Raman and AFM signature of flame-formed carbonaceous 2-D nano-flakes

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Abstract

Flames and combustion devices operated in rich hydrocarbon fuel condition produce a large variety of carbonaceous compounds spanning from low and high molecular weight gas-phase polycyclic aromatic hydrocarbons (PAHs) to 2-D partially aromatic nanometric size compounds and solid soot particles. All these species present different molecular weights and sizes, from few nanometers, 2-3 nm, up to hundreds of nanometers, chemical and physical characteristics, optical and electronic properties.

Both their amount and chemical characteristics are strongly related to the combustion conditions. Indeed, differences in the fuel chemical composition, as well as in the type of the combustion process, i.e. diffusive or premixed, laminar or turbulent, can result on different carbonaceous products. Moreover, other parameter such as temperature, residence time and pressure, can also be used as controller parameters in order to get specific carbon products. The proper choice of the "flame reactor" can, in fact, generate carbonaceous compound having different sizes, micro and nanostructure, light absorption and emission properties. These latter ones are related to the chemical and structural conformation of the formed nanoparticles as well as on their electronic properties, i.e. HOMO-LUMO levels position.

The understanding of the mechanisms responsible for the formation, in rich fuel flames, of the broad set of carbon compounds, from planar PAH molecules to solid state 3-D carbonaceous nanostructures, has been the subject of numerous studies over the last decades [1Libro Capri]. Although these studies were driven by the necessity of more efficient combustion processes and by the necessity of reducing such compounds from the emission of combustion devices, they have lead to a wide knowledge on the chemical kinetic reactions governing the formation and growth of such species, as well as on modelling capabilities and experimental methods allowing to tailor the carbonaceous "by-products" properties by changing the flame synthesis parameters thus allowing a new synthesis method for specific carbon species.

We have produced carbon compounds in laminar hydrocarbon premixed flames burning at atmospheric pressure. Flame products were sampled from the flame by means of a dilution probe operated with nitrogen and collected on-line on a quartz filter. The filters were then analysed by a confocal Raman microscope (Horiba XploRA with λ_{laser}=532 nm).

Morphological analyses were performed by Atomic Force Microscopy, AFM, (NT-MDT NTEGRA prima). To this aim, carbon compounds were collected by thermophoresis, inserting a cold substrate in the flame by means of a pneumatic actuator that assures fast sampling times (about 30 ms). The short sampling time allowed collecting isolated species; freshly cleaved mica was used as substrate to have an atomically flat background in AFM images.

Flames operated with fuel/air mixture slightly richer than the stoichiometric value are blue colored and produce 2-D carbon structure. In fig. 1-left is reported a typical AFM image of an area of 500 nmx500nm, while the height profile across the green line is reported on the right, fig. 1-right. During the sampling time of 30 ms a large number of carbon nano-flakes is collected on the mica substrate. The height of such species is from 0.35 to about 1 nm, as indication of a carbon compound made of a mono-atomic to a few carbon layers. The in-plane shape is roughly circular.

The Raman spectrum of the carbon nano-flakes sampled from a blue-luminosity flame is reported in fig. 2 also, in fig. 3 the Raman bands of the first order and second order part of the spectrum are compared to the one measured in HOPG.

Raman spectrum of flame carbon nano-flakes is characterized by strong signal due to disorder. A broad D band appear close to 1350 cm-1 while the G and D' bands merge in one peak. A fitting procedure of this peak with two Lorentian lineshape show that the G peak is shifted to larger wavenumber respect to the G band of HOPG due to the nanosize of graphitic island [2] and the D' band, at 1620 cm-1, is more intense than G. The strong D and D' signals probably originate by the large amount of edges in our sample being the probed region composed by a many nano-flakes [3]. The Raman spectrum in the overtone and combination bands region add further information on the sample. The position of 2D band confirms the bi-dimensional nature of the flakes. In fact, the center of the band is significantly shifted

towards the lower frequency zone respect the signal of the 2D band from HOPG, closer to the position of a single layer graphene [2]. Nevertheless, differently from a pure graphene the band is much broader, and less intense. Furthermore, the appearance of relevant overtone of G and D' lines and an evident G+D combination band indicate that beside the disorder due to edges, also lattice distortion can be present.

References

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[3] Pimenta, M. A. Dresselhaus G., Dresselhaus M., S., Cancado, L., G., PCCP 9, (2007) 1276-1291

Figures

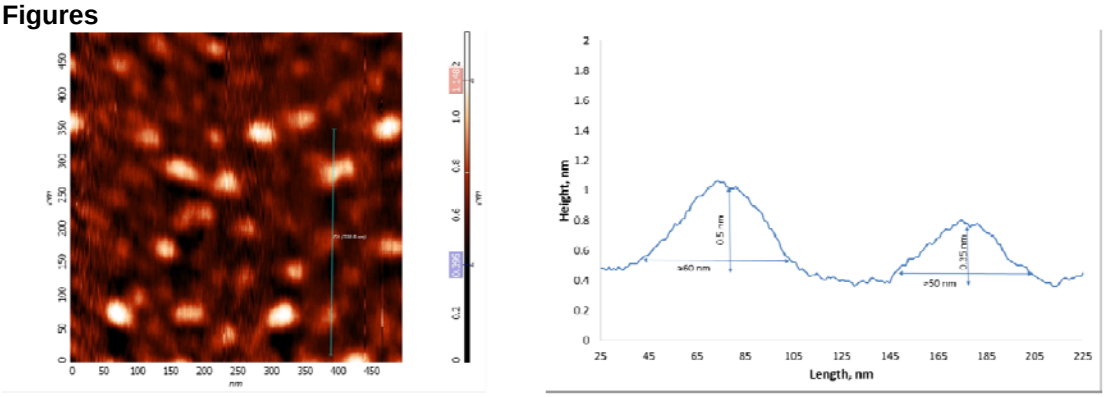

Fig 1 (Left) AFM image of carbon flakes, sampled from blue-luminosity flames, deposited on mica substrate, and (right) height profile along the vertical green nine over the two of the particles.

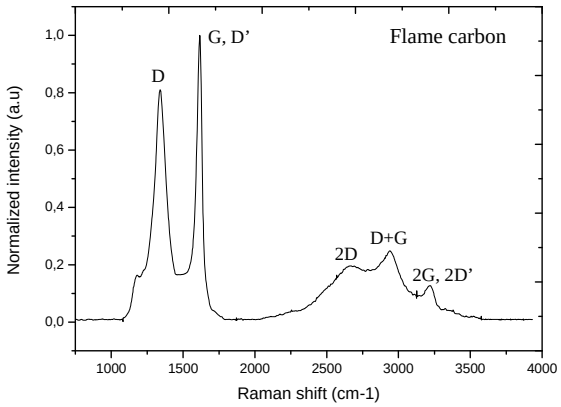

Fig. 2 Raman spectrum of carbon flakes sampled from blue-luminosity flames.

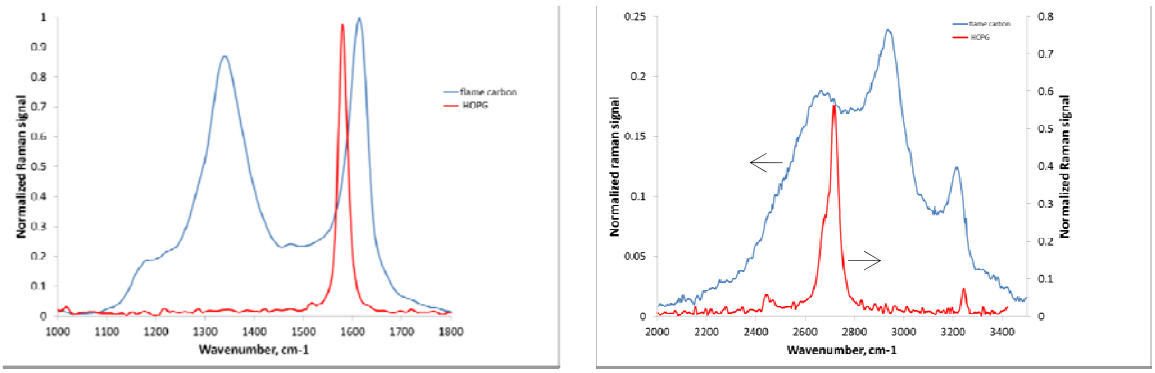

Fig. 3. Raman spectrum of carbon flakes sampled from blue-luminosity flames and HOPG in the first order and second order regions.