Electric field-assisted flame synthesis of Carbon Nanoparticle films

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Abstract

This work summarises the main findings of a joint research activity, carried out within the Italian PRIN Project MagicDust, which couples dedicated experimental campaigns and physical-mathematical modelling to exploit the main features of the electric field-assisted flame synthesis of Carbon NanoParticles (CNPs). The experimental and model results reveal that the new flame synthesis method can produce films with features very different from those obtained by conventional thermophoretic deposition, opening new possibilities in the production of CNP films with tunable properties.

Introduction

Carbon black (CB) is a fascinating material that is successfully adopted in various industrial applications thanks to its nano-sized dimensions, large specific area, chemical stability, mechanical strength, reasonable cost, good electrical conductivity and superhydrophobic properties [1,2]. In the last years, the scientific discovery of the many special features of nanometric particles promoted a new interest in the production of carbon nanoparticle (CNP) films. The CNPs are often manufactured following a top-bottom approach starting from carbon black particles that are processed using different treatments to reduce their sizes to the nanoscale [3,4].

However, combustion science and technology provide sufficient scientific and technological know-how to produce CNPs with virtually tunable size and properties following a more efficient and greener bottom-up approach: using a gaseous fuel with low molecular weight to sustain a highly controlled flame condition, and with accurate positioning and geometry of the CNP collector inside the flame, it is possible to drive the chemical processes that regulate the formation of aromatic structures, so to achieve CNPs with tunable size and properties [5–8]. Furthermore, the process involves a highly efficient combustion process with minimal creation of harmful by-products and the additional benefit of energy production. This bottom-

up approach is known as flame synthesis. Usually, the film formation process is based on the use of thermophoretic forces to deposit particles on a cold substrate immersed in the flame [9,10]. Thereinafter we will refer to this process as FS-Th. Most of the research available in the pertinent literature is based on the production of inorganic films [11–13] and its application to CNPs is the subject of few studies [14,15]. By working at carbon-to-oxygen ratios slightly higher than stoichiometric ones (C/O=0.33 ethylene-air flames), or placing the collector at a very low distance above the burner, it is possible to produce CNPs having sizes close to 10-20 nm, that are very similar to the primary particles obtained from carbon black but have a higher oxygen content that makes them more hydrophilic, a unique property that can be used for several applications alternative to those normally covered by CBs. However, in this flame, both the particle concentration and the thermophoretic deposition rate are low, undermining the process productivity.

The longstanding experience in the field of particle filtration by electrostatic forces suggested that the presence of an electric field in the flame – a plasma characterized by the presence of positive ions, electrons and charged particles – can fasten the deposition rate of CNPs overcoming the limitations of conventional thermophoretic flame synthesis [16,17].

This new process, named Electric field-assisted flame synthesis (FS-eTh in the following), is the topic of this work, which presents a summary of the main results obtained on the production of CNPs in a slightly sooting C/O ethylene-air flame. This study is based on experimental and modelling analysis and compares the characteristics of FS-eTh and FS-Th films and of their parent nanoparticles and agglomerates.

Materials and Methods

CNP films were produced in a flat laminar premixed ethylene-air flame stabilized on a water-cooled McKenna burner. Cold gas velocity was 9.8 cm/s, and the carbon-to-oxygen ratio (C/O) was set to 0.67, which corresponds to a slightly sooting flame. A sketch of the complete setup for CNP film deposition is shown in Figure 1.

CNP film was obtained on different substrates, namely a mica disk, a glass plate, and a glass plate with printed gold electrodes, which were rapidly inserted in the flame. Up to 600 insertions per test were used, the insertion time was 100 ms, and the height above the burner, HAB, was 15 mm. The probe containing the substrate was kept at a fixed electric potential, while the burner was grounded. The electric potential on the substrate was varied from 0 kV up to -3 kV, below the onset of corona discharge, which occurred at -4 kV. In this work, only negative electric potentials were tested, since in the presence of positive polarities, instabilities and flame extinctions were observed, leading to a more complex interpretation of the experimental and model results.

The experimental results consist of an extensive and brand-new set of data on the characteristics of aged CNP films and agglomerates obtained after the dissolution of the CNP films in N-Methyl-2-pyrrolidone: UV-Vis light absorption, Optical band

gaps, Raman spectra, fluorescence, AFM analysis on the morphology of the agglomerates, surface texture, wettability and conductivity measurements were carried out for both FS-Th and FS-eTh processes, allowing highlighting the similitudes and the differences of the produced films and the parent CNP agglomerates.

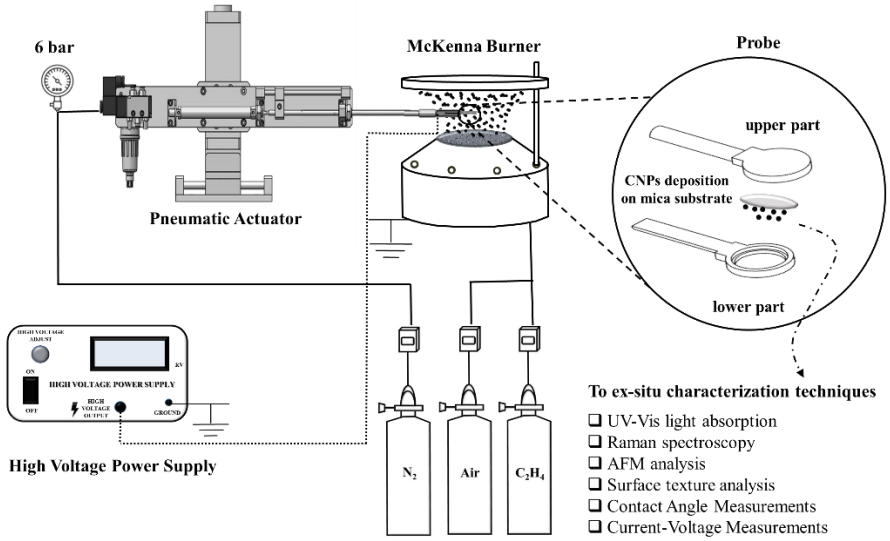

Figure 1. Sketch of the electrophoretic-thermophoretic film deposition setup.

Results and Discussion

To investigate the dynamics of particle deposition under the effect of the electric field, a mathematical model has been developed on the bases of the Langevin equation for momentum balance over a single particle and extensive knowledge of the flame properties in the investigated conditions [18]. The application of the electric field ignites the onset of two other forces in addition to the hydrodynamic and thermal Brownian motion which characterize the conventional thermophoretic deposition: the Coulomb and the electrophoretic forces, acting on charged particles, and the image and dielectrophoretic forces acting on uncharged particles. Indeed, electrophoretic forces also act between charged particles and grounded collectors in the conventional FS-Th process, but they are less relevant than the dominating thermophoretic forces.

The model reveals that the Coulomb electrophoretic force dwarfs the thermophoretic force and gives rise to faster and more perpendicular impacts of the charged particles with the collector. The dielectrophoretic force is relevant only for particles larger than 20 nm, but they represent a negligible fraction of the total CNPs found in the test flame, thus becoming irrelevant in the investigated conditions. Since the fraction of charged particles becomes appreciable only above 5 nm, the electric field-assisted

flame synthesis is more effective for these kinds of particles than for the finer ones [18]. The different impact conditions lead to produce more stable and compact films, not necessarily with a more uniform mesoscale morphology due to local polarization effects. Table 1 summarizes the similarities and differences between CNP films and their parent CNP agglomerates produced by FS-Th and FS-eTh.

Table 1. Overview of the CNP films and agglomerates properties, produced by conventional FS-Th and FS-eTh.

	FS-Th	**FS-eTh**
Length of aromatic islands	~1.36 nm	~1.36 nm
Film growth rate	2.9 nm/s	16.8 nm/s
Selective harvesting?	No	Yes, CNPs larger than 5 nm favoured
Surface texture/Roughness	Low both on nano and mesoscale, with uniform peaks and valleys.	Very high, with irregularities both on nano and mesoscale (flat valleys and many high spiked peaks).
	Volmer-Weber growth mode	Stranski-Krastanov growth mode
Fluorescence	Higher	Lower
CNP agglomerates	Small and unstable	Larger, stable with higher compactness
	Van der Waals's cohesive forces dominant	Electrostatic forces and polarization effects dominant
Optical band gap	~0.5 eV	Thickness-dependent, from ~0.5 eV to ~0 eV
Electrical conductivity	Low and temperature-dependent	Higher and temperature-independent
	~10^{-3} S/cm at 25°C	~10^{-1} S/cm
Wettability/ Contact Angle	Hydrophilic	Transition, Hydrophilic
	CA~13°	CA<40°

The experimental data confirm the model predictions and shed new light on the process dynamics. The Raman spectra indicate that the average size of the graphitic crystallites of the CNPs is unaffected by the presence of the electric field, confirming that the chemistry of CNP formation is not modified by the electric field applied to the sampling probe. The AFM and the surface texture analysis indicate that the morphology is more irregular than that observed for pure thermophoretic deposition, with the formation of large mesoscopic structures of micrometric or submicrometric sizes: while under thermophoretic flame synthesis, the film grows following the Volmer-Weber model, the electric field-assisted flame synthesis produces films which grow following the Stranski-Krastanov model [19]. This result is probably related to the onset of polarization effects in the agglomeration phenomena that gives rise to a preferential orientation of particles in the direction of the electric field,

which is often observed for the deposition of charged particles in electrets.
The AFM and the UV-Vis spectra indicate faster deposition rates, which are consistent with the model predictions. The conductivity and the optical band gap data prove the higher compactness of the deposits formed by FS-eTh as predicted from the CNPs deposition model: the analysis of agglomerates UV-Vis spectra indicates that they are on average much larger and stable for the FS-eTh and their optical band gap is lower than that of pure FS-Th. Besides, the optical band gap of the FS-eTh films indicates that its compactness greatly contributes to the conductivity of the deposits. Another indirect proof of the higher compactness of the FS-eTh deposits comes from the wettability tests, where the presence of large and stable agglomerates moving on the free surface of the droplets is observed. Indirectly, the higher stability of the agglomerates indicates that the FS-eTh is probably less useful for the production of CNPs suspension compared with the conventional thermophoretic flame synthesis.
The experiments also indicate that the hydrophilic character of the FS-Th films is preserved also in the FS-eTh films, which, despite their larger roughness, showed a fast transition from a Cassie-Baxter hydrophobic behavior to a hydrophilic one. On the other hand, this roughness is also representative of a higher surface area of the deposits that is beneficial for several technological applications.

Conclusion

Electric field-assisted flame synthesis emerges as a process useful to overcome the limits of conventional flame synthesis methods and add new degrees of freedom in synthesizing nanoparticles and thin films with unique and tunable properties. The process allows a faster deposition of CNPs and the production of more stable deposits with larger agglomerates, which allows a higher electric conductivity, and an irregular structure with large surface area and hydrophilic properties.
For its advantages in terms of enhanced productivity and the possibility to exploit new features compared with conventional carbon black particles, FS-eTh is worth future investigation and further technological development.

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