Morphology and Electronic Properties of Incipient Soot by Scanning Tunneling Microscopy and Spectroscopy

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MOTIVATION

Formation and emission of soot from incomplete combustion of fossil and bio-derived fuels is a major concern for human health and the environment. One of the most critical steps in soot formation is the onset of particle formation, namely inception and early growth. It is during the earlier phase of formation that flame soot attains the widest variations in terms of physicochemical properties. Immediately behind the flame front, fuel-rich flame chemistry provides the precursor species, including **Polycyclic Aromatic Hydrocarbons** (PAHs), leading to the formation of the first particles.

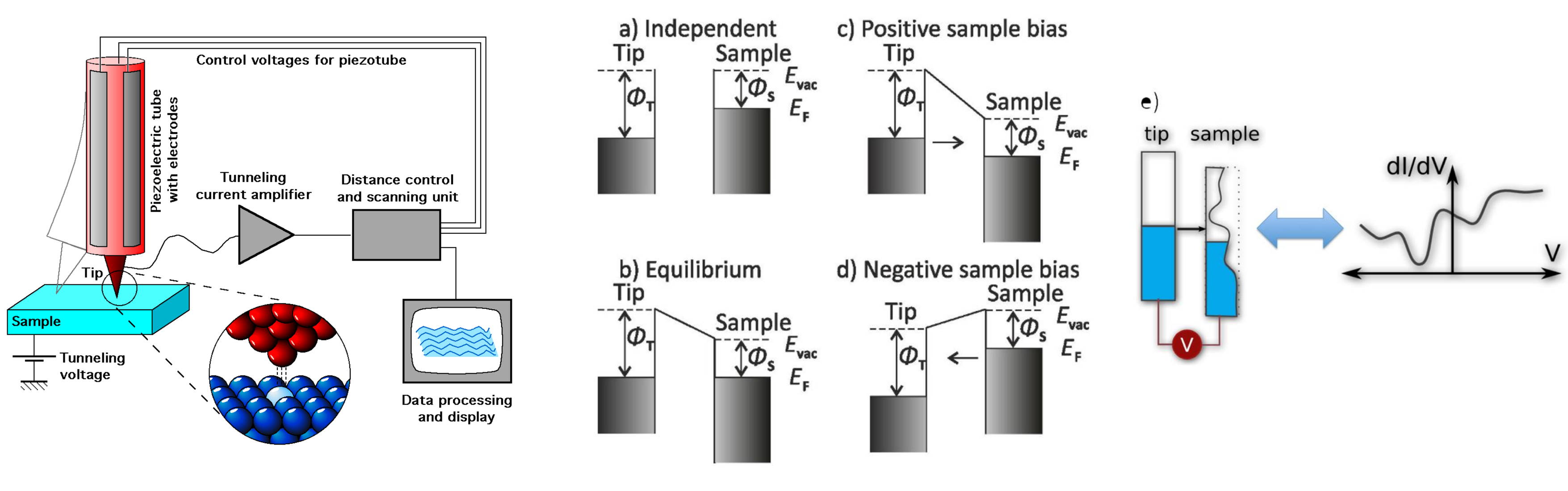
OBJECTIVES

- High-resolution **STM** is utilized to visualize incipient soot particles, for the first time, on a **single particle basis**
- **STS** measurements are carried out, for the first time, to probe the **electronic band gap** of individual, small, **single particles** just a few nanometers in size and **aggregates** of these small particles

SOOT PARTICLES COLLECTION

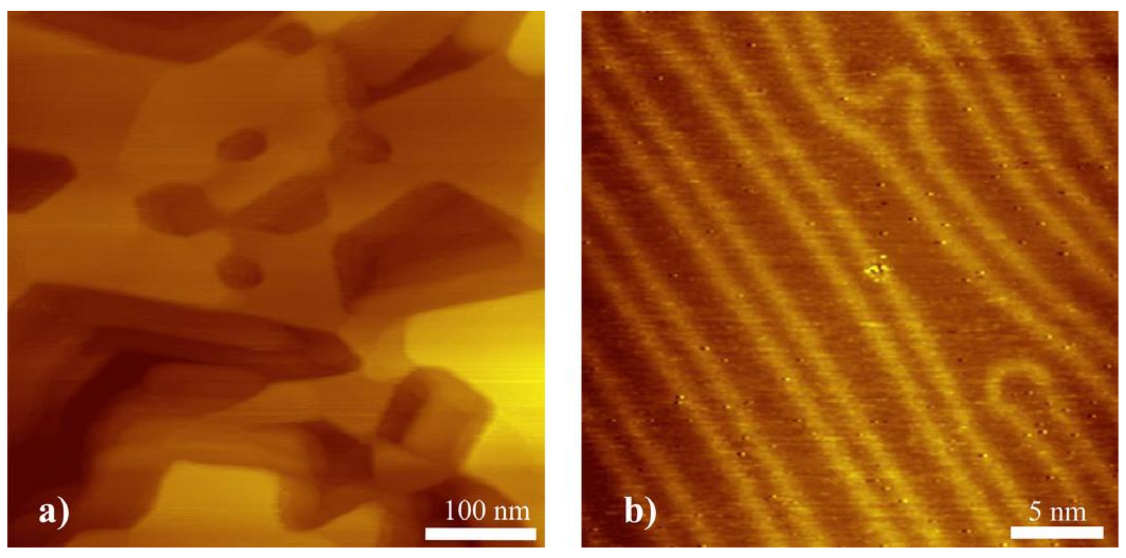
Incipient soot particles were collected from a lightly sooting laminar premixed flame of ethylene and air [2]. The flame has a cold gas velocity of 9.8 cm/s and equivalence ratio ϕ = 2.01, and was stabilized on a water-cooled McKenna burner. Particles were collected thermophoretically by rapid insertion (insertion time 30 ms) using a pneumatic actuator.

SCANNING TUNNELING TECHNIQUES



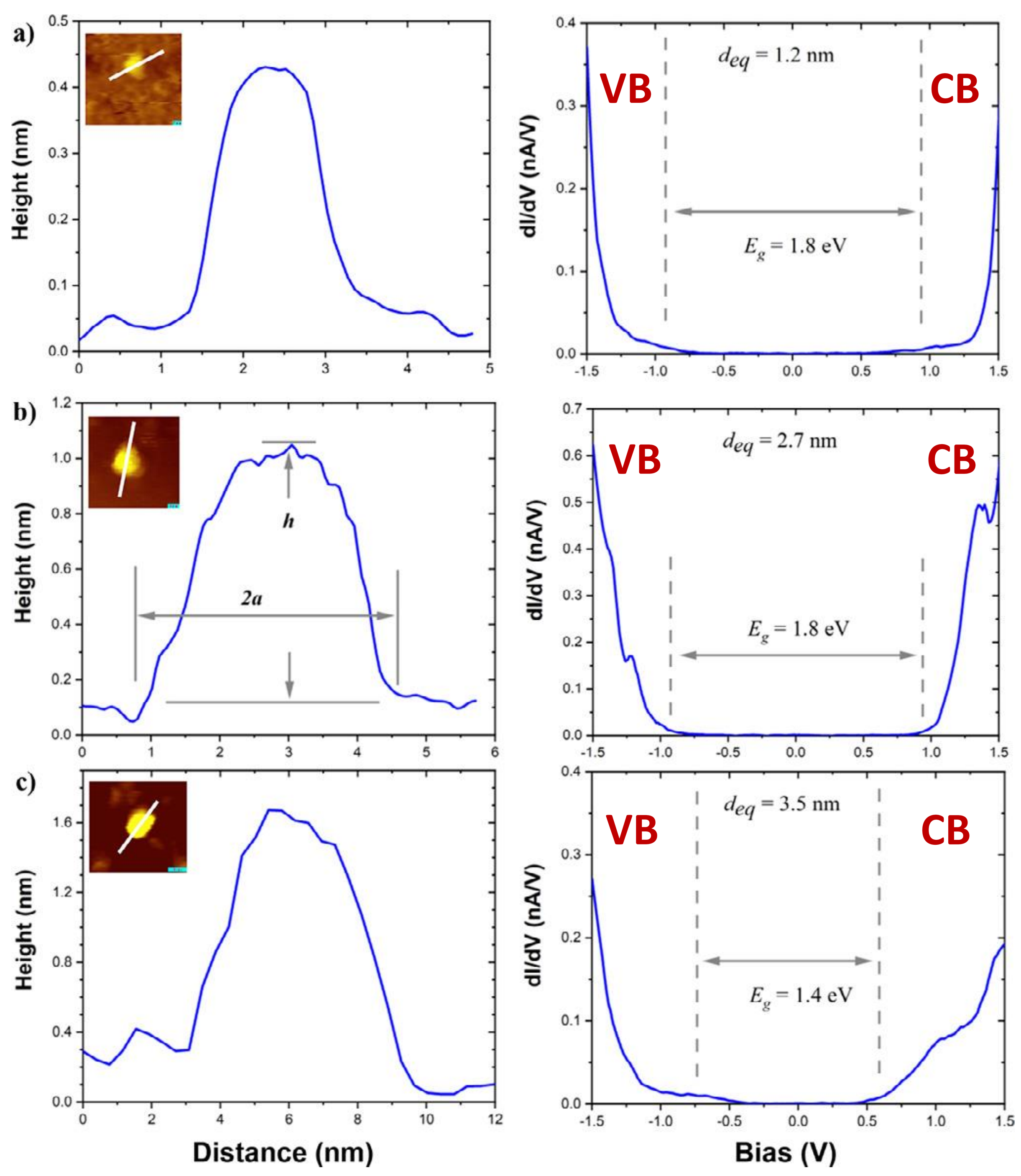
Scanning Tunneling Microscopy (STM) and Scanning Tunneling Spectroscopy (STS)

SUBSTRATE



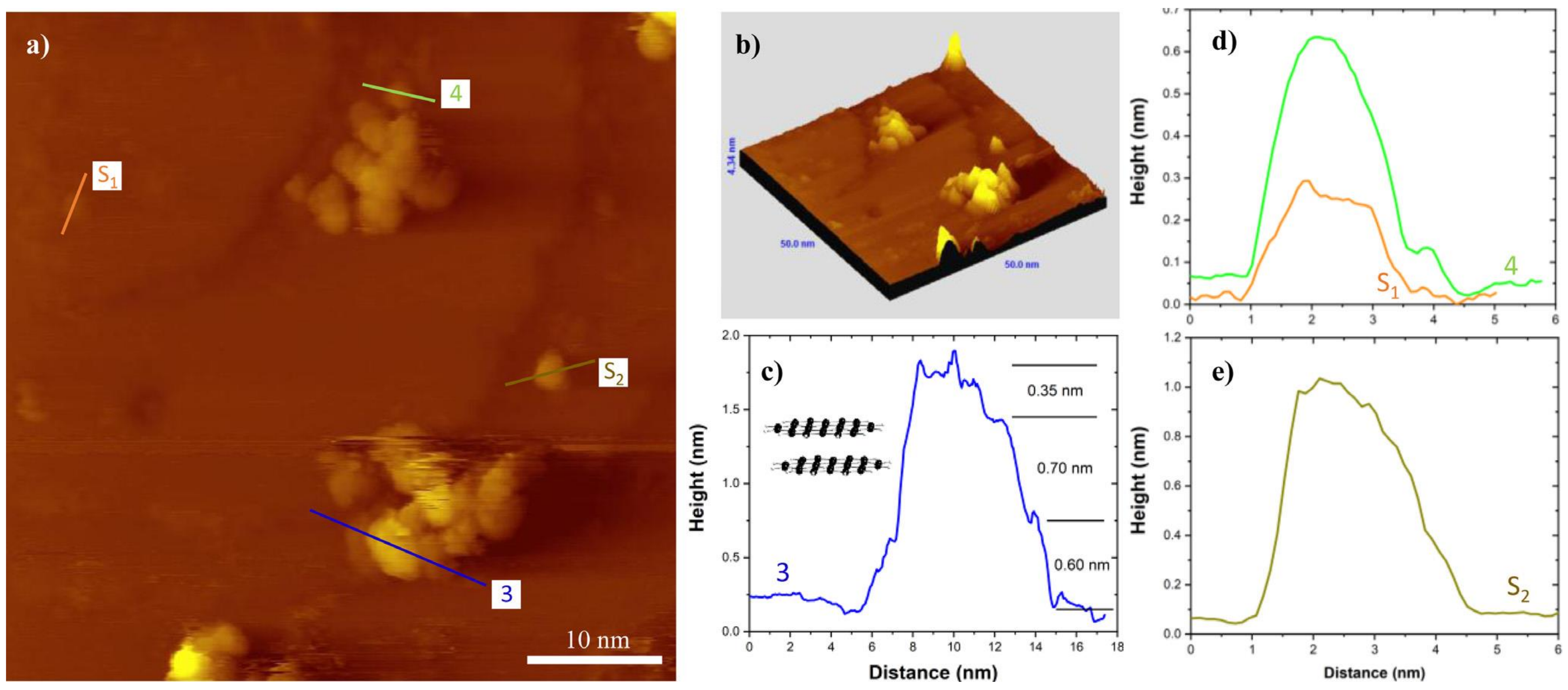
STM images acquired for a gold-on-mica substrate (UHV base pressure of $3 \cdot 10^{-11}$ mbar). (a) A large-scale image (0.5×0.5 μm^2, image acquired using 1.3 V and 0.8 nA) showing atomically flat terraces; (b) a zoom-in image (30×30 nm^2, 1.4 V and 0.7 nA) showing the herringbone reconstruction [1].

ELECTRONIC PROPERTIES AND BAND GAP



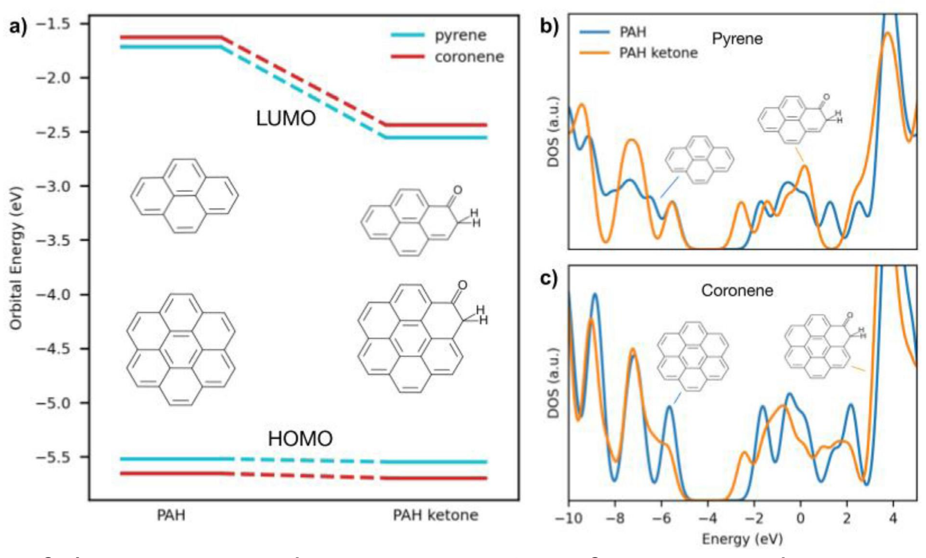
STM images (inset) and height profiles of three representative particles and their corresponding STS differential conductance spectra. STM measurements yield size parameters of (a) a = 1.3 nm and h = 0.4 nm, (b) a = 1.8 nm and h = 0.95 nm, and (c) a = 3.3 nm and h = 1.6 nm. Also marked are the spherical equivalent diameter of the particle probed and its corresponding electronic band gap value.

SIZE AND MORPHOLOGY



(a) STM image of representative aggregates (50×50 nm^2, image acquired using –1.6 V and –0.5 nA). (b) 3D reconstruction of the STM image. (c) - (e) Height profiles along the paths marked in panel (a) with matching colors.

DFT CALCULATIONS



(a) Shift of the HOMO and LUMO energies of pyrene and coronene upon ketonization. (b) Calculated density of states of pyrene and ketonated pyrene, showing the shift in the conduction band; (c) the same calculation for coronene and ketonated coronene.

CONCLUSIONS

- The size of incipient soot particles is **1 to 2 nm**, in agreement with earlier estimates.
- Atomically-flat structures of 1 nm in feature size may be observed, suggesting that the STM holds the potential for **probing PAH clusters** formed during soot nucleation.
- STS measurements on single soot particles (1 to 4 nm) show an electronic band gap value in the range of **1.5 to 2 eV**, and the **band gap value decreases** as the particle size increases.
- The asymmetric feature of the differential conductance spectra and its conduction-band variation among different particles can be explained by **ketonization** of the constituent PAHs or by the presence of PAH **σ-radicals**.
- The (apparent) **quantum confinement** could be explained by an increased probability of oxygenate incorporation or radical presence in the nascent soot particles.

WHAT'S NEXT?

- ➢ **Hydrogenation** seems to promote carbon structural transformation through π-stacking among PAHs, leading to nucleation.
- ➢ After atomic H exposure (10^{-7} mbar, 5-200 s) particles with sizes below 10 nm show a **conversion of semi-conductive to semi-metallic behaviour**.
- ➢ The process of H-atom addition shows **reversibility of band-gap reduction**, in the case of relatively short H exposure.
- ➢ The curvature dependence of the atomic H adsorption may be exploited for **storage and controlled release of hydrogen at room temperature** on flame-generated amorphous CNPs.
- ➢ **Gas sensors** can be designed evaluating the electrical response of CNPs films upon specific gas exposure.

REFERENCES

[1] S. Veronesi et al., *Applied Surface Science*, **2020**, 512, 145658

[2] S. Veronesi, M. Commodo, et al. *Combustion and Flame*, **2022**, 111980