

# SEARCHING FOR FUNCTIONAL PROPERTIES OF CARBON NANOPOWDERS THROUGH LASER PYROLYSIS TECHNIQUE

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## Introduction

The morphological flexibility and their inherent multifunctionality, the high specific area, and chemical activity make carbon nanopowders very attractive for specific applications or nanomaterials with significant improvement of their functional properties. Many of them proved to be compatible with inorganic and/or biologic systems and might be considered as useful materials in medicine and biology (Sijbesma R. et al. 1993). Generally, nanostructured materials, and particularly, carbonaceous ones could interface naturally both with electronic and biologic systems and constitute the future of the micro/nano technologies based on these systems of multifunctional nanomaterials. On the other hand, the carbon nanoparticles existing in environment are an important factor on healthy, either by their toxicity or by interaction with pathogen microorganisms, which can make them more resistant or induce a specific muthagenesis. Carbon nanopowders are oxygen supplier for microorganisms and, at the same time, due to the presence of polyaromatics or heterogeneous atoms existent in the reactive gas mixture, could have an inhibition/poisoning effect (Gavrilă-Florescu et al. 2007).

Composite materials became a versatile class of materials, with an extended potential of applicability, due to their specific mechanical, optical and electrical properties. Regarding these hybrid materials, reasons for expectations suggest that perfection of structure increases with decreasing dimensions of structure (reinforcing element) and ultimate material properties can be reached. Through the use of nano-scale reinforcements, either alone or in conjunction with micro-scale structures, materials can be constructed with superior properties and performance characteristics. In many applications, an appropriate chemical activity and structural order as well as a high specific surface area and a good electrical conductivity are required. The activation of carbon materials improves their functional properties and depends on their structure. Carbon which has not been graphitized becomes less ordered after activation processes; it can be activated more easily than graphitized carbon, which could maintain after activation its structure and relatively low specific area. The degree of structural order could be evidenced by graphite interlayer spacing  $d_{002}$ , crystalline size  $L_a$  in the plane of grapheme layers as well as the electrical resistivity (Weiming Lu et al.2001).

## Experimental

Based on the resonance between the emission line of a CO<sub>2</sub> laser radiation and the infrared absorption band of at least one gas-phase component, the Laser Pyrolysis from Gas-phase Reactants (LPGR) uses as precursors hydrocarbons with a high content of C/mole, either in resonant processes (ethylene, butadiene) or non-resonant ones (acetylene, benzene), when the negligible radiation's absorption by the precursors requires the addition of an energy transfer gas, which can either react or interfere. Through the variation of the experimental parameters, the method allows obtaining carbon nanoparticles with different morphologies providing useful functional properties. Different experiments were performed by varying only one parameter, and maintaining all the others constant. The flow and composition of the reactive gases were changed as well as the laser power density and working pressure. Total flows up to 400 sccm were chosen for the reactive gas mixture; pressure was varied in the range 450–950 mbar and the laser power from 500 to 900 W (power densities from ~ 4000 to 7000 W/cm<sup>2</sup> for a laser beam of 4 mm diameter). The soot obtained were weighed and productivities (g/h) and soot efficiencies (as percentage of soot from the carbon contained in consumed hydrocarbon) were calculated. The experimental parameters and quantitative results obtained in the performed runs showed that by varying hydrocarbon flow, laser power and working pressure, the soot efficiency was up to 46 %; the higher productivity was not a proposed task.

The powder characteristics were investigated by transmission electron microscopy (TEM) using a FEI CM200 FEGTEM microscope coupled with an Oxford Instruments thin window energy dispersive X-ray (EDX) detector

and a Gatan 666 detector for electron energy loss spectroscopy (EELS) analysis. X-ray diffraction (XRD) spectrometry was performed with a Bruker D8 ADVANCE X-ray diffractometer (X-ray tube with Cu anode and Ni filter to remove Cu  $k_{\beta}$  radiation), and Raman spectroscopy with a Raman TM<sup>2001</sup> apparatus (785 nm wavelength in a 180° backscatter configuration and a 30 s integration time). IR investigations of the powder and extracts (Soxlet extraction by toluene) have been recorded by applying the KBr pellet technique. The samples have been used for absorption measurements in the range 400-4000  $\text{cm}^{-1}$  with a Perkin Elmer FTIR spectrometer. The Dynamic Light Scattering technique was used to estimate the aggregation of carbon nanoparticles. XPS spectra for C1s, F1s, O1s and S2p lines were obtained with a VG ESCA3 MKII spectrometer using Al  $k_{\alpha}$  radiation (1486,6 eV), and processed using SPECTRAL DATA PROCESSOR v23 software. C1s line (285 eV) corresponding to the C-C bond has been used as BE reference.

### Some general features of carbon nanopowders synthesized by laser-induced pyrolysis

The morphology investigations of as-synthesized carbon nanopowders reveal the existence of almost amorphous carbon, partial crystalline carbon with small graphene sheets and different carbon nanostructures (e.g. fullerene). The powder is formed by very fine particles (Figure 1a), rather spherical, which may coalesce in bigger particle forming chains, the agglomeration being produced even in pyrolysis flame (different soot nuclei inside the same particle).

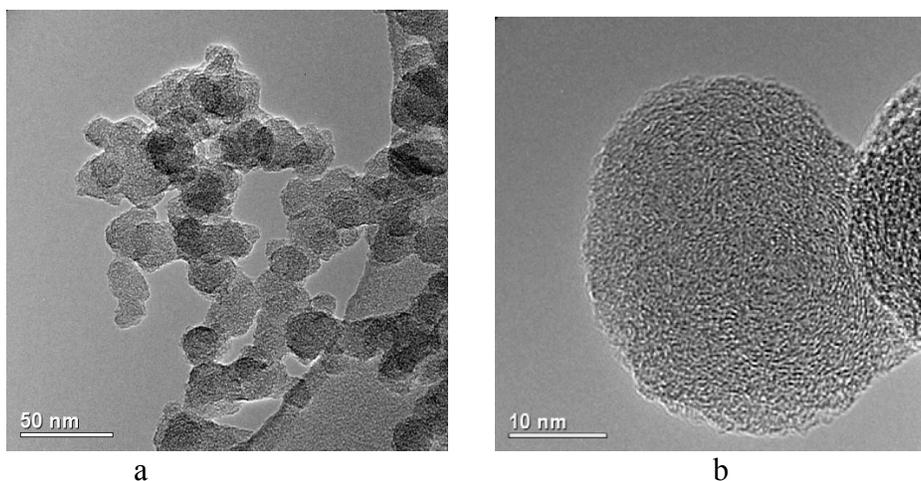


Figure 1. a. TEM image showing the dimension of carbon nanoparticles; b. HREM image of a carbon nanoparticle presenting a turbostratic structure

The size distribution could be fitted with a log-normal function and covers a relatively narrow domain framed in the range of 10-50 nm. Investigations by Dynamic Light Scattering showed the notable existence of aggregates with a main dimension around 500 nm. The diffuse images of diffraction rings (SAED analysis) indicate the absence of a long-range crystalline order whereas XRD patterns – through two broad diffraction peaks attributed to (002) and (10) planes, characteristic to the turbostratic structure – indicate that graphene sheets are already formed and organized as almost parallel layers, spaced at relatively well defined interplanar distance  $d_{002}$  (Figure 1b). The intensity ratio of the D ( $1360 \text{ cm}^{-1}$ ) and G ( $1575 \text{ cm}^{-1}$ ) bands revealed by Raman spectrum correlates with the crystalline size  $L_a$  in the plane of graphene layer [Ferrari et al, 2000], which for the analysed samples showed values between 10 and 30 Å.

### Main experimental parameters

The experimental parameters are rather numerous and their simultaneous effect could have often ill-assorted actions. 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. These could be an energy transfer agent required by a non-resonant synthesis process, an oxidant or other chemical specie required by a specific synthesis process. Reactant flows are controlled as atomic ratios between C and other heterogeneous atoms. The last are related to the formation of some carbon nanostructures and influence the powder 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, and fluorine and sulphur, released during the decomposition of SF<sub>6</sub>, used as sensitizer. Quantified as C/O, C/H or C/F atomic ratios, respectively, their controlled presence could lead to a foreseen major change in soot morphology. The surface of the carbon nanopowder could be fancied as being composed by small-range polyaromatic sheets with very active sites at their border. So, it is possible to assume the active chemical groups are situated in this region and the carbon surface will possess a complex and heterogeneous character. The content in oxygen or other gases, which could influence the chemical properties of the surface, increases with its specific surface and it was shown that solvent extractions do not alter significantly the overall sample's composition [Papirer E.,1996]. However, even small variations could produce changes of surface's properties. So, it is possible that carbon nanopowder could be the subject of surface modification, with the aim to adapt its properties to a special application. By a controlled presence of the heterogeneous atoms in the reactive gas mixture, a foreseen modified surface could be obtained even during the synthesis process. Other important parameters are laser power, pressure in the reactor and the reaction temperature. This last parameter should be evaluated in close relation with laser power and concentration of the absorbing reactant. The residence time in the flame is a sensitive parameter which depends on reaction volume, pressure and temperature as well as on total gas flow [Benzinger W., 1996]. There is a close interdependence between all experimental parameters and the optimization of the process could control the final particle morphology providing useful functional properties. With a facile and good control of the experimental parameters, the laser pyrolysis of the gas/vapor phase reactants proved to be a versatile synthesis method for carbonaceous materials with different morphologies and specific functional properties.

### The influence of the main experimental parameters

*Laser power*, and so the temperature of the process, influences both the particle size and structure of carbon particles. With the increase of this parameter, the particle size generally decreases and the graphitized structure is enhanced. *Gas composition* has an important influence both on particle size and structure.

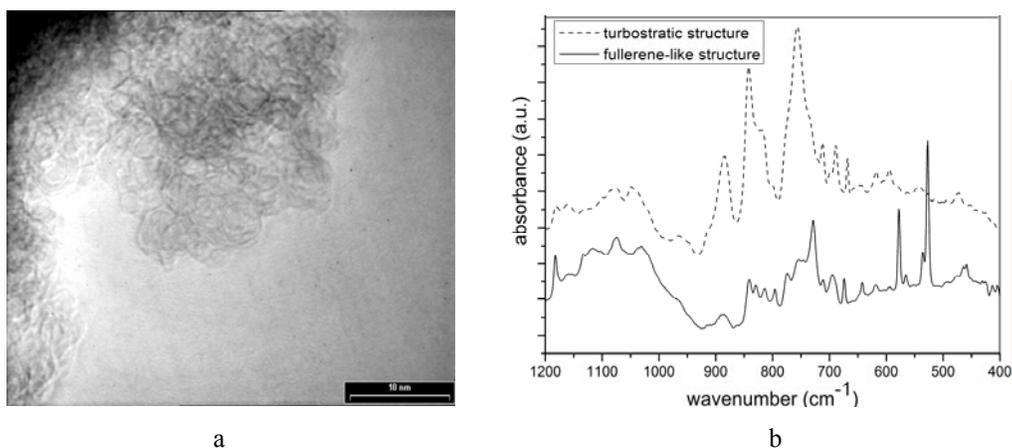


Figure 2. Carbon powder with a fullerene-like structure obtained by laser pyrolysis of a hydrocarbon-based mixture with a controlled quantity of oxygen (C/O at. ratio = 1)

Larger mean diameter (~45 nm) was obtained in the case of ethylene pyrolysis [Morjan I., 2003]. More ethylene in the hydrocarbon gas mixture leads to higher mean particle size. This will continuously decrease in the sequence hydrocarbon/C<sub>2</sub>H<sub>4</sub> (30-35 nm), hydrocarbon/SF<sub>6</sub> (~20-30 nm) and hydrocarbon/SF<sub>6</sub>/N<sub>2</sub>O (<20 nm). Regarding the structure, a fairly concentric arrangement of stacked carbon layers characterises the carbon particles obtained by laser pyrolysis of ethylene or of mixture of ethylene with other hydrocarbon. Oxygen addition produces important change in soot morphology. It is known that oxidation reactions are responsible for the fullerene formation in flames, the elimination of CO from oxidized PAHs being the source of 5-member rings in the PAH's structure. The laser pyrolysis of a reactive gas mixture containing a controlled [Tenegal F. 2001.; Tenegal F. 2003] quantity of oxygen leads to a carbon nanopowder with a fullerene-like structure [Ebrecht M. 1993; Voicu I. 1996]. The electron affinity of fullerene increases the chemical activity of soot surface and, as a component of carbon/composite material, could modify its physical and/or chemical properties [Cataldo F. 2002]. Soot and PAH nucleation and growth are the result of a competition between growth process and oxidation. The available oxidants in the flame are

molecular oxygen, atomic oxygen and OH radical and the elimination of CO from oxydized PAH is a source of 5-member rings in the PAH structure.

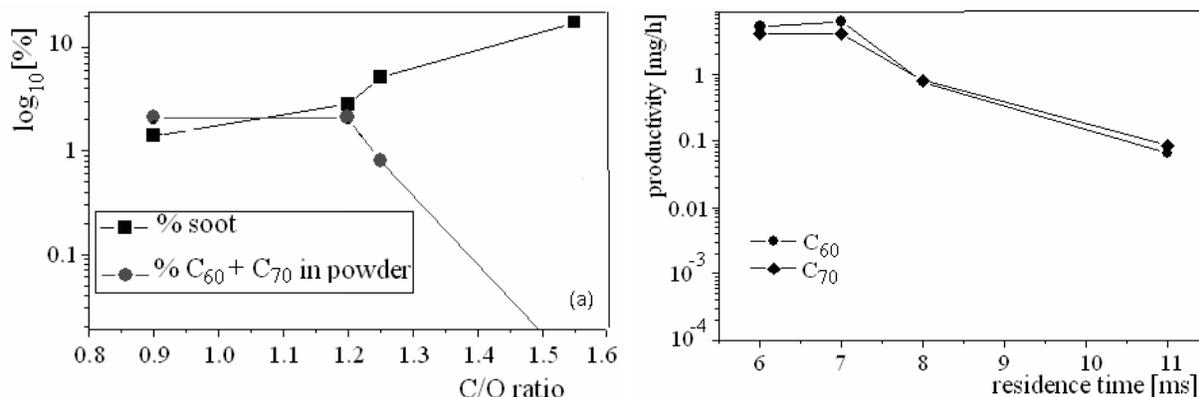


Figure 3. The influence of the C/O atomic ratio (a) and residence time (b) on the equilibrium soot-PAH-fullerene

The equilibrium soot-PAH-fullerene is strongly dependent on C/O atomic ratio (figure 3a) and residence time,  $\tau$  in the flame (figure 3b) [Tenegal F. 2003]. While fullerene yield is decreasing when both C/O atomic ratio and residence time increase, the production of carbon nanopowder is favoured. The equilibrium is also dependent on pressure inside the reactor. This important parameter favours the formation of carbon powder and, according to the global equilibrium prediction for fullerene [Pope C.J. 1996], when pressure decreases the minimum temperature for fullerene formation is shifted towards lower values and the fullerene yield is increased.

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 [Alexandrescu R. et al, 1998]. In this case, carbon particles will present an altered turbostratic structure, with puckered graphene layers due to the insertion of covalent bonded fluorine atoms [Voicu I et al. 2007]. The existence of fluorine and fluorinated radicals 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 [Alexandrescu R. et al. 2003]. The X-ray diffraction patterns of soot synthesized from different gas compositions present, for the peak assigned to (002) planes, larger low angle shift for gas mixture containing  $SF_6$  [Morjan I. et al, 2004]. This is materialized by the increase of the mean distance  $d_{002}$  between the graphene layers, which is changing with C/F atomic ratio. The change is provoked by F and S released due to  $SF_6$  decomposition, by insertion of fluorine atoms; some sulphur appeared to replace fluorine and be attaching to the carbon structure. This could also have a practical consequence as the electrical properties of the carbon powder could be modified. The electrical conductivity of some carbon nanopowders with a density of  $1.23 \text{ g/cm}^3$  was found by other authors [Probst N. et al. 2002] to be in the range of  $5 \cdot 10^{-2} - 1 \cdot 10^{-1} \Omega \cdot \text{cm}$ . The measurements of carbon nanopowders synthesized by laser pyrolysis of a hydrocarbon/ $SF_6$  mixtures, with different C/F atomic ratio and having the same density of powders ( $1.23 \text{ g/cm}^3$ ), showed resistivities in the field of  $1.9 \cdot 10^4 - 5.1 \cdot 10^4 \Omega \cdot \text{cm}$ . This variation could constitute a practical potential for polymer/carbon nanocomposites.

### Surface of carbon powders synthesized by laser-induced pyrolysis

Laser-induced pyrolysis uses a high temperature system based on a high temperature gaseous/vapor mixture composed by hydrocarbon with a high content of C/mole and, sometimes accidentally, other heterogeneous elements like oxygen, fluorine, sulphur, nitrogen etc, which could have major influence on the powder morphology and on the chemical activity of the particles surface. Because these powders could be synthesized in a large variety, with different structures, particle size and aggregation as well as larger or smaller quantities of heteroatoms on their surface, the investigation of either chemical reactivity of the surface and its interaction potential is a challenge. It is considered that these carbon nanopowders are composed not only by pure graphene layers and that heterogeneous atoms are included either in aromatic rings or functional chemical groups localized at the borders of these graphene layers. Their presence leads evidently to a chemical heterogeneity of the surface, which is mainly due to the difference of the electro negativity between heterogeneous and carbon atoms. Due to the presence of  $\sigma$  or  $\pi$

electrons, functional groups like OH, OR (R=radical), NH<sub>2</sub>, etc are classified as electron donors whereas groups like COOH, NO<sub>2</sub> are electron acceptors, because of the unoccupied orbitals. For the qualitative and quantitative evaluation of the functional groups existent on the surface of carbon particles, different methods and techniques are mentioned [Leon y Leon, C. A. et.al.1992; Laine, N.R. et.al., 1963)]. Besides these techniques, the FTIR spectrometry and x-ray photoelectron spectroscopy are used extensively to describe the chemistry of the nanocarbon's surface and to get information on its functionality.

FTIR spectra of the carbon nanopowders are characterized by a strong continuum attributed to carbon as well as by other absorption bands characteristic to polyaromatic hydrocarbons as precursors and/or side products of the carbon nanopowder formation and other carbon nanostructures (fullerenes).

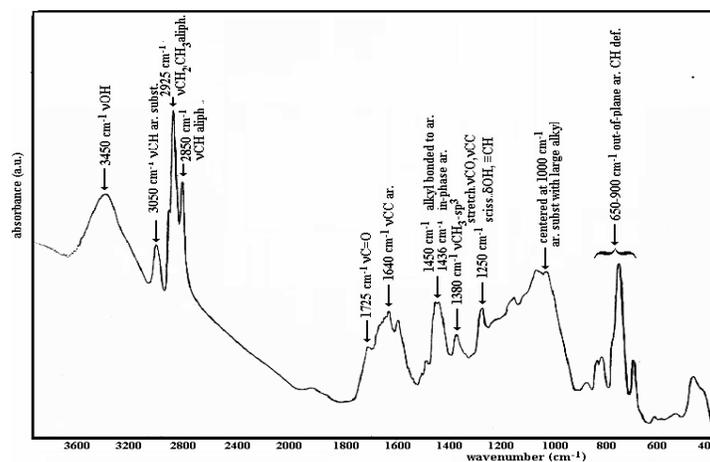


Figure 4. FTIR spectrum of the extract obtained from a carbon powder synthesized by laser pyrolysis of a C<sub>6</sub>H<sub>6</sub>/SF<sub>6</sub>/N<sub>2</sub>O gas mixture

Regarding functional groups, it was shown experimentally that the solvent extract of carbon nanopowder preserve in the great part the composition of genuine powder [Papirer, E., R. Lacroix, and J.-B. Donnet, 1996] and presents a FTIR spectrum with more relevant absorption bands, characteristic to compounds contained by carbon powder. Although the analysis of the FTIR spectrum is extremely laborious if the quantitative interpretation is desired, nevertheless it could show the presence or the absence of a surface with certain particularity. In Figure 4 a FTIR spectrum of the extract obtained from a sample synthesized by a laser pyrolysis of a C<sub>6</sub>H<sub>6</sub>/SF<sub>6</sub>/N<sub>2</sub>O gas mixture is presented.

In the spectral region 4000-1300 cm<sup>-1</sup>, the stretching vibration modes of the important functional groups like OH, NH or CO as well as weaker bands characteristic to S-H, C=C or C≡N could be found. So, in the range 3600-3200 cm<sup>-1</sup> a strong and large band is observed, which is attributed to OH stretching vibration and due to the existence of the OH groups on the surface and to chemisorbed water [Meldrum, B. J. and C. H. Rochester. 1990]. The observed asymmetry of this band at smaller wave number shows the existence of strong hydrogen bonds. The band at ~3050 cm<sup>-1</sup> is due to C-H stretching modes in substituted aromatic compounds. The region between 3000-2800 cm<sup>-1</sup> belongs to alkyl groups and presents two superposed bands, with main peaks at 2925 and 2850 cm<sup>-1</sup>, respectively. The higher intensity of the 2925 cm<sup>-1</sup> peak is due to the simultaneous presence of CH<sub>2</sub> and CH<sub>3</sub> groups [Charcosset H.1990].

Under 2000 cm<sup>-1</sup> the existence of the bands from 1710 and 1640 cm<sup>-1</sup> is attributed to C=O groups [Gómez-Serrano V. et. al. , 1994] and quinone and structures of ionic radicals [Fanning, P .E. and M. A. Vannice. 1993], respectively. The nature of the bands centered on 1750 and 1640 cm<sup>-1</sup> is more complicated because the bands assigned to aromatic rings and the vibration of double bonds (1500, 1600 and 1650, respectively) are superposed on the C=O bands mentioned before. To mention also the bands attributed to species containing nitrogen (an absorption band at 1610-1480 cm<sup>-1</sup> due to -C=N- vibration) [P.Vinke et.al. 1994]. Another broad band in the region 1470-1380 cm<sup>-1</sup> is made up of the superposed bands, which may be attributed to carboxyl/carbonate structures, to OH groups at the surface [Acedo-Ramos M.et.al, 1993], to in-plane vibrations of C=C-H structures at the surface [Meldrum, B. J. and C. H. Rochester, 1990] as well as to C-N- vibrations from the heterocyclic structures [Socrates, G. 1994] The band at 1450 cm<sup>-1</sup> – in the presented case screened by other bands – could be assigned to the vibrations of the alkyl groups directly bent to aromatic ring; at the same case, the aromatic C-H deformations could be the cause of the

relevant absorption from  $1436\text{ cm}^{-1}$  [Wang S.-H. and Peter R. Griffiths, 1985]. The peak appearing sometimes at  $\sim 1380\text{ cm}^{-1}$  could be probably due to  $\text{CH}_3$  groups bent to  $\text{sp}^3$  hybridized carbons.

The peaks in the domain  $1300\text{--}1000\text{ cm}^{-1}$  are generally assigned to phenolic structures from different structural environments [Meldrum B. J. and C. H. Rochester, 1990]. At the same time, this absorption could be also the result of the species with tertiary nitrogen (C-N stretching vibrations at  $1250\text{ cm}^{-1}$ ), embedded in carbon structure. The band from  $1106\text{ cm}^{-1}$  is also frequently met and is attributed to semi-ionic C-F bond; at  $1212\text{ cm}^{-1}$  the absorption could be assigned to covalent C-F bond [Hamwi A. et.al., 1988]. These observations are in agreement with XPS investigations in which C-F bond could change its character from ionic to semi-ionic and then covalent when the fluoridation degree is increased [Palchan, I. et.al., 1989]. Passing through the region centered around  $1000\text{--}1050\text{ cm}^{-1}$  that could be attributed to aromatic compound substituted with large alkyl groups, an important region appears between  $950$  and  $650\text{ cm}^{-1}$ , which can be due to C-H out of plane aromatic deformations. Noting that these deformations are characteristic to the type of substitution from the aromatic ring, the following groups are mentioned:  $890\text{--}850\text{ cm}^{-1}$  (one isolated CH),  $830\text{--}815\text{ cm}^{-1}$  (2 adjacent CH),  $800\text{--}775\text{ cm}^{-1}$  (3 adjacent CH) and  $760\text{--}745\text{ cm}^{-1}$  (4 adjacent CH). It is worth noting the frequent presence of the band centered at  $720\text{ cm}^{-1}$ , which is assigned to  $\text{CH}_2$  groups forming chains with more than 4 carbon atoms. This observation and the existence of intense peaks attributed to alkyl groups suggest the existence of alkyl bridges between the polyaromatic hydrocarbons composing carbon nanoparticles and the existence of saturated cyclic compounds at the edge of the grapheme layers [Jäger C., 2007]. This could explain also the existence of a band around  $830\text{ cm}^{-1}$  that is attributed to the balance vibrations of the  $\text{CH}_2$  groups in cyclic compounds. To mention also the absorption band observed at  $800\text{ cm}^{-1}$ , which could be due to cyclic compounds  $\text{C}=\text{C}$  and  $\text{C}=\text{N}$  with conjugated double bonds [Meldrum, B. J. and C. H. Rochester. 1990]. The FTIR spectrum of the extract could be completed with the characteristics of carbon nanostructures like fullerenes and their derivatives. For the most frequent of them ( $\text{C}_{60}$  and  $\text{C}_{70}$ ) the absorption peaks are situated at  $1460, 1428, 1413, 1180, 1130, 795, 675, 642, 578, 565, 535, 527$  and  $458\text{ cm}^{-1}$  [Voicu I. 1996]. It is worth noting that these carbon nanostructures exist in carbon nanopowders in measurable quantities only if in the reactive gas mixture there is a controlled quantity of oxygen. Fullerene oxides were detected as minor component in fullerene-like carbon powder with the slightly shifted peaks compared to peaks of corresponding non-oxidized species.

The use of ammonia or nitrous oxide in the reactive gas mixture diminishes the surface content of oxygen complexes, mainly that of strong acid surface groups (e.g. carboxylic). Similar situation is met with the band from  $1635\text{ cm}^{-1}$  assigned to quinone and ion-radical structures [Fanning P. E., and M. A. Vannice. 1993]. On the other hand, the enhanced intensities of the bands at  $1330$  and  $880\text{ cm}^{-1}$ , characteristic to nitrogen-containing heterocycles [Vinke, P. et.al., 1994] suggest that the presence of ammonia or nitrous oxide could lead to the nitrogen incorporation in the carbon network, with the formation of pyridine – like structures.

The analysis of XPS spectra obtained on carbon nanopowders synthesized by laser pyrolysis show relevant peaks due to carbon, oxygen, fluorine, sulphur or nitrogen. The carbon nanopowder was pressed on an aluminum foil and the resolution determined with FWHM of Au  $4f_{7/2}$  ( $1,7\text{ eV}$ ). As BE reference, the line C1s at  $285\text{ eV}$ , corresponding to C-C in HOPG was chosen. The C1s spectra were deconvoluted in 6 individual peaks (Figure 5) and attributed, in agreement with the literature data [Biniak S. et.al. 1997; [www.lasurface.com-XPS](http://www.lasurface.com-XPS) data base] as follows:

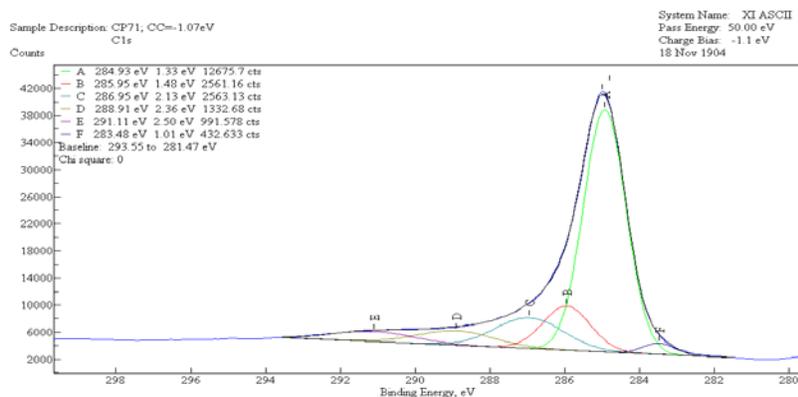


Figure 5. XP C1s spectra obtained on a laser synthesized carbon powder

- Peak A:  $284.93\text{ eV}$ - to graphite carbon;
- Peak B:  $285.95\text{ eV}$  to carbon from alcohol and ether groups or  $\text{C}^*\text{-CF}_n$  and C-O in trifluorobenzene or to non-combined carbon; at the same time, this peak could be attributed also to  $\text{-C-}$

S-S-C- chains; • Peak C from 286,95 eV due to C from carbonyl, graphene layers with bonded fluorine as well as to hydroxyl groups. According to some authors [Atamny, F. et.al., 1992; Xie, Y. and P. M. A. Sherwood. 1989] this peak could be also due to the C-N structures • Peak D: 288.91 eV due to carbon from C=O groups, which belong to the carboxyl or ester structures as well as to that combined with fluorine; • Peak E: 291.11 eV, due to the  $\pi$ - $\pi^*$  transitions in aromatic rings or to the combinations like  $(C^*F_2CHF)_n$  or  $CF_2$ ; • Peak F: 283.5 eV representing carbidic carbon,  $sp^3$  hybridized carbon from diamond network and carbon from aliphatic like  $-(C^*H_2-CH_2)_n-$

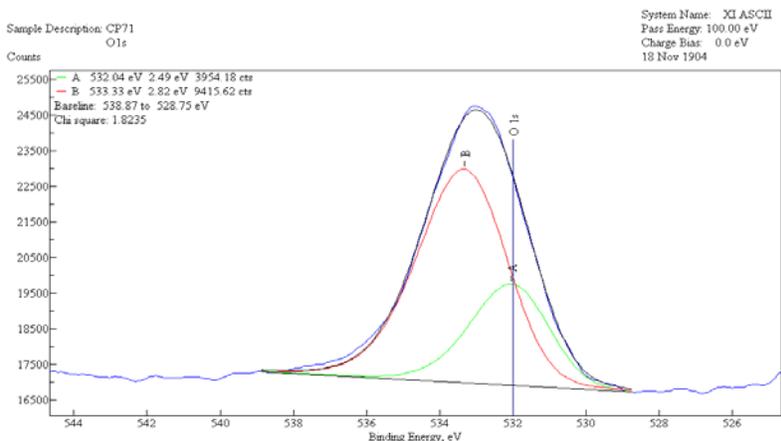


Figure 6. High resolution XP O1s spectrum of the analysed sample

High resolution O1s spectra obtained for the most of carbon powders [Proctor, A. and P. M. A. Sherwood, 1983; Desdemoni E et.al., 1992; Darmstadt H.et.al. 1994] relieve the presence of three peaks corresponding to C=O groups, with binding energies between 530.4eV and 530.8 eV, to C-OH and/or C-O-C groups (energy 532.4-533.1 eV) and to oxygen and/or chemisorbed water (534.8-535.6 eV). For the presented example, spectrum presents after deconvolution the following:

- Peak A, centered on 532,04 eV which, in agreement with the literature data [<http://www.lasurface.com/database/elementxps.php> – XPS data base], could be attributed to adsorbed OH groups, to OH groups bonded to amorphous hydrogenated carbon as well as to the oxygen contamination of the respective powder;
- Peak B, at 533.33 eV, with a weight of 70.4 %, could be attributed to the adsorbed water, to bonds O=C-O, C-O, -C=O in acids, esters and ethers as well as to the bond from the CO molecule.

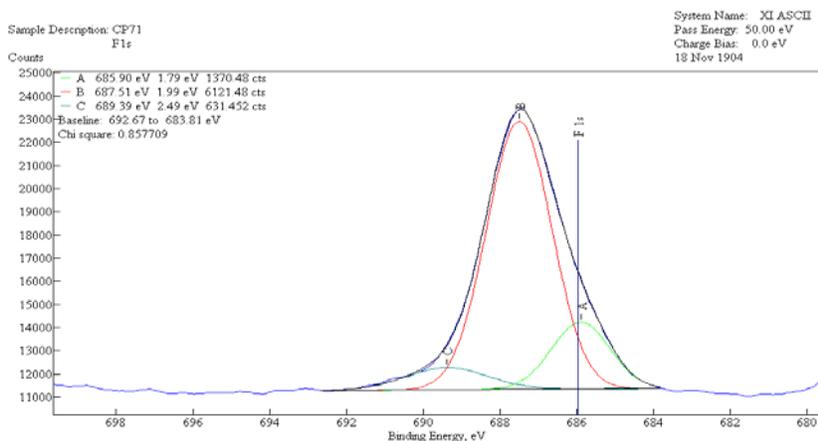


Figure 7. XP F1s spectrum of the analysed sample

Spectrum XP F1s presents after deconvolution peaks attributed to bond that fluorine, with its dual character (ionic and covalent), should have in carbon powder. In spectrum presented in Figure 7 the following peaks are observed:

- Peak A, centered on 685.9 eV that could be attributed to semi-ionic fluorine;
- Peak B, with the value of the binding energy of 687,51 eV has the largest area and could be assigned to covalent bonds of fluorine in CF<sub>x</sub> structure of type I in which C-F bonds are situated at the particle's surface and the border of graphitic domains;
- Peak C, at 689.39 eV, that can be due to covalent bonds of fluorine in CF<sub>x</sub> compounds of type II, in which the bonds are similar to those formed in the fluorinated graphite.

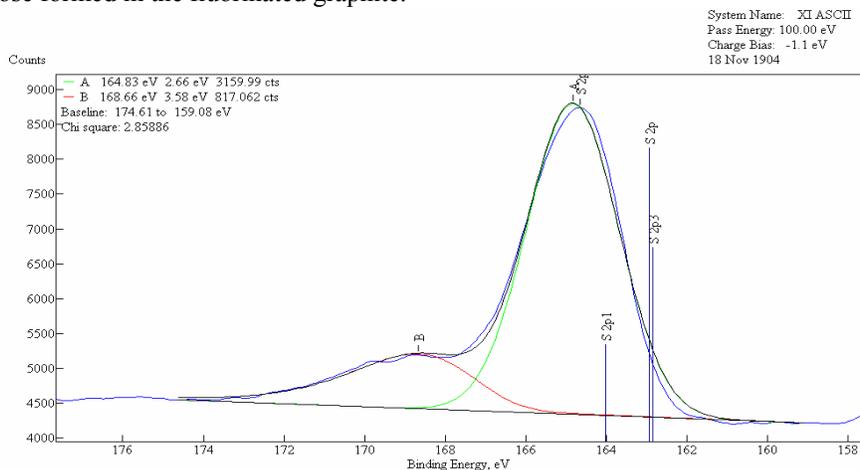


Figure 8. XP S2p spectrum of the analysed sample

As it was mentioned, in non-resonant processes of laser pyrolysis in which sulphur hexafluoride is used as sensitizer, the decomposition of this energy transfer agent releases fluorine and sulphur. The literature data [Feng W. et al. 2006], which refer to XPS analysis of sulphur in carbon powder show that the peak characterized by a binding energy of 164.5 eV could be attributed to free elemental sulphur. The chemisorbed sulphur is revealed by the peak centered in the region 161.8-162.6 eV, organic sulphur is assigned to a peak centered around 163-164.1 eV whereas the oxidized sulphur is evidenced by a peak with a binding energy larger than 167 eV. There is a superposition between the regions of the elemental and organic sulphur. The XP S2p spectrum of sample chosen as example presents after deconvolution two peaks, namely:

- Peak A, center on a binding energy value of 164.83 eV could justify the presence of both elemental sulphur in different forms and sulphur that belong to some organic compounds (e.g. tiofen),
- Peak B, at 168.66 eV, characteristic to oxidized sulphur structures, which preferably bond at the border of the graphene layers and, in convenient concentration, hinders the fluorine insertion between graphene layers of basic structural units composing carbon nanoparticles. This could explain the anomaly observed in the case of samples synthesized from a gas mixture with different C/F atomic ratio (0.5 and 0.8, respectively) where the distance  $d_{002}$  between graphene layers, normally dependent on the quantity of fluorine entered between these planes, was found to be smaller for sample having C/F=0.5 in spite of the fact that in this case the fluorine concentration was larger (but also sulphur concentration). The surface area of the peak A from the spectrum presented in Figure 8 suggest that both organic and elemental sulphur constitute the dominant species existent at the surface of carbon nanoparticles. The results of the elemental analysis on different samples obtained in non resonant laser pyrolysis processes where SF<sub>6</sub> was used as sensitizer, show the existence of a notable quantity of elemental sulphur.

The chemical activity of the particle's surface is related to its microstructure because the reactivity is determined by the density of the grapheme edges opened at surface as well as by the density of the existent chemically active carbon nanostructures (fullerene, nanotubes).

### Some possible applications

The different reactive gas mixtures and the use of suitable experimental parameters lead to the morphologically different carbon nanopowders having specific chemical properties; this was confirmed experimentally by their particular behaviour during the interaction with different chemical or biological systems. Polymer nanocomposites with small quantities (up to 5% by weight) of dispersed nanosized carbon could present a radical alternative to conventional filled polymers.

Preliminary results on the attempt to perform hybrid epoxy, acrylic or polyamide-based polymers reinforced by carbon nanostructures synthesized by laser pyrolysis showed that in the obtained nanocomposites the behaviour of carbon nanopowder depends on its morphology and chemical functionalisation of the surface. A comparison between the characteristics (tensile strength, hardness –Shore-, temperature decomposition) presented by the composites with similar matrix reinforced with different types of fillers shows superior values for the composite polymer – carbon nanopowder and suggests that the new bonds between nanopowder and matrix could contribute to better physical and mechanical characteristics of the final nanocomposite [Gavrila-Florescu L. 2006a]. Due to changes in electrical conductivity observed for carbon nanopowders with different morphologies, the incorporation of conductive particles into a polymer matrix modifies fundamentally the electrical conductivity of the composite, which could be used in application like antistatic materials with moderate conductivity, materials for the cable industry or absorbers at microwave frequencies.

The diversity of particles originated from carbon, existent in dust or aerosols, often influences the microbial development and spreading of the infectious diseases. The carbon nanoparticles existing in the environment are an important factor on healthy, either by their toxicity or by interaction with pathogen microorganisms. Bionanocomposites conceived as a gel with specific nutrients and functional carbon nanoparticles are good culture media to accelerate the growth of aerobic bacteria. The microorganisms grown in the incubation time were investigated by fluorescent markers (Water Soluble Quantum Dots) and proved to present different behaviour in contact with various structures and compositions [Stamatina L.2004] A non typical growth of bacterial colonies, with remarkable growth and well revealed pigmentation at 0.1% carbon concentration was observed [Gavrila-Florescu L. 2006b]. The investigations have put into evidence the cultures of Escherichia Coli, Staphylococcus Aureus and showed the possibility of a rapid identification in the direct copro-parazitologic examination of intestinal parasites like Enterobius or Giardia.

## Conclusions

Carbon nanopowders with different morphologies can be synthesized by laser pyrolysis. The characteristics of the obtained soot could be controlled through the gas composition and experimental parameters. The chemical functionalization of the carbon nanoparticles is an efficient means to improve the interaction with other organic and biologic systems. The interaction with polymer matrix shows enhanced characteristics of the nanocomposites and suggests that the new bonds formed with the matrix depend on the chemical activity of nanopowder. The experimental results showed also that microorganisms in contact with carbon nanoparticles of different structures and compositions have different behaviours. Due to their absorption capacity of the oxygen, carbon nanopowders could play a role of oxygen pump for pathogen microorganisms. The presence of the heterogeneous atoms like fluorine or sulphur have a poisoning effect; they destroy the microorganisms and limit the oxygen transport from the environment.

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