

Tuning the microtexture of carbonaceous particles produced by a spark generator system

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Abstract

The need of easy tools for nanoparticles tailoring is a constant trend topic in science and technology strategic areas and it collects interest ranging from semiconductor research and industry to environmental research fields also in view to ensure suitable standard materials availability.

Carbonaceous particulates generated by Spark Discharge Generators (SDGs) are produced through the vaporization of two electrodes at a tunable potential difference and have been widely used in most research studies involving human inhalation and exposure. These peculiar particulates have been selected to mimic carbonaceous aerosols emitted from combustion processes in terms of mobility diameter and surface characteristics [1]. A number of studies [2, 3] also compares the SDG carbonaceous particulate, chosen as soot model, with diesel engine soots and carbon blacks.

The use of a SDG for production of nanotextured particles is driven by several advantages as an easy-operational method allowing control, reproducibility, versatility and reasonable yields easily improved using parallel SDGs. An important feature offered by the use of SDGs is the possibility to gain large surface-to-volume ratio nanoparticles with high-surface purity [4], namely the absence of undesirable combustion byproducts as tar-like species or polycyclic aromatic hydrocarbons. By acting on the operative parameters (rods, spark discharge frequency, dilution gases) it is possible to varying the nature of the generated particulate (carbonaceous, metallic, metal-oxides or composites), with the possibility to finely control the particle size distribution, concentration and overall chemical-physical features, including morphology at nanoscale level. The most widely system used for research studies, being the first commercially available SDG, is the Palas GFG 1000.

In this work we pose attention to the nanotexture tuning (strictly linked to the chemical reactivity and, in turn, to the surface chemistry) of carbonaceous Palas GFG particles produced from graphite rods by acting on three parameters: gas carrier (nitrogen, argon), gas purity, discharge frequency (50, 300 Hz). The chemical reactivity and the surface chemistry of the particles have been evaluated by thermogravimetry (TG) and infrared spectroscopy (FTIR), respectively, as a function of the Palas operating parameters, crossing the findings with the morphology and internal structural characteristics inferred by transmission electron microscopy (HRTEM).

Particles production and characterization methods. In the aerosol generator (GfG 1000, Palas GmbH, Karlsruhe), two 6 mm diameter graphite rod electrodes (purity 99.999%) are mounted at an interdistance of about 2 mm and an argon stream (3.5 L/min carrier gas flow, purity 99.999%) is fed through a narrow slit into the space between the electrodes to remove all primary particles and ions between the electrodes before the next spark. At the chamber exit, the aerosol is diluted in a concentric annular nozzle by nitrogen or argon at different purity (30 L/min gas flow rate, minimum purity 99 and 99.999%, hereinafter 2.0 and 5.0, respectively. The nominal amount of O₂ impurity is 3 ppm in the case of 5.0 and over 3 ppm in the case of 2.0). The spark discharge frequency was settled at 50 and 300 Hz and the carrier flow rate at 3.5 L/min.

The eight samples produced by the spark generator (named: N₂ 2.0 50 Hz, N₂ 2.0 300 Hz, N₂ 5.0 50 Hz, N₂ 5.0 300 Hz and Ar2.0 50Hz, Ar 2.0 300 Hz, Ar 5.0 50Hz, Ar 5.0 300 Hz) and

collected on a polytetrafluoroethylene (PTFE) filter (Fluoropore, Millipore, 0.45 μm porosity), located downstream of the generator, for a sampling time of 30 min each, were off-line analyzed.

The FTIR analysis was performed in attenuated total reflectance (ATR) mode in the 3600–400 cm^{-1} on a Nicolet FTIR spectrometer *i10*. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) imaging were performed on a FEI Tecnai G2 F20 transmission electron microscope equipped with a field-emission gun. Nanoparticle reactivity in an oxidative environment was evaluated by thermogravimetric analysis (TGA) performed on a PerkinElmer Pyris 1 thermogravimetric analyzer (air, 30 mL/min from 50 up to 750 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$).

Particles characteristics. The HRTEM imaging and the thermal reactivity (Figure 1) revealed a straight relation between the nature of the inert gas and the sizes of both particles core and carbon shell. In all of the cases, HRTEM evidenced an overall structural inhomogeneity, although primary particles are clearly discernible. The averaged primary particle size is considerably smaller compared with the typical chain-like structured nanoparticulate produced in combustion systems (flames and engines) [5].

In the case of Ar-type Palas carbonaceous particulates, small and quite widely distributed (average diameter spanning from 1 to 6 nm) well-defined primary particles are discernible with short graphene segments arranged concentrically and parallel to the particle perimeter. These structures can be easily classified as the widely accepted GfG soot [1-3], characterized by an overall fulleroid shape with closed carbon shells and scarcely non-smooth surface, associated with a not negligible oxygen content (Figure 2, lower panel). Looking at the N_2 -type Palas carbonaceous particulates, completely different nanostructures tend to emerge. The surface structures are smoother with hollow cores and longer outer graphene layers.

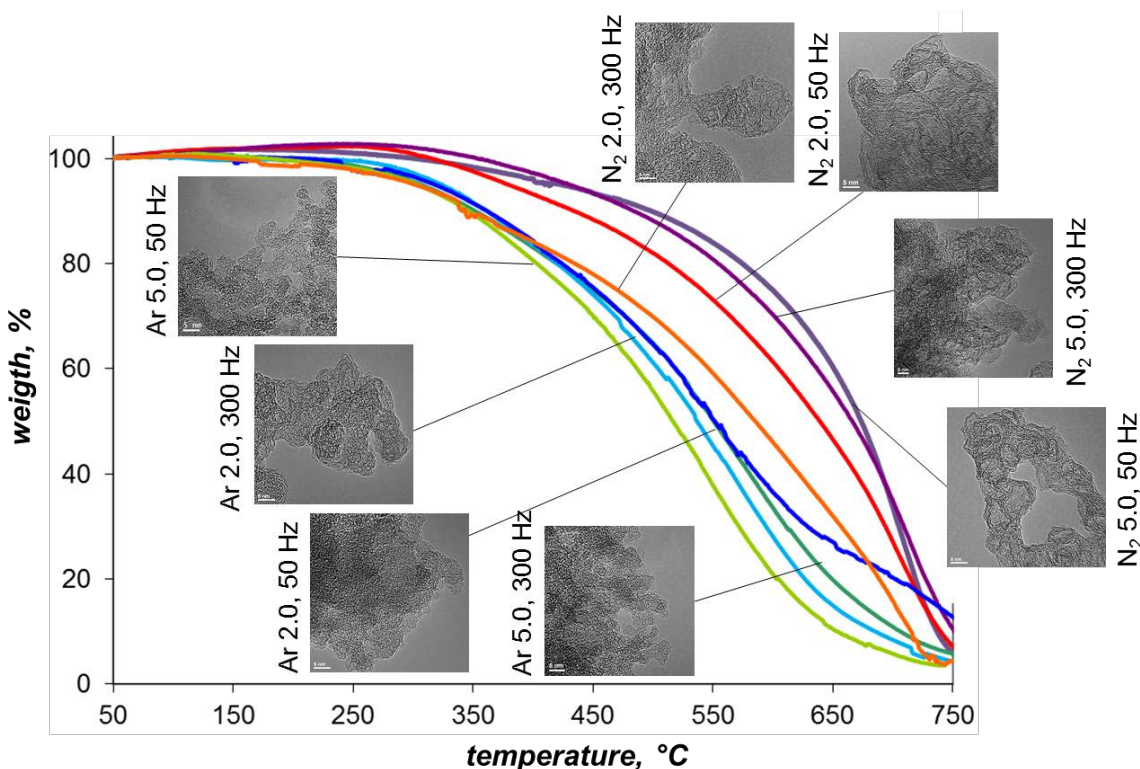


Figure 1. TG plots and HRTEM images (scale bar 5 nm) of Ar-type and N_2 -type Palas carbonaceous particulates.

The TG profile of the graphite-based particulate exhibits a continuous weight loss with a clearly different initial starting culminating, in both Ar and N_2 -type carbonaceous particulates cases, with complete sample combustion after 750 $^{\circ}\text{C}$. The Ar-type carbonaceous particulates

exhibit an early weight loss starting (250°C) compared to N₂-type Palas ones (350 °C). The difference in the oxidation behaviors of the Ar-type and N₂-type Palas carbonaceous particulates is strictly associated with the different microstructures revealed by HRTEM. The differences in surface curvature degree (i.e. different defective surfaces) expose different sites to oxidation: the strongly curved fulleroid structure of the primary particles surface exhibited by the Ar-type carbonaceous particulates can be easily functionalized with reactive groups resulting in an easier oxidation. By contrast, the N₂-type carbonaceous particulates exhibit a higher resistance against oxidation compared to the Ar-type Palas ones that is most likely due to the larger graphenic crystallites imaged by HRTEM. As a general rule, large crystallites give a low ratio of edge site to basal plane carbon atoms, thus a lower surface area for reactive groups attack [5].

The Ar-type Palas carbonaceous particulates show two pronounced weight loss: the first at about 400°C most likely driven by the combustion of functionalized defect-rich primary particles [1], the second weight drop due to the combustion of large primary particles or agglomerates with less defective/functionalized surfaces and, eventually, also to surface-bonded fullerenes produced in the spark-discharge of graphite.

The FTIR spectra of the samples are reported in Figure 2. Spectra are baseline-corrected, height-normalized and shifted for clarity.

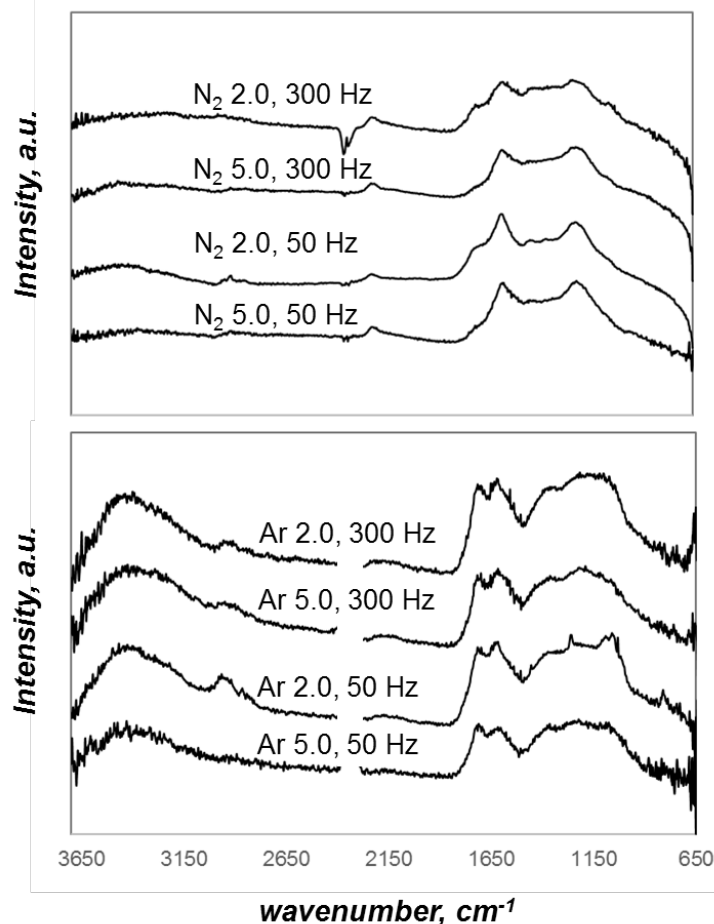


Figure 4. FTIR spectra of Ar-type and N₂-type Palas carbonaceous particulates.

The FTIR spectra profiles of the eight samples are quite similar and reflect the complex character of the carbonaceous networks constituting the carbonaceous particles. The infrared signals are mostly located in three regions: broad bands between 3100 and 3600 cm⁻¹ (exchangeable protons from oxygen-containing functional groups and adsorbed water), low-intensity signals between 2800 and 3100 cm⁻¹ (stretchings of aromatic and aliphatic C–H groups, most likely from impurities in the graphite rods and in the argon carrier gas),

overlapping signals between 1750 and 1100 cm^{-1} ascribable to the stretching and bending absorptions of different functional groups (both O and N-containing, in addition to adsorbed water).

The FTIR spectroscopy allow to associate the more fulleroid Ar-type carbonaceous particulates with highly defective non-smooth surface to a high oxygen content (i.e. C=O of carbonylic and carboxylic groups peaked at 1710 cm^{-1}). In the case N₂-type carbonaceous particulates, bands associated to the presence of N can be observed: the signal at 2200 cm^{-1} are attributable to C-N triple bond stretching while the signals in the 1500-1800 cm^{-1} and the 1000-1300 cm^{-1} regions are ascribable to some C-N stretching and N-H bending absorption modes [6].

Interestingly, the influence of gas purity appears to be negligible in the case of Ar-type carbonaceous particulates, while, in the case of N₂-type carbonaceous particulates, a light enhancement of the C=O band is observable when low purity dilution gas was used, in both spark discharge frequency conditions. The slightly higher oxygen amount in N₂-type carbonaceous particulate produced in presence of a low purity dilution gas explains the lower resistance toward oxidation (Figure 1) compared to the N₂-type carbonaceous particulates produced by using the higher purity dilution gas and the nanostructural features resembling those observed in the case of Ar-type carbonaceous particulates.

This preliminary survey demonstrates that tunable microtextures of carbonaceous particles are obtainable by a spark generator system by simply acting on the generator operating conditions and on the quality of gas supply. Moreover, it assessed that the use of N₂ as dilution gas allows the incorporation of small quantities of N in the carbonaceous particulate network.

References

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