

Measuring Domain Sizes in Graphene-Based Carbons

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INTRODUCTION

Whether graphene-based carbons are under the form of films or bulk, dense materials, many of the overall properties (transport, thermal, mechanical) depend on the domain sizes, that is to say mostly the lateral extension (L_a) - and thickness (L_c) in a lesser extent - of the crystallites, regardless of their turbostratic or graphitic structure. Since the sixties and mostly based on the work by Warren and Ruland, X-ray (and neutron) diffraction is a well-known technique for estimating L_a and L_c parameters, but several methods can be found. Other methods are also used for long, namely Raman spectroscopy, and transmission electron microscopy (TEM) imaging. All have their limitations or were not fully quantitative. This work is discussing the degree of relevance of each of the three methods, and is introducing new approaches we have developed - or are currently developing - in order to reach better reliability and/or simplicity in estimating domain sizes in graphene-based carbons.

MATERIALS AND METHODS

Materials: Carbon materials subjected to the various analytical procedures are isotropic or anisotropic pyrolytic carbons and graphitizable pitch cokes.

X-Ray diffraction: The X-ray data were collected on a Bruker D8 Advance diffractometer equipped with the Lynxeye detector using the Cu $K\alpha$ radiation at 0.1541 nm (filtered by Ni) and the Bragg-Brentano configuration. The Scherrer equation was applied while considering the Warren correction factor (1.84) or the Scherrer correction factor (0.9), depending on the case.

Raman spectroscopy: Raman spectra were acquired on various spectrometers in order to use excitation wavelengths ranging from IR to UV.

Transmission electron microscopy: Lattice fringe images exploited by means of quantitative image analysis were acquired with a Philips CM30 equipped with a ultra-twin objective lens, a LaB₆ electron source, and operated at 150 kV.

RESULTS AND DISCUSSION

A plot such as in Figure 1 requires the L_a sizes of a reference sample series to be first obtained, which is usually carried out by X-ray diffraction. However, accounting for the asymmetry of the hk bands (typically 10) while it modulates into two hkl peaks (typically 100 and 101) during the turbostratic to graphitic transformation is not simple. Hence, we compared various quantitative exploitation methods found in the literature for X-ray diffraction patterns, including the well-known method developed by Warren

long ago¹⁾, and that proposed more recently by Shi et al²⁾, with the latter being claimed to improve the former significantly. Considering that determining the correction factor and its variation in the course of the graphitization process makes the pattern analysis a complex issue, we also made an attempt to find a method preventing to use any correction factor but the regular Scherrer factor.

A thorough Raman investigation was then carried out on both some pyrocarbons and the pitch coke series. Because all the fitting procedures in the literature have no physical meaning, a new fitting procedure of the Raman spectra was first determined³⁾, based on the existence of a double scattering process due to the bouncing of the photoelectron by the graphene edge. Consequently, this process probability is as higher as the domain size is smaller. This allowed the various band widths and heights to be measured accurately, from which we found that the well-known Tuinstra-Koenig law ($I_D/I_G = f(1/L_a)$) cannot apply over the whole range of L_a size, specifically below $L_a = \sim 10$ nm. We therefore propose to use the width of the G band, which was found to vary linearly with increasing L_a within the range of small domain sizes.

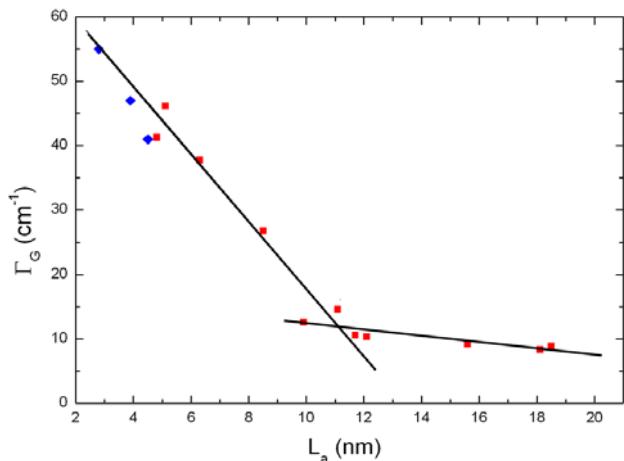


Fig. 1. The plot of the half-width at half-maximum of the G band in function of the L_a size (obtained from XRD) for anisotropic pyrocarbons (diamonds) and a 1000-to-2500°C treated pitch coke series (squares) shows linear domains making much easier and accurate the estimation of L_a than with the Tuinstra-Koenig law. The slope change matches the beginning of the turbostratic/graphitic transition

L_a sizes from X-ray diffraction were then compared with direct measurements carried-out by means of image analysis of TEM lattice fringe images of pyrocarbon samples. Various nanotextural parameters were drawn from this analysis, including L_1 (i.e., the average diameter of straight, continuous graphene) and L_2 (i.e., the average diameter of distorted, continuous graphene). The variation of the nanotextural parameters from TEM was also correlated with that of the Raman parameters.

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REFERENCES

1. Warren, B.E. (1941) "X-ray diffraction in random layer lattices", *Physical Review*, Vol.59, p.693-698.
2. Shi, H., Reimers, J.N., Dahn, J.R. (1993). "Structure-refinement program for disordered carbons", *Journal of Applied Crystallography*, Vol.26, p.827-836.
3. Mallet-Ladeira, P., Puech, P., Toulouse, C., Cazayous, M., Ratel-Ramond, N., Weisbecker, P., Vignoles, G.L., Monthioux, M. (submitted). "A Raman study to obtain crystallite size of carbon materials: a better alternative to the Tuinstra-Koenig law", *Carbon*.