



# Physicochemical evolution of nascent soot particles in a laminar premixed flame: from nucleation to early growth



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## ABSTRACT

In this work, particle inception and early growth stages were investigated in an ethylene/air premixed flame by the evolution of the particle size and structure with flame residence time. Particle size distribution was measured by a scanning mobility particle seizer and chemical–physical investigation was carried out by Raman microspectroscopy, UV–visible light absorption and cyclic voltammetry.

From early inception of particles, just downstream the flame front, to the formation of primary soot particles, in the post-oxidation flame zone, particles participate in a series of chemical and physical reactions that strongly modify their nanostructure and physicochemical properties, resulting in different optical and electronic characteristics. The results presented in this study show that the evolution from a mono-modal to a bi-modal size distribution is associated to a particle graphitization process consisting of a slight increase of the in plane average size of the polyaromatic units within the particles,  $L_a$ , and on the formation of stacks of polyaromatic planes. These outcomes suggest that in our flame conditions particle coagulation/coalescence has a major role in the initial soot formation, affecting both physical and chemical particle properties.

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## 1. Introduction

Fine and ultrafine carbonaceous particles emitted from both stationary and automotive combustion systems have long been recognized as a serious problem for their detrimental effects on human health and on the environment [1–3]. This has been the leading motivation for many years of research in the field of soot formation and characterization in combustion processes.

Soot particles are generated from the incomplete combustion of hydrocarbons as results of a considerable complex network of chemical and physical processes which occur in a very short time scale, of the order of few milliseconds, and in a unique high temperature and chemical reactive environment that is the flame. Although the soot formation process in combustion has been the subject of a considerable number of experimental and numerical studies and has been greatly debated over the years [4–7], the complete understanding of the mechanism standing behind the chemistry and physics of the entire process has not been accomplished yet.

Among all the key steps participating in the soot formation process, particle nucleation is doubtless the most critical to describe. The

need for a more predictive understanding of the particle inception in flames has been actually long recognized. Preliminary experimental studies aimed at investigating just nucleated carbonaceous nanoparticles in flames date back to almost twenty years ago [6], and much more work in this field has been done from then on [7–11].

In fuel-rich flames, the incomplete combustion of part of the fuel molecules results in thermal decomposition radical products, close to the flame front, which later recombine forming benzene via cyclization reactions as well as naphthalene and other larger polycyclic aromatic hydrocarbons (PAHs) onward in the post-flame region [12]. Detailed analysis of the formed PAH compounds molecular structure and concentrations, is crucial in describing the soot formation process. Indeed PAHs represent the building blocks, at the molecular level, of the solid soot particles. The yield, the morphology, the nano-structure, and the chemical composition of the primary soot particles depend on the combustion conditions and on the fuel chemical composition [13–16].

Most of the experimental studies on flame-formed soot particles have been mainly focused on the analysis of gas-phase PAH molecules and/or mature soot particles and remarkable progresses have been reached in characterizing them both qualitatively and quantitatively. A considerable lack of knowledge rises when trying to describe the transformation of gas-phase compounds into solid carbonaceous particles, i.e. the particle nucleation process.

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## Nomenclature

PAH	polycyclic aromatic hydrocarbons
PAC	pericondensed aromatic compounds
PSD	particle size distribution
CV	cyclic voltammetry
HAB	height above the burner
SMPS	scanning mobility particle sizer
DMA	differential mobility analysis
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital
$d_m$	mobility diameter
$d_p$	real (mass-equivalent) diameter
$E_g$	optical band gap
PL	photoluminescence
$L_a$	in-plane correlation length of aromatic island
BSU	basic structure unit

Two major clustering pathways have been theorized over the years to describe carbonaceous particle inception in flame [8]. The first one considers particle nucleation as the physical interaction of two or more gas-phase pericondensed aromatic compounds, PACs, via van der Waals attractive forces. PACs of relatively low sizes, few hundreds mass units, once colliding begin to stick each other to form dimers which in turn may collide with other pericondensed aromatic molecules forming trimers and/or with other dimers forming tetramers and so on [17]. The physical assembly of two or more PACs, and the further mass growth through the condensation of other PAC molecules, has become an attractive route for modeling soot nucleation and has been extensively used over the years in many numerical studies. However, many aspects regarding this mechanistic picture are currently under debate, they include: smaller size and geometry of the PAC molecules for which physical dimerization, due to van der Waals attractive forces, becomes favored and/or relevant at flame conditions; reversibility of the process; contribution of aliphatic chains; non-planarity of the polyaromatic molecules due to the inclusion of five-member rings [18–21]. The second pathway considers that particles begin to form by means of a sequence of polymerization reactions, i.e. purely-chemical pathway, that starting from parent polyaromatic hydrocarbons and relative oligomers, i.e. aromatic units linked by C–C bonds, with few hundreds atomic mass units allows the molecular mass to grow up to thousands of mass units [22]. Once formed, oligomeric structures may also undergo physical clustering via inter/intra van der Waals attractive molecular forces among polyaromatic domains to form stacks of parallel displaced aromatic units.

The development of detailed mechanisms capable to catch not only the size and the number distribution of the formed particles, but also the chemical and physical evolution of the particles themselves is part of the ongoing research [23–26]. Additionally, there are both experimental and numerical evidences suggesting that the relative contribution of the above two mechanisms to the soot inception process may be strongly dependent upon the combustion conditions [27–30].

Both pathways give rise to the formation of carbon nanoparticles which later may undergo coagulation/coalescence in addition to mass growth by heterogeneous reactions on the particle surface operated by acetylene addition and/or by condensation of molecular gas-phase PAHs, that ultimate in the formation of the primary soot particles. These latter can be further transformed later on in the flame undergoing carbonization, i.e. dehydrogenation, and oxidation reactions.

Experimentally, soot precursor nanoparticles with sizes of only few nanometers were first detected nearly two decades ago by two independent groups: in a laminar premixed flame via in-situ

ultraviolet scattering/extinction measurements by D'Alessio and co-workers [6, Part I-5], and in a co-flow laminar diffusion flame via thermophoretic sampling followed by ex-situ transmission electron microscopy by Dobbins [6, Part III-17]. More recently, remarkable progress has been obtained by using on-line nano differential mobility analysis measurements in both laminar premixed [31–35] and diffusion [36,37] flames. These studies clearly pointed out that particle size distribution (PSD) in laminar flames is generally bimodal with a lower-size mode of the PSD peaked at particle diameters near or below 3 nm and a larger-size mode corresponding to primary soot particles. These sets of data corroborated the existence of soot precursor nanoparticles of few nanometers previously detected by in-situ light absorption and scattering measurements in the ultraviolet spectral region [38,39]. Furthermore, PSDs in laminar premixed flames have been also reported to be highly dependent on the flame C/O ratio and residence time [35], flame temperature [40], and fuel chemistry [41].

Beside the mechanistic approach used to describe the early stages of the soot formation process, it remains quite well accepted that freshly nucleated carbonaceous particles can differentiate from the larger primary soot particles not only with respect to their different size but also in terms of their physicochemical properties, i.e. chemical and morphological composition, physical state, hydrogen to carbon (H/C) ratio, optical and electronic properties, spectroscopic behavior, coagulation efficiency and hydrophobic/hydrophilic character. Therefore a deeper knowledge on the physicochemical properties and on the differences of these two classes of carbonaceous particles is relevant on the development of more predictive soot modeling approaches, and on the understanding of their relative role on the climate change and on the human health in addition to the possible use of such carbon nanoparticles as materials with tailored optical/electronic properties.

In some recently published studies [42,43] the characterization of particles of different modes of the PSD allowed to evidence that a relevant difference among them was the degree of three-dimensional ordering in their carbon structure. In other words these studies reported that in soot forming flames the formation of stacks of polyaromatic domains takes place in the particles of the larger mode of the PSD, thus also producing an abrupt variation of the optical properties of the particles. What is still missing is a detailed investigation of the evolution of particle structure and growth with flame residence time. This is the main objective of the present study, which also aims at producing a database of the evolution of particle size and composition along the flame, which is of interest for developers of particle dynamic/kinetic models for soot formation.

In this work the initial evolution of carbon nanoparticles in a laminar premixed flame has been investigated by on-line differential mobility analysis, off-line Raman microspectroscopy, UV–visible spectroscopy and cyclic voltammetry (CV). The results presented in this study are discussed in order to gain further insights on the chemical and physical processes involved in soot formation and their effect on particle properties.

## 2. Experimental

An atmospheric pressure laminar premixed ethylene-air flame was stabilized on a water cooled sintered bronze McKenna burner having a diameter of 6 cm. The cold gas velocity was set at 9.8 cm/s and carbon to oxygen (C/O) atomic ratio was maintained constant at 0.67 (equivalence ratio  $\phi = 2.03$ ). Ethylene was chosen being one of the principal product of the decomposition of hydrocarbons and it is usually used, together with methane, as representative of the combustion of aliphatic hydrocarbons. It can be also formed during the decomposition of oxygenated compounds even if in this latter case other important intermediates are formed. Premixed flame was used because it is a one dimensional reactor in which it is possible to isolate chemical aspects of the process from the fluid dynamic of the

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