Applied Surface Science 255 (2009) 5511–5514

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Heterogeneous atoms in laser-induced synthesis of carbon black

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ARTICLE INFO

Article history:
Available online 17 September 2008

Keywords:
Pyrolysis
Laser
Nanocarbon
Heteroatom

ABSTRACT

Based on a high temperature hydrocarbon/heterogeneous atoms system of well-established composition, the formation of carbon nanostructures by laser-induced pyrolysis is related to the presence of heteroatoms in the reactants. In this paper, the goal is to underline the influence of some heteroatoms on the morphology and functionalizing nanostructured carbon materials by changing both gas composition and experimental parameters, with the focus to drive these materials into a regime where they can naturally interface with the surrounding matter. To investigate, in the versatile laser pyrolysis method, how to in situ modulate – through the presence of heterogeneous atoms – the characteristics of carbon nanopowders claimed by specific application is a challenge. Some preliminary results confirm experimentally their particular behavior during interaction with polymer matrices of some nanocomposites.

1. Introduction

The unique manifold of carbon to occur in a great variety of species used to a large number of highly specialised applications is a consequence of its great chemical flexibility in allowing the different hybridization degrees in one structure. This leads to an unlimited possibility of structures which can accept foreign elements (hydrogen, boron, nitrogen, oxygen, etc.) both on its surface and within the structural framework, with a possibility of a continuous modelling of properties. During synthesis process, these atoms are included either in aromatic rings or functional chemical groups localized at the borders of these graphene layers and lead evidently to a chemical heterogeneity of the surface. The activation of carbon materials improves their functional properties, depends on their structure and could be modulated in situ by the controlled presence of heteroatoms in the reactive gas mixture. These could be beneficial or deleterious as their effective participation in the process may lead to the formation of certain nanostructure or can yield strong carbon–heteroatom bonds and thus playing an inhibition role. The discoveries and intense studies in the field of carbon nanoparticles [1,2] led to a multidisciplinary field of investigations and proved to be in the great part compatible with inorganic and biologic systems [3].

2. Experimental

The process of laser pyrolysis is based on the interaction between the emission of a CO_2 laser line and the infrared absorption band of a reactant gas in a small, well-defined volume into the flux reactor. The technique proved to be a versatile and efficient method for the synthesis of carbon nanopowders because the high temperature gradients and fast reaction times involved in the process lead to very fine powders with controlled size and morphology and uniform particle size distribution [4]. The carbon sources were hydrocarbons with a high content of C/mole, used either in resonant (ethylene: $\nu_7 = 971\ \text{cm}^{-1}$) or non-resonant processes (acetylene: $\nu_5 = 730.3\ \text{cm}^{-1}$, $\nu_3 = 3281.9$ and $3294.9\ \text{cm}^{-1}$ and benzene: $\nu_4 = 673\ \text{cm}^{-1}$, $\nu_{14} = 1038\ \text{cm}^{-1}$ and $\nu_{13} = 1486\ \text{cm}^{-1}$), when ethylene or sulphur hexafluoride were employed as sensitizer; this energy transfer agent could either react or interfere through its decomposition products, and make the final particle morphology difficult to control experimentally [5]. The experimental set up consists of a high CW CO_2 laser (10P20 emission line at $944\ \text{cm}^{-1}$), a stainless steel reaction chamber, gas flow and pressure control systems as well as a powder recovery device [6]. The characteristics of synthesized carbon nanopowders were analysed as a function of the nature of reactant gases and experimental parameters and investigated by electron microscopy (TEM, HREM), and FTIR spectrometry. The complementary data regarding the particles' size and aggregation were obtained by dynamic light scattering (DLS) investigations.

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doi:10.1016/j.apsusc.2008.09.021

3. Results and discussion

The nature of the reactive gases refers to hydrocarbons with a high content of carbon/mole or to other chemical components required by a specific pyrolysis process like the unavoidable energy transfer agent required by a non-resonant synthesis process, an oxidant or other chemical specie claimed by a specific synthesis. The heterogeneous atoms could react or interfere and are related to the formation of some carbon nanostructures thus having a notable influence on the powder's characteristics. Quantified as C/X atomic ratios (X = O, F, S, N, etc.), their controlled presence leads to a foreseen major change in soot morphology. In this respect, it is worth noting the atoms of oxygen – important factor determining fullerene formation, hydrogen – as one of composing elements of hydrocarbon, or fluorine and sulphur, released during SF_6 decomposition, used as sensitizer. The presence of nitrogen or/and nitrogen oxides which proceed from the decomposition of nitrous oxide used frequently as oxidizer, chemically modifies the carbon black surface increasing significantly the fraction of carbon nanoparticles linked to the matrix surface [7] or graphting carbon black surface by amine groups to improve the control of its distribution in elastomer blends [8], etc.

Carbon nanopowders synthesized by laser-induced pyrolysis is composed by very fine particles sizing between 10 nm and 50 nm, which coalesce in bigger particles forming chains. Size measurements performed by DLS technique on diluted exploratory samples (~0.003 g to 100 ml toluene) – synthesized from C_2H_2/C_2H_4, $C_2H_4/C_6H_6/N_2O$ and C_6H_6/C_2H_4 reactive gas mixtures –, after 10 min of dispersion with an ultrasonic bath, allowed to estimate particles mean diameter to be 1200 nm, 250 nm, and 400 nm, respectively (Fig. 1a).

Laser-induced pyrolysis of pure hydrocarbons leads to carbon nanopowders with a turbostratic structure [6]. The controlled presence of oxygen in the reactive gas mixture changes drastically the structure to the fullerene-like one (Fig. 1b); FTIR spectrum of soot obtained from a reactive gas mixture containing oxygen shows typical peaks (e.g. 578 cm^{-1}, 565 cm^{-1}, 535 cm^{-1}, 527 cm^{-1} and 458 cm^{-1}) attributed to fullerene, whereas in the FTIR spectrum of sample with turbostratic structure the absorption bands assigned to PAH due to aromatic C–H deformations in the range of 700–900 cm^{-1} are very well revealed (Fig. 1c). Soot and PAH nucleation and growth are the result of a competition between growth process and oxidation. The laser pyrolysis of a reactive gas mixture containing a controlled [9,10] quantity of oxygen leads to a carbon nanopowder with a fullerene-like structure [11]. The electron affinity of fullerene increases the chemical activity of soot surface and modifies its physical and/or chemical properties [12]. Other functional groups containing oxygen (not presented here) were identified by FTIR or X-ray photoelectron spectroscopy (XPS) techniques.

The unavoidable presence of sensitizer in off-resonance conditions could lead to the presence of heterogeneous atoms like fluorine and sulphur, released in these specific experimental conditions by the decomposition of sulphur hexafluoride used as energy transfer agent [5]. The evidence for the presence of different products of SF_6 dissociation comes from the IR spectra of the exhaust gases or from investigations with a TEM with an energy-dispersive X-ray spectrometer. These experimental data certify the existence of fluorine and fluorinated radicals, which could influence the powder's morphology and limit the formation of different carbon nanostructures. It was shown that both soot and fullerene yield are inferior to the runs where SF_6 was avoided [13]. In this case, carbon particles will present an altered turbostratic structure, with puckered graphene layers due to the insertion of covalent bonded fluorine atoms [14].

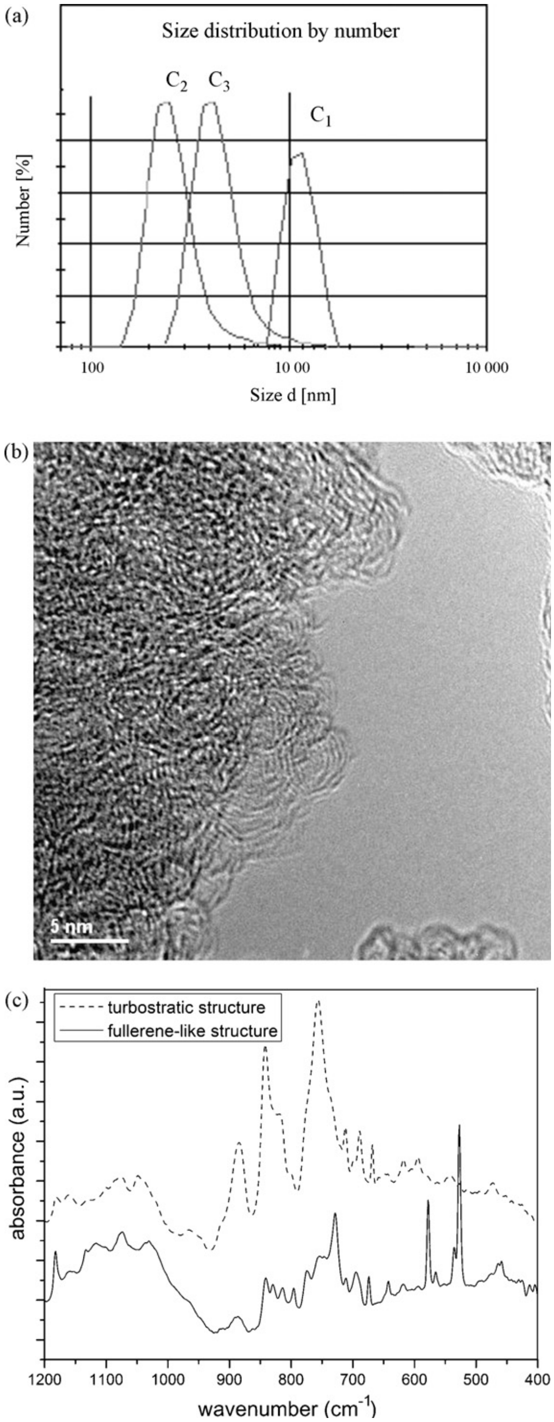

Fig. 1. (a) Mean size of particles' agglomerates of samples C1, C2, C3 synthesized by laser pyrolysis from C_2H_2/C_2H_4, $C_2H_4/C_6H_6/N_2O$ and C_6H_6/C_2H_4 reactive gas mixture, respectively; (b) HREM image of carbon nanopowder with fullerene-like structure; (c) FTIR spectra characteristic to turbostratic and fullerene-like structure.

The ratio hydrocarbon/sensitizer flow rate is expected to strongly influence the reaction temperature. With the decreased sensitizer content, the flame temperature decreases, and probably limiting the complete dissociation of the hydrocarbon molecules, preserves more aromatics available for continued molecular growth. Thus, samples obtained from a mixture having smaller SF_6 concentration are characterised by an increasing graphitic nature (Fig. 2), when graphite fringes begin to align and order over