Research paper

Electrical characterization of flame-soot nanoparticle thin films

Gianluigi De Falco[a], Mario Commodo[a,*], Mario Barra[b,c,**], Fabio Chiarella[b,c], Andrea D'Anna[d], Alberto Aloisio[c,e], Antonio Cassinese[b,c], Patrizia Minutolo[a]

[a] Istituto di Ricerche sulla Combustione, CNR, P.le Tecchio 80, 80125 Naples, Italy
[b] SPIN-CNR Division of Naples, Piazzale Tecchio, 80, I-80125 Naples, Italy
[c] Dipartimento di Fisica "E. Pancini", Università degli Studi di Napoli Federico II, Italy
[d] Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli Federico II, P.le Tecchio 80, 80125 Naples, Italy
[e] INFN Sezione di Napoli, Naples, Italy

ARTICLE INFO

ABSTRACT

Carbon nanoparticles, with diameter d ~ 10 nm, were produced in a premixed ethylene-air flame and used to grow self-assembled thin films by thermophoretic deposition on Si^{++}/SiO_2/Gold multilayer substrates inserted in flame.

The particles' size was measured by a Scanning Mobility Particle Sizer. UV–vis light absorption, Raman spectroscopy and Atomic Force Microscopy were used for the chemico-physical and morphological investigation of the carbon nanoparticle thin films. The electrical characterization was then performed in different environmental conditions with the basic aim to assess the potentiality of these films to be employed as electrically-active components in electronic and sensing applications.

The films are composed by the aggregation of nanoscale grains whose size increases with the deposition time and are consequently highly porous with the electrical conduction properties showing a dependence on thickness suggesting a percolation-like behavior. Raman spectrum indicates that the chemical/structural composition of the film does not change with deposition time and consists in small graphitic crystallites with constant size.

The electrical measurements show also the ohmic behavior of the IV curves. Moreover, an ambipolar response of the CNPs channels, when investigated in the field-effect configuration, was observed and, in parallel with conductivity, charge carrier mobility values were found to increase with thickness.

1. Introduction

In the recent years, nanoscale materials are attracting growing interest because of their unique properties, which are often superior or complementary to their bulk counterparts and may pave the way for novel applications. The unique characteristics of nanoparticles, like high surface to volume ratio, chemically active surface, highly tailorable electrical and optical properties, allow their use in solar cells, light emitting diodes, and other applications (biological labeling, sensors and catalysis) [1]. Particularly interesting is the subset of carbon materials, as fullerenes, nanotubes, nanowires, graphene and other carbon based materials, which show the additional benefits of flexibility and chemical stability [2,3].

Nanostructured materials are produced by a variety of methods [4]. Among all, combustion processes are particularly interesting and may offer relevant advantages since they are autothermic, one step, fast, low cost, and scalable to industrial level [5]. Furthermore, by changing the process conditions, combustion synthesis allows the formation of the most varied carbon nanostructures, from graphite to diamond, fullerenes, nanotubes, graphene and graphene-like materials [6–10].

Most of the materials produced by flame synthesis consist of singlet particles or aggregates, and are collected as powders or nanostructured films. The deposition of low kinetic energy particles produced in gas phase has been used to produce nanostructured thin films starting from the original work by Fuchs [11]. The size and composition of the original particles is important for determining the quality of these films [12], however, the further assembling of the nanoparticles to grow reproducible high quality films is likewise challenging. These kinds of films have been deeply investigated in the past because of their great potential and various applications can be found in literature especially as gas sensors [13], and mostly for inorganic compounds [14–16]. However, interesting electronic applications have been presented also for carbon cluster assembled thin films by Bongiorno et al. [17] using a supersonic cluster beam deposition.

The low energy deposition of particles produced by flame synthesis can be obtained by exploiting the temperature gradient between the aerosol and a cold substrate inserted in flame, which produces a thermophoretic force that moves the particles towards the substrate. The low kinetic energy of the particles guarantees that, when landing on the substrate, particles undergo neither fragmentation nor diffusion and relaxation processes so that the film greatly retains the structural properties of the aerosol used as building blocks [11,17]. Hence, by controlling these properties, it is possible to tailor the structural and functional properties of the film itself. The thermophoretic deposition is therefore emerging as a very attractive method for a low cost, simple and one-step film preparation that does not require the use of solvents, although in the case of carbon films has been used principally for analytical purposes [18,19].

Soot nanoparticles formed in combustion have been often associated to adverse effects for the environment and considered an unwanted byproduct although they present similarities with the carbon black, which is instead widely used in the industry for applications such as conductive filler, antistatic agent, and in electronic equipment related material [20]. Only very recently, candle soot, CS, is attracting some interest as a novel material. Pioneering works have indeed shown that CS can be used for a variety of applications in electronic devices [21,22], as photoluminescent carbon dots [23,24], catalyst [25] or as a coating material for superhydrophobic [26,27] or superamphiphobic surfaces [28]. Soot particles may therefore have a promising potential for industry since it is a quasi-graphitic structure like carbon black although these two compounds differ substantially [29]. Indeed, soot generally includes an organic carbon fraction and its chemical and physical properties, such as size, morphology and composition, are strongly dependent on the flame parameters, for example, particle residence time in flame, temperature, pressure, fuel and type of combustor [30–33]. Such tunability in particle composition is particularly appealing for those applications in which a precise control of the chemico-physical properties of the nanoparticles constituting the film are particularly important.

The objective of this work is therefore to investigate the morphological and electrical properties of flame soot nanoparticle thin films with the aim to explore new applications like low cost electronics or nanosensors.

The combustion reactor which allows to better control and to tailor the properties of the produced particles is a fuel-rich laminar premixed flame burning a simple hydrocarbon fuel as ethylene. Indeed, this is the simplest configuration, free of any fluid dynamic complexity, in which the mechanisms of particle formation and dynamics have been widely investigated over tens of years and are currently better known [31,32]. Early nucleated carbon nanoparticles (CNPs) are about 1–2 nm in size [34], are composed by sp^2 carbon [35] arranged in small aromatic islands, have a bandgap of 1.5–2 eV [36,37], absorb radiation predominantly in the ultraviolet range and emit radiation by fluorescence [38]. In addition, such combustion-produced nanoparticles (CPNs) are potentially good electron acceptor material when blended with a hole acceptor material [39]. Increasing the residence time in flame, particles undergo growth and carbonization processes transforming in nearly spherical particles, with diameters of tens of nanometers, which eventually agglomerate forming chain-like aggregates. These mature soot particles contain turbostratic graphite crystallites, have H/C ratio of the order of 0.1 [40], have a lower optical band gap, of the order of fractions of eV, and therefore absorb light over a wide spectral range from the UV to IR and possess a rather large electrical conductivity [41,42]. From the above, it is clear that appropriately selecting the particles during their ageing process allows tailoring the properties of the sampled particles.

In this work, carbon nanoparticles, CNPs, have been synthesized in ethylene/air fuel-rich premixed flames and preliminarily characterized in terms of their size by using a Scanning Mobility Particle Sizer. Through a thermophoresis-based set-up, CNPs thin films were formed on multilayer substrates with the perspective of technological applications since it allows simultaneous detection of the film conducting properties and the possible occurrence of the field-effect phenomenon. The films herein considered were analyzed through a wide set of complementary techniques including UV–vis light absorption, Raman spectroscopy and Atomic Force Microscopy. A multi-approach electrical characterization (i.e IV, Field-effect, I vs Time measurements) was finally performed with the basic aim to assess the potential of these films to be employed as electrically-active components in real devices (e.g. environmental sensors, supercapacitors, etc.).

2. Experimental

2.1. Flame soot NPs synthesis

Soot CNPs were produced in a flat laminar premixed ethylene-air flame stabilized on a water cooled syntherized bronze McKenna burner. This flame configuration allows the most suitable combustion environment for experimental and modeling studies of flame chemistry and soot particle physicochemical evolution. In such flame reactor, the temperature and the specie concentrations only depend on the height above the burner (HAB), which has a direct correspondence with the flame residence time [43]. The fuel mixture was composed by ethylene and air with carbon to oxygen atomic ratio C/O = 0.72, with the cold gas-stream velocity v = 9 cm/s. Different nanoparticles were collected by changing HAB.

The size distribution of the soot CNPs in aerosol phase, $dN/dlnD_p$, with D_p the particle size, was measured on-line by Scanning Mobility Particle Sizer (SMPS). To this aim, combustion products were withdrawn from the flame centerline by means of a tubular dilution probe as described in previous studies [44–46]. A sketch of the experimental apparatus for particle size distribution, PSD, measurements is reported in Fig. 1a.

The sampling probe was made of a stainless steel tube (1 cm outer diameter and 0.5 mm wall thickness), with a 0.2 mm side pinhole through which flame gases were sampled and diluted in nitrogen following a procedure reported elsewhere [44–46]. PSDs of the flame-formed CNPs were measured by a TSI 3938 SMPS systems.

2.2. Thermophoretic deposition, thin film generation and characterization

Films of soot NP were produced by the in-flame deposition of particles on a substrate rapidly inserted in flame, i.e. the residence time of the substrate in flame is 100 ms, as illustrated in Fig. 1b. As will be showed afterwards, the nanoparticles in the flame studied in this work have $D_p \sim 10$ nm. In this case, the deposition is primarily controlled by the thermophoretic force [15] produced by the thermal gradient between the hot environment in which the particles are suspended and the cold substrate [18]. The kinetic energy of the particles impinging on the substrate is therefore determined by the thermophoretic velocity, V_{th}, which depends on the thermal gradient, ∇T, the density, ρ_{gas}, and the dynamic viscosity, μ_{gas}, of the medium in which the particles are suspended, while it does not depend on the particle size [18]:

$$V_{th} = -0.55 \frac{\mu_{gas}}{\rho_{gas}} \frac{\nabla T}{T} \tag{1}$$

For our experimental conditions, the temperature gradient can be estimated by a simplified model that assumes a constant stagnation thermal boundary layer (λ) in front of the substrate, in which a linear particle concentration and temperature profile are assumed [15]. Since during each insertion the residence time of the substrate in flame is very small, 100 ms, the substrate temperature can be assumed constant and equal to 350 K [18], while the flame temperature outside the boundary layer is about 1650 K. Gas properties were approximated as for