 88 (2022): 100956.



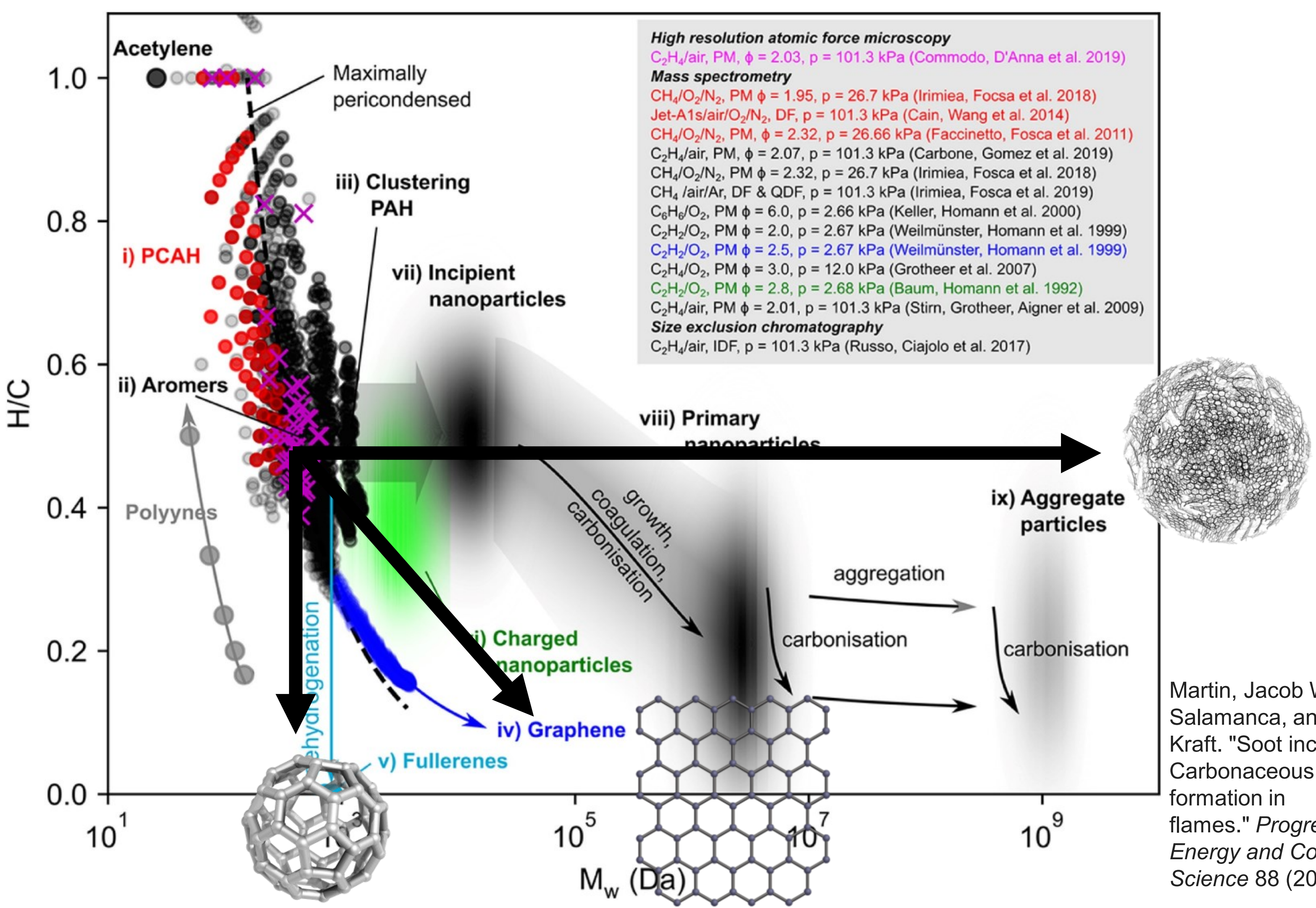
Homann 1999



Fortugno, Paolo, et al. Carbon 186 (2022): 560-573.



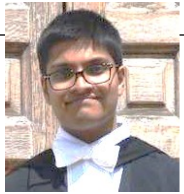
Leon, Gustavo, et al. "The role of oxygenated species in the growth of graphene, fullerenes and carbonaceous particles." *Carbon* 182 (2021): 203-213.



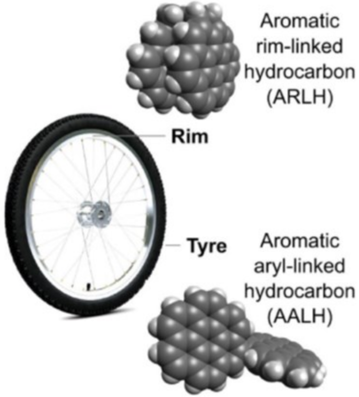
Martin, Jacob W., Maurin Salamanca, and Markus Kraft. "Soot inception: Carbonaceous nanoparticle formation in flames." *Progress in Energy and Combustion Science* 88 (2022): 100956.

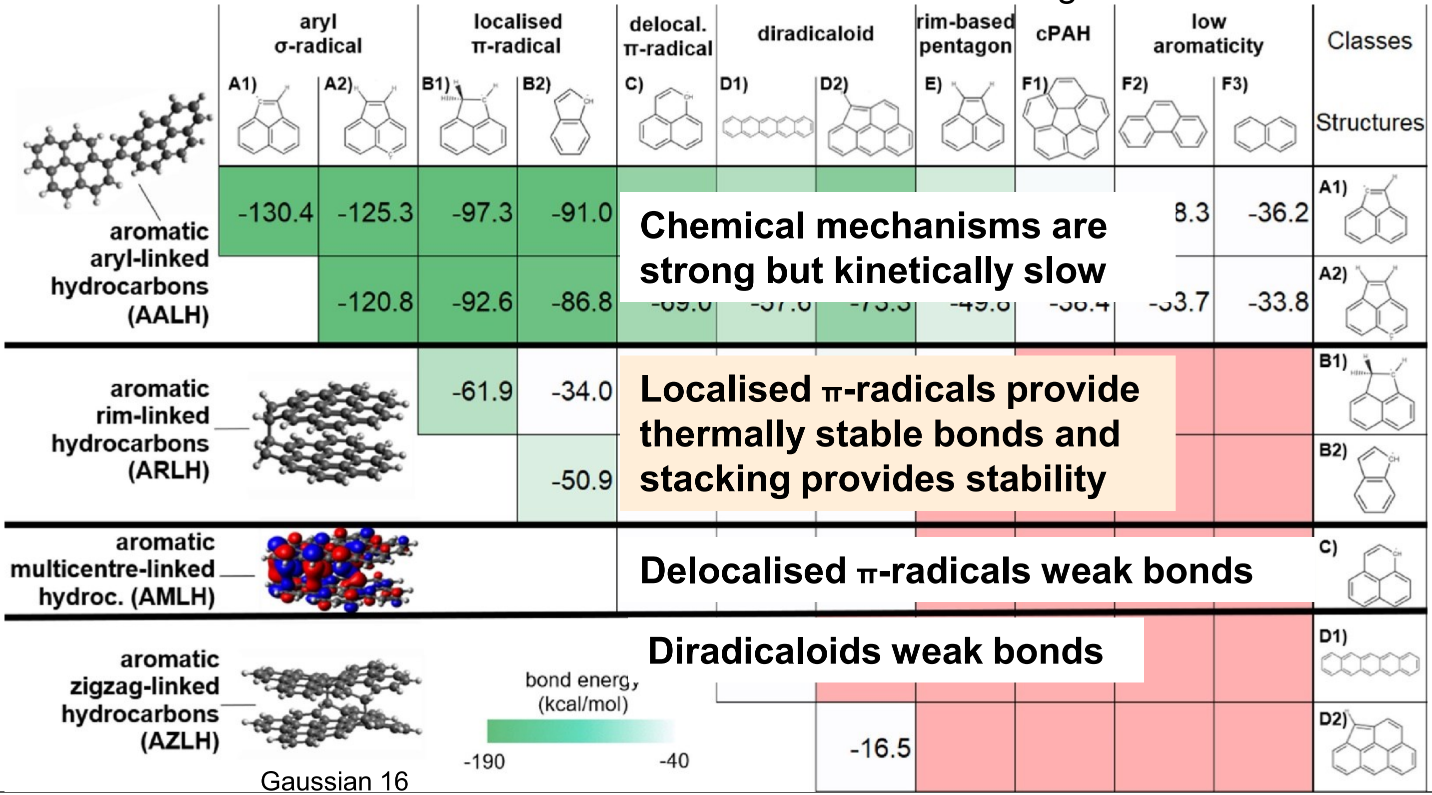
Kinetics of chemical mechanisms

Strong bonds but kinetics are slow



Angiras Menon





Chemical mechanisms are strong but kinetically slow

Localised π-radicals provide thermally stable bonds and stacking provides stability

Delocalised π-radicals weak bonds

Diradicaloids weak bonds

M06-2X/cc-pVTZ//B3LYP/6-311G(d,p)

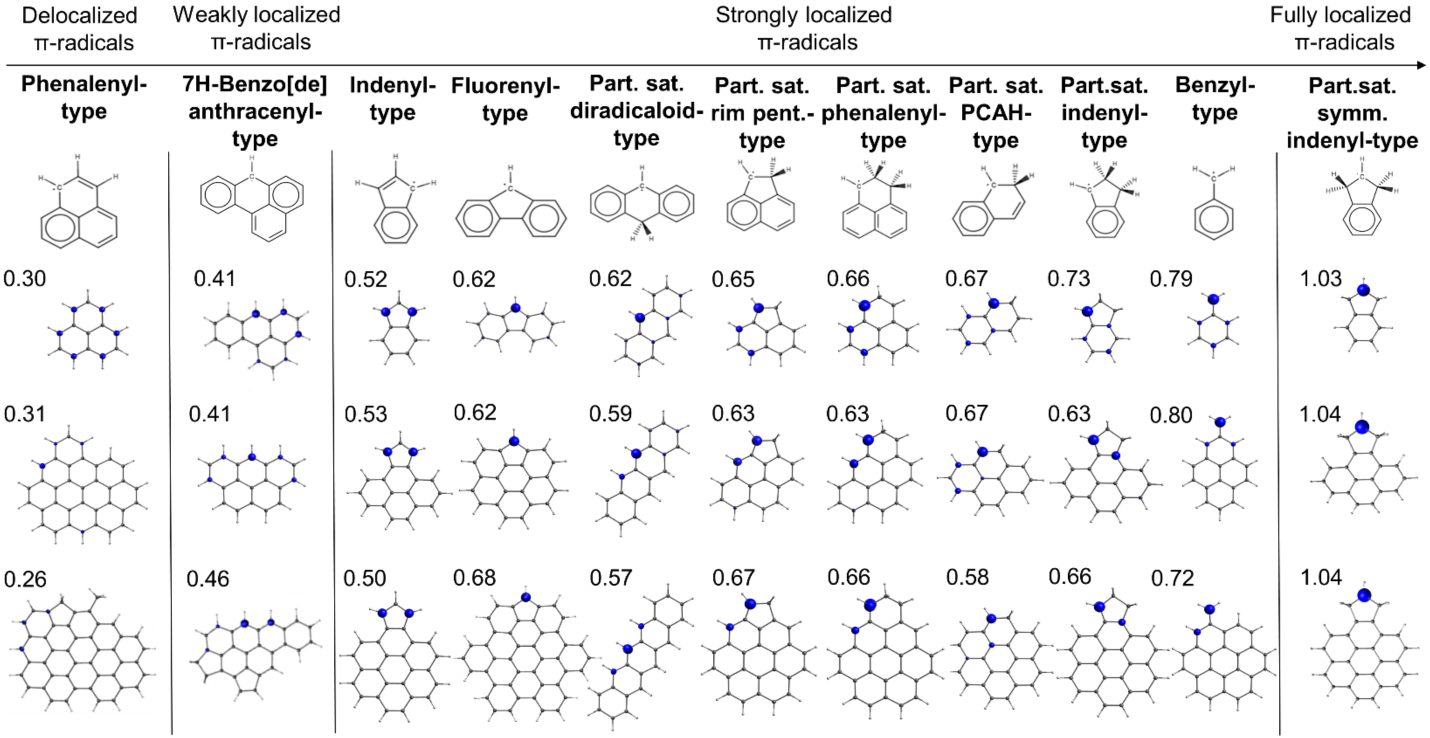
Martin, Jacob W., et al. "Reactivity of polycyclic aromatic hydrocarbon soot precursors: implications of localized π-radicals on rim-based pentagonal rings." *The Journal of Physical Chemistry C* 123.43 (2019): 26673-26682.

Menon, A., Martin, J. W., Akroyd, J., & Kraft, M. (2020). Reactivity of polycyclic aromatic hydrocarbon soot precursors: Kinetics and equilibria. *The Journal of Physical Chemistry A*, *124*(48), 10040-10052.

Electrons pinned to the edge

Localisation of π-radicals due to aromaticity

Selvakumar, Praveen K., et al. "Role of π-Radical Localization on Thermally Stable Cross-Links Between Polycyclic Aromatic Hydrocarbons." *The Journal of Physical Chemistry A* 127.33 (2023): 6945-6952.



Praveen Selvakumar

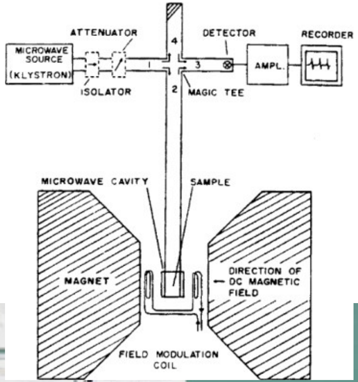
Electrons pinned to the edge

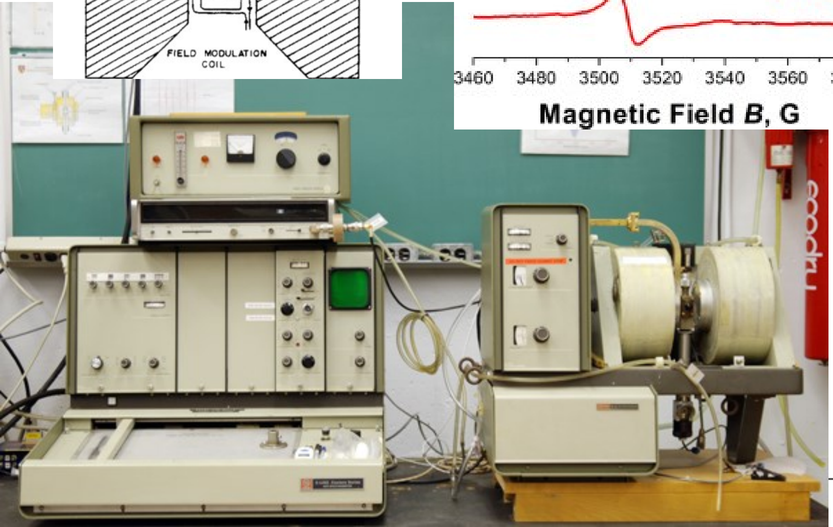
Alessandro Faccinetto

Xavier Mercier

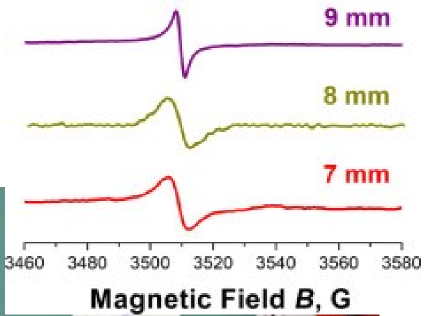
Herve Vezin

Electron paramagnetic resonance

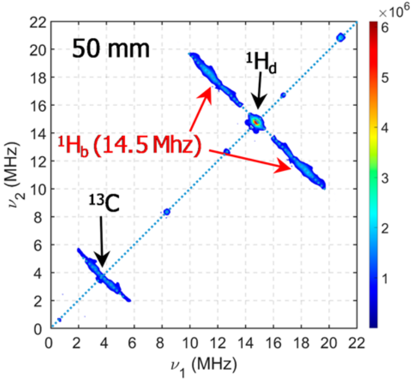




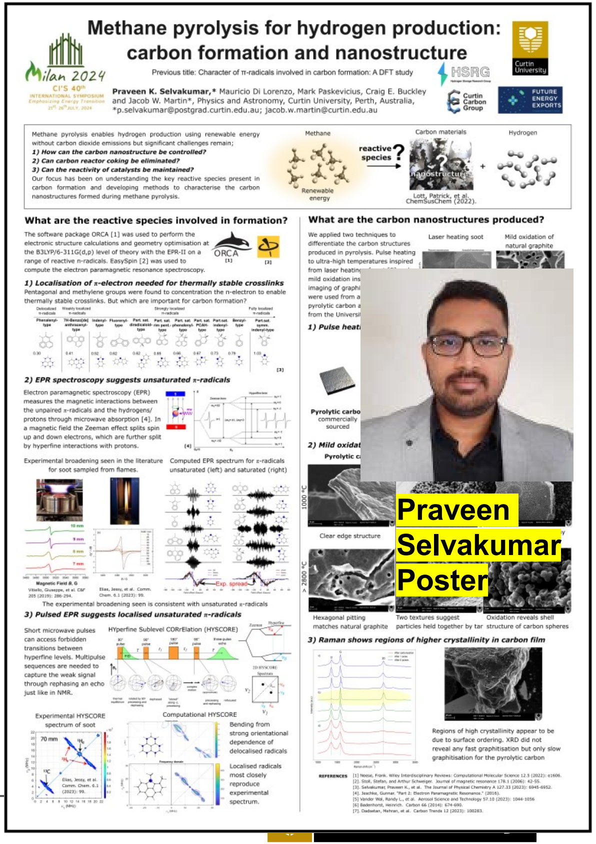
Vitiello, G., De Falco, G., Picca, F., Commodo, M., D'Errico, G., Minutolo, P., & D'Anna, A. (2019). Combustion and Flame, 205, 286-294.



Elias, J., Faccinetto, A., Vezin, H., & Mercier, X. (2023). Communications Chemistry, 6(1), 99

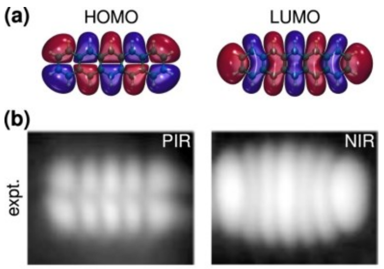


Evidence for localised pi-radicals from pulsed EPR experiments.



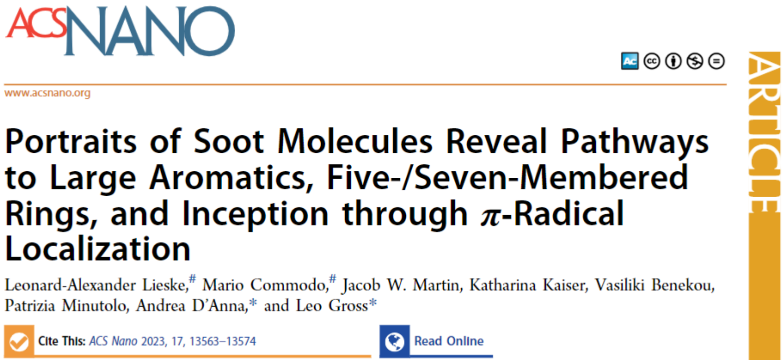
Electrons pinned to the edge

STM - pi-electrons



Leonard-Alexander Lieske

Vasiliki Benekou


ACS NANO

www.acsnano.org

ARTICLE

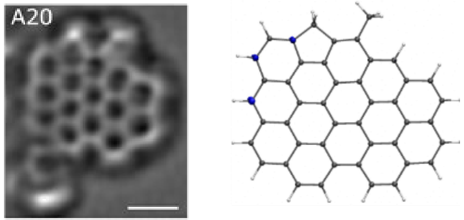
Portraits of Soot Molecules Reveal Pathways to Large Aromatics, Five-/Seven-Membered Rings, and Inception through π-Radical Localization

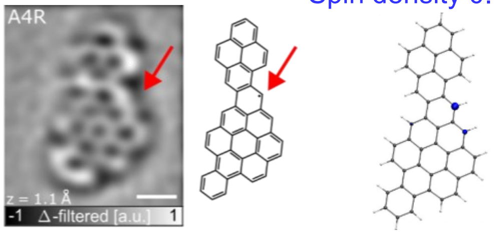
Leonard-Alexander Lieske,# Mario Commodo,# Jacob W. Martin, Katharina Kaiser, Vasiliki Benekou, Patrizia Minutolo, Andrea D'Anna,* and Leo Gross*

Cite This: ACS Nano 2023, 17, 13563−13574

Read Online

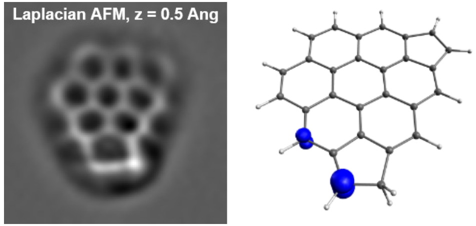
Spin density 0.26

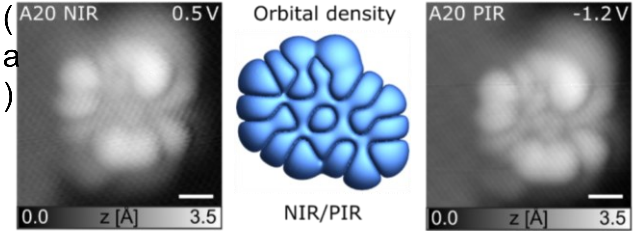


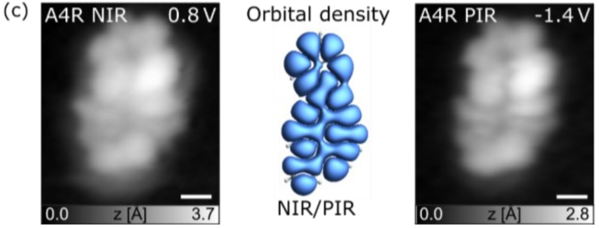


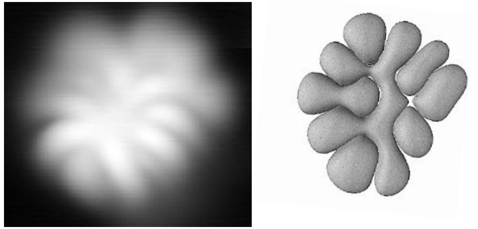
Spin density 0.41

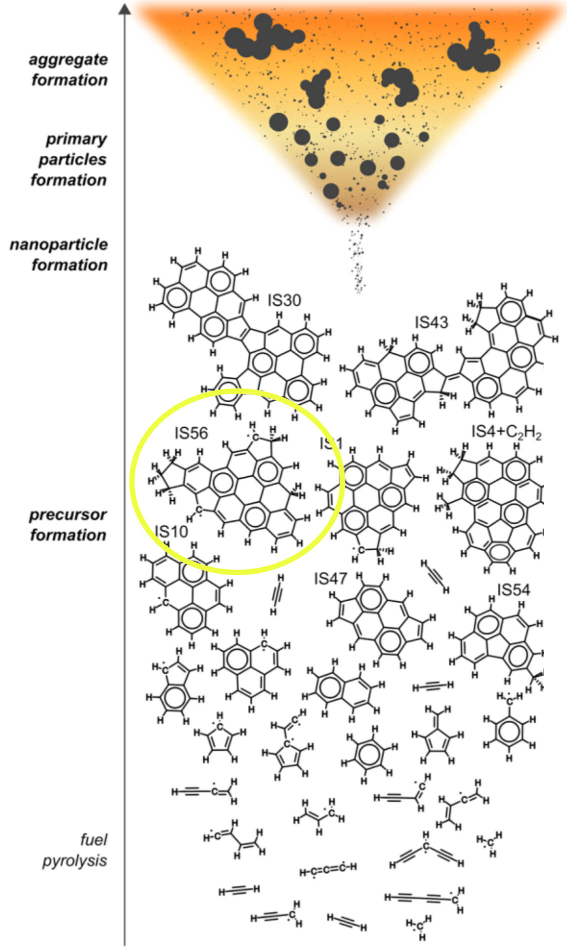
Spin density 0.67

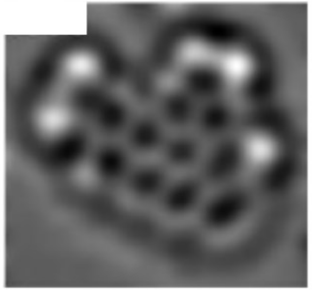


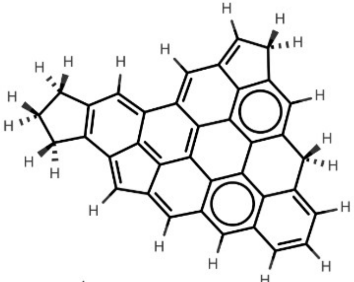




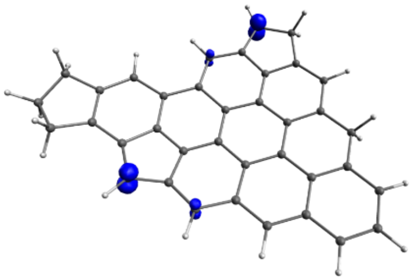


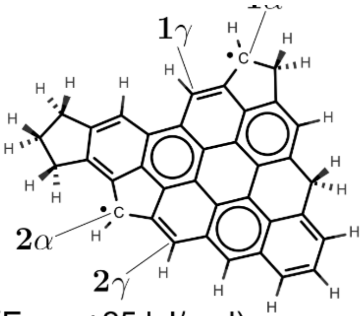






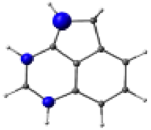
$^1A_1$ – singlet

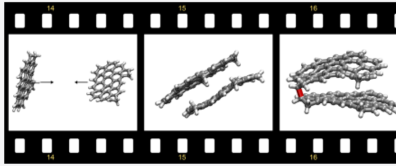




$^3A_1$ – triplet diradical (E_{ST} = +25 kJ/mol)

DLPNO-CCSD(T)/cc-pVTZ





JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
pubs.acs.org/JACS

π-Diradical Aromatic Soot Precursors in Flames

Jacob W. Martin,[▽] Laura Pascazio,[▽] Angiras Menon, Jethro Akroyd, Katharina Kai
Mario Commodo, Andrea D'Anna, Leo Gross, and Markus Kraft*

Cite This: J. Am. Chem. Soc. 2021, 143, 12212−12219 Read Online

ACCESS | Metrics & More | Article Recommendations | Sup

ABSTRACT: Soot emitted from incomplete combustion of hydrocarbon fuels contributes to global wa
disease. The mechanism by which soot nanoparticles form within hydrocarbon flames is still an unsolved
science. Mechanisms proposed to date involving purely chemical growth are limited by slow reaction ra
relying on solely physical interactions between molecules are limited by weak intermolecular interactions t
temperatures. Here, we show evidence for a reactive π-diradical aromatic soot precursor imaged using
microscopy. Localization of π-electrons on non-hexagonal rings was found to allow for Kekulé aromatic soo
triplet diradical ground state. Barrierless chain reactions are shown between these reactive sites, which
aromatic rim-linked hydrocarbons under flame conditions. Quantum molecular dynamics simulation
condensation of aromatics that survive for tens of picoseconds. Bound internal rotors then enable the reacti
and become chemically cross-linked before dissociation. These species provide a rapid, thermally stable ch
nanoparticle formation and could provide molecular targets for limiting the emission of these toxic comb

■ INTRODUCTION

Soot emitted into the atmosphere contributes to global warming, and when deposited on ice, soot lowers ice's albedo, increasing melting.[1] Recent estimates place the atmospheric radiative forcing of black carbon at 0.5−1.0 W/m^2, similar to that of methane.[1] Additionally, soot and other <2.5 μm combustion products ($PM_{2.5}$) have been directly correlated with increased morbidity and respiratory diseases.[2] Most pressing is preliminary evidence that an increase of only 1 μm/m^3 of $PM_{2.5}$ in the urban environment is associated with an 11% increase in COVID-19 related deaths (in preliminary data from the USA).[3] Recent lockdown measures also demonstrated how quickly soot emissions can drop in the atmosphere with a 12% reduction in $PM_{2.5}$ emissions in 50 major cities

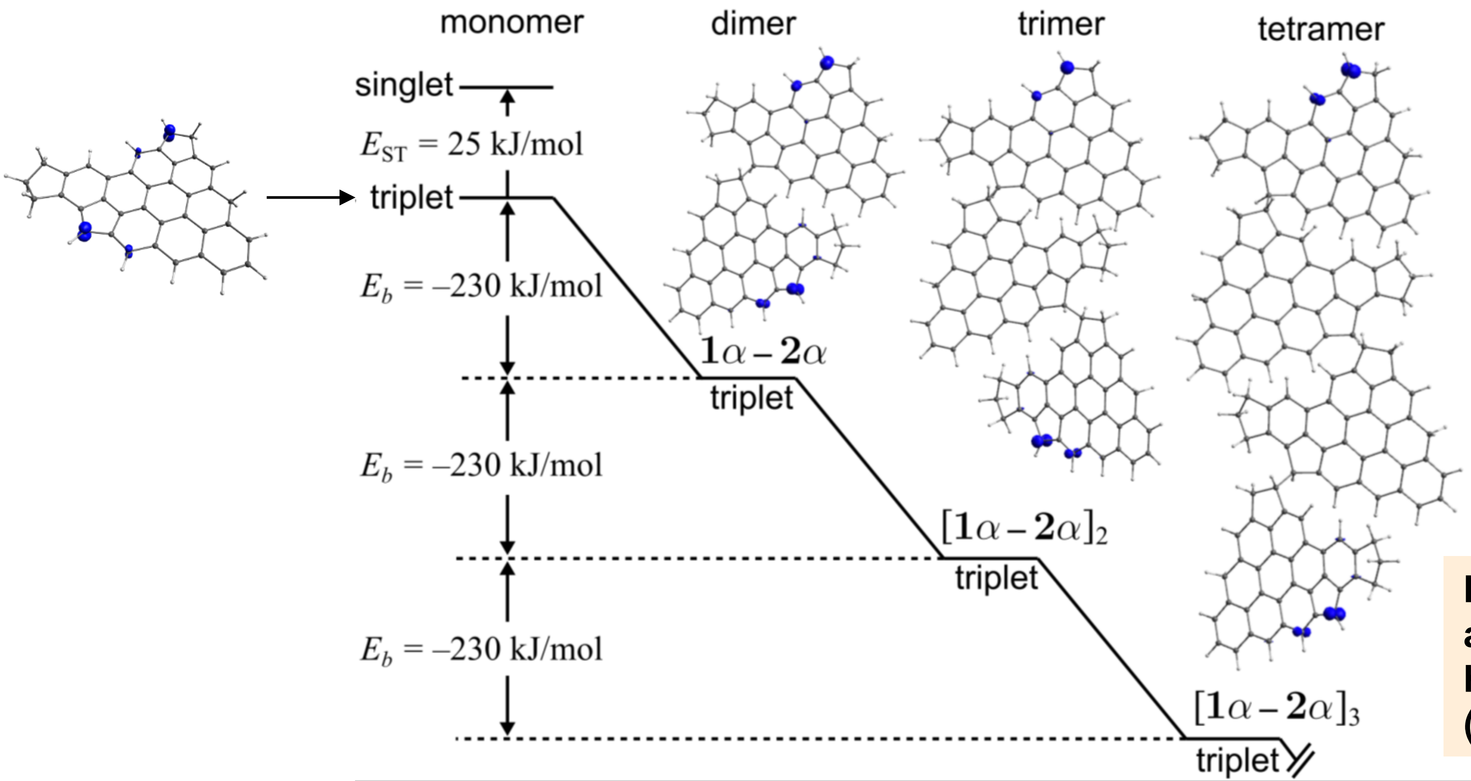
are found in the atmospheres of pla
Titan.[6]

No predictive model yet exists
particle formation, inhibiting our al
pollutants from combustion systems
produce and tune new nanomater
formation is inception (or nuclea
aromatic soot precursors cluster to
Figure 1). Three main requirements
transformation: (1) The species invol
reaction where reactivity or cond
through subsequent monomer additio
must be thermally stable with bond e

Received: May 15, 2021

Polymerisation

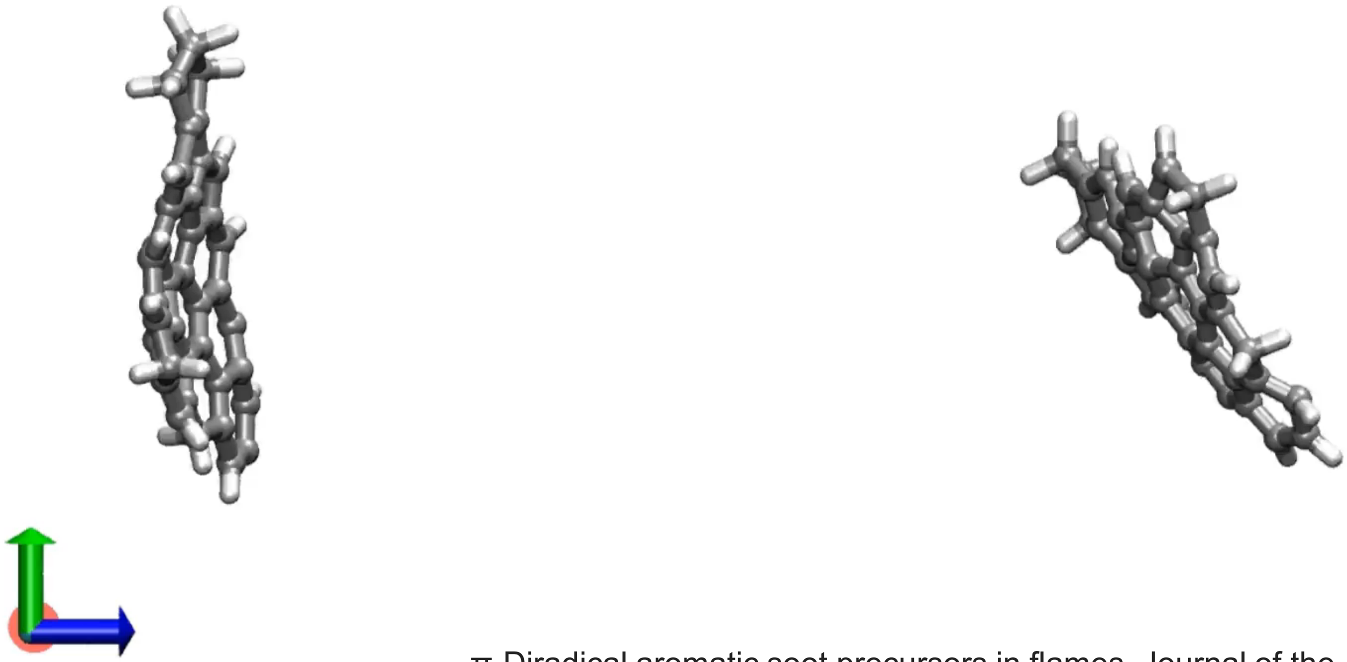
Barrierless chain reactions



Polymerisation of aromatic rim-linked hydrocarbons (PARLH).

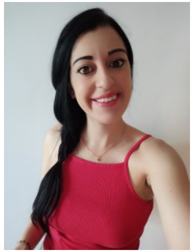
IS56
CLASSIC MD

MM (GROMACS): OPLS intramolecular and isoPAHAP intermolecular
QM (ORCA): meta hybrid GGA DFT BS-M06-2X/def2-SVP



0.00 ps

π-Diradical aromatic soot precursors in flames. Journal of the American Chemical Society. 2021 Aug 2;143(31):12212-9.

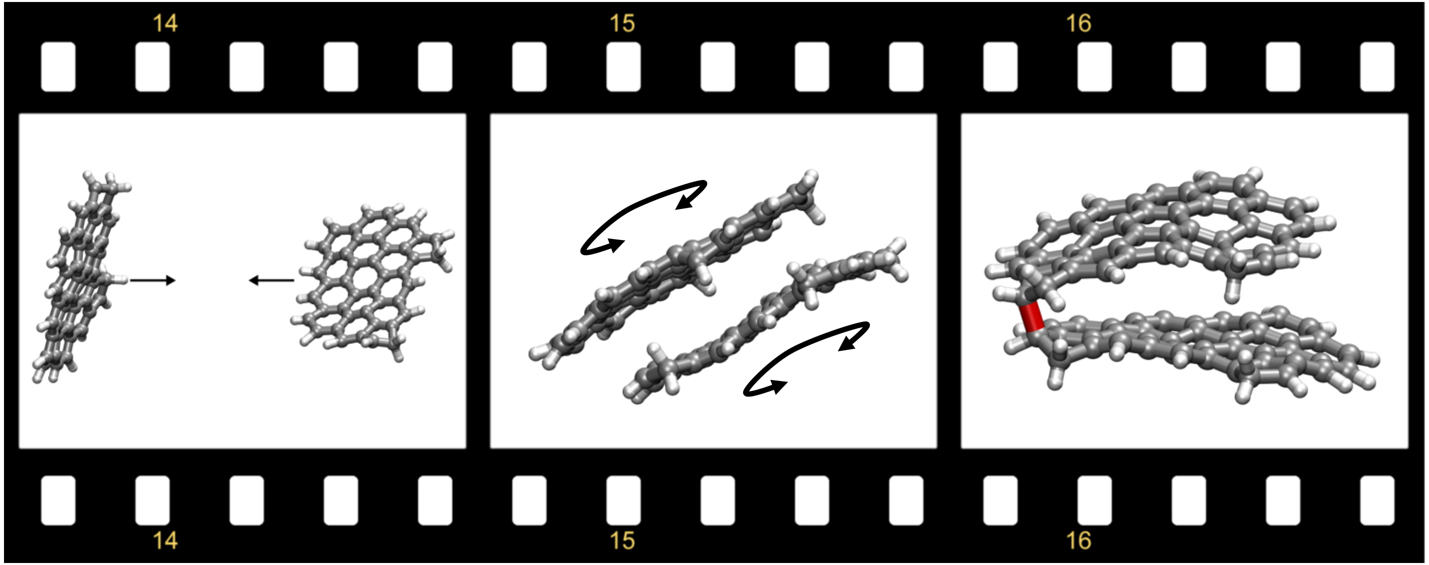


Laura Pascazio

Localised π-diradical

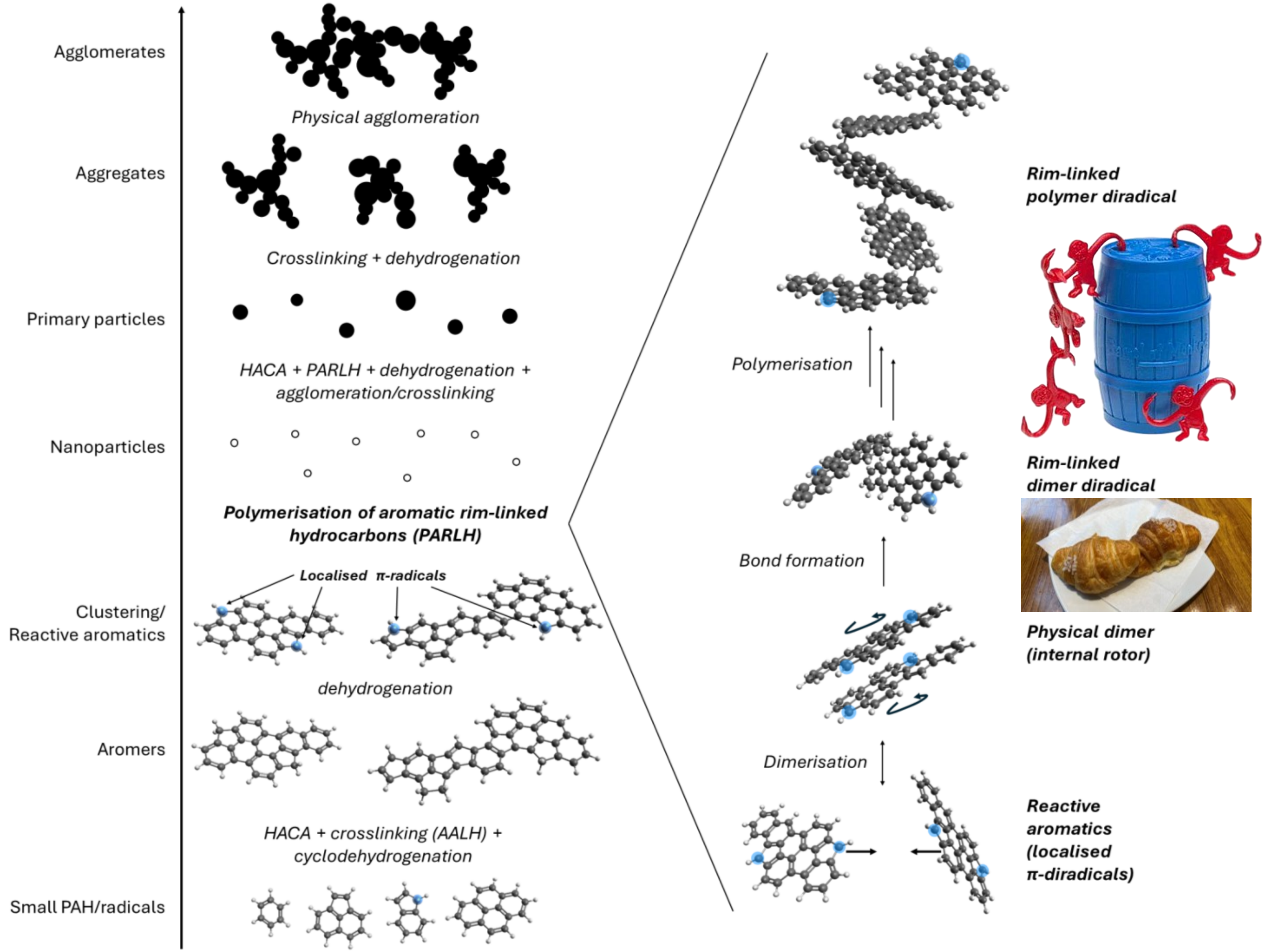
Condensation followed by bond formation – Physical + Chemical

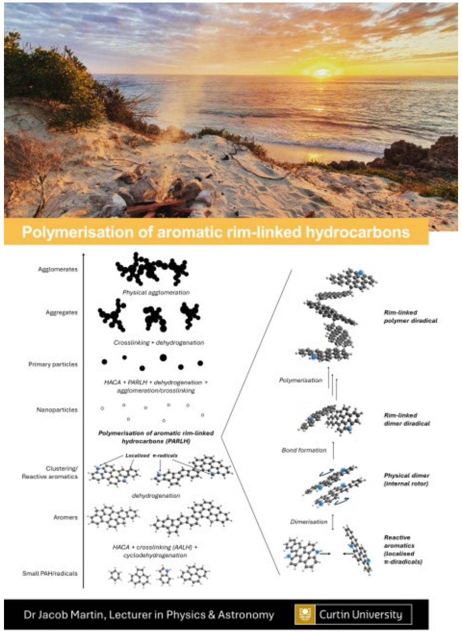
π-Diradical aromatic soot precursors in flames. Journal of the American Chemical Society. 2021 Aug 2;143(31):12212-9.



"We thus suggest that the activation of internal rotation creates "collisional events" between the edges of the rotating PAH that offer the opportunity for reaction to take place."
Frenklach and Mebel 2020

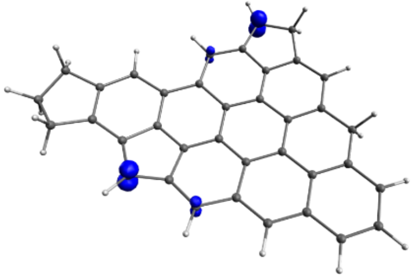
Physical condensation occurs first then internal rotors enable the reactive sites to find each other and react (not found for σ-diradicals).

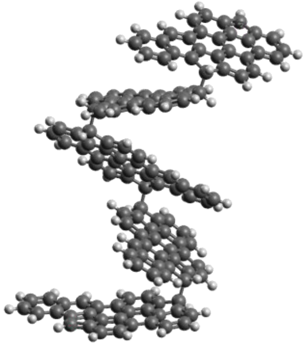

Agglomerates
Physical agglomeration
Aggregates
Crosslinking + dehydrogenation
Primary particles
HACA + PARLH + dehydrogenation + agglomeration/crosslinking
Nanoparticles
Polymerisation of aromatic rim-linked hydrocarbons (PARLH)
Localised π-radicals
Clustering/ Reactive aromatics
dehydrogenation
Aromers
HACA + crosslinking (AALH) + cyclodehydrogenation
Small PAH/radicals
Polymerisation
Rim-linked polymer diradical
Rim-linked dimer diradical
Bond formation
Physical dimer (internal rotor)
Dimerisation
Reactive aromatics (localised π-diradicals)


Polymerisation of aromatic rim-linked hydrocarbons
Dr Jacob Martin, Lecturer in Physics & Astronomy
Curtin University

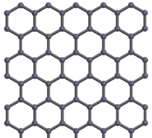
Summary

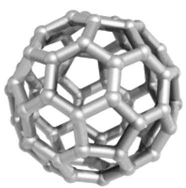
1. Identify key reactive species

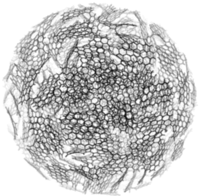


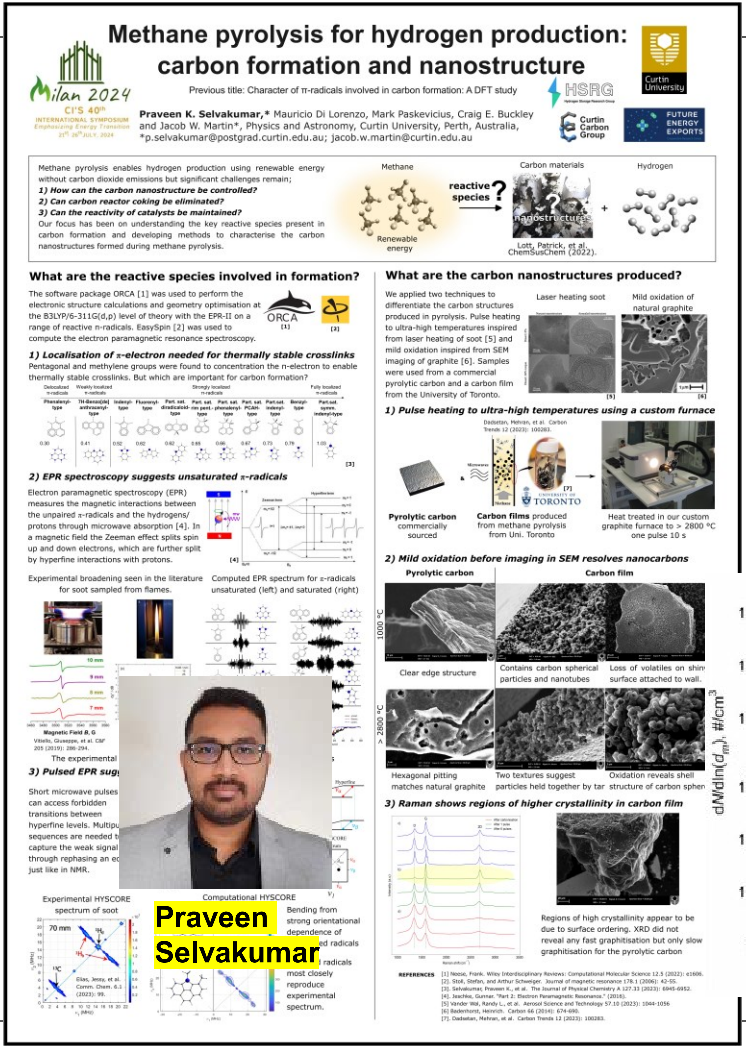


2. Control carbon nanostructures produced in pyrolysis



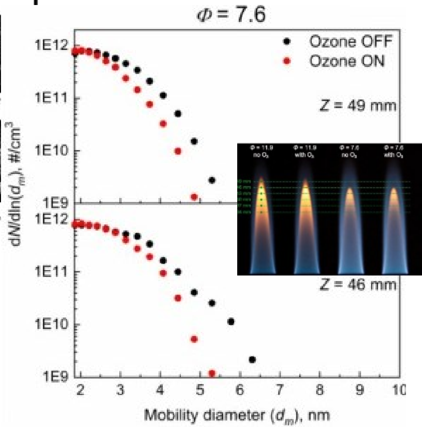






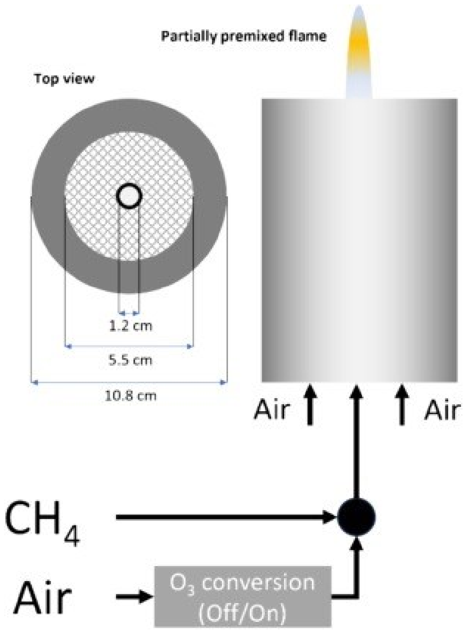
Praveen Selvakumar

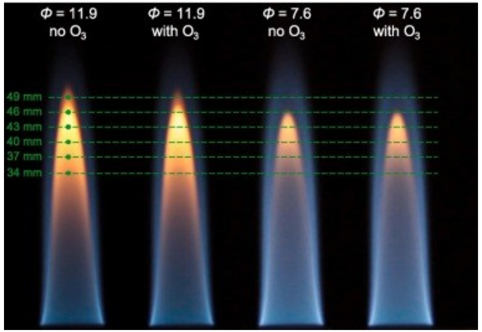
Luca Basta
Poster
Ozone injection

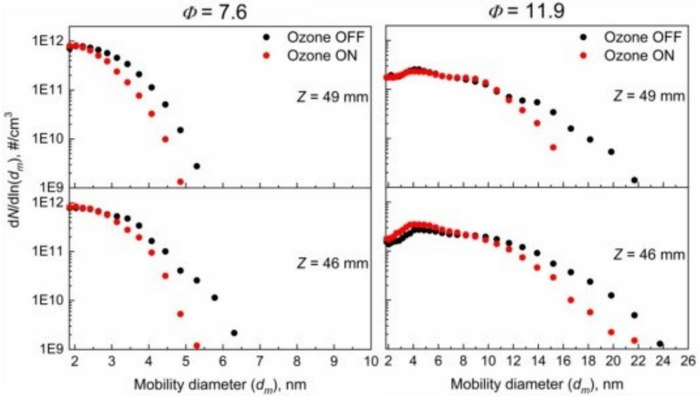


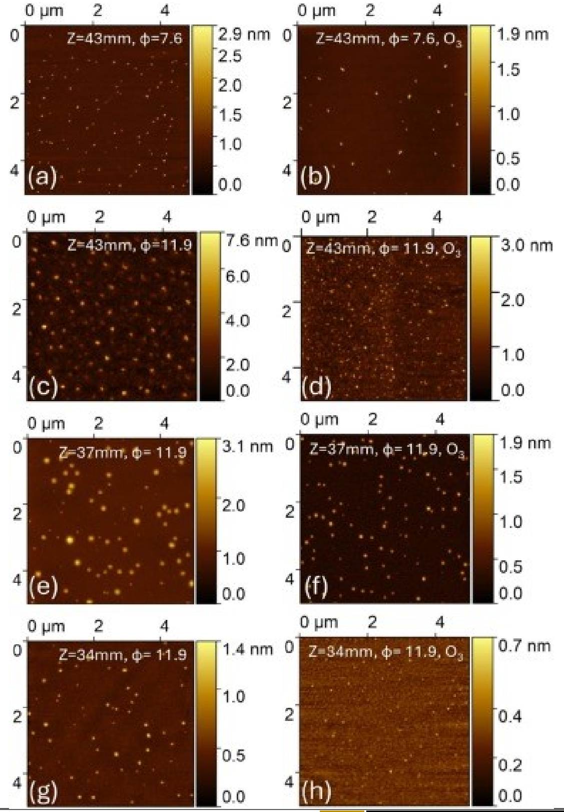
Ozone injection

Luca Basta
Poster









Basta, Luca, Alessia Pignatelli, Fabio Sasso, Francesca Picca, Mario Commodo, Patrizia Minutolo, Jacob W. Martin, and Andrea D'Anna. "The effect of ozone on soot formation in partially premixed laminar methane/air flames." *Fuel* 373 (2024): 132342.