

Carbon 2015 Satellite Workshop:

**Multi-Scale Structure/Properties in Bulk Carbon Materials:**  
*Structure determination, physical & chemical properties characterization, modelling,  
from the nanometer to the meter*

Technische Universität – Dresden, Germany – July 10-11, 2015

**TENTATIVE PROGRAMME**

All names given in this programme refer to the *presenting persons*, not necessarily the authors  
Friday, July 10<sup>th</sup>:

<b>8:00</b>	<b>Arrival and registration check</b>
8:30	Welcome address: <i>Pr. Gerard L. Vignoles, University Bordeaux, LCTS, France</i> <i>Dr. Marc Monthieux, CNRS, CEMES, Toulouse, France</i> <i>Pr. Hubert Jäger, TU Dresden, Germany</i>
<b>9:00 – 10:00</b>	<b>Invited talk 1</b>
	“Carbon Nanostructure: Characterization by HRTEM and XPS and Alteration by PLH” <i>Pr. Randy Vander Wal, Penn State University, University Park, PA, USA</i>
10:00 - 10:30	Coffee break
<b>Contributing talks</b>	
10:30 - 10:50	“Thermal stability from soft to hard hydrogenated amorphous carbons analyzed using in-situ Raman spectroscopy. Application to tokamak carbon deposits” <i>Dr. Cédric Pardanaud, Aix-Marseille Univ, PIIM, France</i>
10:50 - 11:10	“Crystallite size $L_a$ of heat treated carbons from the endocarp of babassu coconut by Raman spectroscopy” <i>Pr. Francisco G. Emmerich, Fed. Univ. Espírito Santo, Vitória, Brazil</i>
11:10 - 11:30	“Quantitative maps of orientation and anisotropy degree from PLOM observation” <i>Pr. Gerard L. Vignoles, University Bordeaux, LCTS, France</i>
11:30 – 11:50	“Investigation of activated carbons by HRTEM, X-ray scattering and Raman spectra” <i>Dr. Pascaline Pré, ENS Mines Nantes, France</i>
12:00 – 13:15	Lunch
<b>13:30 – 14:30</b>	<b>Invited talk 2</b>
	“Multi-scale Structure/Properties Relationships in Nuclear Graphites” <i>Dr. Gareth Neighbour, Oxford Brookes University, UK</i>
<b>Contributing talks</b>	
14:30 - 14:50	“Measuring and Quantifying Structural Changes in Irradiated Nuclear Graphite” <i>Dr. Anne A. Campbell, ORNL, USA</i>

14:50 - 15:10	“A size-dependent thermodynamic model for graphitic crystallites integrating the binary interactions of sulfur/hydrogen with carbon up to 2500 K” <i>Dr. Philippe Ouzilleau, Polytechnique Montréal, QC, Canada</i>
15:10 - 15:30	“Activated carbon xerogels from chemical activation of hydrothermally activated glucose-graphene oxide hybrids” <i>Pr. Juan Tascón, INCAR-CSIC, Oviedo, Spain</i>

Friday, July 10<sup>th</sup> (cont'd):

<b>15:30 – 16:30</b>	<b>Poster session</b> with coffee break
	“Insights on structures of the large polycyclic aromatic hydrocarbons systems featuring coal tar pitch and naphthalene pitch” <i>Dr. Barbara Apicella, IRC-CNR, Italy</i>
	“XPS and NEXAFS synchrotron spectroscopy of PAH relevant in combustion and environment field”, <i>Dr. Barbara Apicella, IRC-CNR, Italy</i>
	“Porous texture and surface chemistry effects on CO <sub>2</sub> capture by ordered mesoporous carbons ”, <i>Pr. Juan Tascón, INCAR-CSIC, Oviedo, Spain</i>
	“Synthesis of graphene for thin film solar cell applications”, <i>Diana Marcela Aranzales Ochoa, Universitat Jaume I, Castellón de la Plana, Spain</i>
	“Re-arrangement of ions in nanoporous carbon supercapacitors studied by in-operando small-angle X-ray scattering”, <i>Dr Christian Prehal, Montanuniversität Leoben, Austria</i>
	“Quantitative analysis of HRTEM images of carbonaceous materials and correlation with its oxidative behaviour”, <i>Alexandra Zygoianni, CPERI-CERTH, Thessaloniki, Greece</i>
	“Characterization of Nanoporous Carbide-Derived Carbons by Combined Transmission Electron Microscopy, Nitrogen/Carbon Dioxide Physisorption, and Raman Spectroscopy”, <i>Dr. Pascaline Pré, ENS Mines Nantes, France</i>
	“Evolution of soot nanostructure in premixed hydrocarbon flames”, <i>Dr. Pascaline Pré, ENS Mines Nantes, France</i>

<b>16:30 - 17:30</b>	<b>Invited talk 3</b>
	“Hierarchical Porous Carbide-Derived Carbons for Energy Storage” <i>Dr. Stefan Kaskel, TU Dresden, Germany</i>

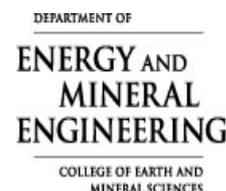
<b>Contributing talks</b>	
17:30 - 17:50	« Soot characterization by SEM tomography » <i>Gizem Okyay, EM2C-ECP, Châtenay-Malabry, France</i>
17:50 - 18:10	“Multi-wavelength Raman spectroscopy studies of graphene-based carbons with various domain sizes” <i>Dr. Marc Monthieux, CEMES-CNRS, Toulouse, France</i>

19:00 - 22:00	DINNER
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Saturday, July 11<sup>th</sup>:

<b>Invited Talk 4</b>	
9:00 - 10:00	“... <b>TBD</b> ...” <i>Dr. Walter Schütz, Future Carbon AG, Germany</i>
10:00 - 10:30	Coffee break
<b>Contributing talks</b>	
10:30 - 10:50	“Carbon phase diagram around the triple point graphite/liquid/vapor” <i>Pr. Aleksandr Savvatimskiy, Acad. Sci. JIHT Moscow, Russia</i>
10:50 - 11:10	“Melting temperature measurement for graphite HAPG under fast current heating” <i>Dr. Arseniy Kondratiev, Acad. Sci. JIHT Moscow, Russia</i>
11:10 - 11:30	“Three dimensional bilayer graphene” <i>Pr. Peter J. Harris, University of Reading, UK</i>
11:30 - 12:10	“Graphene-like legos for building structural models of carbon materials obtained from cellulose” <i>Dr. Natalia Woźnica, University of Silesia, Chorzow, Poland</i>
12:15 - 13:30	Lunch
<b>Invited talk 5</b>	
13:40 – 14:40	“Energy Storage and Carbon Nanostructures” <i>Pr. Gotthard Seifert, TU Dresden, Germany</i>
<b>Contributing talks</b>	
14:40 - 15:00	“An energy landscape for carbon network solids” <i>Pr. Nigel Marks, Univ. Curtin, Perth, Australia</i>
15:00 - 15:20	“Graphite melting: Atomistic kinetics bridges theory and experiment” <i>Dr. Vladimir Stegailov, Acad. Sci. JIHT, Russia</i>
15:20 - 15:40	“Non-Graphitic carbons modeling and critical analysis of structural parameters determined from diffraction and lattice fringe analyses” <i>Patrick Weisbecker, CNRS, LCTS, Bordeaux, France</i>
15:40 - 16:00	“Mechanical properties of pyrocarbons – from molecular to macroscopic scale” <i>Dr. Jean-Marc Leyssale, University Bordeaux, LCTS, France</i>
<b>16:00 - 16:45</b>	<b>Coffee break &amp; Concluding remarks</b>

Invited lecture at the Carbon 2015 spinoff workshop “PyroMaN II” – Dresden, July 2015



## **Carbon Nanostructure: Characterization by HRTEM and XPS and Alteration by PLH**

**Randy L. Vander Wal**

*John and Willie Leone Family Department of Energy and Mineral Engineering and the EMS Energy Institute, Penn State University, University Park, PA 16802*

Carbon is a very versatile material. Synthesized in various forms, characterization is fundamental for relating properties to performance in sundry applications. Two well-known methods are TEM and XPS. TEM as an instrument offers both microscopy and spectroscopy. It is best associated with bright-field imaging. To render this structural information quantitative, image analysis algorithms have been developed and vetted against traditional techniques for measures of  $L_a$  by Raman spectroscopy and  $L_c$  by X-ray diffraction. Applications of the image analysis algorithms include understanding the formation of carbon and its reaction potential.

Two-dimensional curvature in carbon lamellae stems directly from cyclopentadiene (C<sub>5</sub>) and related species. GC-MS measurements of species have shown this while kinetic models provide support for this inference. Here analysis algorithms are applied to TEM for archeological purpose – to identify species contributing to the carbon formation. Conversely quantitative TEM can differentiate the nanostructure of varied model carbon materials to create structure-property relations between nanostructure and oxidative reactivity. It can also be applied sequentially to understand reaction mode and concurrent structural changes due to radiation.

XPS is a spectroscopic technique with capability for elemental composition and bonding state. Elemental analysis is useful for characterizing emissions, engine deposits and carbon aerosols. By providing the  $sp^2/sp^3$  bonding ratio, XPS can follow the degree of carbonization as in biochar formation, track graphitization or monitor surface functionalization of carbons such as graphene oxide. TEM and XPS will be shown as complementary techniques by examples.

As a different diagnostic, pulsed laser heating (PLH) is a thermal processing technique using a high intensity pulsed laser light to heat materials to very elevated temperatures. We have applied it to composite carbons used as heat shield material, pyrolysis carbons and the carbon allotropes in nanoscale form. As an optical technique, PLH can heat these materials uniformly. Interest in these carbons arises from using PLH as a characterization technique to understand their formation by derivitization of structure. The suite of TEM tools documents the structure of graphitic nano-onions while XPS details their bonding character. Selected highlights will be presented as time permits.

**Biographical Sketch**

Dr. Vander Wal is a professor in the John and Willie Leone Family Dept. of Energy and Mineral Engineering at Penn State University. His general research theme is nanomaterials for energy engineering. Under this rubric his research has encompassed the areas of energy control, conversion, efficiency, generation and storage, with focus upon carbon allotropes and materials. Related environmental interests lie in combustion-generated soot: its measurement via laser-based methods and its characterization by microscopic and spectroscopic techniques. Parallel analytical interests are in micro-plasma-based environmental and mineral analyses. After graduating with a PhD in Chemical Physics, Dr. Vander Wal was a fellow at Sandia National Labs, rose to senior scientist while working at NASA with research spanning space and aeronautic programs prior to arriving at Penn State.

## Hierarchical Porous Carbide-Derived Carbons for Energy Storage

Stefan Kaskel\*

\* *Dresden University of Technology, Department of Inorganic Chemistry, Bergstraße 66, 01062 Dresden, and Fraunhofer IWS, Dresden, Germany*

Metal- or semi-metal atoms can be selectively removed from their carbides in the presence of halogens such as chlorine gas at high temperatures. This etching reaction produces a highly microporous ( $d < 2$  nm) carbon network known as carbide-derived carbon (CDC). The size distributions of CDC micropores are rather narrow as compared to other porous carbon materials, such as physically or chemically activated carbons. This makes CDCs highly suitable for applications in gas storage, separation or as electrode materials in supercapacitors. In the last years we reported various approaches for the generation of CDCs with hierarchical pore architectures starting from polycarbosilanes as SiC precursors to generate porous carbon materials with bi- or trimodal pore size distributions for applications in supercaps and Li-S-batteries. In the present contribution an overview about strategies for pore design in electrode materials applications will be given with specific capacities significantly exceeding a value of 240 F/g in aqueous electrolyte. Furthermore, extremely high reversible capacities of more than 800 mAh/g (related to the mass of the active material) and outstanding cycling performance were determined for the large-pore CDCs when used as a cathode material in lithium-sulfur cells, which are one of the most promising future generation battery systems. Sulfur loadings up to 75 wt.% and high areal loadings were achieved with high sulfur utilization even at low electrolyte/sulfur ratios. Dry processing was identified as a beneficial and scalable production method for the electrodes. The use of hard carbon anodes allows the investigation of cathode-intrinsic degradation effects since lithiated hard carbons were identified to sustain more than 1400 cycles in Li/S-systems.

### References

S. Kaskel et al. *J. Power Sources* (2014), 251, 417-422; *Adv. Funct. Mater.* (2014), 24(9), 1283; *Energy Mater.* (2014), 4(2), 1300645/1-1300645/9, *Chem. Commun.* (2014), 50, 3208-3210; *Angew. Chem. Int. Ed.* (2013), 52(23), 6088-6091; *Carbon* (2012), 50(11), 3987-3994; *Angew. Chem. Int. Ed.* (2012), 51(30), 7577-7580.

Invited lecture at the Carbon 2015 spinoff workshop “PyroMaN II” – Dresden, July 2015

## **Energy Storage and Carbon Nanostructures**

**Gotthard Seifert**

*Theoretische Chemie, Technische Universität Dresden, D-01062 Dresden, Germany*

New concepts for energy storage for mobile applications are of high actual interest. Here we demonstrate the potential of Carbon based nanostructures as storage material for mechanical energy and for hydrogen storage. We consider the twisting of single carbon nanotubes and ropes of single walled carbon nanotubes as mechanical energy carrier. The mechanical energy storage capacity of such carbon nanotube systems can surpass significantly that of advanced Li-ion batteries. Furthermore, we evaluated the hydrogen storage capacities of Carbon based nanostructures. Compact storage of hydrogen is the key challenge facing adoption of hydrogen as fuel for mobile applications. A promising approach to increase the storage densities is the adsorption of molecular hydrogen in porous environments. We have studied in detail the role of the host structure, the pressure and temperature dependence as well as the importance of quantum effects on the hydrogen storage capacity of a broad range of materials. These two - rather different - approaches make Carbon nanostructure based systems interesting for the application in hybrid drives.

# Measuring and Quantifying Structural Changes in Irradiated Nuclear Graphite

*A.A.Campbell<sup>1</sup>, Y.Katoh<sup>1</sup>, K.Takizawa<sup>2</sup>*

<sup>1</sup>*Oak Ridge National Laboratory, Oak Ridge, TN, USA*

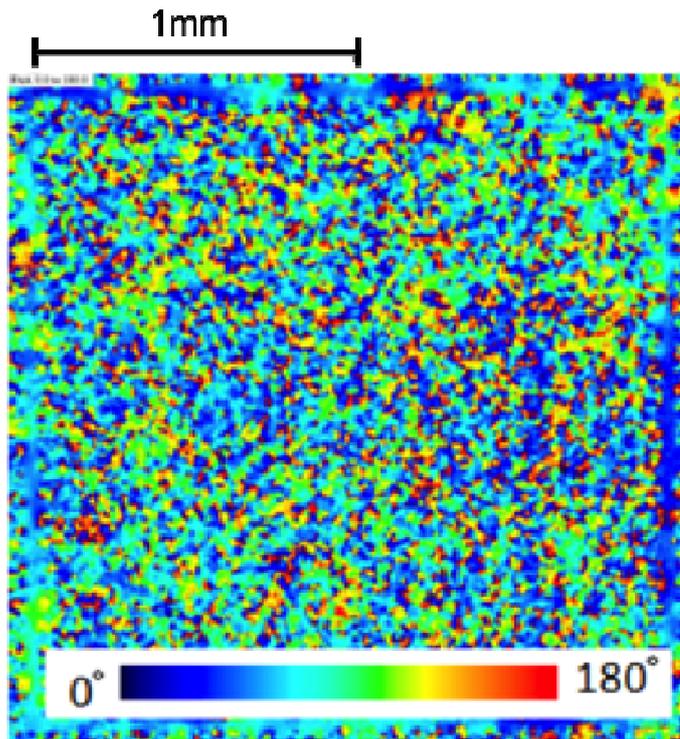
<sup>2</sup>*Tokai Carbon Co., Ltd., Japan*

Graphite has been used in the nuclear industry for over 70 years, since the first chain reaction in Chicago IL in 1942. It is an ideal core material because it can perform dual roles as a neutron moderator (low Z and low neutron absorption cross section) and a structural material (high strength, high thermal conductivity, and exceptional high temperature capability). When graphite is in a reactor environment, the high temperature and neutron damage cause these beneficial properties to change, but unfortunately these changes are different for every grade of graphite. The primary differences between the grades is the microstructure, which is controlled by the manufacturing process, and until recently there has been insufficient investigations into how the microstructure changes due to irradiation and how this correlates to the observed changes in macroscopic properties (i.e. volume, Young's modulus, thermal conductivity, electrical resistivity, strength).

The difficulty associated with (micro)structural characterization of graphite is the fact that the features of interest have dimensions ranging in size from a few meters down to a few angstroms. Such features include, for decreasing size, anisotropy (component-scale 1's m – 10's cm), filler particles ("grain size" <1 $\mu$ m – >1mm), pores and microcracks (<1 $\mu$ m – >1mm), Mrozowski cracks (sub-grain elliptical cracks <1nm – 10's nm in thickness and 10's – 1000's nm in length), crystallite size (regions with perfect graphite crystalline structure 10's – 1000's nm), and lastly atomic spacing (few Å). This range of nano- to macro-sized features requires multiple measurement techniques, but it is preferable to determine which techniques can interrogate multiple features to reduce the amount of work performed on the post-irradiation activated specimens.

Work is being performed at Oak Ridge National Laboratory (ORNL) to investigate the effect of neutron irradiation, in the High Flux Isotope Reactor (HFIR), on fine-grain graphite, grade G347A from Tokai Carbon Co., Ltd. These irradiations are studying the effect of a temperature range from 280°C-800°C and neutron damage as high as 35 displacement-per-atom. Like other nuclear graphite grades, G347A undergoes significant dimensional, physical, thermal, and electrical property changes as a result of exposure to neutron irradiation. This comprehensive irradiation program is also allowing us to investigate how the microstructure of this fine-grain graphite changes due to the range of irradiation conditions.

This presentation will first discuss which techniques are being investigated for their applicability to graphite, and what difficulties and successes arose with each technique. These techniques include: micro-ellipsometry, X-Ray diffraction, optical microscopy, micro-tomography, porosimetry (both N<sub>2</sub> and Hg), and Raman spectroscopy. An example of the micro-ellipsometry measurement is shown in Figure 1. The result shows the rotational orientation of graphite basal planes, highlighting that there are small regions with preferred orientation but overall the material is close to isotropic. In addition we will also present and discuss of the current findings of the effects of irradiation on these various microstructure features, and how these changes do and do not correspond to changes observed in the macroscopic materials properties.



**Fig. 1:** Measurement and analysis results from ellipsometry performed on G347A. The ellipsometry data is the fast axis angle, which is a measure of the rotation of the basal planes.

Research sponsored by the Tokai Carbon Co., Ltd. under contract NFE-09-02345 with UT-Battelle, LLC.

# Crystallite size $L_a$ of heat treated carbons from the endocarp of babassu coconut by Raman spectroscopy

Enrique R. Yapuchura, Alfredo G. Cunha, Jair C.C. Freitas, Francisco G. Emmerich\*  
Federal University of Espirito Santo, Vitoria-ES, Brazil

This work deals with the characterization by Raman spectroscopy of the endocarp of babassu coconut (a native biomass in the Northeast and Central Brazil) subjected to heat-treatment temperatures (HTT) from 800 to 2200° C [1]. During the carbonization process, large structural changes in the studied non-graphitizable carbon material are produced. The Raman spectra of all samples present the usual D and G bands characteristic of several graphitizable and non-graphitizable carbonaceous materials.

Measurements of the values of average in-plane crystallite size  $L_a$  obtained with X-ray diffraction (XRD) [2] were used to verify the linear relationship (developed for nanographites [3]) between the inverse of  $L_a$  and the ratio of the integrated intensities of the D and G Raman bands ( $I_D/I_G$ ), taking into account the laser excitation energy ( $E_L$ ).

It was observed that the dependence of  $L_a$  on the laser excitation energy was fundamental for combining the Raman measurements obtained at different laser energies into the same curve. However, the straight line of  $(I_D/I_G) E_L^4$  as a function of  $1/L_a$  with the best correlation coefficient for the heat-treated endocarp of babassu coconut samples does not pass through the origin as in nanographites [3]. Our results indicate that for non-graphitizable carbons such as the heat-treated endocarp of babassu coconut the expression requires the addition of a negative constant term (a linear coefficient) in linear relationship of  $(I_D/I_G) E_L^4$  as a function of  $1/L_a$ . The obtained equation was:  $(I_D/I_G) E_L^4 = 388 (1/L_a) - 35.2$ , where  $E_L$  is measured in [eV] and  $L_a$  in [nm]. The comparisons of the values of crystallite size  $L_a$  obtained by XRD and Raman spectroscopy are shown in Table 1.

**Table 1** - Values of crystallite size  $L_a$  obtained by XRD [2] and Raman spectroscopy with two different  $E_L$  values for the endocarp of babassu coconut with HTT from 800 to 2200° C.

HTT (°C)	$L_a$ - XRD (nm)	$L_a$ - Raman ( $E_L = 1.96$ eV) (nm)	$L_a$ - Raman ( $E_L = 2.33$ eV) (nm)
800	3.0	3.2	3.0
1000	3.3	3.4	3.3
1200	3.9	3.5	3.7
1400	4.0	4.2	3.8
1600	4.2	4.5	3.8
1800	4.6	4.8	4.3
2000	5.3	5.3	5.9
2200	5.6	5.8	5.8

[1] Yapuchura E.R., Characterization by Raman spectroscopy of heat treated carbons from the endocarp of babassu coconut, Federal University of Espirito Santo, Brazil, MSc Dissertation, (2014).

[2] Emmerich F.G., de Sousa J.C., Torriani I.L., Luengo C.A., Applications of a granular model and percolation theory to the electrical resistivity of heat treated endocarp of babassu nut, Carbon, vol 25, p. 417–424 (1987).

[3] Cañado L.G., Takai K., Enoki T., Endo M., Kim Y.A., Mizusaki H., Jorio A., Coelho L.N., Magalhães-Paniago R., Pimenta M.A., General equation for the determination of the crystallite size  $L_a$  of nanographite by Raman spectroscopy, Appl Phys Lett, vol 88, p. 163106–8 (2006).

# Three dimensional bilayer graphene

*Peter J. F. Harris*

*Electron Microscopy Laboratory,*

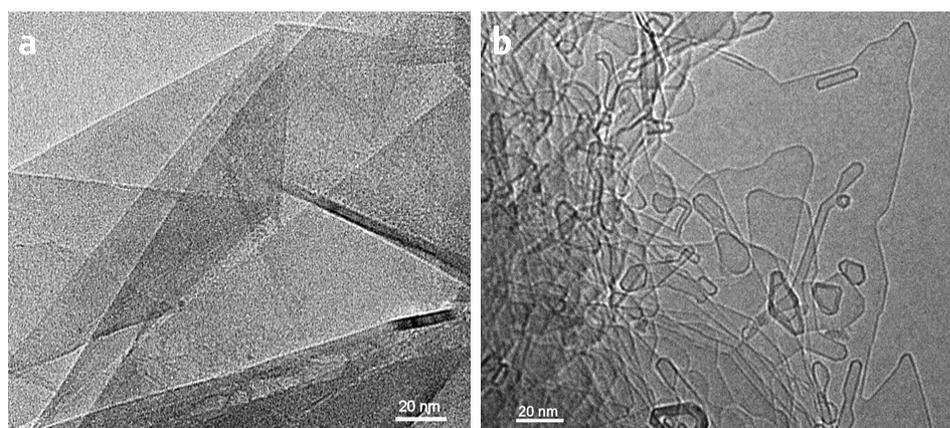
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This paper describes a new form of carbon, which consists of hollow, three-dimensional shells bounded by bilayer graphene. The new carbon is produced very simply, by passing a current through graphite rods in a commercial arc-evaporation unit [1-4].

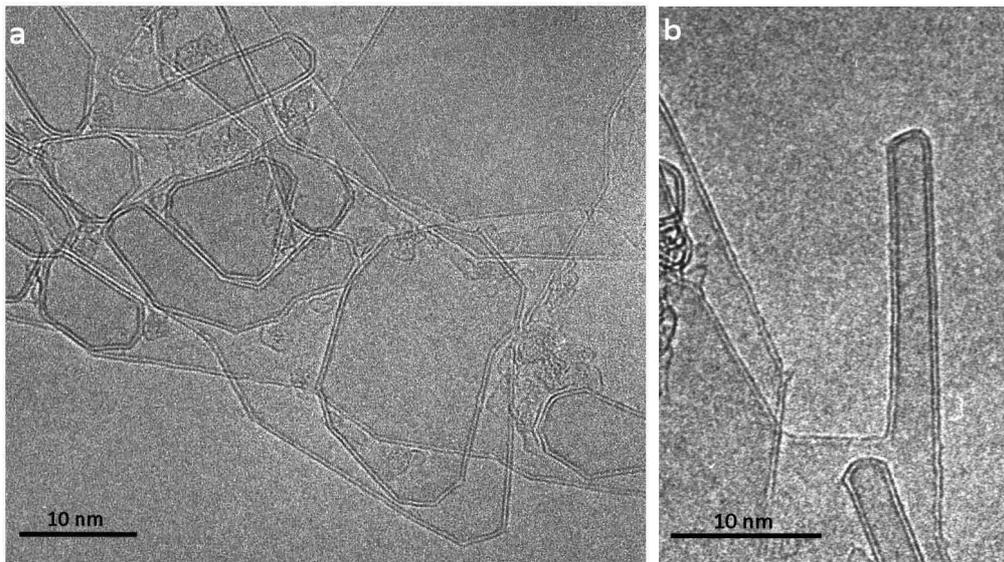
A typical image of material from a fresh graphite rod is shown in Fig. 1 (a). As expected, this consists mainly of flat crystallites, ranging from a few 100 nm to about 5  $\mu\text{m}$  in size, containing up to 100 layers. The crystallites were often folded and buckled, and were covered with small amounts of finely-divided material. However, nanotubes or other fullerene-related structures were not seen in the fresh graphite. The carbon collected from the graphite rods following arcing contained some “normal” graphite, but this was accompanied by many regions which had a very different appearance. One of these areas is shown in Fig. 1 (b). Here, the outline of the structure is much more irregular than in the fresh graphite, with many curved and unusually-shaped features. The material is decorated with numerous short nanotubes and nanoparticles.



**Fig. 1:** (a) Transmission electron micrograph of carbon from fresh graphite rod. (b) Micrograph at same magnification showing transformation in structure following passage of current.

A higher magnification image of the material following arcing is shown in Fig. 2 (a). It can be seen that this largely consists of bilayer graphene. A striking feature of the carbon is that nanotubes are often observed to be seamlessly joined to the larger regions. An example can be seen in Fig. 2 (b). This strongly suggests that the large bilayer structures are three-dimensional rather than flat, since it is difficult to envisage a way in which nanotubes, with their circular cross-section, could be connected to flat, bilayer, graphene without being seriously distorted, at least in the vicinity of the junction.

The structural transformation of graphite as a result of the passage of an electric current (i.e. by Joule heating), has now been observed by a number of groups [e.g. 5-7]. For example, Huang *et al.* [6], reported experiments in which samples of graphene prepared from highly orientated pyrolytic graphite (HOPG) were Joule-heated inside a transmission electron microscope. This produced a radical restructuring of the graphene rather similar to that



**Fig. 2:** (a) High resolution TEM image of transformed carbon showing bilayer structure. (b) Image showing bilayer nanotube joined to larger structure.

described here, except that the final structures were made up of single-layer rather than bilayer graphene. Like other authors in this field, Huang *et al.* discussed the process in terms of the sublimation and edge reconstruction of flat graphene. However, as already pointed out, there are good reasons for believing that the material produced by this transformation is in fact three-dimensional. Recently, evidence in support of this idea has been obtained using tomography and electron energy loss spectroscopy [4].

It is interesting to consider possible applications for the new carbon described here. One area for which the material appears particularly suitable is as an electrode material for supercapacitors. Compared with microporous carbon, this material has relatively large pore sizes (typically of the order of a few 10s of nm), which would greatly facilitate the penetration of electrolyte ions into the pores. Preliminary measurements also suggest it has a relatively high electrical conductivity, which is clearly advantageous for electrode materials.

Currently our work is focused on scaling up production of this new carbon.

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- [1] Harris, P.J.F. Ultrathin graphitic structures and carbon nanotubes in a purified synthetic graphite. *Journal of Physics: Condensed Matter*, **21**, 355009 (2009).
  - [2] Harris, P.J.F. Structural transformation of graphite by arc-discharge. *Philosophical Magazine*, **91**, 2355-2363 (2011).
  - [3] Harris, P.J.F. Hollow structures with bilayer graphene walls. *Carbon*, **50**, 3195-3199 (2012).
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  - [7] Barreiro, A. *et al.* Graphene at high bias: Cracking, layer by layer sublimation, and fusing. *Nano Letters*, **12**, 1873-1878 (2012).

# Melting temperature measurement for graphite HAPG under fast current heating

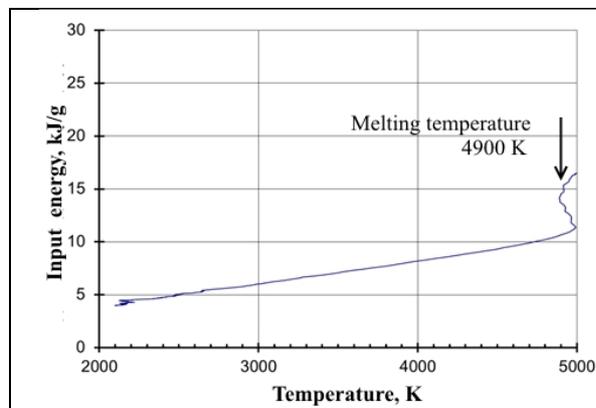
A.M. Kondratyev, S.V. Onufriev, A.I. Savvatimskiy

Joint Institute for High Temperatures, Moscow, Russia

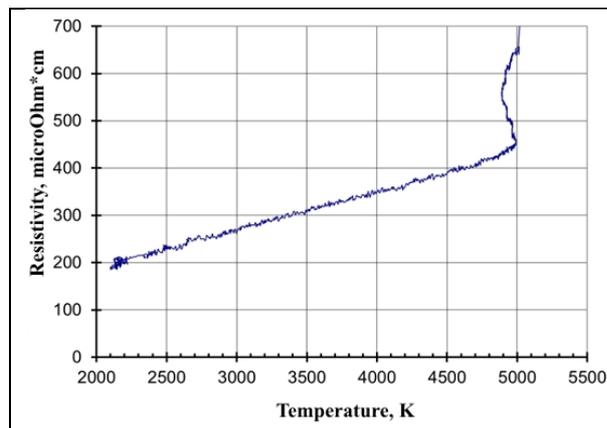
Nowadays HAPG is significantly important since this material becomes popular among the community of high-energy density physics at both laser facilities and x-ray free electron lasers. A mosaic crystal is generally considered as numerous small perfect crystallite domains of micrometer and sub-micron size which are oriented, almost but not exactly, parallel to one another. The term *Highly Annealed Pyrolytic Graphite* (HAPG) is present in the literature since the 1960's for bulk specimen, and was re-introduced by Legall et al. in 2006 year for a new kind of pyrolytic graphite developed by Optigraph GmbH (Berlin, Germany). [1].

HAPG – it is highly annealing pyrolytic graphite; anisotropic; density  $2.25 \text{ g/cm}^3$ . It looks like HOPG, but as a result of annealing the specimen in this experiment has the mosaicity to be  $\sim 0.08^\circ$  on a  $1 \times 1 \text{ mm}^2$  scale.

We report two results of fast heating HAPG graphite as seen in fig.1 and fig.2.



**Fig.1.** The dependence of input energy (Joule energy) against temperature for specimen with 40 micron thick (width 5 mm, 15 mm long). Current pulse heating 16 kA; melting point was reached in the time interval 4 microseconds.



**Fig.2.** The dependence of the resistivity (referred to initial dimensions) against temperature for the same specimen. Resistivity of HAPG at the melting point is lower than for other grade of graphite [2].

These studies have a financial support from Russian National Foundation (RNF), grant 14-50-00124.

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# An energy landscape for carbon network solids

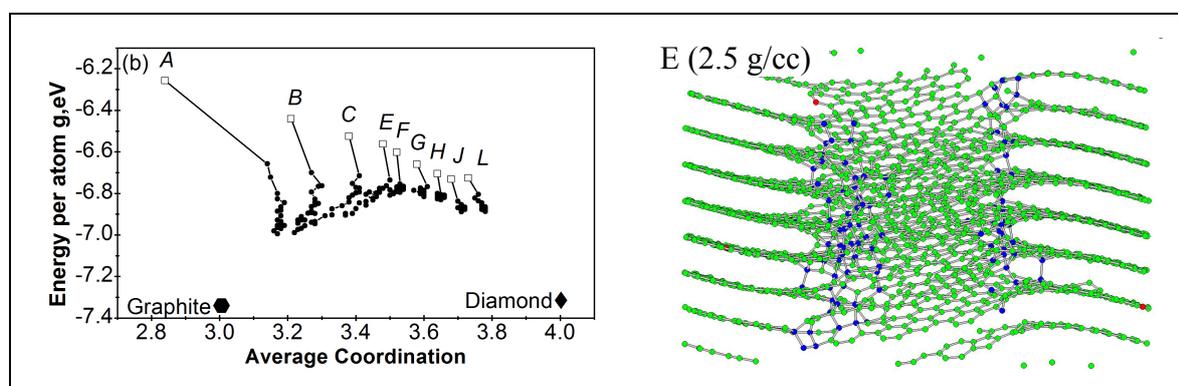
R. C. Powles<sup>1</sup>, N. A. Marks<sup>2</sup>, D. W. M. Lau<sup>3</sup>, D. G. McCulloch<sup>3</sup>, D. R. McKenzie<sup>1</sup>

<sup>1</sup>School of Physics, The University of Sydney, Sydney, NSW 2006, Australia

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Carbon network solids show a rich diversity with many distinct structural classes. Transitions between classes can be induced by annealing and mechanical compression, frequently with unexpected results. To understand these connections and develop an overall picture of how the structures are connected energetically, we have performed molecular dynamics (MD) simulations of compression and annealing using the Environment Dependent Interaction Potential for carbon [1]. Figure 1 shows data from the annealing simulations in which fully amorphous structures transform over time into more stable structures that are predominantly either  $sp^2$  or  $sp^3$  dominated. The image is an example of an annealed structure with a density of 2.5 g/cc, comprising two graphite-like domains.



**Fig. 1:** Left: Data from the annealing simulations. Initial structures (labeled A–L) are fully amorphous with a high energy per atom. Annealing transforms the structures in the direction of either graphite or diamond; the critical density which separates the two domains is around 2.7 g/cc. Right: An example structure from the domain which evolves towards graphite.

Using the MD data we have constructed an energy landscape that includes both amorphous and crystalline bonded networks [2]. The landscape, representing a minimum free energy surface, is constructed as a function of density and the degree of crystallinity and is used to explain experimental observations. We use the landscape to explain: (1) why some carbon structures show full recovery from deformation while others deform permanently, (2) why annealing of non-crystalline materials grown in a low pressure pure carbon vapor quenching process always lead ultimately to graphite and not to diamond and (3) why room temperature compression of graphitic carbons leads to a reversible amorphization. The tetrahedrally bonded amorphous structure is predicted to have the lowest free energy at sufficiently high pressures and temperatures and therefore is expected to occur as the endpoint of rapidly quenched shock compression processes of carbon structures.

[1] NA Marks, Physical Review B, **63**, 035401 (2001).

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# A size-dependent thermodynamic model for graphitic crystallites integrating the binary interactions of sulfur/hydrogen with carbon up to 2500 K

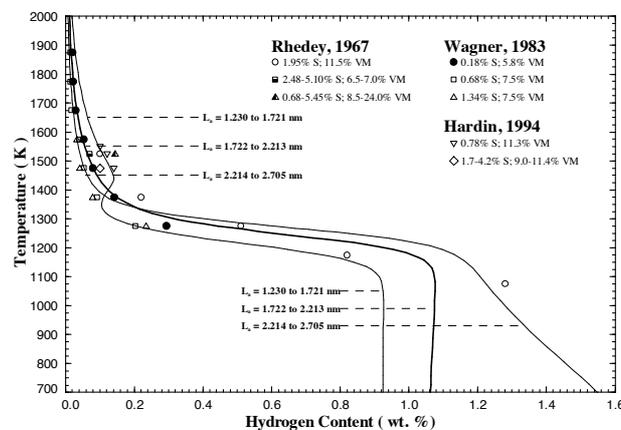
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It is well known that the most useful forms of carbon materials in common industrial applications are bulk carbon materials (for example, petrochemical cokes). The understanding of the properties of such bulk materials has fueled in the last decades numerous research articles both focusing on experimental observations and the proper definition of the behavior of bulk carbon materials that can be derived from these observations. The production of predictive calculations for the properties of bulk carbon materials is a research problematic still relevant to this day as such calculations would have to simultaneously account for the interactions of chemical composition and the fact that the crystalline structure of such materials is strongly impacted by surface energies (due to its inherent nanometric scale).

This work presents a recent predictive model for the basic thermodynamic properties of the crystalline phase of bulk carbon materials (i.e. graphitic crystallites). The effect of hydrogen and sulfur contents is included in this model. This model allows the calculation of the relative enthalpy and absolute entropy of graphitic crystallites. The application of such a model through the use of a well proven Gibbs energy minimization technique allows the production of results as previously presented in [1] for the carbon/hydrogen system (presented in Fig. 1 below).



**Fig. 1:** Comparison of the predicted dehydrogenation of idealized cokes crystallites with available experimental data (see [1] for Full Reference Details)

A key aspect of the model is that the predictive calculations can be performed for average crystallite length  $L_a$  and crystallite stack height  $L_c$  from a few nm to infinite size crystallites (very large values of  $L_a$  and  $L_c$ ). The validation of the model is made through the correct prediction of both the thermal dehydrogenation (above 1000K) and the high temperature desulfurization (above 1500K) of industrial cokes. The validation calculations were done for graphitic crystallites with values of  $L_a$  and  $L_c$  between approximately 1 nm and 45 nm. Future development of the model will focus on calculating appropriate surface energies.

[1] Ouzilleau P. et al., A size-dependent thermodynamic model for coke crystallites: The carbon–hydrogen system up to 2500 K, *Carbon*, vol. 85, 99-118 (2015)

[2] Ouzilleau P. et al., A size-dependent thermodynamic model for coke crystallites: the carbon-sulfur system up to 2500 K, Submitted to *Carbon* in December 2014, under review

# Thermal stability from soft to hard hydrogenated amorphous carbons analyzed using *in-situ* Raman spectroscopy. Application to tokamak carbon deposits

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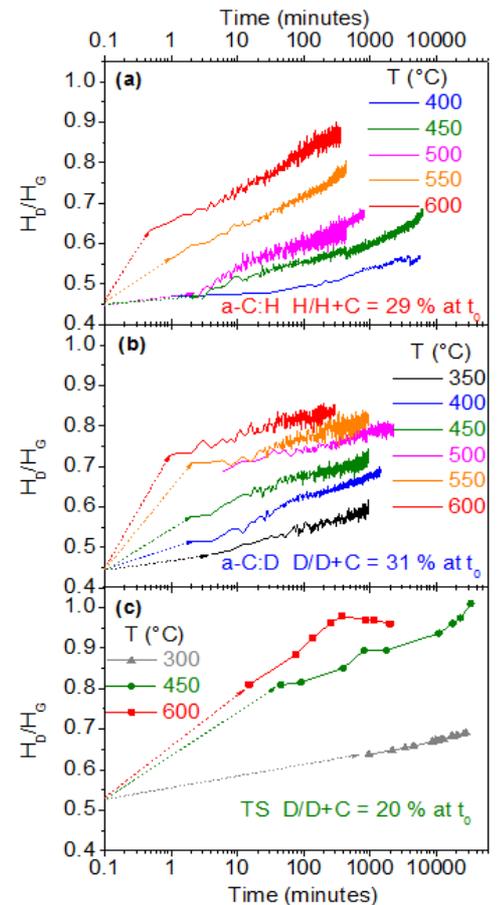
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Carbon was often used as the first wall of tokamaks. A complete analysis of the D retention in the Tore Supra tokamak, including both *in-situ* gas balance measurements and *ex-situ* post-mortem characterizations, has revealed that deuterium was depleted in the deep layers of the deposits, indicating that an unexpected long term D-release occurred.

To mimic the variety of hydrogenated deposits found in Tore Supra, we used several reference samples and heated them to relevant temperatures (120-1000°C). These samples had various C(sp<sup>2</sup>)/C(sp<sup>3</sup>)/H contents and were PECVD layers with properties ranging from soft to hard films (DC bias from -100 to -300 V corresponding respectively to H/(H+C) equal to 37 and 29 at.%). We have studied the thermal stability of these samples using single wavelength *in-situ* Raman microspectroscopy, recording their evolution during hours or days (see fig. 1). Ultra High Vacuum thermal desorption spectroscopy and ion beam analysis were done separately for comparison. We have identified selected Raman parameters as C(sp<sup>3</sup>)-H and/or C(sp<sup>2</sup>)-H sensitive. For example, for the -300 V DC bias sample, carbon reorganization with aromatization and loss of C(sp<sup>3</sup>) occurs in the first 100 minutes at 500 °C. This process occurs more rapidly with higher initial H content.

Our study [1-4] focuses on a method to obtain quantitative information from the spectral analysis compared to other techniques. We applied this method for reference samples and deposits produced in the Tore Supra tokamak to get insights into their structure and on the long term D release processes.



**Fig. 1.**  $H_D/H_G$  isotherms. (a) a-C:H sample with 29% of initial H content. (b) a-C:D sample with 31% of initial D content. (c) Tore Supra samples with roughly 20 % of initial D content.

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[2] C. Pardanaud, *et al.*, Long Term H-Release from Amorphous Carbon Evidenced by in Situ Raman Microscopy under Isothermal Heating, *Diamond and Related Materials*, 37, 92 (2013)

[3] C. Pardanaud, *et al.*, Multiwavelength Raman spectroscopy analysis of a large sampling of disordered carbons extracted from the Tore Supra tokamak, *Vibrational Spectroscopy*, 70, 187-192 (2014)

[4] C. Pardanaud, *et al.*, Thermal stability and long term hydrogen/deuterium release from soft to hard amorphous carbon layers analyzed using *in-situ* Raman spectroscopy. Comparison with Tore Supra deposits, *Thin solid films* (2015), DOI: 10.1016/j.tsf.2014.10.062

# Multi-wavelength Raman spectroscopy studies of graphene-based carbons with various domain sizes

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The Raman spectrum of graphenic materials is composed of two main bands, the G band corresponding to optical C=C mode, and the D band corresponding to either a breathing of the hexagons for highly defective materials [1] or to a mode in the Brillouin zone selected by a double resonant process for weakly defective materials [2]. Hence, the domain size (i.e., the average diameter of defect-free graphenic area  $L_a$ ) is a major parameter influencing the Raman spectrum.

In this work, we investigated the shape of Raman spectra for various graphenic materials exhibiting  $L_a$  sizes within the low (< 2 nm), intermediate (~2-10 nm), and large (> ~10 nm) range while varying the excitation wavelength. We attempted to address the physics behind and compared with different approaches used in the literature.

It is concluded that the linewidth of the G band is a good indicator for estimating  $L_a$  sizes in the range ~2-10 nm. The whole broadening of the G band with decreasing  $L_a$  accounts for both (i) the opposite dispersive behavior of the transversal (TO) and longitudinal (LO) optical branches and (ii) the double-resonant and non-resonant Raman scattering processes. This approach should allow the Raman spectra of a large variety of carbon materials to be modelled. It is particularly relevant when considering low maturity carbonaceous rocks such as gas shale, for which Raman spectra can be modelled in a more reliable manner than with the empirical approaches often used in the literature.

*This work was supported by the ANR program as part of the PyroMaN project ANR-10-BLAN-0929-02.*

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[2] Thomsen, C. and Reich, S. (2000). "Double resonant Raman scattering in graphite", Phys. Rev. Lett., Vol.85, p.5214.

# Investigation of activated carbons by HRTEM, X-ray scattering and Raman spectra

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Activated carbon are nanoporous materials composed of assemblies of highly defective graphene sheets which are cross-linked and locally arranged in stacks with a common orientation over very limited regions called continuous domains. Imaging by HRTEM gives a partial view of the disordered arrangement of the carbon skeleton, in the form of dark fringes representative of the edges of the graphene sheets which are parallelly aligned along the electron beam. The nanotexture of a large panel of various activated carbons (ACs) produced from different activation conditions and raw materials was characterized with a new HRTEM image processing method based on morphological modeling [1]. This method provides with a fine quantitative description of the spatial arrangement of the defective grapheme fragments constitutive of the carbon skeleton. Different degrees of disorder of the AC nanostructures could then be pointed out considering the size and the surface density of the continuous domains .

Comparison with micropore size data derived from N<sub>2</sub> and CO<sub>2</sub> adsorption isotherms suggests that the ultra-microporosity is located within the continuous domains, in the spaces enlarged by the intra-planar or edge defects of the grapheme layers, whereas super-micropores (0.7-2 nm) of more irregular shape, are delimited by the random arrangement of the continuous domains.

The analysis of the shape of the X-ray scattering curves reveals some interesting trends in relation with the micropore size distribution. Especially, the occurrence of a pronounced shoulder in the intermediary s-vector range is shown to be specific to materials exhibiting a significant volume of super-micropores. The intensity variation in the s-vector range representative of the micropore scattering also increases with the fraction of super-microporosity.

The analysis of the Raman spectra after deconvolution enlightens variations which could be related to some of the nanotextural data (fringe lengths and tortuosity) and to the ultra-microporosity fraction of the ACs [2].

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## Carbon phase diagram around the triple point graphite/liquid/vapor

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Experiments on phase diagram of carbon around its Graphite/Diamond/Liquid have been carried out by several authors, as summarized by F. P. Bundy [1,3]. Bundy's and Togaya's [2] experiments were fulfilled by millisecond pulse electrical heating under high pressure. P, T phase diagram of carbon was constructed by Bundy, on the basis of experimental studies until 1994 year (see figure, curves in red). Bundy chose 5000 K as the most reliable value for triple point graphite/liquid/vapor.

More recently, it has been attempted to predict this phase diagram on the basis of computational chemistry [4]. This prediction is reported in figure (curves in black). As we can see, there are several common points and discrepancies between these two approaches. The reader clearly sees the computed graphite melting line (green) in the figure goes to temperatures lower than 4000 K at low pressures, in contradiction with most experiments. The computations of the graphite/diamond equilibrium curve are slightly inaccurate with respect to reported experiments in the graphite/diamond area; they are much more inaccurate in the prediction of the melting lines (too low).

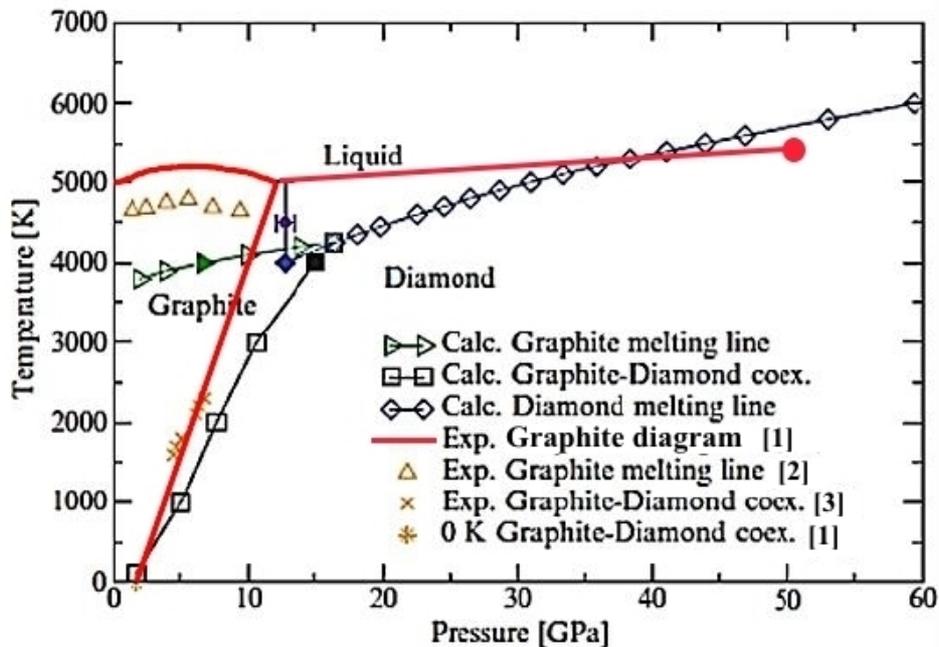


Figure.1. Carbon P-T phase diagram (experimental [1-3] and calculated approach [4]).

Recent calculations [5] have brought new lights on this apparent contradiction between theory and experiments. First, the authors compare the capabilities of AIREBO and LCBOP-II potentials used in calculations, and reveal some weak points. Second, they provide computations of the effective melting temperature as a function of the heating rate. Fig.2 gives experimental and numerical data for different heating rates for carbon specimens. The black curves are our results for AIREBO and the green curves are our estimates for LCBOP-II. The dash-dotted lines show the graphene melting determined in [5] (crosses) and in [6].

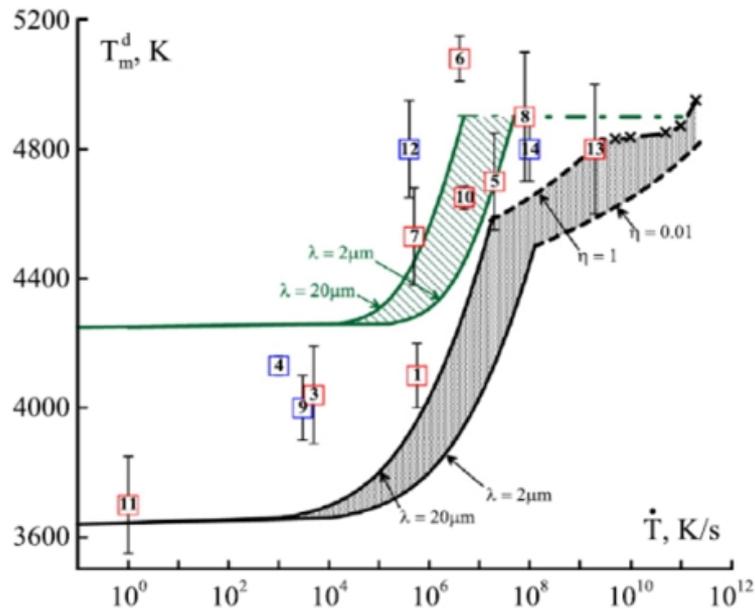


Fig.2. [5] – Dependence of the graphite melting temperature detected in experiments with respect to the heating rate. The red symbols show the electrical pulse heating and the blue ones show the laser heating experiments). The solid lines show the region of  $T_m^d(\dot{T})$  for an average grain size of  $\lambda = 2\text{--}20\ \mu\text{m}$ . The dashed lines show the region for the critical liquid phase fraction  $\eta = 0.01\text{--}1$ .

From figure 2, it appears that the scatter of the measured melting temperature ( $T_m$ ) values can be at least partly explained by the ease of graphite superheating due to its unusually slow melting kinetics.

We may note that under melting of rapidly heated substances the low diffusion rate of the defects to the liquid/solid interface prevents the saturation of the solid by the defects at the equilibrium density. Fast experiments prove (for metals, carbides and carbon) that before the melting of a crystal, there appeared Frenkel point defect pairs that eased melting; this effect gives increasing in heat capacity just before melting. That is why the value of  $T_m$  is nearly a constant for different heating rate in the experiments of last years. However, this effect (creation of Frenkel pairs) was not reported in [5] and other calculations. The detailed content of [5] will be discussed by the authors in the other report at the Workshop.

These studies have a financial support from Russian National Foundation (RNF), grant 14-50-00124.

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[6] K. V. Zakharchenko, A. Fasolino, J. H. Los, M. I. Katsnelson, *J Phys: Cond Matt* **23**(20), 202202 (2011).

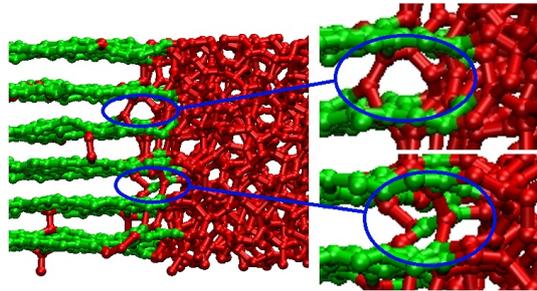
## Graphite melting: Atomistic kinetics bridges theory and experiment

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Graphite is one of the most wide-spread carbon allotropes. Unique thermophysical properties of graphite result in its important role in science and engineering. However, the experimental data on graphite melting temperature still remain controversial despite the long history of investigation. The experimental results of several works cover the wide span from 3800 to 5000 K that is an essentially larger uncertainty than the errors of individual experiments (the detailed analysis of the experimental works is presented in [1]).

Here we report the extended results of our recent works [2,3] in which we had deployed the molecular dynamics (MD) method to study the kinetics of two competing processes in graphite: the heterogeneous melting at the solid-liquid boundary and the homogeneous melting due to the spontaneous formation of liquid phase nuclei.



**Fig. 1:** A part of the MD simulation box with the phase boundary. Graphite layers are shown in green, atoms with other coordinations (disordered structure, interstitials) are shown in red. The interplanar interstitial-like defects formation is found to be a main melting front propagation mechanism.

Using the MD method we have shown that melting in graphite proceeds much slower than in other solids. We have calculated the rates of heterogeneous and homogeneous melting mechanisms as well as the thermodynamic melting temperature of graphite and the single graphene layer decay temperature for the AIREBO interatomic potential. These results combined in a simple mesoscopic model that takes into account a typical microstructure of graphite specimens, have allowed us to describe a large set of experimental results on the detected graphite melting temperatures at different heating rates. These results suggest that at the heating rates higher than  $\sim 10^6$  K/s graphite specimens in most cases become superheated, the solid-liquid transition temperature becomes higher than the equilibrium melting temperature and is influenced mainly by the specimen microstructure and the energy deposition process.

The slow melting kinetics of graphite together with the pressure and temperature effects on porosity of commonly used graphite specimens can explain the observed maximum on the experimentally detected melting temperature dependence on pressure as a kinetic effect without the hypothesis about a liquid-liquid phase transition in liquid carbon.

The work was supported by the Russian Science Foundation (Grant No. 14-19-01487).

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# Activated carbon xerogels from chemical activation of hydrothermally activated glucose-graphene oxide hybrids

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Graphene oxide is made up of bidimensional carbon sheets decorated with a high density of oxygenated functional groups, which confer it certain unique characteristics such as a high dispersibility in water and polar organic solvents, a relatively high reactivity and an ability to self-assemble into monolithic gels under hydrothermal conditions. Besides these properties, recent works have demonstrated that graphene oxide sheets act as a morphology-directing agent in the preparation of monolithic carbon gels. Thus, under hydrothermal conditions, addition of small amounts of graphene oxide to carbohydrate solutions has been reported [1] to induce the formation of carbon monoliths instead of micrometric spheres.

In this work, we report on the characteristics of micro/mesoporous carbon xerogels prepared through a two-step procedure [2]. The first step involves hydrothermal carbonization of glucose in the presence of graphene oxide as a morphology-directing agent. The second step consists of chemical activation of the resulting monoliths with KOH. We studied the effect of several operation variables (graphene oxide/glucose ratio, temperature and time of hydrothermal treatment, amount of activating agent and activation temperature) on the morphology and porous texture of the obtained materials.

The carbon xerogel monoliths obtained after the first step (hydrothermal carbonization) consisted of a random assembly of thin sheets (<30 nm) derived from the dehydration and condensation of glucose on the surface of graphene sheets, as catalyzed by the acidic sites present on the graphene oxide surface. The sheet thickness was a function of the graphene oxide/glucose ratio. Chemical activation of the above monoliths with KOH led to xerogels with high surface areas and pore volumes (up to 2000 m<sup>2</sup>/g and 1.15 cm<sup>3</sup>/g, respectively). Suitable selection of the KOH/xerogel ratio and the activation temperature allowed one to closely control the porosity characteristics in the obtained materials. Thus, activated xerogels either possessing almost exclusively narrow microporosity (<1 nm), or incorporating also wide micropores and narrow mesopores could be obtained using specific activation conditions.

Finally, the obtained xerogels were tested as adsorbents for CO<sub>2</sub> and dyes (rhodamine B, fuchsin basic, methyl orange). The CO<sub>2</sub> uptakes (up to 4.9 mmol/g at 273 K and 1 bar) correlated well with the volume of narrow micropores. A comparison with recent results from the literature indicates that these uptakes are relatively high taking into account the porosity development in the obtained adsorbents. Likewise, the activated carbon xerogels exhibited adsorption capacities for bulky dyes (between 600 and 700 mg/g) that are comparable to those reported to date for efficient carbon-based adsorbents. Therefore, the xerogels described here can also be potentially used for the effective adsorption of bulky dyes from wastewater.

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## Mechanical properties of pyrocarbons – from molecular to macroscopic scale

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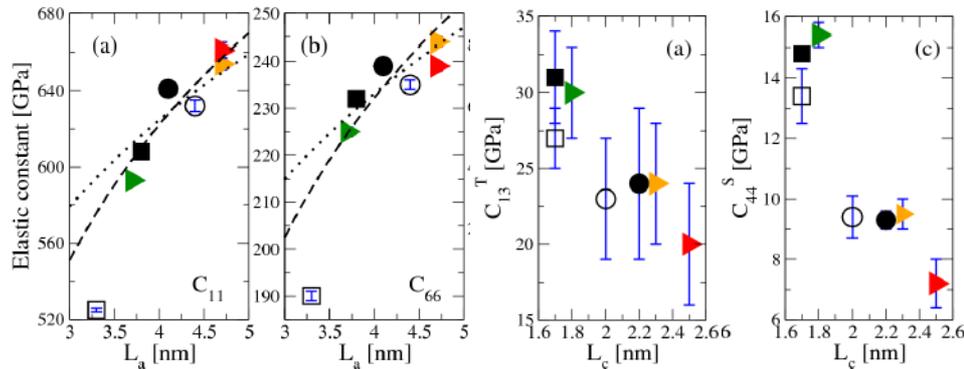
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Laminar pyrocarbons are employed in carbon/carbon and other thermostructural composites for aerospace and energy applications, due to their outstanding thermal and mechanical properties at extreme temperatures. The design of pyrocarbon-containing materials requires a good knowledge of these properties. Unfortunately, they are strongly varying with their structure and texture at various scales, themselves a function of the processing conditions. Moreover, they are difficult to measure experimentally, because bulk pyrocarbon sample are difficult to prepare. Modeling is therefore a precious help to address these issues.

Virtual mechanical tests have been carried out by Molecular Dynamics on a series of pyrocarbon models recently obtained by the IGAR (Image-Guided Atomistic Reconstruction) technique [1], as well as graphene and graphite for sake of comparison. Results are effective elasticity tensors, Young moduli and Poisson coefficients, which may be related to structural and textural parameters of these materials. Figure 1 depicts the evolution of  $C_{11}$  and  $C_{66}$  (in-plane tensile and shear stiffness coefficients) with the in-plane coherence length  $L_a$  and of  $C_{13}$  and  $C_{44}$  (Poisson effect and shear moduli concerning crossed directions) with the graphenic stacking height  $L_c$ .



**Figure 1.**  
Correlations  
between  
elasticity tensor  
elements with  
structural  
parameters  $L_a$   
and  $L_c$ .

These nanoscale properties will be discussed in front of the actual properties as determined by experiments. Up to now, they seem to be in discrepancy. Texture effects, as well as possible buckling are considered as sources of these differences.

[1] Farbos, B., Weisbecker, P., Fischer, H.E., Da Costa, J.-P., Lalanne, M., Chollon, G., Germain, C., Vignoles, G.L., Leyssale, J.-M. Carbon 80 (1), 472-489 (2014)

# Quantitative maps of orientation and anisotropy degree from PLOM observation

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Polarized Light Optical Microscopy has been one of the first techniques employed to characterize anisotropic carbons, which are birefringent. A very popular technique is the determination of extinction angles between crossed nicols, which has been recently turned quantitative on flat carbon deposits [1].

We propose here an analysis method that yields measurements of optical anisotropy (that can be translated into an effective extinction angle) that are resolved in space (i.e. there is one measurement per image pixel) and are given simultaneously with the local orientation. Such determinations are performed with a set of micrographs of the same area (unintentional displacements are corrected by software) taken with distinct absolute orientations of the polarizer and of the analyzer

It is therefore possible to create maps of orientation and of the degree of anisotropy, superposed to the natural light images of a given area of a carbon material. Figure 1 illustrates the procedure on a C/C composite with a multilayer pyrocarbon matrix. The distinct types of pyrocarbon (Rough and Smooth Laminar) are very well distinguished; moreover, the columnar structure of the deposits is well revealed by the procedure.

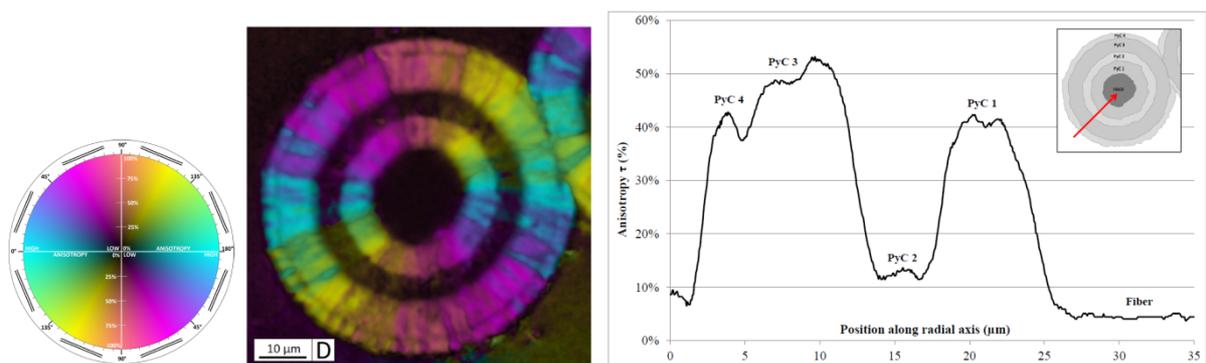


Fig 1 – Left: legend (color for orientation angle, darkness for isotropy); middle : multilayer pyrocarbon deposit around a carbon fiber; right : radial anisotropy degree profile

[1] A. Gillard et al., Carbon , in revision (2015)

# Non-Graphitic carbons modeling and critical analysis of structural parameters determined from diffraction and lattice fringe analyses

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Large models (>200 000 atoms) of highly anisotropic non-graphitic carbons have recently been obtained using an image guided atomistic reconstruction (IGAR) method [1]. This method used experimental HRTEM images and allowed obtaining accurate models in the directions of the graphenic planes while the graphene layers stacking was underestimated, mainly due to the projection effect in the TEM imaging process.

New variations of the IGAR method have been developed in order to overcome the projection effect difficulty and to apply the method to less anisotropic carbons. They differ by replacing the existing image generation routines by a-priori syntheses of 3D images.

- The first approach is based on “polycrystalline” turbostratic structures; the 3D blocks used to guide the atoms are made of Voronoi tessellations filled with 002 fringes spaced 0.34 nm apart along variable stacking directions. Frontiers between grains are flat planes. A comparison of a 3D block and of an atomistic model is shown figure 1.
- The second approach is based on Gabor filters (Gaussian kernel functions modulated by sinusoidal plane waves). Gabor kernels are scattered in the 3D block with given density, orientations, sizes and aspect ratios. Contrary to the “polycrystal” approach, frontiers between grains are less clearly defined.

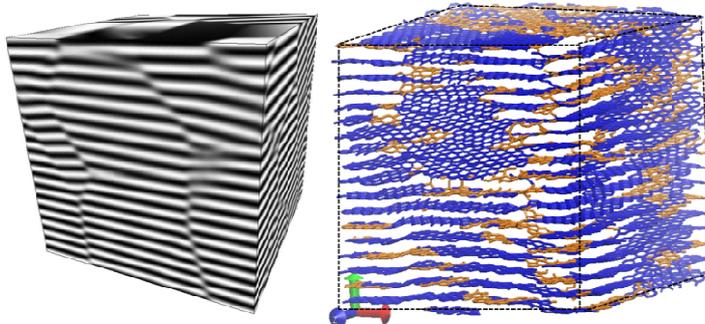


Figure 1: a 3D image used as an input for the atomistic construction (“polycrystal” method) and the corresponding model (26000 atoms)

Several models have been obtained using both methods with various domain sizes, anisotropy degrees and densities. Results will be presented in term of statistics (three coordinated atoms, 5-7 membered rings...). Not only the simulated HRTEM images, but also the estimated structure factors and pair distribution functions will be compared with experimental results obtained on various pyrocarbons. Then various questions will be addressed, namely (i) the domain boundaries shapes and (ii) the correlation between the real domain sizes and the apparent lengths (coherence lengths, fringe lengths) obtained by the usual characterization techniques: XRD, HRTEM. A recently developed method of lattice fringes images analysis [2], using orientation maps, will be used to analyze the simulated HRTEM images.

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[2] J.P. Da Costa, P. Weisbecker, B. Farbos, J.-M. Leyssale, G.L. Vignoles, C. Germain. Investigating carbon materials nanostructure using image orientation statistics. CARBON 84 (2015) 160-173

# Graphene-like legos for building structural models of carbon materials obtained from cellulose

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Activated carbons are greatly valued for their largely expanded specific surface. The activated carbons in this study were obtained from carbonized cellulose by chemical activation with NaOH. Both materials before and after activation were investigated. Properties of these materials depend on their atomic scale structure. According to earlier structural models developed by R. Franklin disordered carbons consists of linked microcrystallites of graphite. Discovery of fullerenes and nanotubes took development of structural models of activated carbons even further - it provided the idea of incorporating curved, defected structures based on carbon honeycomb lattice into models. This idea helps to explain in a better way their highly developed specific surface.

To approach the question of the atomic structure of the samples we combined experimental methods such as high resolution transmission electron microscopy, wide angle neutron scattering (WANS), wide angle X-ray scattering (WAXS), and Raman spectroscopy with computer simulations. The WANS measurements were carried out at the Institut Laue-Langevin in Grenoble using D4 neutron diffractometer for liquids and amorphous materials and the WAXS measurements at the European Synchrotron Radiation Facility in Grenoble, France using the High-Energy X-ray Beamline (ID15B).

The main building unit in our study was a defected multi-layered graphene flake. As the small size of the coherently scattering regions places the material structure on the vague borderline between amorphous and crystalline materials, the data was analyzed in real and reciprocal space. In order to process data in real space one of correlation functions was utilized, the chosen one was Pair Distribution Function (PDF), which provides information about atomic distances within the sample. For reciprocal space structure factors were calculated. Diffraction data (along with computed models) analyzed in real and reciprocal space allowed the size of those flakes to be determined as well as gave insight into the types of defects present in the system. In those simulations, a two-step approach was taken. First, the paracrystalline model was used as a simple, yet powerful tool to estimate the parameters of the model (such as dimension, number of layers). Based on the results from the first step, models including physically reasonable defects were constructed and relaxed with molecular dynamics. Defects proved to be reasonable in this study were mono-vacancy, di-vacancy and Stone-Thrower-Wales type of defect. Information gained from analysis of the data obtained from Raman spectroscopy and high resolution transmission microscopy was used to validate selected models. A good agreement between experimental data and proposed models was obtained.

# SYNTHESIS OF GRAPHENE FOR THIN FILM SOLAR CELL APPLICATIONS

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Graphene, since the demonstration of its easy isolation of graphite in 2004 has been attracting enormous attention in the scientific community. Because of its unique properties like transparency, conductivity, flexibility, stability at atmosphere conditions [1], high raw material availability, it has been used for technological applications in many areas as electronics and optoelectronics, photovoltaics, medicine, etc.

In the beginning, the graphene has been applied in photovoltaics for replacing the indium tin oxide (ITO) used as the transparent electrodes of organic solar cells [2]. Recently, it was involved into the conversion and conduction layers of a perovskite-type photovoltaic cell [3]. In these devices the graphene and titanium dioxide combine to serve as the charge collector while perovskite acts as the sunlight absorber.

However, there no data until now that relate the use of graphene as a back conductive contact layer in thin film solar cells. The back contact in these cells is made out of metals like Au, Pt, Ag, Cu, Ni, Al, etc. and its fabrication is a much-studied part of materials engineering field. Nevertheless, Molybdenum is preferable among the others metals, because withstands corrosion against Se and S, especially for chalcogenides-type cells (Fig.1). Thus, we propose the substitution of molybdenum for graphene in the back contact conductive layer. The morphological and structural characteristics of the graphene will determine the reliability and efficiency of the final device.

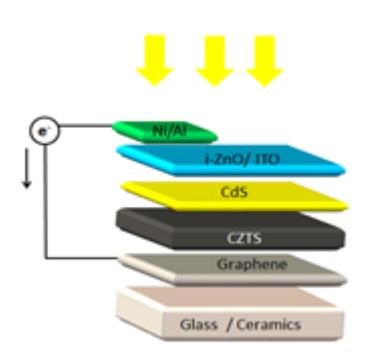


Figure 1. Schematic layout of kesterite thin film solar cell, where graphene is used as a back contact.

In this work we describe a graphene synthesis using chemical exfoliation of graphite by modified Hummers method. Different preparation parameters are changed for example temperatures, concentration and reaction times. That further impact on a layer adherence and electrical properties were studied. Further on, the obtained graphene was deposited on glass or ceramic substrates by spin coating technique, substituting the molybdenum (Mo) back contact

layer completely. For attainment of successful photovoltaic device, coating compatibility in the solar cell system has been analyzed. The developed material was characterized structurally and microstructurally by X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy, Scanning and Transmission Electron Microscopy (SEM/TEM) and Atomic Force Microscopy (AFM), among others.

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## **XPS AND NEXAFS SYNCHROTRON SPECTROSCOPY OF PAH RELEVANT IN COMBUSTION AND ENVIRONMENT FIELD**

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Detailed information on the chemical and physical structure of the nanometric carbon species accompanying soot formation and emission are important to assess their possible health and environmental effects as well as to identify the pathways involved in soot inception and growth. Consequently, there is an increasing demand for diagnostic techniques capable to determine properties of nanoparticles not easily accessible to traditional analytical methods. The present work aims to contribute in developing a new analytical approach with synchrotron radiation for the analysis of PAH that, beside to be emitted as individual molecules, mimic the basic units (aromatic layers) of fine and ultrafine particles. Some PAH standards, selected among the most abundant combustion-formed PAH, have been suitably volatilized and on-line analysed in gas phase. Their electronic structures have been studied by means of synchrotron radiation spectroscopy at the carbon K-edge: X-ray Photoelectron spectroscopy (XPS) and Near Edge X-ray Absorption Fine Structure (NEXAFS).

The XPS spectra of the standard molecules have been measured in order to determine the C1s ionization potentials. The molecules under study have many non-equivalent carbon atoms, which are expected to produce several overlapping C 1s photoelectron lines.

The C1s band characteristics (position, amplitude, etc.) have been studied and correlated with the PAH structure, which differs in the rings number, condensation degree, five-ring presence. The XPS data were matched with the NEXAFS ones for achieving information also about the local environment (up to ca. 6 Å) around a specific type of absorber atom. In particular details could be obtained about the distance to neighboring atoms, their type and number, and the local geometry around the absorber. Experimental data have been interpreted for some PAH by comparison with theoretical calculations. The interpretation in collaboration with a theoretical research group will be extended to all the other PAH.

On the basis of the findings obtained from the experiments on PAH in gas phase, some insights on the C1s band of XPS spectrum of combustion-formed soot particles were given too.

# Insights on structures of the large polycyclic aromatic hydrocarbons systems featuring coal tar pitch and naphthalene pitch

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Fossil fuel-derived and synthesized pitches, consisting of a complex mixture of numerous aromatic hydrocarbons, are important resources of polycyclic aromatic hydrocarbons (PAH) that can be treated for the manufacturing of various carbon-based materials as graphite electrodes, carbon anodes, carbon fibers and composites fibers. The quality of the pitch-derived carbons is strictly dependent on the complex composition and properties of pitch precursors. Details on the PAH composition of parent pitches and the related soft interactions and assembly mechanism, are important for determining final pitch properties achieved after the heat treatment, typically involved in the production of carbon artefacts. Besides, pitches are readily available mixtures of large PAH which can be used in the place of purposely-synthesized individual PAH, as realistic models of the different nanosized  $sp^2$  domains featuring ordered and disordered carbon materials. The study of their chemical characteristics and spectroscopic features can hence be useful to infer the structural characteristics of  $sp^2$  nanostructures in disordered carbon materials.

Large unsubstituted and substituted monomeric aromatic compounds, along with oligomeric systems where aromatic units can be connected by e.g. C-C single bonds (oligo-aryl type), -CH groups, ether bridges, are considered to be the basic constituents of both coal tar [1,2] and naphthalene-derived pitches [3]. As a consequence of their different source, coal tar pitch (CP) and naphthalene pitch (NP) have quite different properties as softening point, coke yield, etc., in spite of their similar H/C atomic ratio (around 0.5) and aromatic nature. In this work the comparative study of their properties was carried out by a multi-array analytical approach including heptane and toluene extractions. A detailed characterization of parent pitches and solvent separated fractions was performed. Composition and thermal behavior were analyzed by gas chromatography-mass spectrometry, size exclusion chromatography, thermogravimetry and laser desorption-mass spectrometry to compare the volatility and thermal stability in relation to their solubility and molecular weight distribution. Specific structural features were measured by infrared, UV-visible and fluorescence spectroscopy. The cross-check of the information obtained by different methodologies, picking up from each technique the most important information, was useful to deepen and validate the characterization of very structurally different large PAH systems featuring both pitches. The deep spectroscopic analysis used to get insights on structural features as aliphatic/aromatic hydrogen distribution and aromatic moieties allowed to differentiate between the class of ortho fused PAH, featuring CP, and the class of aromatic naphthalene moieties interspersed with aliphatic (mainly naphthenic) groups, which makes up NP.

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# Characterization of Nanoporous Carbide-Derived Carbons by Combined Transmission Electron Microscopy, Nitrogen/Carbon Dioxide Physisorption, and Raman Spectroscopy

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Carbide-derived carbons (CDCs) are nanoporous carbon materials produced by the selective extraction of metal- or semi-metal atoms from carbide precursors, e.g. by high-temperature chlorine treatment. CDCs are characterized by high specific surface areas and are widely applied in adsorption and electrochemical energy storage [1]. CDCs such as DUT-38 (DUT-Dresden University of Technology) [2] exhibit a hierarchical porosity which can be finely tuned by adjustment of the synthesis parameters. However, as it is typical for highly microporous carbon materials, CDCs have a highly disordered nanostructure resulting in the formation of micropores of irregular shape. In this study, we present a pore structure analysis of hierarchical CDC materials combining high resolution transmission electron microscopy (HRTEM) imaging, physisorption and Raman spectroscopy. At low magnification, HRTEM images show a high density of mesopores of regular shape created by the metal particle removal. At larger magnification, HRTEM fringe images were processed with a home-made software [3], revealing significant variations in the nanotextural properties of the materials with the synthesis temperature. The information so obtained was completed by Raman spectra analysis. These investigations show the precise control over the hierarchical pore structure of the CDCs provided by the chlorine treatment.

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# Evolution of soot nanostructure in premixed hydrocarbon flames.

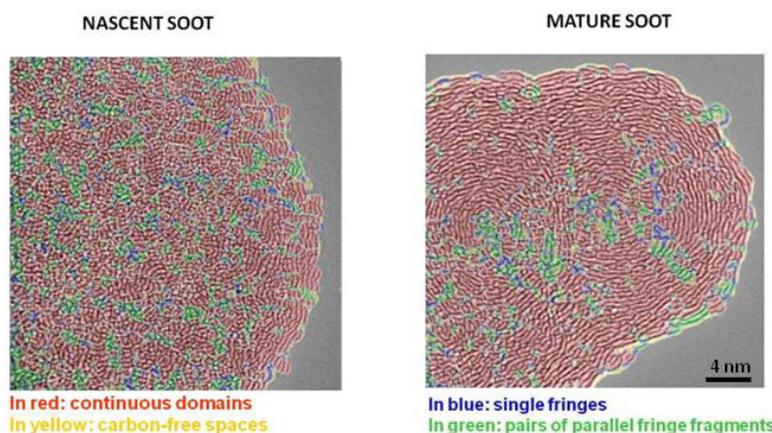
*P. Pré<sup>1\*</sup>, B. Apicella<sup>2</sup>, C. Russo<sup>2</sup>, D. Deldique<sup>3</sup>, M. Alfe<sup>2</sup>, V. Gargiulo<sup>2</sup>, A. Tregrossi<sup>2</sup>, A. Ciajolo<sup>2</sup>, J.N. Rouzaud<sup>3</sup>*

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The evolution of soot nanostructure along their formation region in rich-hydrocarbon premixed flames of benzene, ethylene and methane was examined from fringe image processing obtained by High Resolution Transmission Electron Microscopy (HRTEM) [1]. The gain in the soot structural ordering and loss of defects along the flames was pointed out by measuring the variations in the fringe lengths, tortuosity and local curvature radii, as well as in the size and surface density of the continuous domains. The observed domains reveal the formation of concentric arrangements of parallel fringe increasing in size with the degree of soot maturation in the flame.



**Fig.1:** Extraction of the continuous domain units after HRTEM image processing of ethylene soot sampled at different heights above the burner : 4 mm (left) and 14 mm (right).

The fringe length variations were found in good agreement with the coherent layer length  $L_a$  determined after Raman spectra deconvolution and calculation of the intensity ratios of the G and D bands [2].

In addition, these observations were related to the changes in the aliphatic and aromatic hydrogen content derived from a newly developed FT-IR quantitative method and to the measurement of the soot absorption coefficient [3].

This study gives new and pertinent insights in the different dehydrogenation and soot mass growth processes observed for the different hydrocarbon flames.

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# Re-arrangement of ions in nanoporous carbon supercapacitors studied by in-operando small-angle X-ray scattering

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Electrosorption of ions in the confined geometry of carbon nanopores plays an important role for rapid energy storage or capacitive deionization. In contrast to volume-dominated redox reactions, supercapacitors store energy electrostatically utilizing the opposed charges of electrons and ions at the electrode-electrolyte interface via formation of an electrical double-layer. There exist only a few in-situ techniques allowing a direct view on the ion transport within the nanopores.

We employ in-operando small-angle X-ray scattering (SAXS) and X-ray transmission (XRT) measurements to study the ion re-arrangement within nanoporous carbons of in-situ supercapacitor cells during charging and discharging. Activated carbons and titanium carbide derived carbons (TiC-CDC) were used as electrode materials revealing dependencies of the ion behavior on both pore size and shape. As shown by our data, in aqueous electrolytes with high ionic strength, *globally* the charge within the carbon electrode is accommodated by so-called ion exchange, whereas *locally* counter-ions move preferably towards the pore walls upon charging [1]. Interestingly a similar *local* reordering of ions as a function of the applied voltage was observed even for carbons with an average pore size smaller than 1 nm.

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# Porous texture and surface chemistry effects on CO<sub>2</sub> capture by ordered mesoporous carbons

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Adsorption by porous carbons is a promising technology for CO<sub>2</sub> capture thanks to the possibility of developing materials with high specific surface areas and well-defined pore structures. Moreover, it has been proved that incorporation of basic functionalities (especially nitrogen functional groups) into the carbon network improves the CO<sub>2</sub> adsorption capacity at low pressures and high temperatures. The objective of this work is to clarify the effects of different types of N-, O- and P-containing functionalities on CO<sub>2</sub> adsorption on a series of carbons with ordered porosity.

Ordered micro/mesoporous carbons were prepared using SBA-15 as template and 3-aminobenzoic acid as precursor. A polyamide/SBA-15 silica composite was carbonized at various temperatures in the presence of different amounts of phosphoric acid [1]. The adsorption capacity of the resulting materials was measured at subatmospheric pressures at three different temperatures (0, 25, 50 °C).

The use of different H<sub>3</sub>PO<sub>4</sub> concentrations led to porous carbons exhibiting high pore volumes and a great variety of functional groups, which were identified and quantified using XPS [2]. Both the textural and surface chemical properties of the carbons could be easily controlled by varying the H<sub>3</sub>PO<sub>4</sub> concentration and carbonization temperature. H<sub>3</sub>PO<sub>4</sub> modified the pyrolysis mechanism of the thermally polymerized precursor and induced the progressive degradation of both structural order and mesopore arrangement when phosphoric acid concentrations >50 wt.% were used. On the contrary, low H<sub>3</sub>PO<sub>4</sub> concentrations led to mesoporous carbon materials with very narrow PSDs and high retention of nitrogen at the carbon surface.

A clear conclusion from this work is that CO<sub>2</sub> adsorption at 0 °C and 1 bar essentially depends on the narrow micropore volume, being almost unaffected by the surface chemistry. Thus, the largest CO<sub>2</sub> uptake at this temperature (5.04 mmol/g) was obtained for the carbon with the most developed ultramicroporous structure. Unlike this, CO<sub>2</sub> adsorption at 25 or 50 °C and 1 bar was clearly influenced by the surface chemistry (heteroatom nature and concentration) of the carbons. Thus, the CO<sub>2</sub> uptake increased with increasing amount of N-containing groups, the opposite occurring with O- and P-containing groups. Among the N-containing functionalities, the pyrrolic ones provoked the largest improvements in CO<sub>2</sub> adsorption; the effects of pyridinic and quaternary groups were weaker. The highest isosteric heats of adsorption at zero coverage were obtained for the samples with the highest surface concentrations of nitrogen (i.e., those synthesized in the presence of low H<sub>3</sub>PO<sub>4</sub> concentrations). This is consistent with the positive effect of the nitrogen functional groups. Such N-doped carbons can constitute suitable selective adsorbents for CO<sub>2</sub> capture in post-combustion conditions.

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# Quantitative analysis of HRTEM images of carbonaceous materials and correlation with its oxidative behaviour

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Soot emissions from both stationary and mobile diesel engines are a major contributor to negative health effects and environmental pollution. Soot particles are dangerous due to the large number of harmful substances that they carry and because of their minuscule size, they can travel deep into our lungs and even enter the bloodstream. The currently applied method for reducing soot emissions includes the use of diesel particulate filters (DPF's) with periodical thermal oxidation of soot. Therefore, a better understanding of how soot morphology and nanostructure affect the reactivity toward oxidation can be used to create more efficient methods of soot reduction and removal.

To date, a variety of methods have been used to characterize the carbon nanostructure (size, orientation and organization of carbon lamella) including X-ray diffraction, Raman spectroscopy and High Resolution Transmission Electron Microscopy [1, 3, 4, 6]. However, HRTEM is the only method that can provide the configurations of the graphene layers of soot. Vander Wal et al. [2] studied the soot microstructure via HRTEM image analysis and argued that soot oxidation rate notably depends on the length and curvature of the graphene segments.

In the present work, which is an extension of previous work on diesel soot characterization via Raman microspectroscopy [5] a method for the analysis of HRTEM images of carbonaceous materials is developed. In particular, this study describes the development of an image analysis algorithm to extract quantitative nanostructure properties from HRTEM images of carbonaceous materials. Through this procedure, known as lattice fringe analysis, information about fringe length, tortuosity and separation distance within primary carbon particles is obtained. The algorithm is implemented using MATLAB and in order to validate the acquired results, a comparison is made between the aforementioned results and those obtained by Image J analysis, a Java-based image processing program.

The developed algorithm is applied not only to diesel soot, as well as to other types of carbonaceous materials, such as graphite and carbon black.

The analysis of three to four different areas of HRTEM images for each material is performed to get representative information on carbon nanostructure. Statistical results are presented in the form of histograms (Figure 1) and show that the developed algorithm provides the capability to determine different carbon nanostructures between carbonaceous materials of various origins. Moreover, it is observed that fringe tortuosity and separation distance as descriptors of structural order are related to the soot reactivity. A correlation with Raman parameters and results from X-ray diffraction analysis is also performed.

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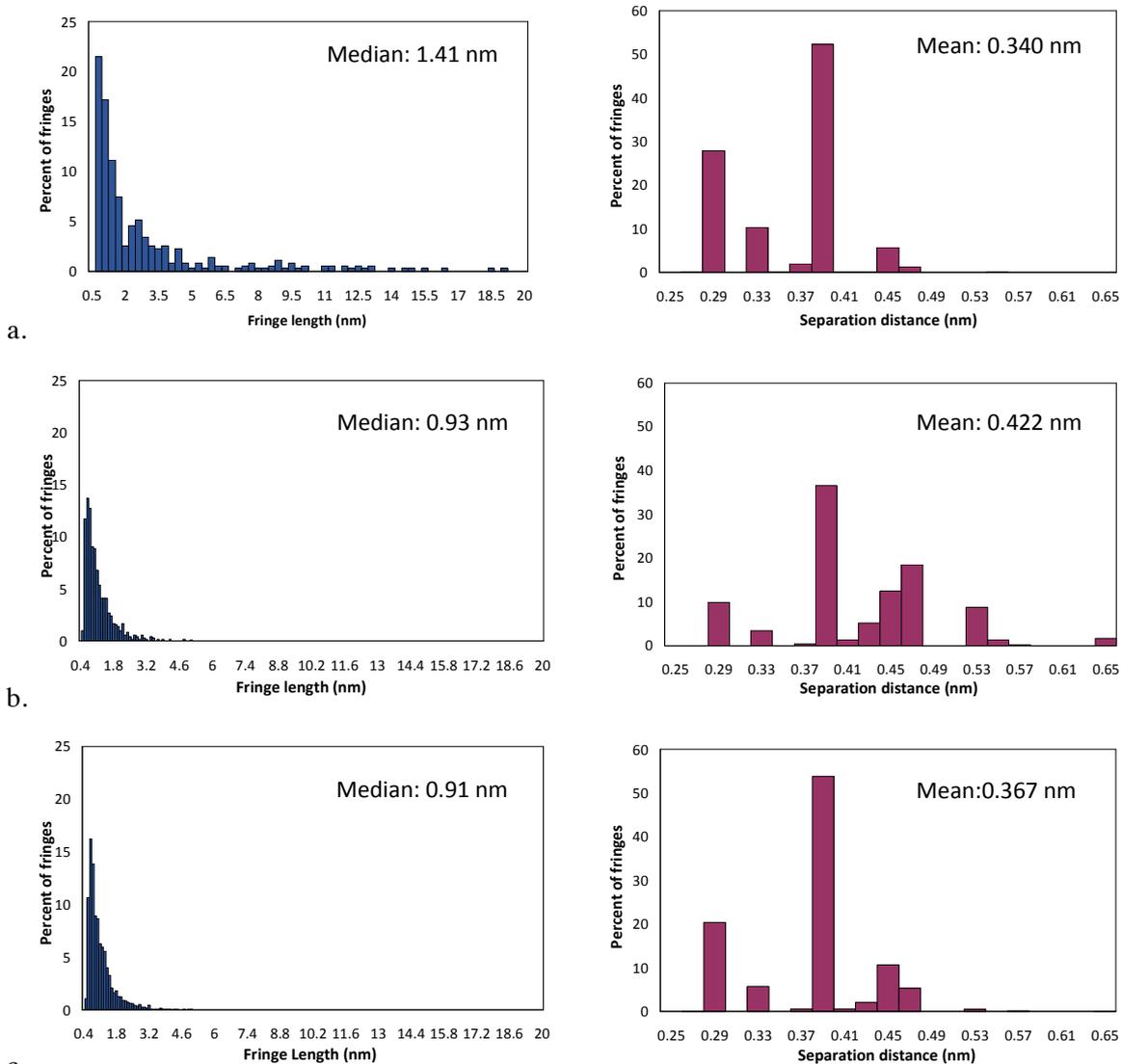
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**Figure 1.** Quantification of HRTEM images via Lattice fringe analysis: Fringe length and separation distance analysis for: a. Commercial Graphite, b. Carbon Black and c. Diesel soot.