Advances in Scanning Probe Microscopy Techniques for Soot Characterization

Consiglio Nazionale delle Ricerche
STEMS
Istituto di Scienze e Tecnologie per l'Energia e la Mobilità Sostenibili

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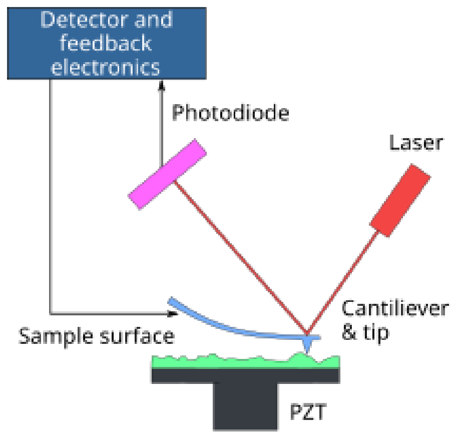
7th International Workshop on the measurement and computation of reacting flows with carbon nanoparticles

Politecnico di Milano
July 20th-21st, 2024

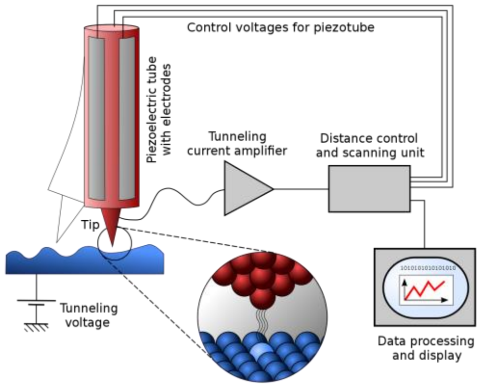
Scanning Probe Microscopy Techniques

✓Atomic Force Microscopy (AFM)



✓Scanning Tunneling Microscopy (STM)

Gerd Binnig and Heinrich Rohrer (IBM Zürich) the Nobel Prize in Physics in 1986



✓ **3D morphological information (microscopy)**

✓ **Physicochemical information (spectroscopy)**

Atomic Force Microscopy

ELSEVIER
Combustion and Flame 132 (2003) 181–187
Combustion and Flame

Morphological characterization of the early process of soot formation by atomic force microscopy

A. C. Barone*, A. D'Alessio, A. D'Anna
Dipartimento di Ingegneria Chimica, Universita' di Napoli "Federico II," Napoli, Italy

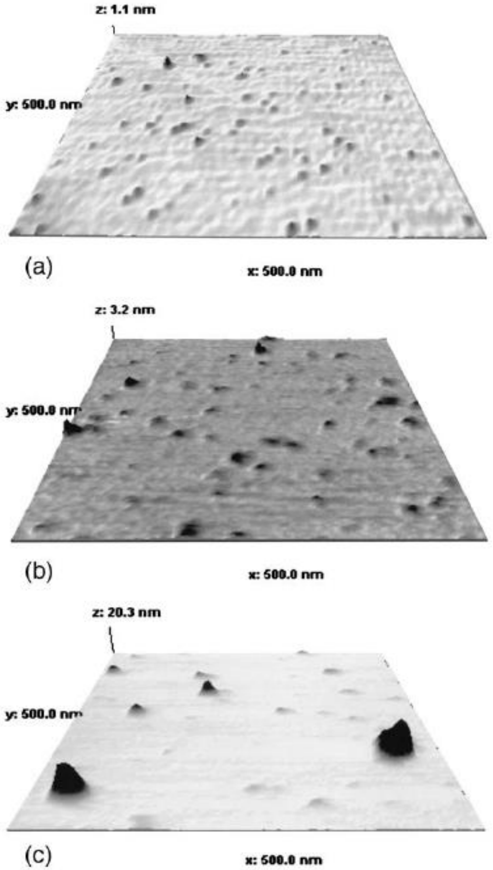
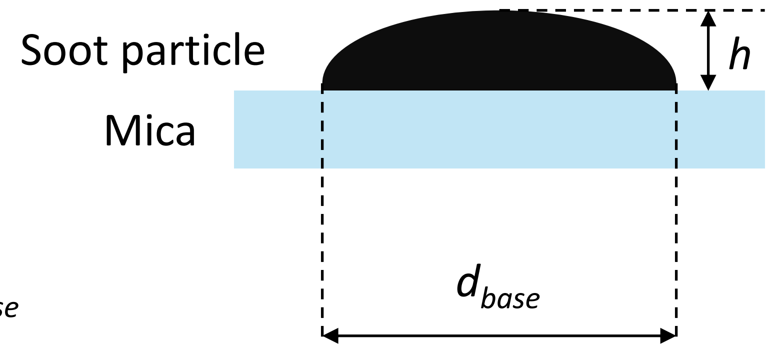


Fig. 3. AFM 3D images of particles collected on mica for a C_2H_4/Air flame, at different heights above the burner: (a) H_{AB} = 4 mm, (b) H_{AB} = 6 mm, (c) H_{AB} = 8 mm.



Sphericity ratio (SR) = h/d_{base}

Equivalent diameter (ED) = $(6V_P/\pi)^{1/3}$

Sgro et al. Chemosphere (2003)

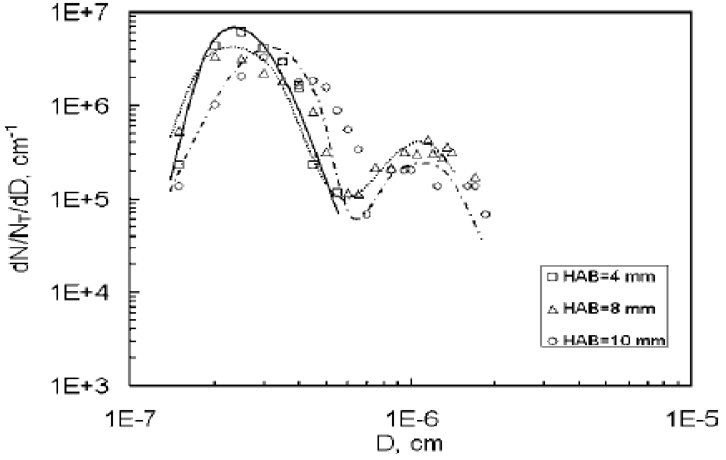
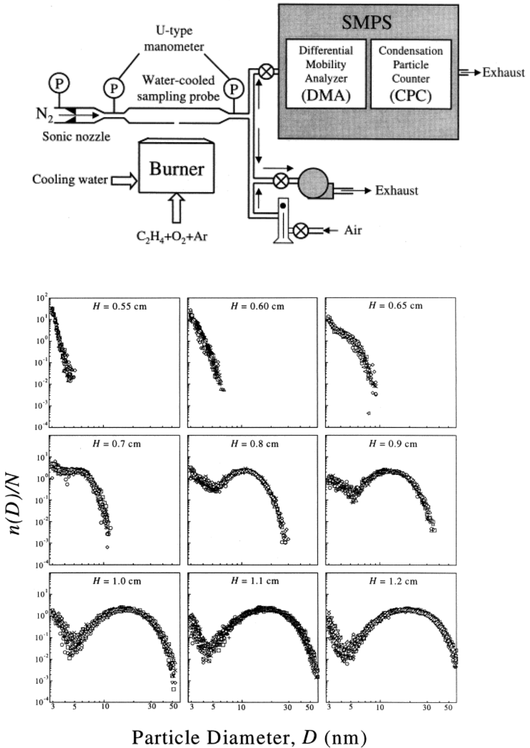
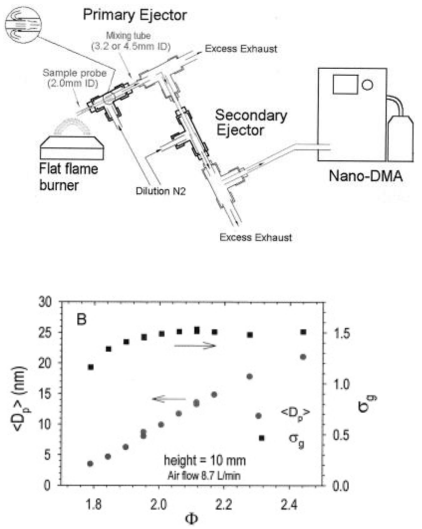


Fig. 1. Normalized size distibution curves by AFM relative to a C/O = 0.77 flame at different heights on burner: H_{ab} = 4 mm (squares), H_{ab} = 8 mm (triangles), H_{ab} = 10 mm (circles).

Zhao et al. Combust. Flame (2003)



Maricq et al. Combust. Flame (2003)



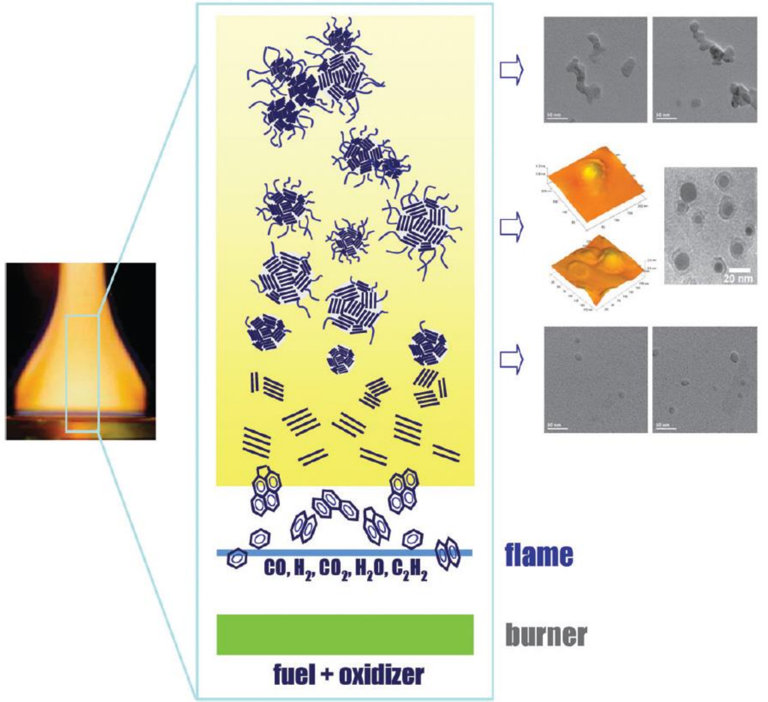
Atomic Force Microscopy

PAPER www.rsc.org/pccp | Physical Chemistry Chemical Physics

Micro-FTIR study of soot chemical composition—evidence of aliphatic hydrocarbons on nascent soot surfaces†

Jeremy P. Cain,[a] Paul L. Gassman,[b] Hai Wang*[a] and Alexander Laskin*[b]

Received 19th November 2009, Accepted 16th February 2010
First published as an Advance Article on the web 19th March 2010
DOI: 10.1039/b924344e



Contents lists available at SciVerse ScienceDirect
Combustion and Flame
journal homepage: www.elsevier.com/locate/combustflame
ELSEVIER

The evolution of soot morphology in a laminar coflow diffusion flame of a surrogate for Jet A-1

Mohammadreza Kholghy[a], Meghdad Saffaripour[a], Christopher Yip[b], Murray John Thomson[a,*]
[a] Department of Mechanical and Industrial Engineering, University of Toronto, 5 King's College Road, Toronto, Ontario M5S 3G8, Canada
[b] Department of Chemical Engineering and Applied Chemistry, University of Toronto, 160 College Street, Toronto, Ontario M5S 3E1, Canada

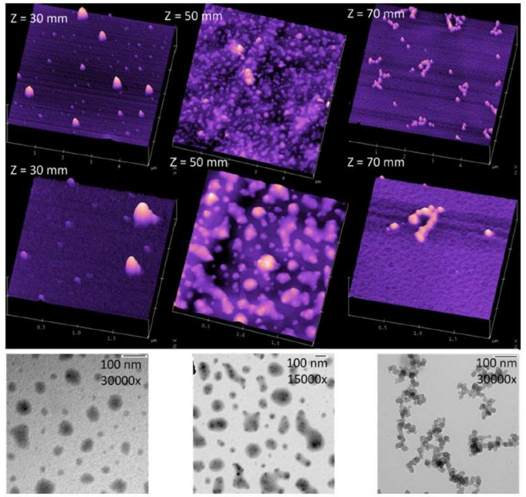


Fig. 11. AFM and TEM images of soot particles samples along the flame centerline at different heights above the fuel tube exit. Note the different length scale of the middle TEM image. Note the difference length scale between the first and the second rows of AFM images. Note that the AFM and TEM images are not of the same particles but rather the same grids.

Contents lists available at ScienceDirect
Particuology
journal homepage: www.elsevier.com/locate/partic
ELSEVIER

Application of flame-formed carbon nanoparticle films for ethanol sensing

Pegah Darvehi[a,1], Luca Basta[b,1], Mario Commodo[a,**], Patrizia Minutolo[a,*], Andrea D'Anna[b]
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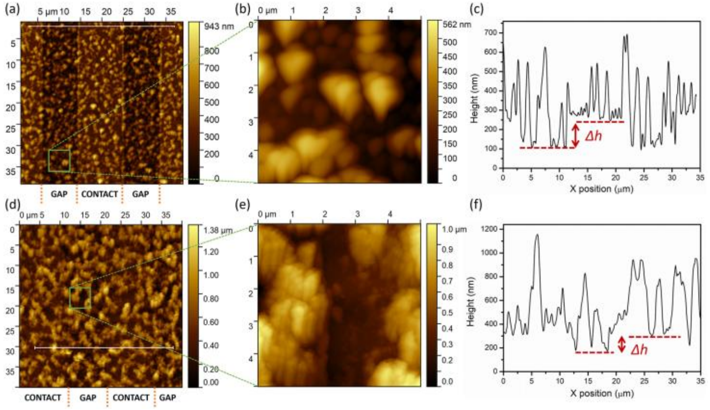
[b] Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli Federico II, P.le Tecchio 80, 80125, Napoli, Italy



Atomic Force Microscopy

ELSEVIER
Combustion and Flame 132 (2003) 181–187
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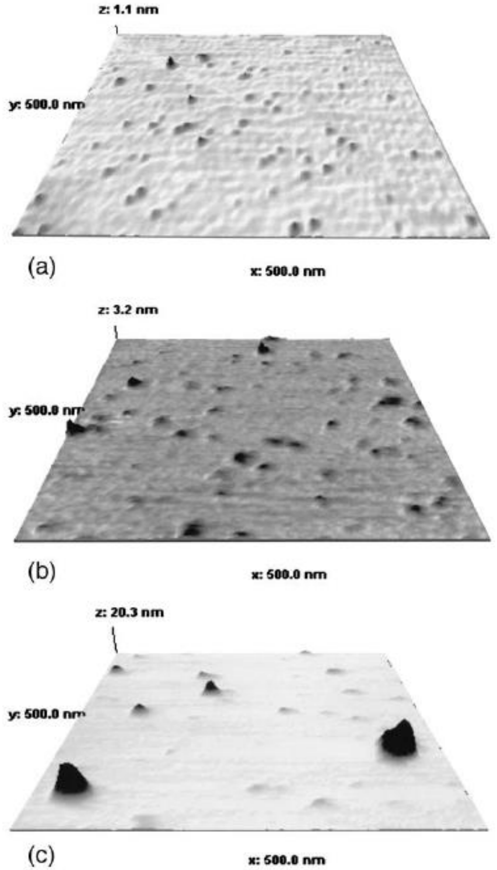

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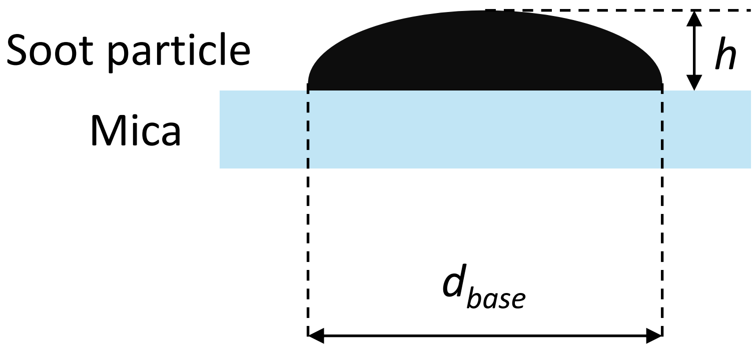
PERGAMON
Chemosphere 51 (2003) 1079–1090
CHEMOSPHERE
www.elsevier.com/locate/chemosphere

Detection of combustion formed nanoparticles

L.A. Sgro [a,*], G. Basile [a], A.C. Barone [a], A. D'Anna [a], P. Minutolo [b], A. Borghese [c], A. D'Alessio [a]
[a] Dipartimento di Ingegneria Chimica, Università degli Studi di Napoli Federico II, Piazzale Tecchio 80, 80125 Napoli, Italy
[b] Istituto di Ricerche sulla Combustione, CNR, Piazzale Tecchio 80, 80125 Napoli, Italy
[c] Istituto di Motori, CNR, Via Marconi 8, 80125 Napoli, Italy



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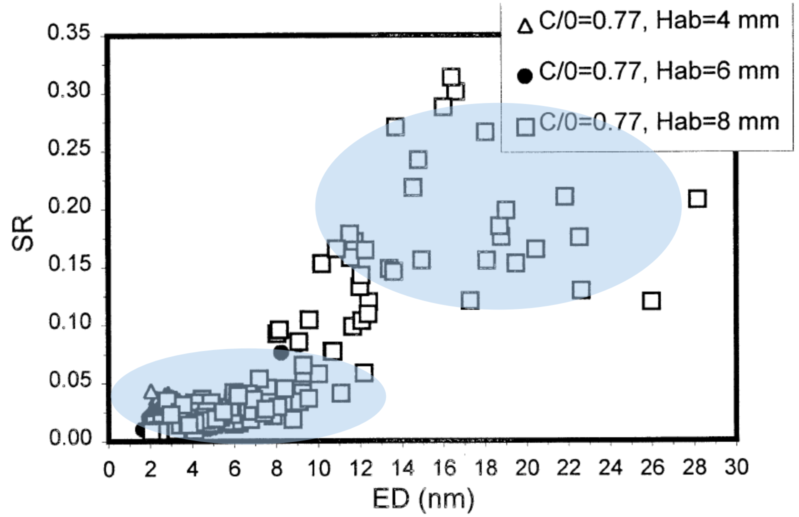


Fig. 8. Ratio of particle height with respect to their diameter (SR) as a function of the particle equivalent diameter (ED) in the C_2H_4/Air flame, C/O = 0.77, for H_{AB} equal to 4 mm, 6 mm and 8 mm.

*A deformation of the nanoparticles due to impact depends upon the nature of the intermolecular forces that bind together the clusters. A rather loose interaction should produce viscoelastic structures, whereas more rigid and **larger particles might be tied up by chemical bonds**.*

Nanoindentation experiments by AFM – Mechanical properties – Cross-linking

Taylor & Francis

Combustion Science and Technology

ISSN: 0010-2202 (Print) 1563-521X (Online) Journal homepage: https://www.tandfonline.com/loi/gcst20

Mechanical Properties of Soot Particles: The Impact of Crosslinked Polycyclic Aromatic Hydrocarbons

Laura Pascazio, Jacob W. Martin, Maria L. Botero, Mariano Sirignano, Andrea D'Anna & Markus Kraft

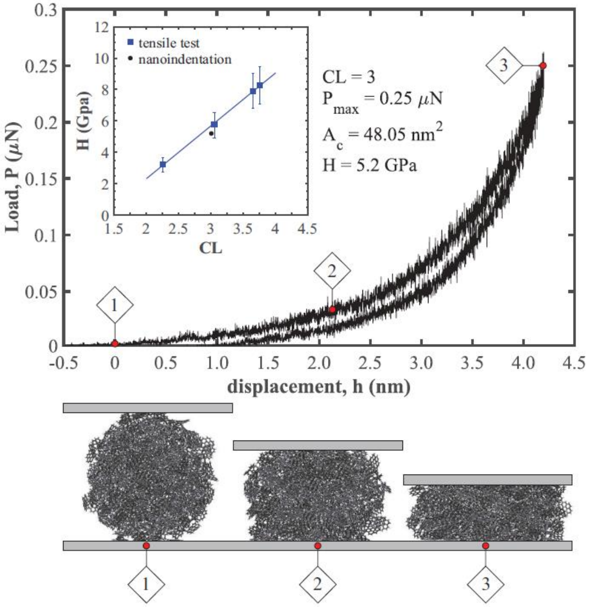


Figure 9. Load–displacement diagram and snapshots at different deformations (indentation depths) for a particle of crosslinked coronene molecules with *CL*= 3. The insert shows a comparison between the hardness determined from the tensile test and the nanoindentation simulations.

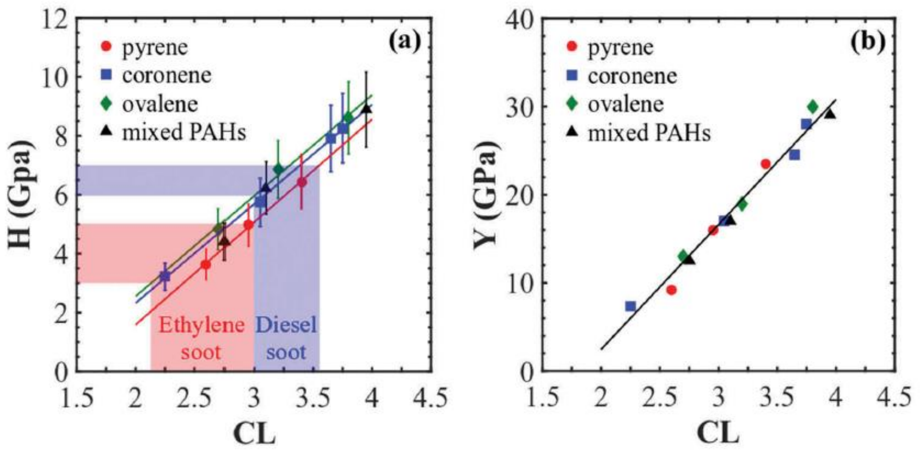


Figure 6. (a) Hardness (*H*) versus degree of crosslinking (*CL*) for the empirically determined values from the reactive force field uniaxial tensile tests using *K*= 1.4 (with error bars showing *K*= 1.2–1.6). The hardness values determined for diesel soot and ethylene soot are also shown for comparison (Bhowmick and Biswas 2011; Bhowmick, Majumdar, Biswas 2011). (b) Young's modulus (*Y*) versus degree of crosslinking (*CL*).

- *The results show that the hardness grows with the degree of crosslinking in the structure.*
- *The hardness of soot suggests that soot maturation involves crosslinking and carbonization processes and that a 3D network of crosslinked PAH is present in mature soot.*
- *The transition from the liquid-like behavior of incipient soot particles to the solid state (mature soot) at flame temperatures may be related to an increase in the crosslinking density.*

Nanoindentation experiments by AFM – Mechanical properties – Cross-linking

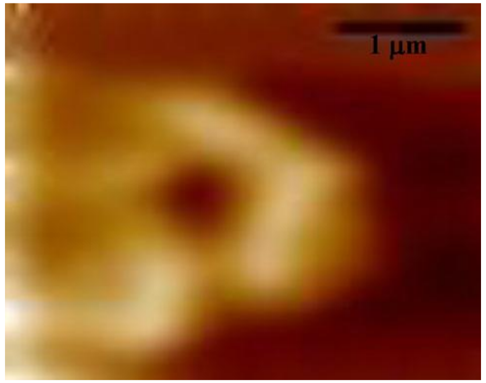
Tribol Lett (2011) 44:139–149
DOI 10.1007/s11249-011-9831-5

ORIGINAL PAPER

Relationship Between Physical Structure and Tribology of Single Soot Particles Generated by Burning Ethylene

Hiralal Bhowmick · S. K. Biswas

Image of an indent of an agglomerate



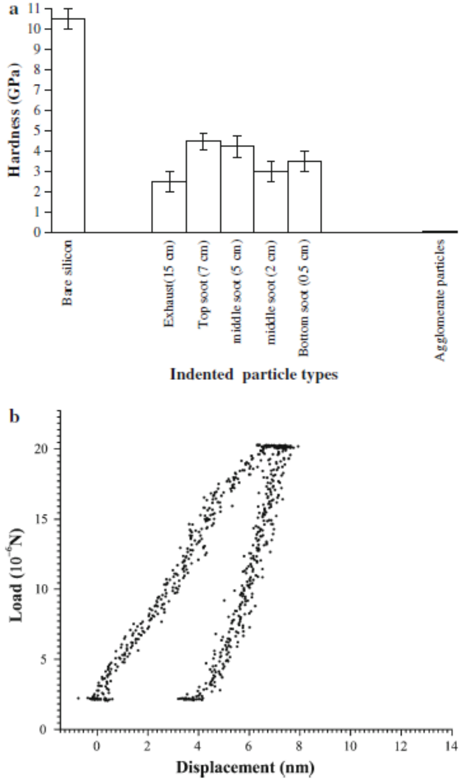


Fig. 2 a Hardness of flame soot and bare silicon. b A typical load–displacement characteristic of a soot particle (h = 0.5 cm) obtained by nanoindentation

applied sciences
MDPI

Article

Exploring Nanomechanical Properties of Soot Particle Layers by Atomic Force Microscopy Nanoindentation

Gianluigi De Falco [1,*], Fiorenzo Carbone [1], Mario Commodo [2,*], Patrizia Minutolo [2] and Andrea D'Anna [1]

[1] Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli "Federico II", 80125 Napoli, Italy; fio.carbone@studenti.unina.it (F.C.); anddanna@unina.it (A.D.)
[2] Istituto di Scienze e Tecnologie per l'Energia e la Mobilità Sostenibili, STEMS-CNR, 80125 Napoli, Italy; patrizia.minutolo@stems.cnr.it
* Correspondence: gianluigi.defalco@unina.it (G.D.F.); mario.commodo@stems.cnr.it (M.C.)

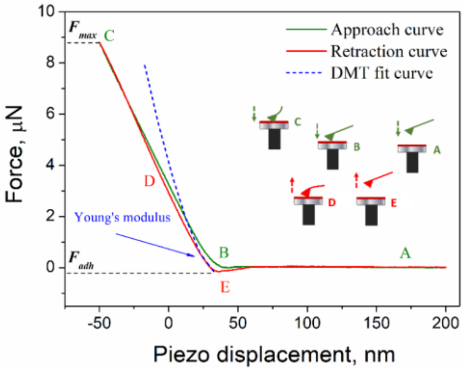


Figure 1. A typical force–distance curve measured on PEN during approach (green line) and retract (red line) of AFM probe to and from the sample surface.

Table 2. Hardness and Young's modulus measured by AFM nanoindentation on Sample #1 and Sample #2 and compared to PEN and HOPG. Errors are reported as the mean standard deviation from >20 independent measurements.

Sample	Hardness H, GPa	Young's Modulus E, GPa
Sample #1	0.75 ± 0.05	4.2 ± 0.3
Sample #2	0.90 ± 0.05	7.2 ± 0.4
PEN	0.70 ± 0.05	3.8 ± 0.3
HOPG	2.40 ± 0.10	7.5 ± 0.3

Atomic Force Microscopy: Interactive forces

Aerosol Science and Technology

Taylor & Francis

ISSN: 0278-6826 (Print) 1521-7388 (Online) Journal homepage: www.tandfonline.com/journals/uast20

Flame-Formed Carbon Nanoparticles: Morphology, Interaction Forces, and Hamaker Constant from AFM

Gianluigi De Falco, Mario Commodo, Patrizia Minutolo & Andrea D'Anna

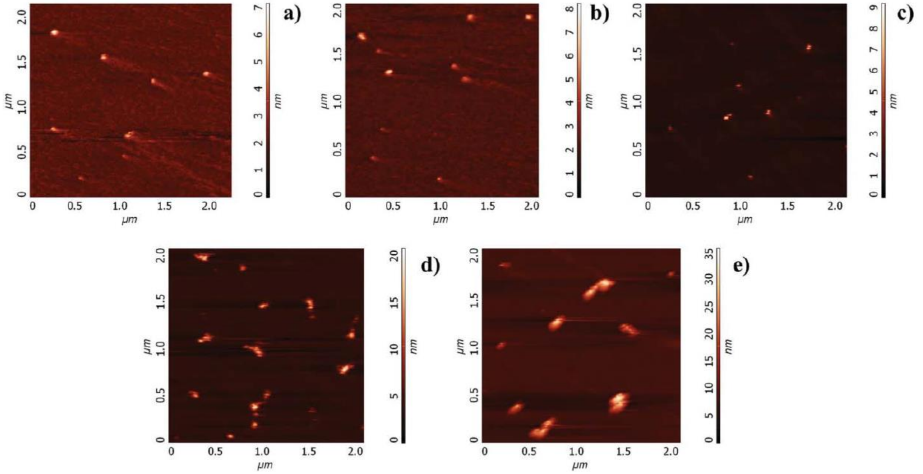


FIG. 4. AFM contact images of particles collected from flames with different equivalence ratio: (a) $\Phi = 1.85$; (b) $\Phi = 1.89$; (c) $\Phi = 1.95$; (d) $\Phi = 2.16$; (e) $\Phi = 2.58$.

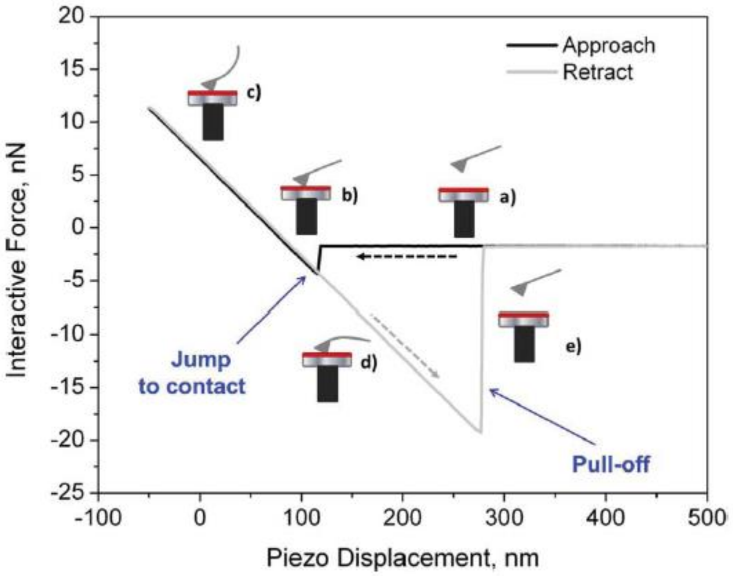
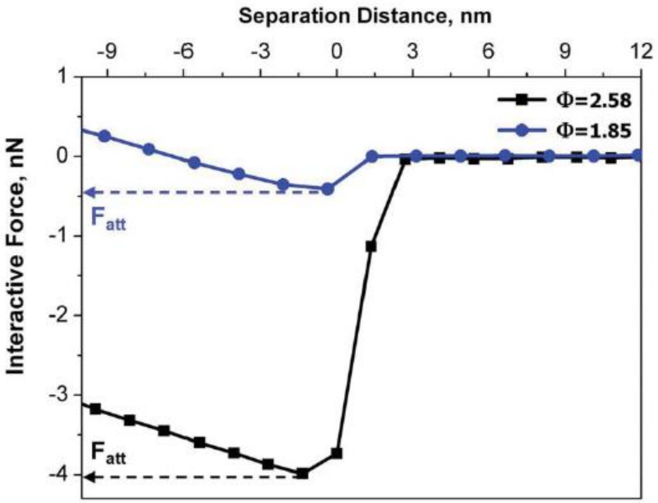


FIG. 1. A typical experimental force–distance curve measured by AFM. The black line refers to the approach of the cantilever to the sample surface, while the gray line refers to retraction from the sample surface.

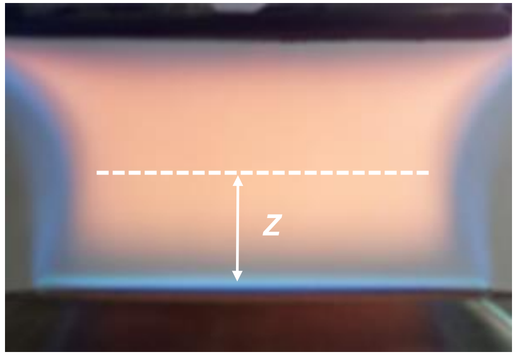


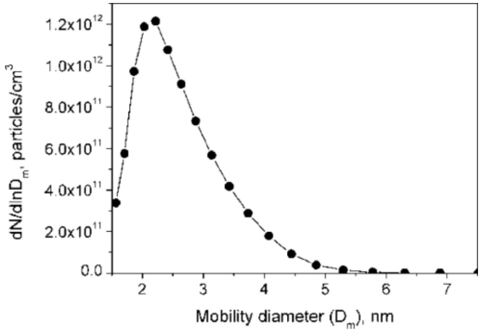
Average Hamaker constants

	Hamaker constant A, 10^{-19} J
HOPG	4.7 ± 0.3 [a]
Particles at $\Phi = 2.58$	3.5 ± 1.6[b]
Particles at $\Phi = 2.16$	2.2 ± 0.9[b]
Particles at $\Phi = 1.95$	1.5 ± 0.5[b]
Particles at $\Phi = 1.89$	0.98 ± 0.01[b]
Particles at $\Phi = 1.85$	0.95 ± 0.01[b]
Benzene	0.5[c]
Aliphatic	0.1[c]

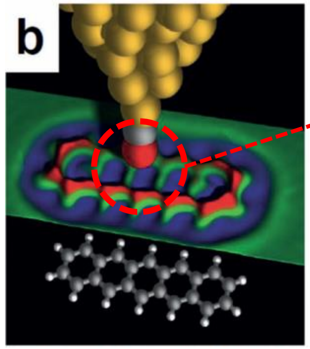
[a]Lee et al. (2002); [b]this study; [c]Israelachvili (2011).

HR-AFM – Soot molecules imaging





Gross et al. Angew. Chem. Int. Ed. (2018)

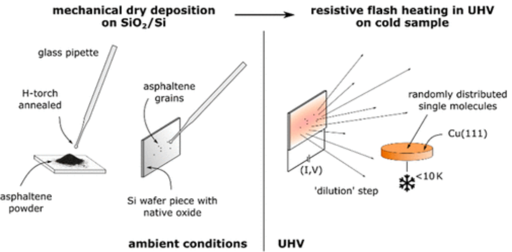


Carbon monoxide–functionalized tip to probe repulsive forces above single molecules

Sample preparation:

Gently pressing the filter onto a piece of silicon wafer

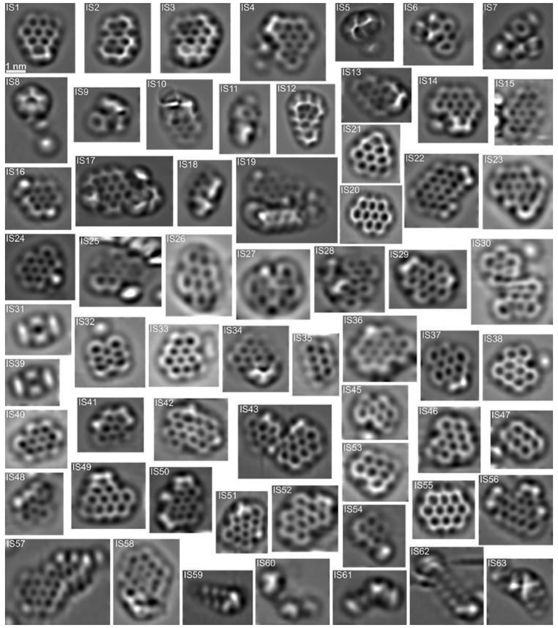
Particles sublimed from silicon wafer – flash-heated – to evaporate the molecules on a cold substrate for STM/AFM characterization

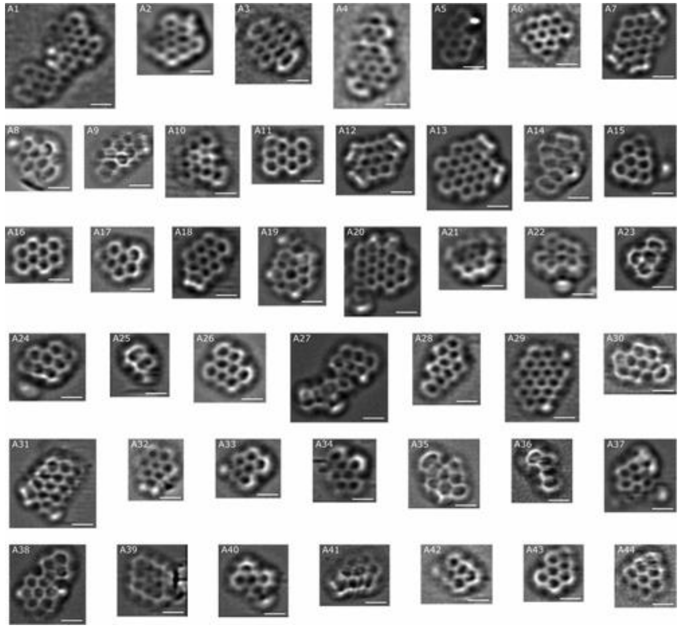


Schuler et al. Energy Fuels (2020)

The Z = 8 mm data are reported in:
Schulz et al. PCI 37, 2019, 885-892
Commodo et al. C&F 205, 2019, 154-164

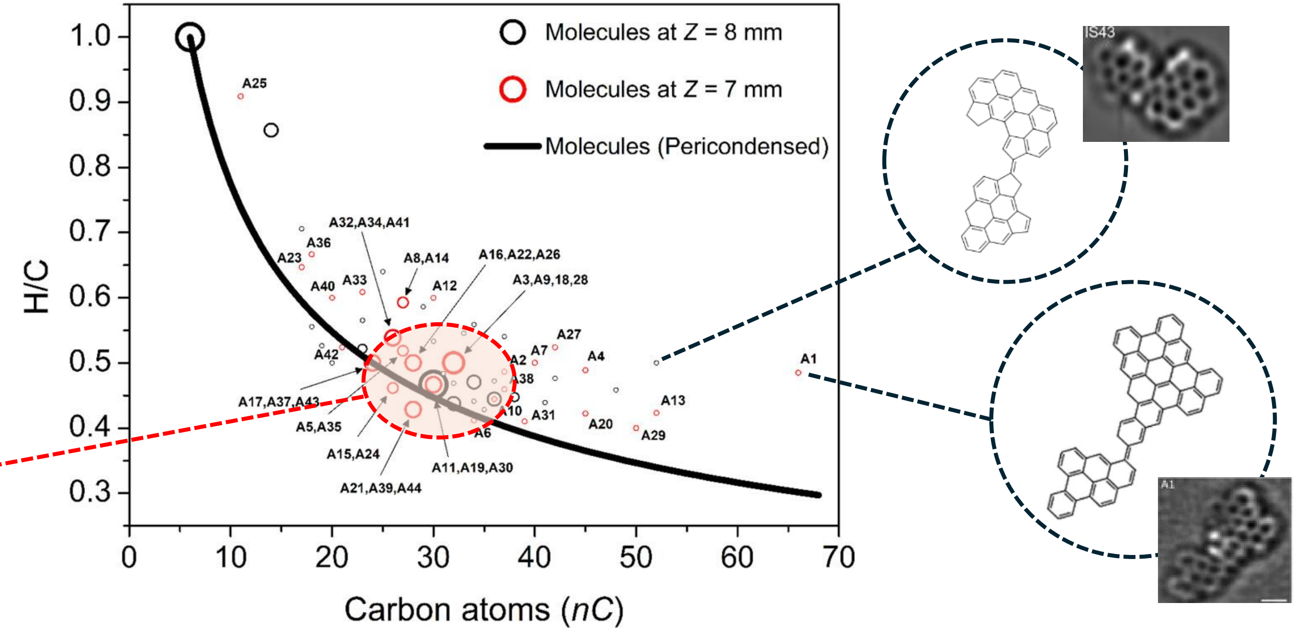
The Z = 7mm data are reported in:
Lieske et al. ACS nano 17, 2023, 13563-13574





28-30 carbon atoms

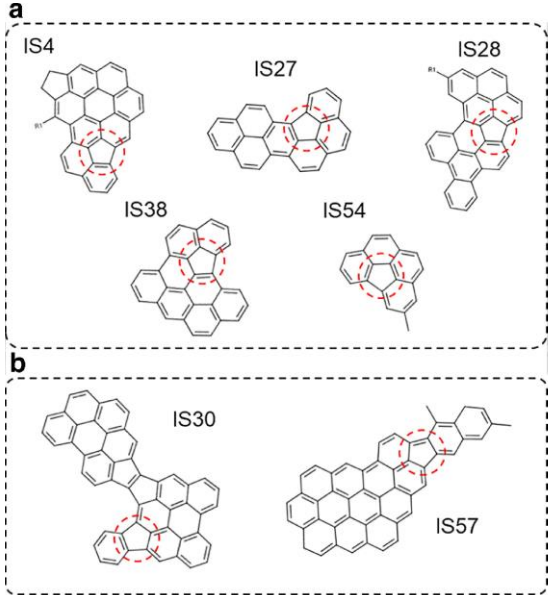
0.45-0.5 H/C



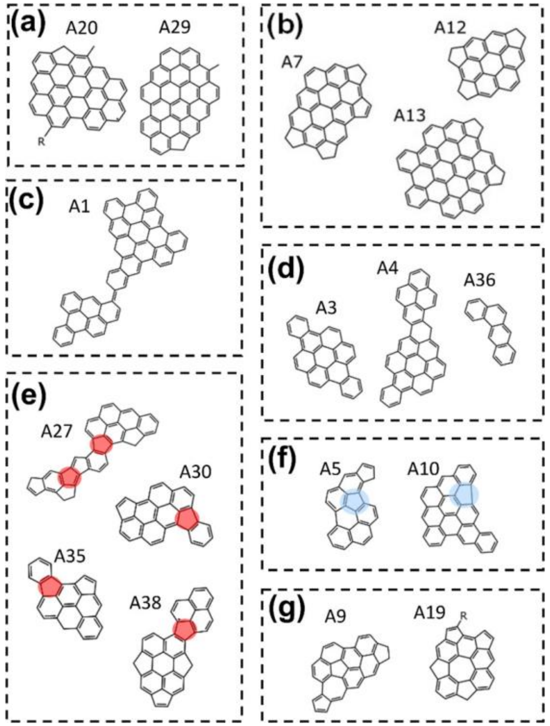
HR-AFM – Soot molecules imaging

molecules with **partially internal penta-rings**:
(a) molecules incorporating benzo[ghi]fluoranthene-type moieties;
(b) molecules incorporating fluoranthene-type moieties.

Promoting curvature

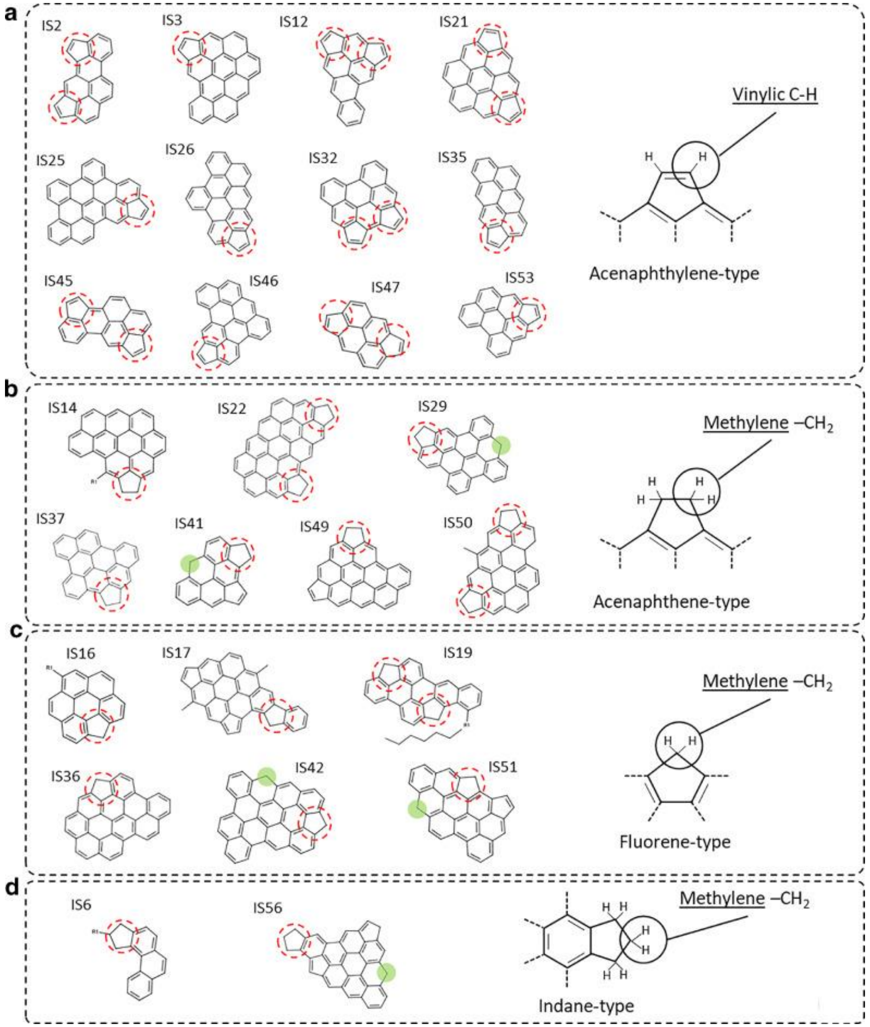


Lieske et al. ACS nano 17, 2023, 13563-13574



(a) Aromatic pericondensed structures with **high molecular mass**; (b) molecular species presenting substantial compact **pericondensed structures** but moving away from the maximally pericondensed line due to the **aliphatic pentagonal rings at their periphery**; (c) **cross-linked aromatic molecule**; (d) extended catacondensed and (e) pentalinked **elongated structures**; (f) aromatic molecules with **partially embedded pentagonal rings**. Highlights refer to molecules incorporating benzo[ghi]fluoranthene-type moieties in which the five-membered ring is incorporated in one PAH core (blue); molecules incorporating fluoranthene-type moieties in which the five-membered ring is bridging two PAH cores (red); and (g) **aromatic molecules incorporating both five- and seven-membered rings**.

Commodo et al. C&F 205, 2019, 154-164

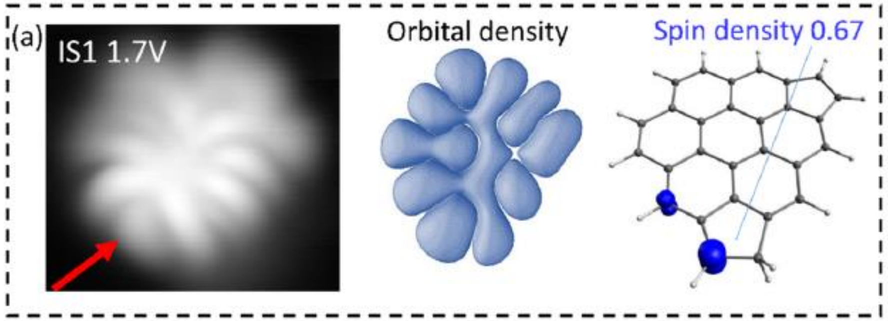


molecules with **peripheral penta-ring**:
(a) Molecules incorporating **acenaphthylene-type moieties**; (b) molecules incorporating **acenaphthene-type moieties**; (c) molecules incorporating **fluorene-type moieties**; (d) molecules with **indane-type moieties**. Green dots indicate the position of **methylene groups** on peripheral benzenoid rings.

HR-AFM – Soot molecules imaging

Presence of resonantly stabilized π-radicals

Lieske et al. ACS Nano 17, 2023, 13563-13574



Commodo et al. C&F 205, 2019, 154-164

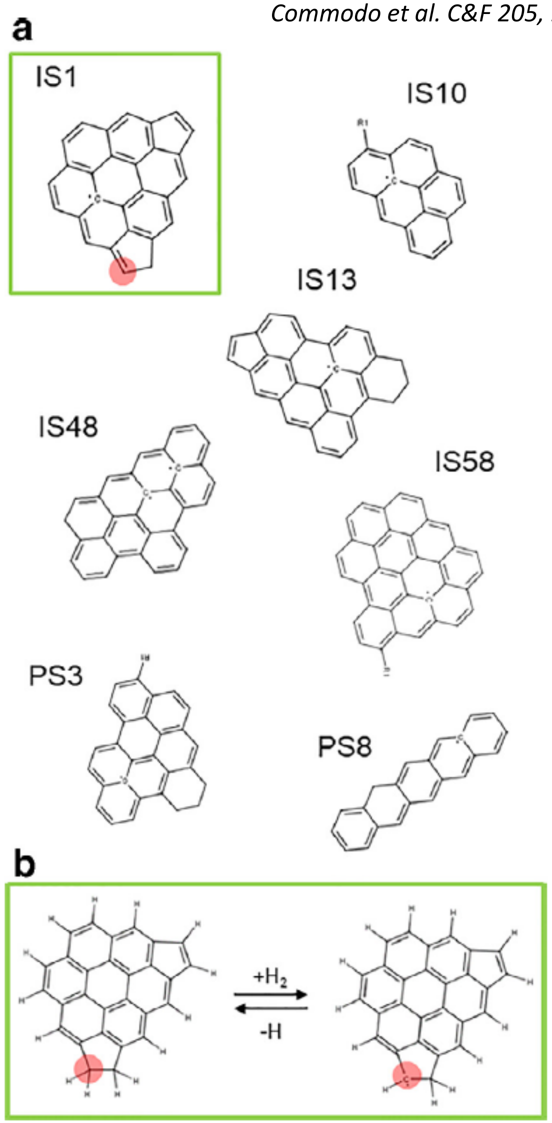
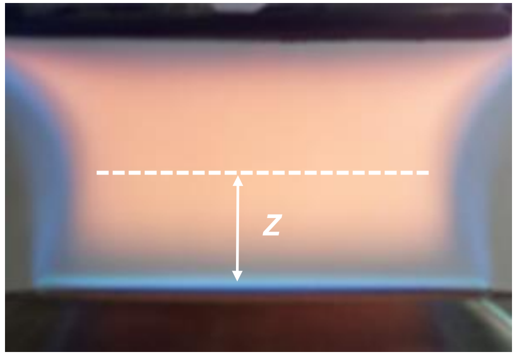
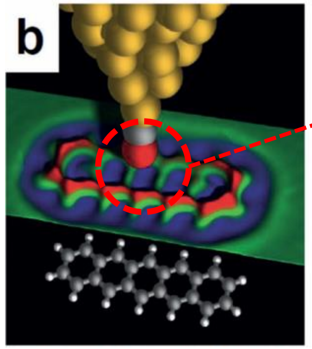


Fig. 8. (a) Proposed structure of imaged molecules with radical character. Note that multiple resonant structures are possible for all radicals depicted here. (b) Possible mechanism for the formation of a π-radical (forward reaction, one hydrogen is removed from the π-system resulting in a π-radical $+H_2$) and a methylene group (backward reaction, one hydrogen is added to the π-radical) in **IS1**. The carbon atom where a radical could have been formed is highlighted in red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

HR-AFM – Soot molecules imaging



Gross et al. Angew. Chem. Int. Ed. (2018)



<u>Carbon monoxide–functionalized tip to probe repulsive forces above single molecules</u>

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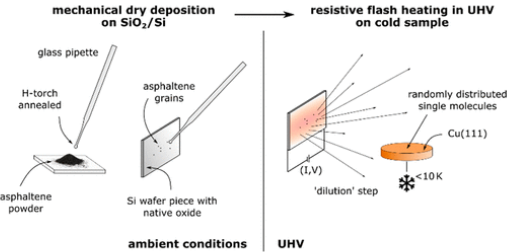
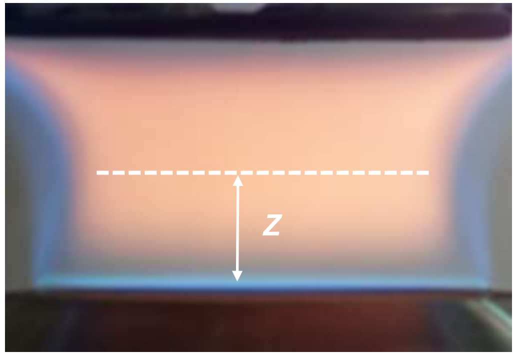


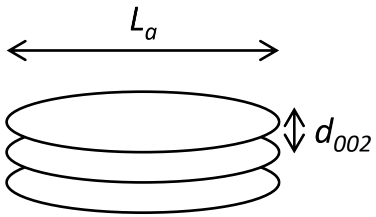
Schuler et al. Energy Fuels (2020)

Main outcomes:

- Presence of **pentagonal rings**;
- Presence of sp3 carbons in **methylene (-CH2-) bridges**;
- Presence of **aliphatic chains** was observed;
- Presence of **aromatic π–radicals**;
- Presence of **cross-linked aromatic compounds**;
- The size of aromatics moieties in incipient soot is **0.8-1.0 nm**; with an average *H*/*C* ratio of **0.45/0.5**.

HR-AFM and Raman Spectroscopy

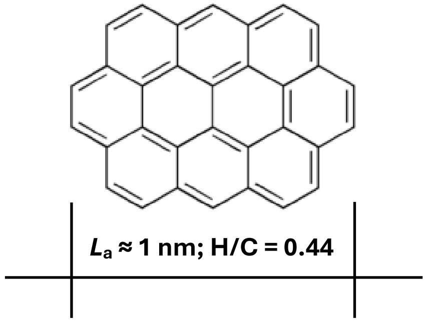




$$L_a^2(\mathrm{nm}^2) = 5.4 \cdot 10^{-2} \cdot E_L^4(\mathrm{eV}^4)\frac{I(\mathrm{D})}{I(\mathrm{G})}$$

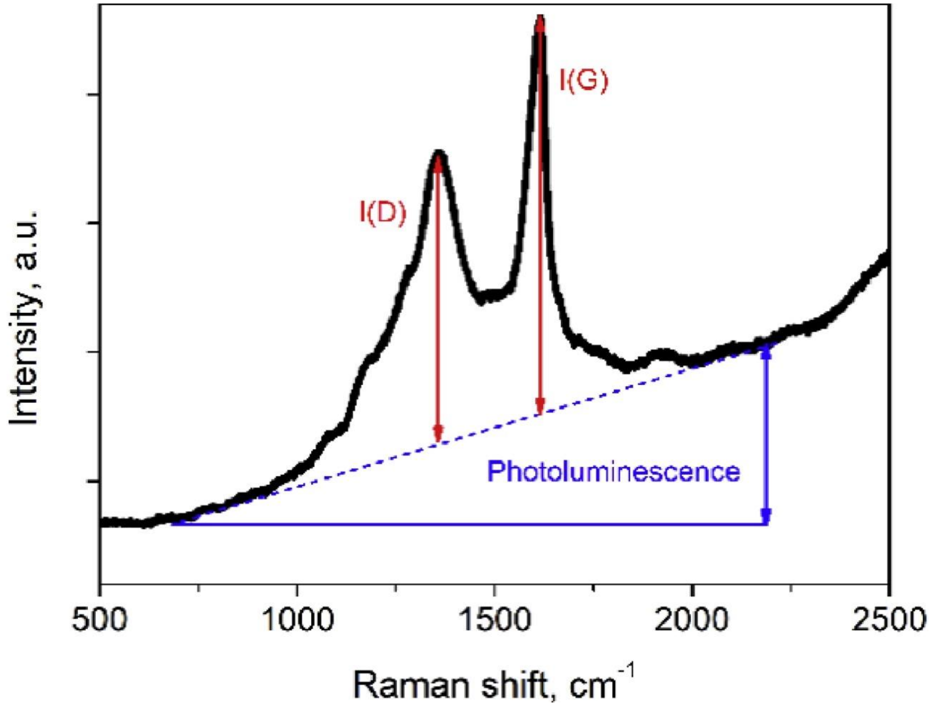
Ferrari, Basko/Nature Nanotech. (2013)

For L_a < 2 nm



L_a ≈ 1 nm

Schulz et al. Proc. Combust. Inst. 37, 2019, 885-892



G → Graphite peak
D → Disorder peak

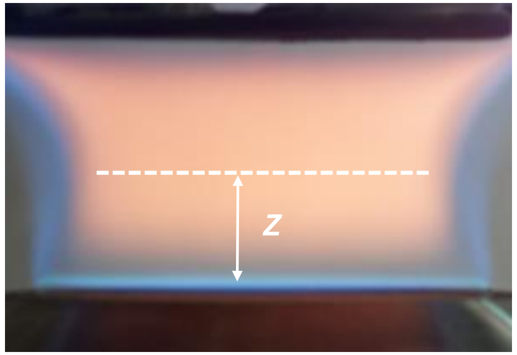
Aromatic islands in nascent soot are about 1 nm in size;

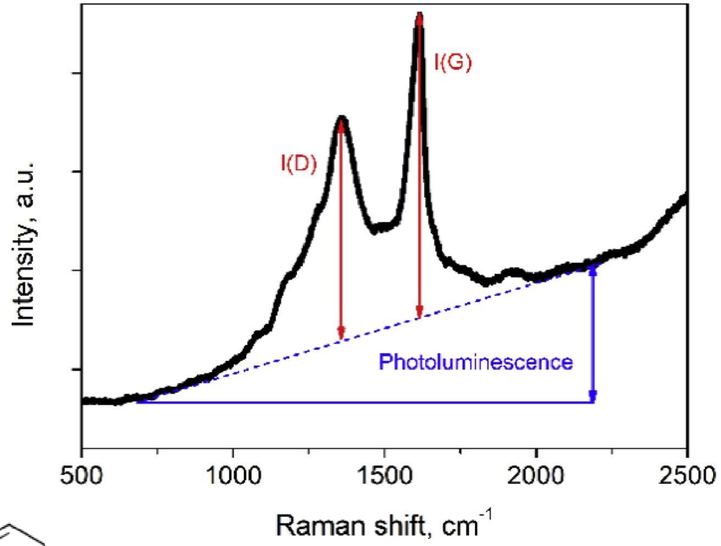
This value remains almost constant in the early growth/particle aging process;

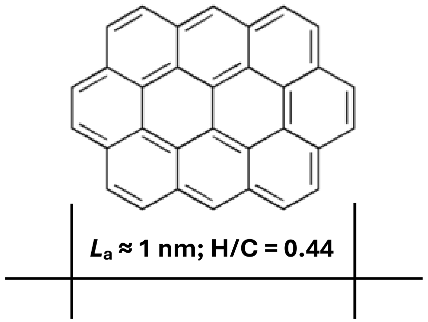
The value is consistent with the many HR-TEM observations (even for rather mature soot).

2D growth is mostly attained at the onset (maybe right before?) of the formation process

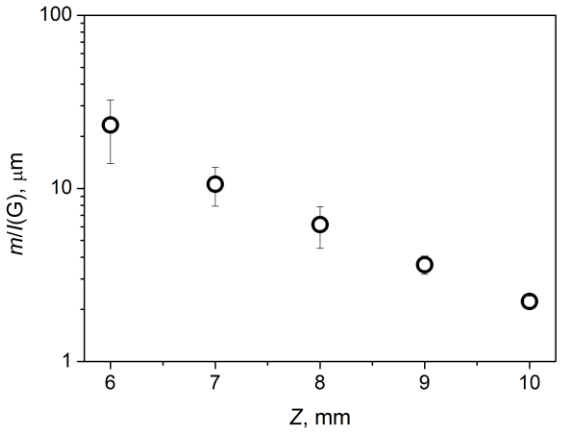
HR-AFM and Raman Spectroscopy

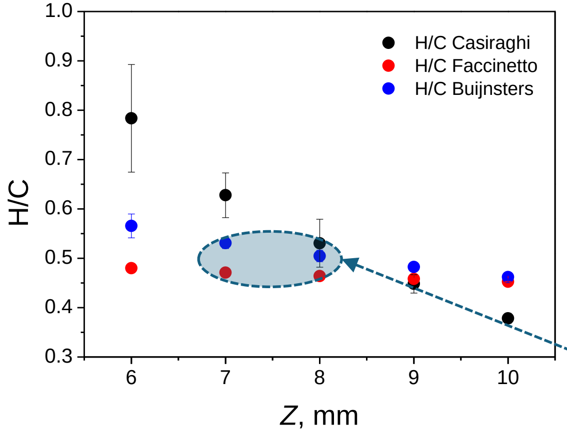






Baseline (photoluminescence) contribution:



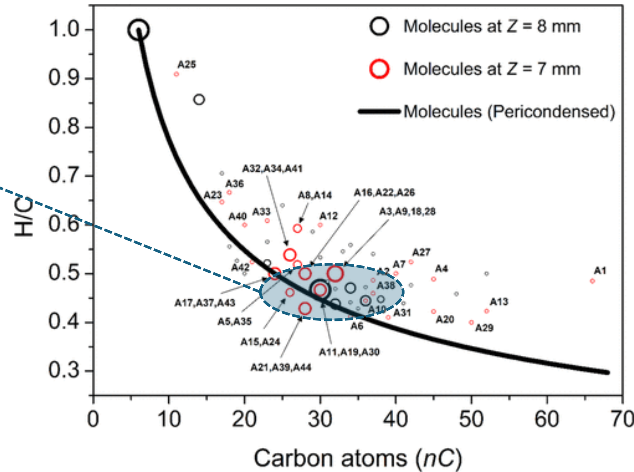


$$H\ [at.\%] = a + b * \log(\frac{m}{I(G)})$$

Casiraghi et al. Diam. Relat. Mater. 14 (2005) 1098–1102
(Hydrogenated amorphous carbon - a-C:H)

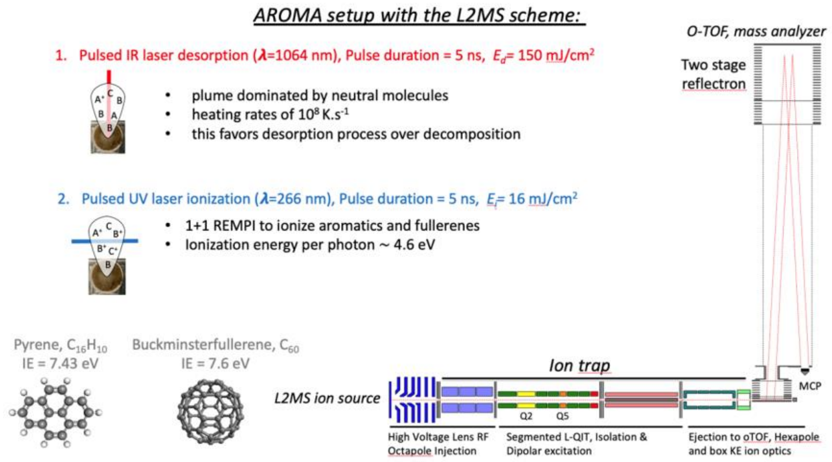
Buijnsters et al. J. Appl. Phys. 2009
(Hydrogenated amorphous carbon - a-C:H)

Faccinetto et al. Comm. Chem. 2020
(soot from diffusion flame)

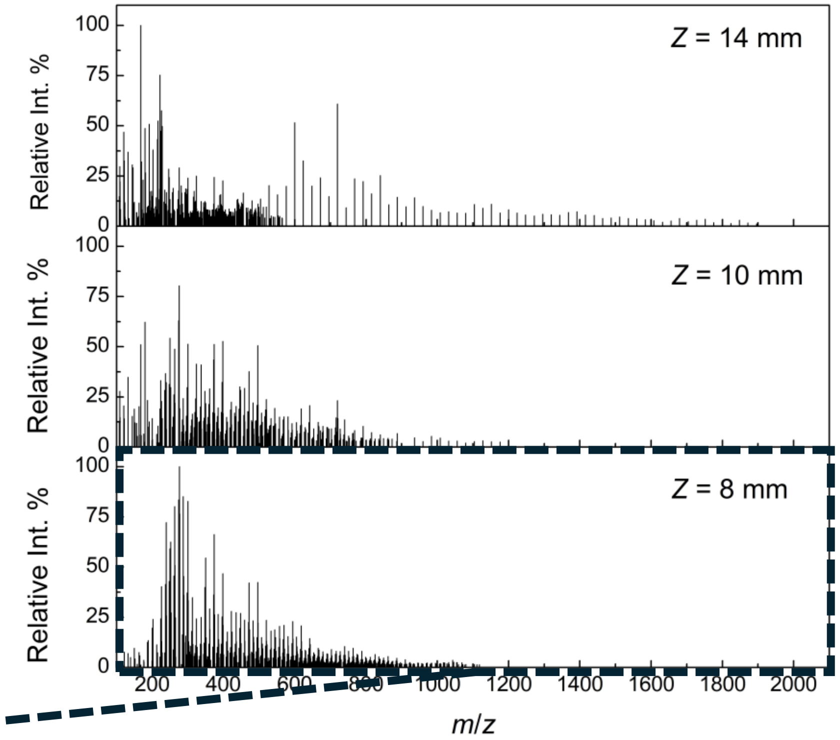


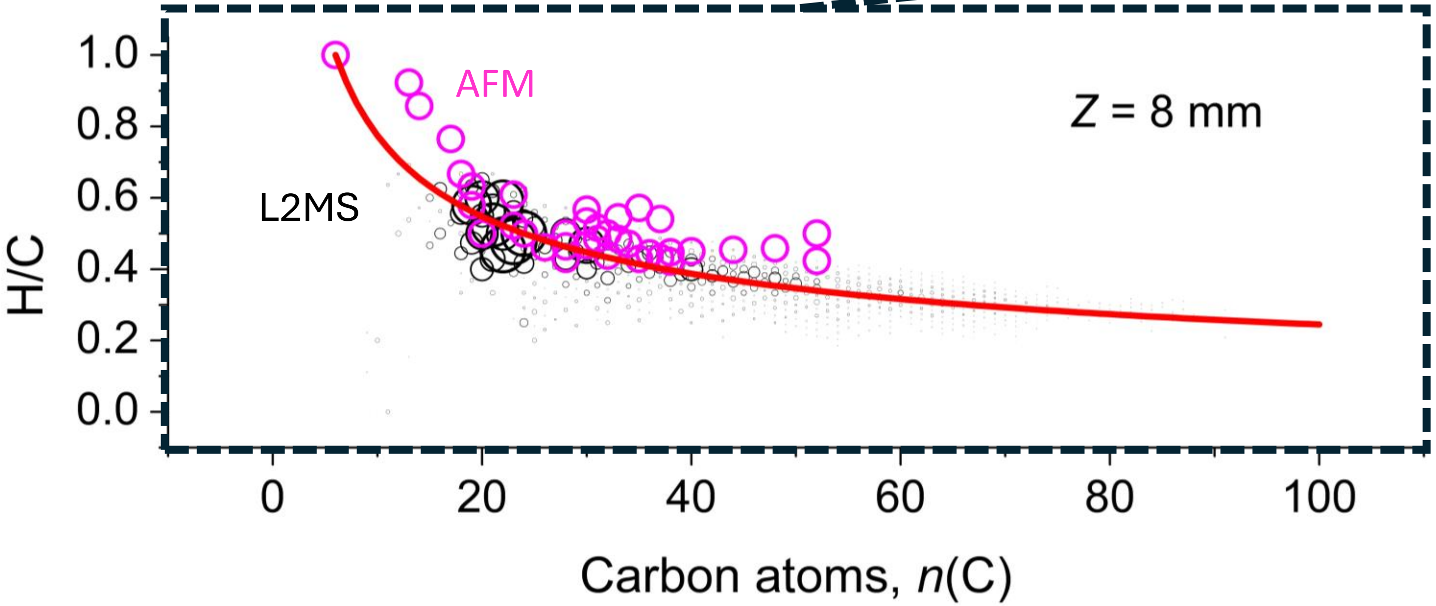
HR-AFM and L2MS

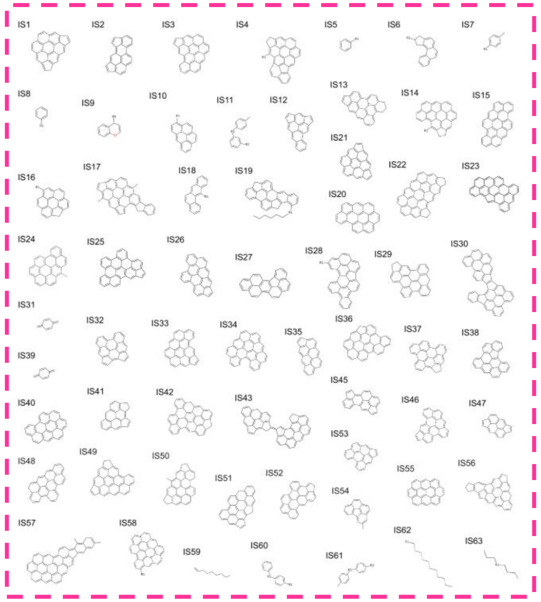
Sabbah, et al. Astrophys. J., 843 (34) (2017)



Sabbah, et al. Proc. Combust. Inst. (2021)

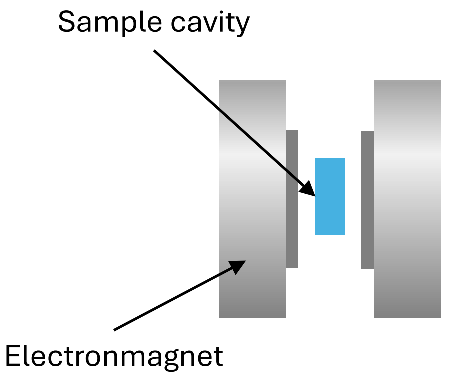


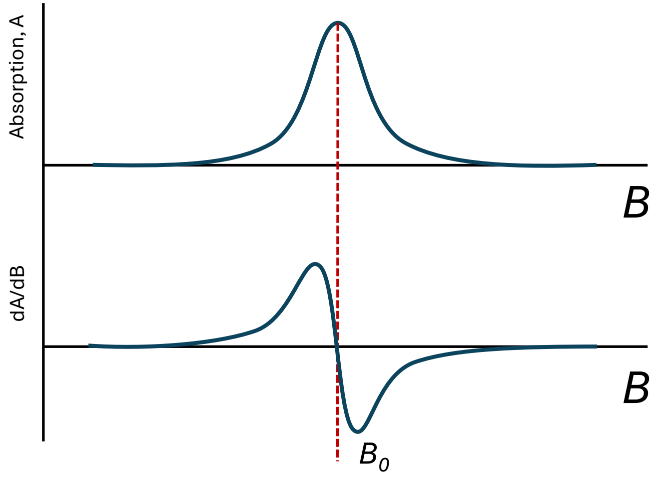




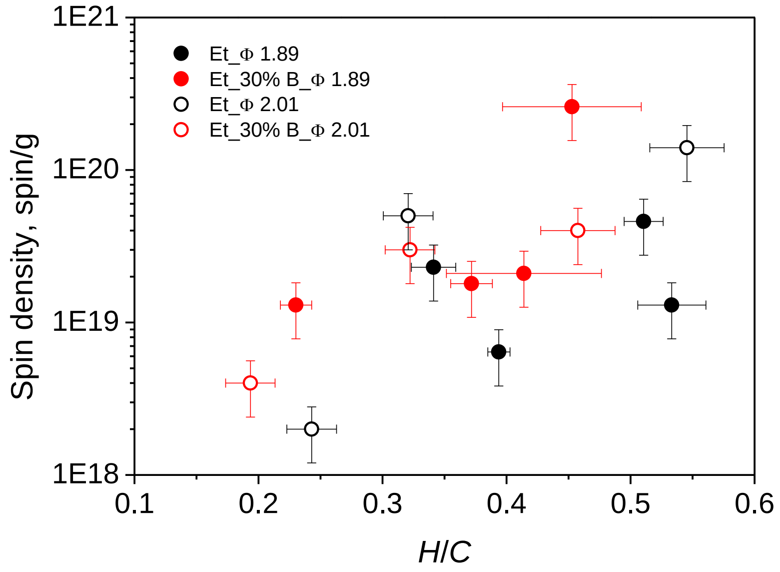
HR-AFM

HR-AFM and Electron paramagnetic resonance spectroscopy (EPR)

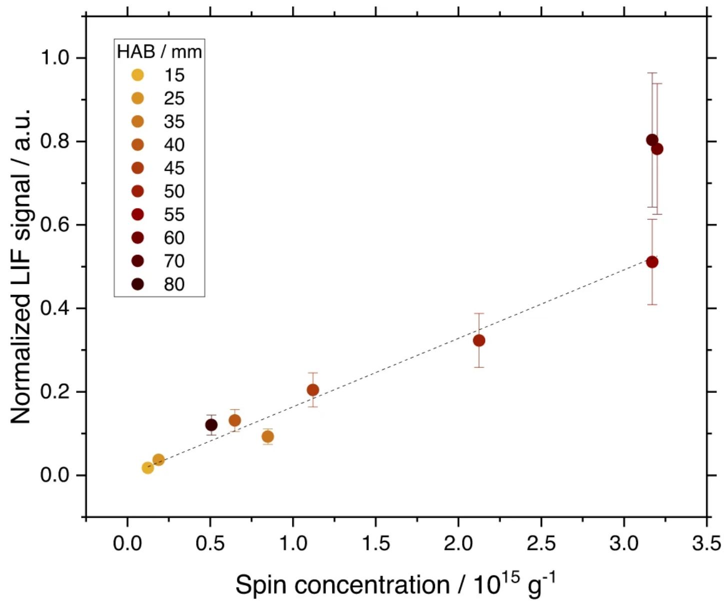




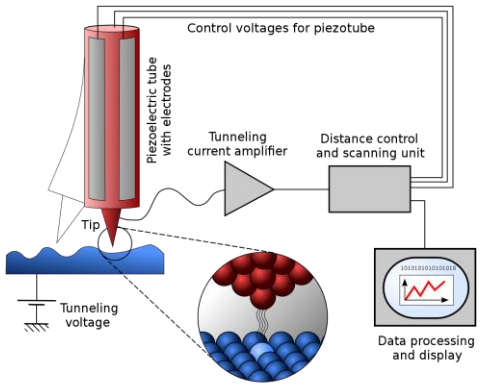
Commodo, et al. PROCI (2021)



Elias, Faccinetto, Vezin, Mercier Comm. Chem. (2023)

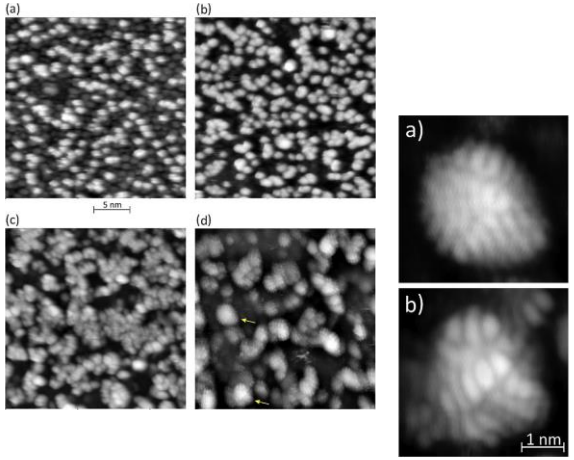


Scanning tunneling microscopy (STM) and Spectroscopy (STS)

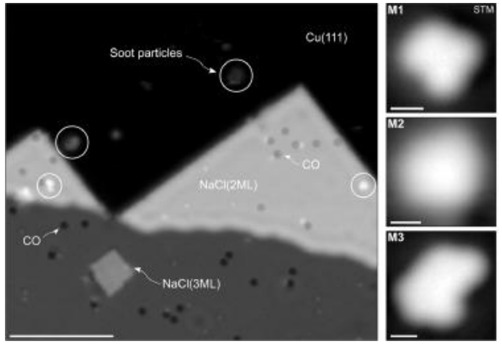


Scanning tunneling microscopy (STM)

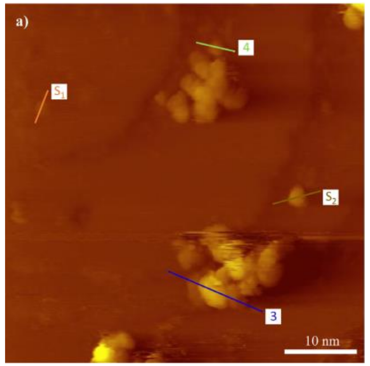
C.S. Wang, N.C. Bartelt, R. Ragan, K. Thürmer
Revealing the molecular structure of soot precursors
Carbon 129 (2018) 537e542



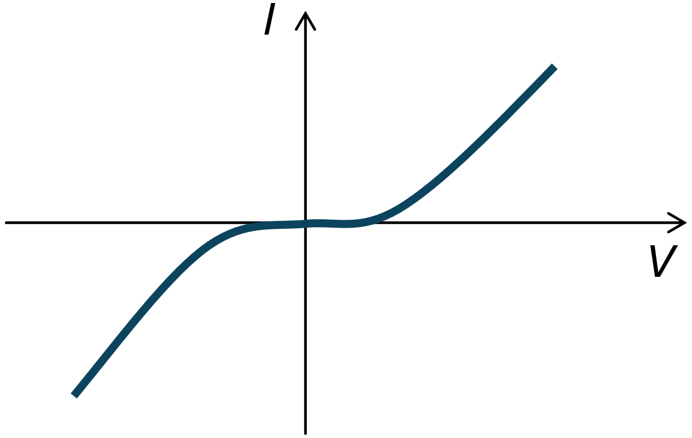
F. Schulz et al.
Proc. Combust. Inst. 37 (2019) 885–892

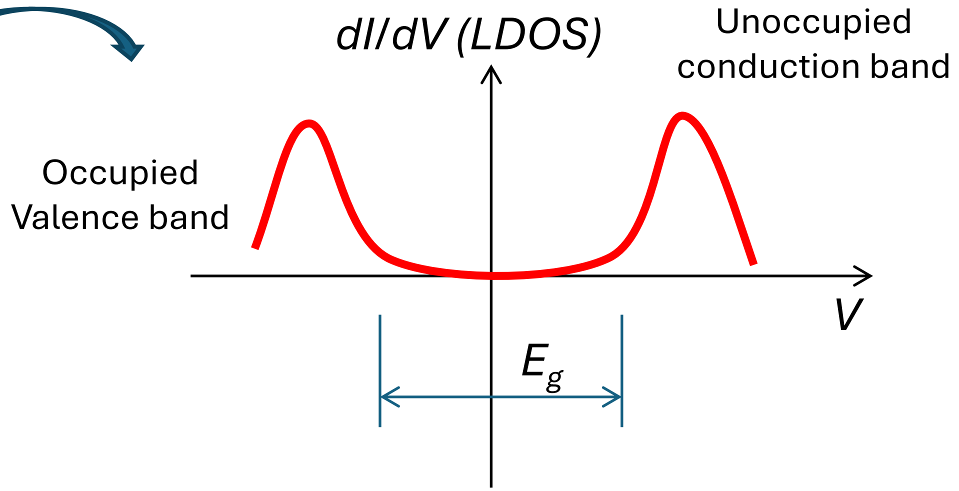


Veronesi et al. Comb. Flame 243 (2022) 111980

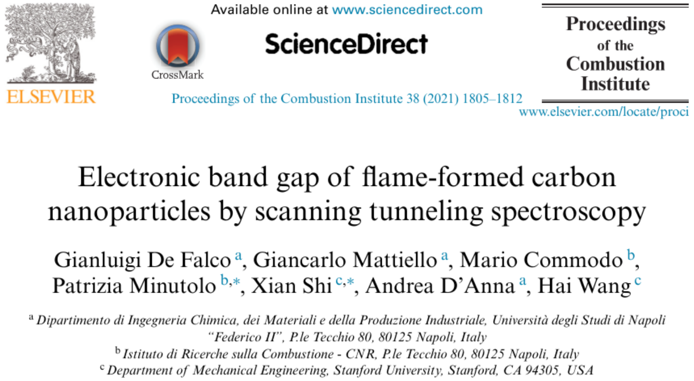


Scanning tunneling spectroscopy (STS)





Scanning tunneling microscopy (STM) and Spectroscopy (STS)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Proceedings of the Combustion Institute 38 (2021) 1805–1812

www.elsevier.com/locate/proci

Electronic band gap of flame-formed carbon nanoparticles by scanning tunneling spectroscopy

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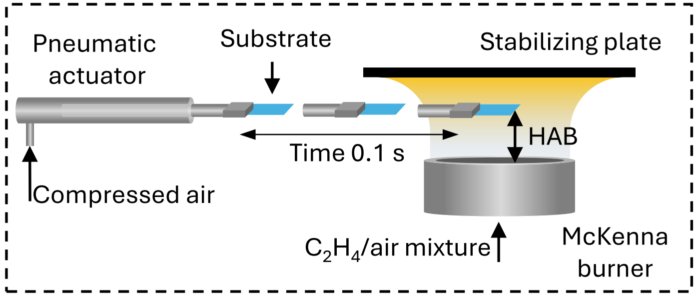
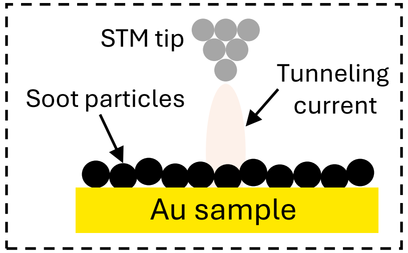
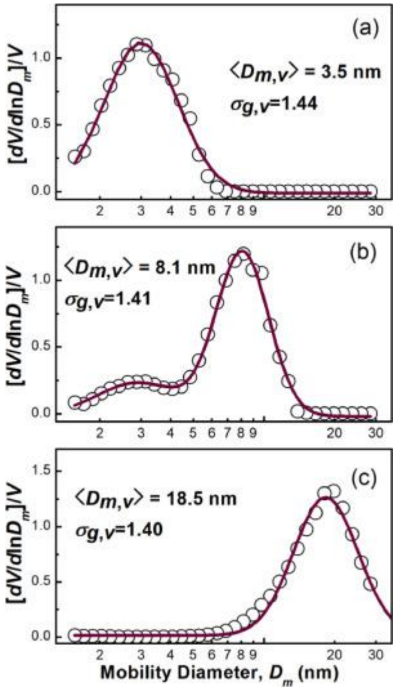
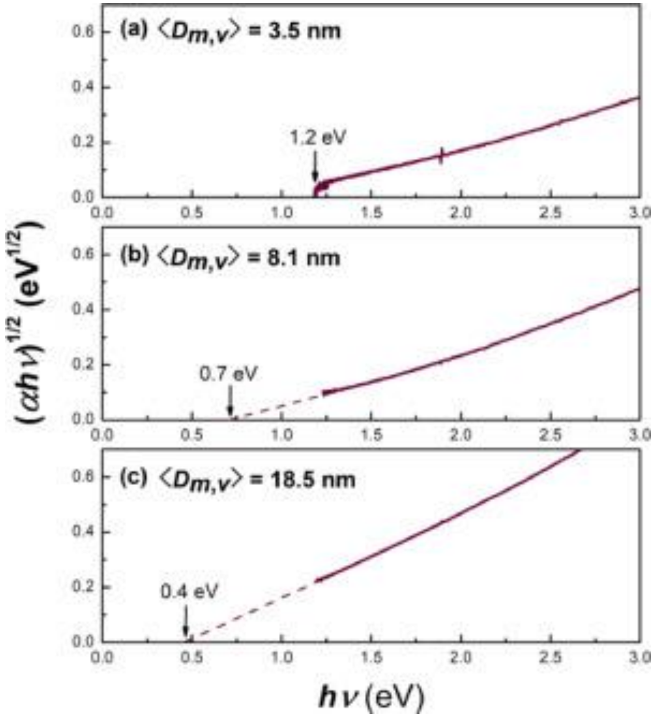
[b] Istituto di Ricerche sulla Combustione - CNR, P.le Tecchio 80, 80125 Napoli, Italy

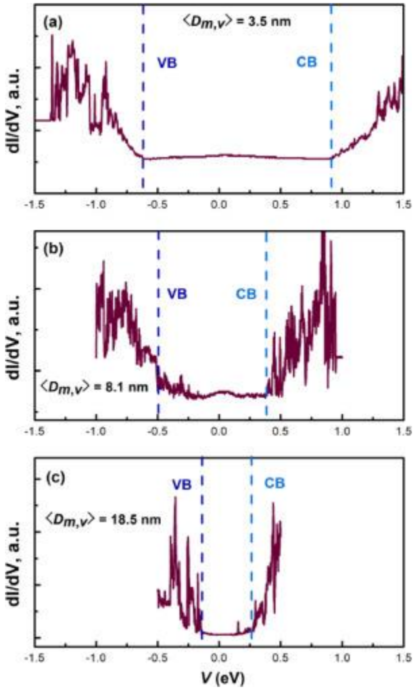
[c] Department of Mechanical Engineering, Stanford University, Stanford, CA 94305, USA

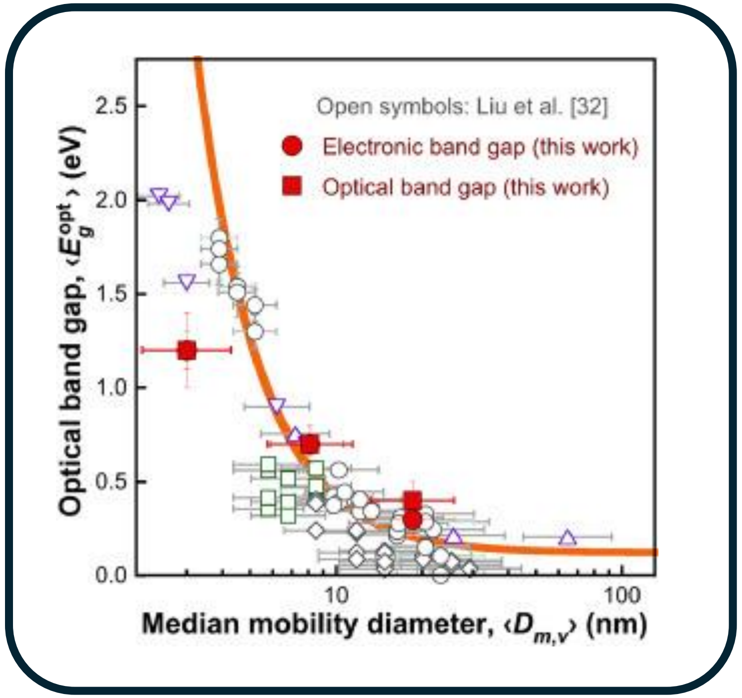




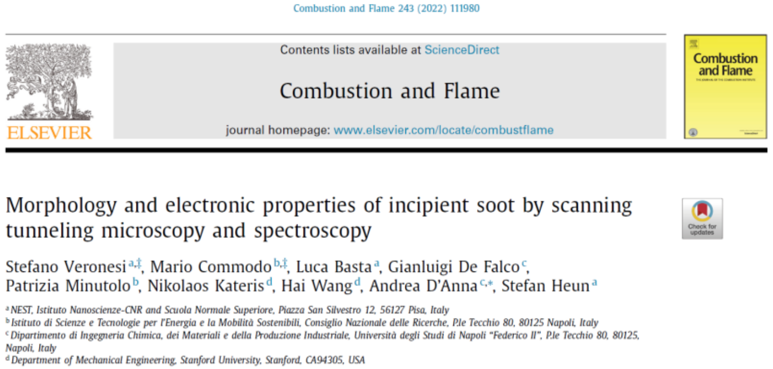








Scanning tunneling microscopy (STM) and Spectroscopy (STS)


Combustion and Flame 243 (2022) 111980

Contents lists available at ScienceDirect

Combustion and Flame

journal homepage: www.elsevier.com/locate/combustflame

Morphology and electronic properties of incipient soot by scanning tunneling microscopy and spectroscopy

Stefano Veronesi[a,‡], Mario Commodo[b,‡], Luca Basta[a], Gianluigi De Falco[c], Patrizia Minutolo[b], Nikolaos Kateris[d], Hai Wang[d], Andrea D'Anna[c,*], Stefan Heun[a]

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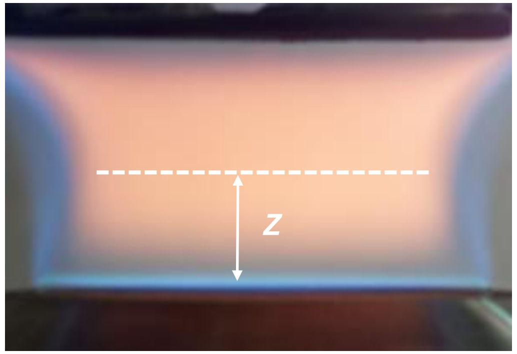
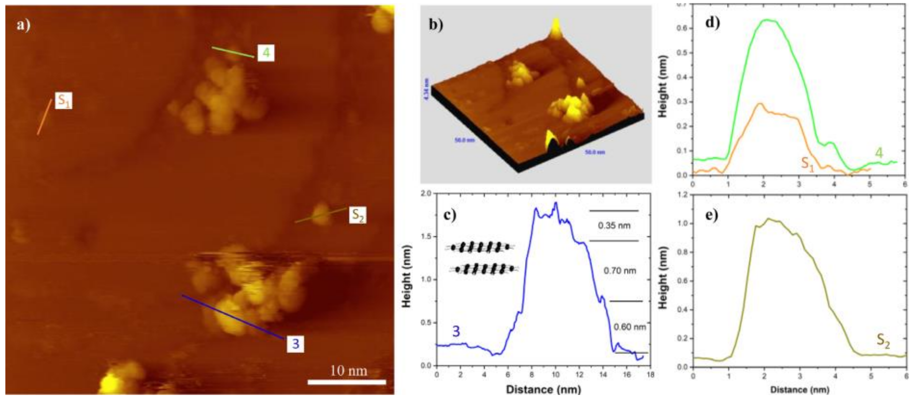
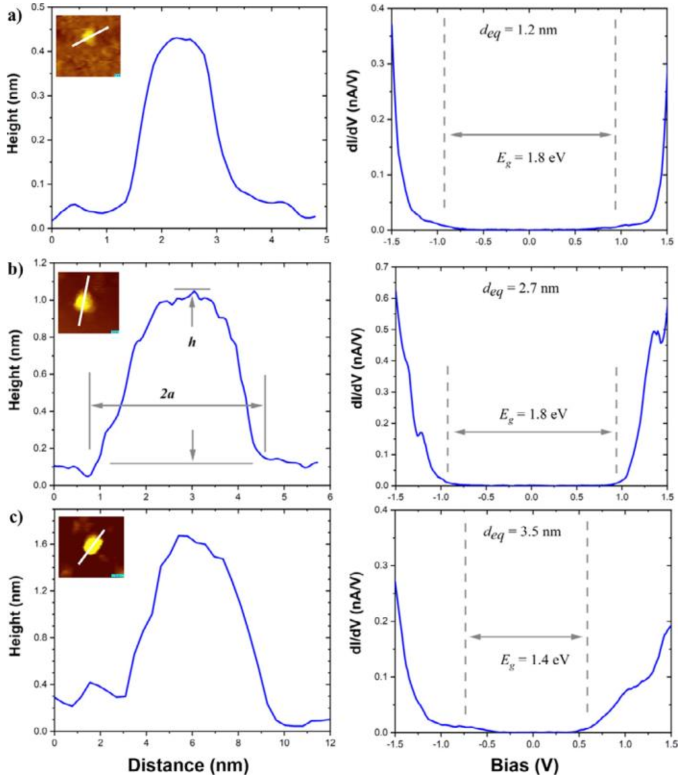
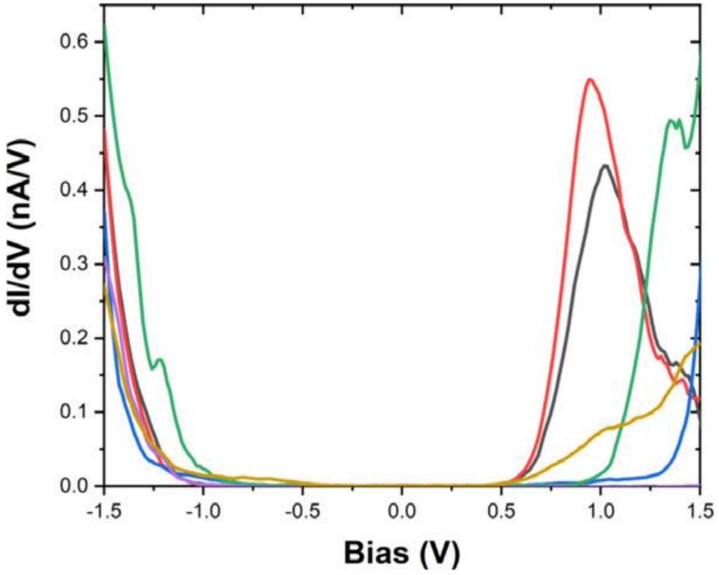
[d] Department of Mechanical Engineering, Stanford University, Stanford, CA94305, USA









STS differential conductance spectra of several particles, all with spherical equivalent diameter < 5 nm

Conclusions and outlook

AFM and HR-AFM

- ✓ 3D Morphological information of soot: from inception to early growth;
- ✓ Physicochemical properties of the particles (hardness, degree of cross linking, interaction forces);
- ✓ HR-AFM: Detailed topological information of the aromatics present at the soot inception point;
  - ✓ Try to get information on a single particle level (by nanoindentation and or force-distance curve);
  - ✓ Implement other AFM based methods: conductive-AFM? TERS?

1J03: Toward resolving flame-formed carbon nanoparticle structure through conductive atomic force microscopy;
N. Montes, E.S. Genter, N. Kateris, A.S. Jayaraman, H. Wang

5G09: Flame synthesis of soot/TiO2 nanoparticle composite films with improved electrical properties characterized by Scanning Probe Microscopy;
G. De Falco, L. Basta, M. Commodo, P. Minutolo, A. D'Anna

Conclusions and outlook

STM/STS

- ✓ 3D Morphological information of soot: STM can have even higher resolution than AFM for clusters and particles;
- ✓ Electronic properties of the soot particles – direct measure of the local E_g;
  - ✓ Try to get information on a single particles level (better STM resolution on the single particles);
  - ✓ Probe local E_g to possibly identify degree of staking and/or cross-linking (and in general E_g vs. particle size – thus improving and or validating current E_{opt} measurements);
  - ✓ Correlate particle chemical/structural properties with the electronic properties (also in view of applications as a material).

Thank you for your attention