

# Exploring Flame-Formed Carbon Nanoparticle Thin Films for Sensing Applications

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## Abstract

Carbon-based nanostructured materials offer exciting potential due to their unique properties. This research explores using flame synthesis as a simple and cost-effective method, to create carbon nanoparticles (CNPs) for sensor applications. Thermophoretic sampling then deposits CNPs as thin films, ideal for miniaturized sensors. By controlling flame and sampling conditions, CNP properties like size, structure, and composition can be tuned. These CNP films exhibit good electrical conductivity, biocompatibility, and sensitivity, making them promising candidates for gas and temperature sensors. The resulting films are conductive, lightweight, and biocompatible, making them ideal for sensor applications. This study demonstrates a one-step process for creating active components for rapid and sensitive temperature and gas sensors using flame-synthesized CNPs without further treatment, highlighting the potential of this approach for rapid and cost-effective sensor development.

## Introduction

Carbon-based advanced materials exhibit remarkable versatility and have been revealed to hold great potential for functional applications due to their exceptional combination of good electrical conductivity, high chemical and thermal stability, ideal optical properties, and low toxicity. Indeed, their use in energy harvesting media, optoelectronic and sensing devices, and flexible active materials, among numerous other potential applications, have been recently gathering more and more interest [1]. This has fueled significant advances in the development of novel carbon-based nanomaterial synthesis routes.

In particular, thanks to the spontaneous formation of carbon nanoparticles (CNPs) in fuel-rich flames, these highly reactive environments have been exploited as a starting

point for production techniques of several carbon materials, such as fullerenes, carbon nanotubes, carbon black, graphene, and soot [2]. Among them, CNPs which are formed at the early growth stages (starting from the inception point) exhibit particularly interesting properties, even without pre- or post-deposition treatments, such as chemical surface functionalization or temperature treatment. In fact, at the beginning of the formation process CNPs are constituted of large polyaromatic molecules (PAHs) that can aggregate via physical van der Waal forces and chemical cross-linking [3,4]. Moreover, at higher flame residence time, through coagulation and surface reactions, particles can grow, and larger primary particles can be formed [5]. Hence, a fine tailoring of both the flame reactor and the flame synthesis parameters allows for the tunable production of CNPs that possess engineered properties, such as size, amorphous versus graphitic-like composition ratio, and electrical and optical characteristics [6,7].

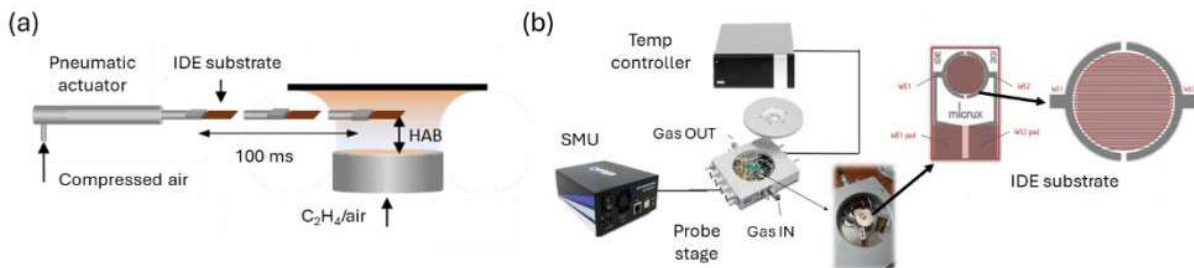
Furthermore, in those practical applications that require thin film production, like the miniaturization of electronic devices or the development of battery electrodes, flame synthesis offers an effective bottom-up assembly method [8,9]. Indeed, nanostructured, self-assembled uniform thin films can be produced via thermophoretic sampling, which relies on the thermophoretic force that pushes flame-generated particles from the hot flame toward a cold substrate rapidly inserted into the flame [10]. The resulting deposition mechanism has been shown to present a ballistic-like nature and to produce a self-affine, fractal, and porous structure, made of voids and grains [6]. Notably, the properties of the generated film depend on the properties of the original precursor particles, together with the total deposition time [11]. Hence, there has been a lot of interest in using CNP thin films in sensing applications due to their capacity to conduct electricity, their biocompatible, very sensitive, flexible, and lightweight nature, as well as the ease of their production.

Here we report on the development of cost-effective temperature and gas sensors via a straightforward one-step process based on the synthesis of CNPs in flames and subsequent particle thermophoretic sampling, without the need for any further physico-chemical treatment. The response of the resulting sensing devices toward ambient temperature or ethanol vapor exposure is investigated, confirming the potential of the flame-synthesis procedure to produce effective active layers for rapid and sensitive sensors.

## Experiment

A laminar premixed ethylene/air flame at atmospheric pressure stabilized on a water-cooled sintered bronze McKenna burner with a diameter of 6 cm is used for the production of the carbon nanomaterial in fuel-rich, sooting conditions. The flame equivalent ratio is  $\phi = 2.32$  (carbon to oxygen atomic ratio of 0.77) and the cold gas velocity is  $v = 9.8$  cm/s. The height above the burner (HAB), which in this system directly corresponds to the flame residence time, is set to 10 and 14 mm, in order to collect CNPs up to 25 nm of average diameter [12]. Thin-film Inter Digitated gold electrodes (from Micrux, ED\_IDE1-Au) are utilized as substrates, with a channel

width-to-length ratio of  $W/L = 49000$ . The self-assembly of the CNP thin films is obtained by exploiting thermophoretic deposition via multiple quick insertions of 100 ms each (see Fig. 1a), for a total deposition time in the range of 1 to 5 s, depending on the number of insertions (from 10 to 50). A rapid insertion time is set in order to prevent excessive heating of the substrate which would cause a decrease in the thermophoretic force and, therefore, negatively affect the sampling efficiency. Atomic Force Microscopy (AFM) is performed to obtain the morphological characterization of the samples, using a Scanning Probe Microscope NTEGRA Prima (from NT-MDT), operating in a semi-contact mode with supersharp silicon probes (from NANOSENSORS, SSS-NCHR) with a tip radius of 2 nm (nominal). Structural properties are extracted with Raman spectroscopy measurements, performed with an Xplora Raman microscope (from Horiba), using a 532 nm laser beam of less than 1 mW optical power and a 100x objective lens with numerical aperture  $NA = 0.9$ . To obtain the electrical characterization the samples are put on a variable-temperature probe stage (from Linkam, HFS600E-PB4) with tungsten probes and electrical connectors mounted in a gas-tight chamber (see Fig. 1b). Current-voltage ( $I-V$ ) curves are run using a Source Measuring Unit (from Ossila, SMU x200). A controlled atmosphere of variable ethanol concentrations is obtained with a controlled evaporator mixer (from Bronkhorst, CEM).

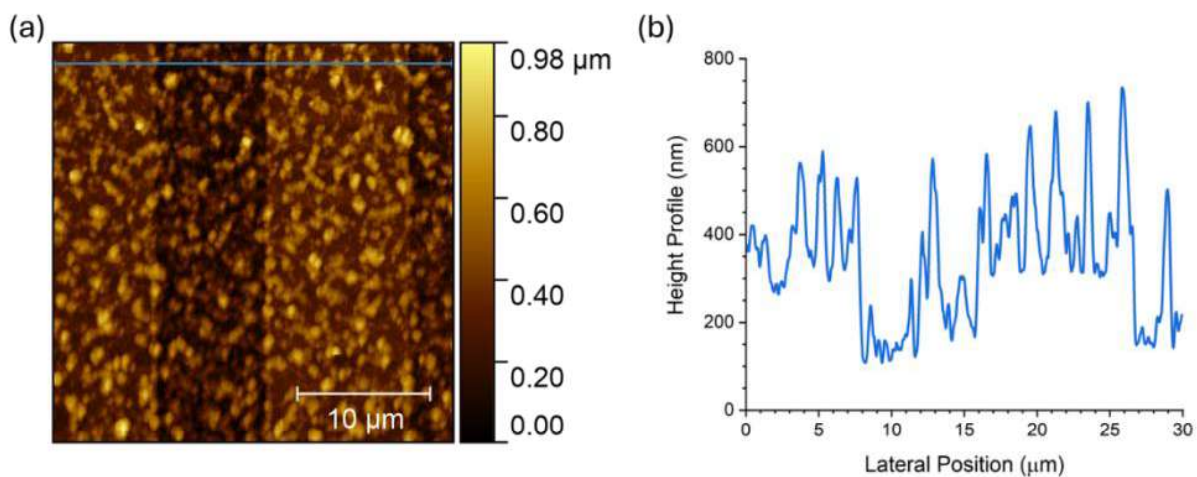


**Figure 1.** Scheme of the (a) thermophoretic sampling process and of the (b) electrical measuring and sensing setup (with a detailed zoom of the IDE substrate).

## Results and Discussion

The surface morphology was visualized with semi-contact AFM (as shown in Fig. 2a). The collected CNP thin film exhibits a granular structure with higher and lower concentrations of grains, typical of thermophoresis-based and other ballistic-like deposition procedures. Underneath the CNP film, the electrode pattern is still recognizable, both in the AFM image and in the height profile taken across the electrodes (as shown in Fig. 2b). With different numbers of insertions and, therefore, different total insertion times, the amount of collected carbon material can be varied. Moreover, by collecting at different HAB values, particles of diverse sizes and varying electrical characteristics can be selected. Indeed, by changing the flame residence time, different regimes of the soot formation process can be explored, and particles from either the nucleation (at lower HAB) or the coagulation (at higher HAB) zones can be gathered. It has already been reported that CNPs of different sizes and levels of growth present different electronic bandgap values. The latter

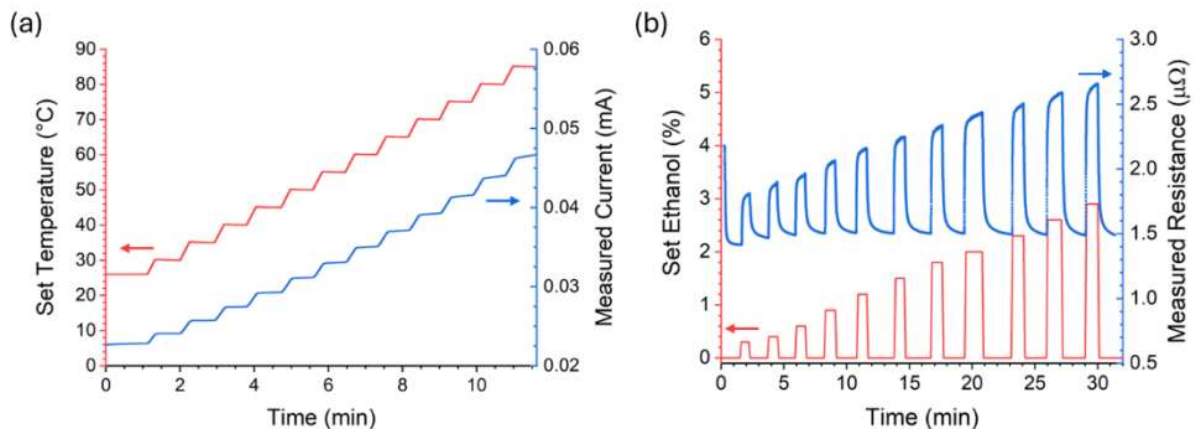
decreases with the increasing of the particle size, coherently with both a quantum confinement size-dependent effect and a variation in the chemical composition [7,13]. This parameter tuning allows CNP films of variable thickness and electrical properties, and an optimal value can be reached. For thin-film-based electrical measuring techniques, for instance, it is usually advantageous to obtain active films possessing a high resistance. High resistivity films, in fact, allow a low current flow and, therefore, both a negligible self-heating effect and a lower electrical power consumption. This would be obtained with a low amount of material that still is enough for the creation of a continuous percolative network of semiconductive CNPs. On the other hand, when the collected carbon material increases, the complexity of the film surface increases as well, as can be derived from higher surface roughness and developed interfacial area ratio values measured with AFM in case of a higher quantity of collected CNPs. As a result, the active surface exposed to the ambient temperature or atmosphere composition increases as well, allowing for an improved sensitivity. Therefore, here, we collected CNPs at different HABs (with a similar number of insertions), opting for a lower HAB = 10 mm when avoiding self-heating was crucial and a higher HAB = 14 mm otherwise.



**Figure 2.** (a) AFM height image of an exemplary  $30 \times 30 \mu\text{m}^2$  area on the sample with 20 insertions at HAB = 14 mm. The CNP self-assembled thin film covers the whole surface of the sample (both the higher gold contact areas and the lower glass gap regions). (b) Height profile collected along the blue line in panel (a), showing the height jump between the covered gold contacts and the covered glass gaps.

In our granular CNP thin films, the current flow is allowed via the tunneling of electrons between neighboring particles which form a continuous percolative network between the electrodes. This phenomenon can be enhanced by the thermal excitation of the electrical carriers. Indeed, increasing the temperature, the number of excited carriers increases, and, therefore, the current rises (as shown in Fig. 3a). This temperature-dependent current response can be exploited to develop a temperature sensor that possesses a high absolute temperature coefficient of resistance ( $TCR \sim -100 \times 10^{-4} K^{-1}$ , denoting a good sensitivity toward

temperature changes) and a reliable response calibration from room temperature (RT) up to 85 °C (with a calibration fit residual lower than 0.1 K) [14]. In contrast, if exposed to gas molecules with a polar nature, such as ethanol, their physical adsorption on CNPs can induce charge transfer and the freezing of electrical carriers. This results in an increase of the film resistance with the increase of the ethanol concentration in the atmosphere (as shown in Fig. 3b). Hence, a sensor for ethanol gas has been designed and tested for a gas concentration between 0 and 2.9%, obtaining fast response and recovery times (both shorter than 20 s) and great sensitivity (up to 0.22 1/(ethanol concentration%)) [15].



**Figure 3.** (a) Current response (shown as the blue curve) measured at 10 V on the sample with 40 insertions at HAB = 10 mm during a stepwise temperature increase from RT up to 85 °C (red curve). (b) Resistance response (shown as the blue curve) measured at 2 V on the sample with 50 insertions at HAB = 14 mm during the variation of ethanol concentration (red curve).

## Conclusions

In this work, flame-based synthesis of carbon nanoparticles was demonstrated to be a feasible technique for the production of nanostructured thin films to be used as active layers in sensing electronic devices. The electrical response of the CNP thin-films to temperature and atmosphere gas composition was studied revealing good sensitivity and reliability. This, together with the ease and low cost of the material microfabrication process, and the non-toxicity and biocompatibility of carbon-based materials, makes these films ideal for sensing devices in several conditions. Moreover, the synthesis technique illustrated here allows the depositing of the film on a variety of substrates and with arbitrary design. That paves the way to embed temperature and gas sensors in a variety of commercial products where temperature analysis and ethanol gas detection are required.

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