SCANNING SPREADING RESISTANCE MICROSCOPY FOR ELECTRICAL CHARACTERIZATION OF FLAME GENERATED PARTICLES

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Abstract
Combustion formed carbonaceous particles may have features similar to carbon compounds used in new technologies like optoelectronic and energy storage and conversion. Such species can roughly be distinguished into two classes: organic particles with diameter D=2-10 nm, which have molecular-like spectroscopic properties, and soot which is constituted by amorphous carbon in form of chain-like clusters of primary particles with D~50nm. Their physical-chemical properties of both classes can be tailored by changing the flame parameters, like temperature, fuel/air ratio etc. A detailed knowledge of the composition and properties of produced compounds is required to evaluate their potentialities as a low cost new nano-structured material. In this work, soot nanoparticles were produced in a laminar premixed rich ethylene-air flame. We used scanning spreading resistance microscopy (SSRM) for the electrical characterization of soot particles collected via thermophoresis on mica substrates rapidly inserted into the flame. The I-V characteristic of layers of carbonaceous soot particles have been measured and compared in terms of number of insertions in the flame, i.e. amount of soot particles. The results obtained in the present works show that SSRM is a very interesting and promising diagnostic tool for soot characterization. Furthermore, such results may lead to the development of soot sensors based on their electrical properties.

1. INTRODUCTION
In the recent years, there was an emerging interest toward engineered carbon-based nanoparticles of tailored composition and structures for a variety of possible applications including drug delivery, coating for photovoltaic cells, new nano-sized materials and they are playing a major role in today's science and technology [1]. Innovative and inexpensive synthesis processes are now in great demand and combustion seems to be a viable method for their production.
It is well-known that hydrocarbon flames operated in fuel rich-conditions produce carbonaceous solid particulate matter, which are generally considered as an unwonted by-product and an atmospheric pollutant [2]. Flame-generated

nanoparticles have the potential to be considered as a new low cost carbon-based material, characterized by a nearly-molecular size and an unique active surface. Under this light, a full knowledge of composition and properties of combustion-formed nanoparticles is required to investigate the possible fields of application; studies on electrical conductivity can be useful the develop innovative technologies, such as soot sensors based on conductometric measurements principle, or optoelectronic devices realized with combustion-formed particles layers.

In this work, we have collected carbonaceous nanoparticles produced by premixed flames of ethylene and air, by means of thermophoretic sampling, in order to obtain quite uniform layers of nanoparticles on substrates. Samples were then analyzed by Atomic Force Microscopy (AFM), which furnishes 2D and 3D topological maps of material deposited on atomically flat mica substrates. Local electrical conductivity measurements were performed by means of Scanning Spreading Resistance Microscopy (SSRM). SSRM is a new, powerful electrical characterization technique for semiconductors, based on AFM [3]. A conductive probe is used to scan the sample in contact mode, while a DC bias is applied between the tip and a second contact; the resulting current flowing through the sample is measured using a lock-in logarithmic amplifier. Unlike other scanning probe-based techniques, such as Scanning Tunneling Microscopy, SSRM offers the possibilities of measuring independently topography and conductivity of the samples [4].

2. EXPERIMENTAL

The experimental combustion system consists of a flat, laminar premixed flame of ethylene and air, stabilized on a McKenna burner, with a cold gas velocity of 10 cm/s. A pneumatic actuator was used to insert mica muscovite discs (9 mm in diameter, 0.15 mm tick) in the flame with a constant sampling time for each insertion, ranging from 10 ms to 100 ms; the cold surface of the substrate produces a strong temperature gradient with respect to the hot combustion gases, making particles move towards the surface by thermophoretic forces, where they impact and deposit.

Topography and conductivity measurements of the samples were then performed by means of NT-MDT NTEGRA scanning probe microscope, equipped with conductive Au-coated silicon AFM tips (NT-MDT, type CGS-10); mica discs were mounted on a sapphire substrate with spring contact for electrical measurements. Surface topography has been measured in semicontact AFM mode, in order to obtain 3D topological maps which allows to determine the level of coating of the substrates. Surface conductivity mapping has been obtained by operating the SPM in Scanning Spreading Resistance Microscopy mode. Scanning of the tip over the cross section of the sample in SSRM mode provides a two dimensional map of the local spreading resistance with a spatial resolution set by the tip radius, simultaneously with contact AFM topographic images. After the scanning is complete, local I/V characteristic curves can be obtained by measuring the current in a selected point of the scanned area, as a function of bias voltage applied in a defined range (up to a maximum of -10V to +10V). At a given voltage, the current measured by the instrument is given by the total circuit resistance, which is the sum between the resistance of the sample, the resistance of the tip and the resistance of the contact between the sample and the tip (considering other resistances negligible); the latter two resistances can be usually considered constant and negligible compared to the sample resistance for conductive tips and reasonable sample resistance [5].

3. RESULTS AND DISCUSSION

Preliminary results were obtained from an ethylene/air flame with a C/O ratio equal to 0.85 and a cold gas velocity of 10 cm/s, inserting the mica substrate at a height above the burner of 15 mm.

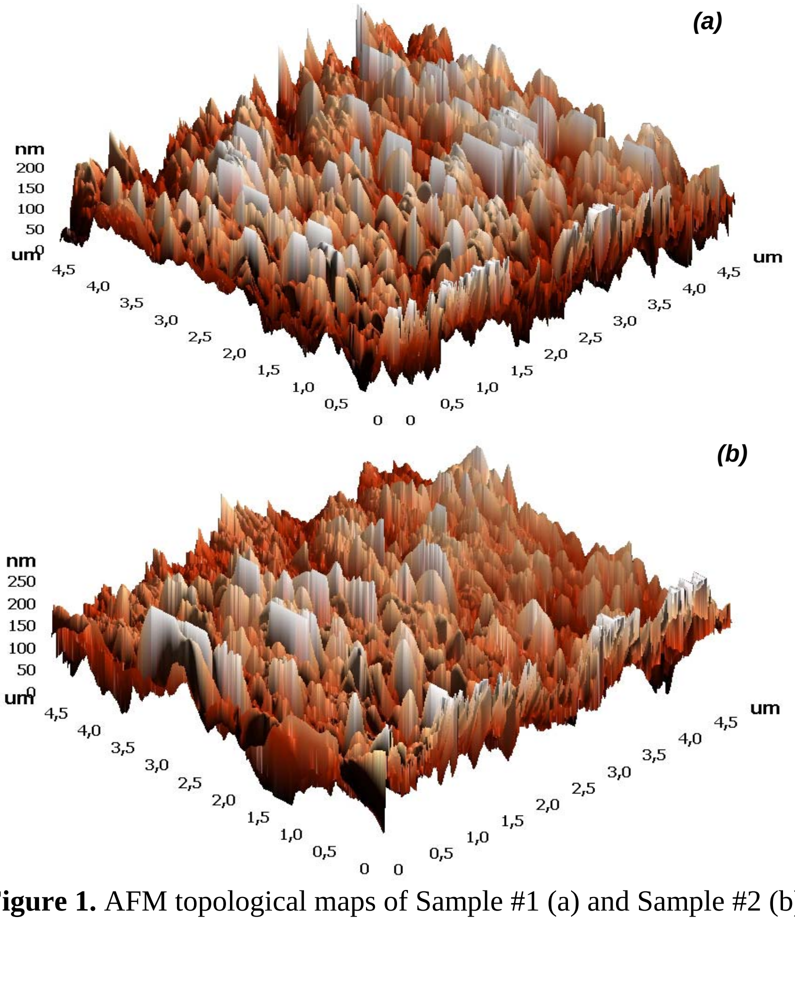

Figure 1. AFM topological maps of Sample #1 (a) and Sample #2 (b).

The time of each insertion (t_{ins}=50 ms) was keeping constant. With the selected experimental conditions, carbonaceous particulate matter constituted by soot particles was collected.
Two different samples were analyzed, with a total number of insertions of the substrate in flame of 50 (Sample #1) and 100 (Sample #2).
AFM topological maps of the two samples surfaces are shown in Fig.1. Both samples show a good level of coating, higher for the sample collected with the higher number of insertions, with an almost uniform film of carbonaceous particles covering the whole mica substrate. From AFM images it is possible to estimate thickness of the two layers, approximately equal to 170 nm for Sample #1, and 250 nm for Sample #2.
Fig. 2 reports the SSRM images of Sample #1 and Sample #2, both obtained with an applied bias voltage of 10 V. SSRM images show that the sample surface conductivity is appreciable and some current flows through the whole surfaces, although the current distribution over the surface is quite inhomogeneous. The average conductivity of carbonaceous particles film sampled with 50 insertions is about 2 nA, while the average conductivity of carbonaceous particles film sampled with 100 insertions is higher (about 10 nA), demonstrating that increasing the number of insertions allows to collect a more uniform layer of particles, with a higher packing degree between particles.

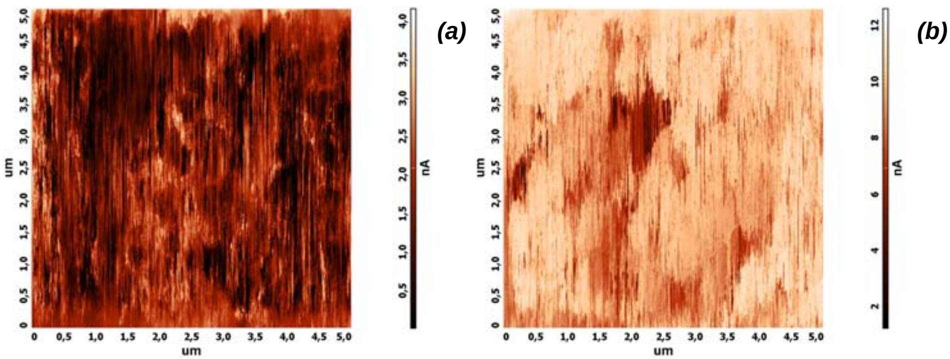

Figure 2. SSRM images of Sample #1 surface (a) and Sample #2 surface (b).

Subsequently, local current/voltage characteristics of the material was calculated, choosing, from the spreading resistance maps, points on which higher currents were measured scanning for I/V curves. I/V characteristics are reported in Fig. 3, for Sample #1, and Fig. 4, for Sample #2; blue curves are for V changed from minimum to maximum value, red curves are for V changed from maximum to minimum values. Both curves are symmetric and non-linear, indicating a non-ohmic electrical behavior. Also, I/V characteristics show that electrical conductivity of flame-generated carbon particles film sampled with 100 insertions is higher than that of carbonaceous particles film sampled with 50 insertions.

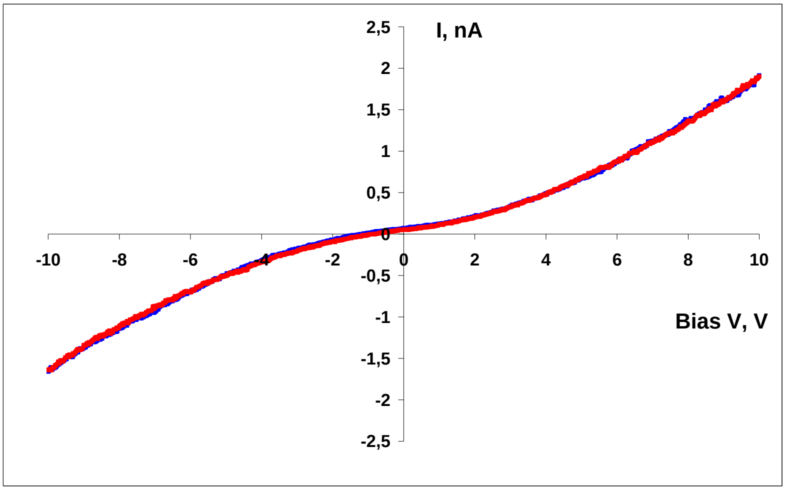

Figure 3. SSRM measured local I/V characteristic of Sample #1.

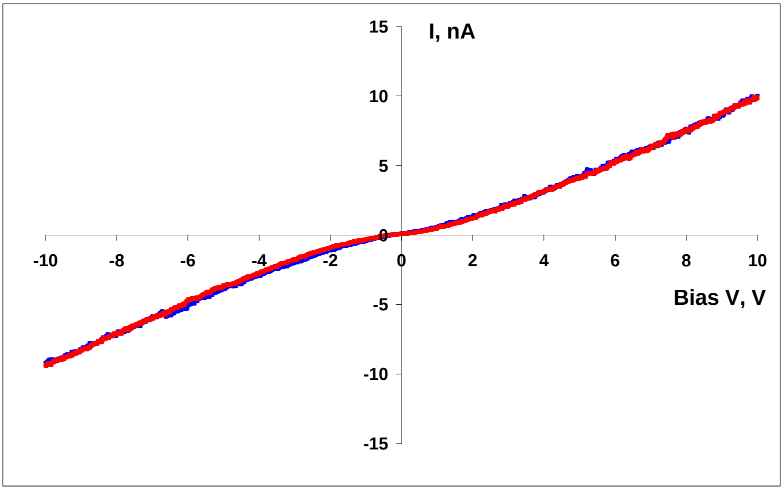

Figure 4. SSRM measured local I/V characteristic of Sample #2.

From electrical characterization performed with SSRM technique, a preliminary estimation of electric current density, defined as the flux of current through the cross-sectional area, can be done. Assuming that cross-sectional area of soot particles layer is proportional to the square value of layer thickness, for an applied bias voltage of 1 V current density is almost equal to 350 mA/cm^2 for Sample #1, and 800 mA/cm^2 for Sample #2.

4. CONCLUSIONS

To conclude, a preliminary study of electrical properties and behavior of flame-generated carbon nanoparticles has been conducted by means of Scanning Spreading Resistance Microscopy. SSRM is a very powerful and helpful technique to analyze combustion-formed particles layers collected by thermophoresis, since it allows to investigate simultaneously the topography of the surface, and so the degree of coating of the substrate, and the electrical conductivity of materials, linking together topological and electrical collected data. First results show that soot particles layer have a non-ohmic electrical behavior; increasing the total residence time of the substrate in flame produces a more higher and homogeneous layer, and increases also electrical conductivity of materials. Additional works need to be performed to investigate sampling conditions that allow to obtain a completely uniform layers of materials, and to characterize electrical properties of the materials under different conditions (e.g., in nitrogen or in carbon dioxide atmosphere).

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