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Determination of crystallite size in polished graphitized carbon by Raman spectroscopy

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A series of polished and unpolished sp^2-nanostructured carbons "nanographites" obtained from the pyrolysis of various precursor types have been systematically studied by both Raman spectroscopy and x-ray diffraction. The ratio between the intensities of the disorder-induced D band and the first-order graphite G band (I_D/I_G) commonly used up to now to estimate the "crystallite" diameter L_a displays, in the case of polished graphitized sp^2 carbons, clear spatial heterogeneities and can lead to the overestimation of the intrinsic structural disorder. The full width at half maximum of the G band, which is shown to be insensitive to the polishing process, exhibits a linear dependence on the mean "crystallite" diameter [$\text{FWHM}(G) = 14 + 430/L_a$] and therefore can be used for an accurate structural characterization of these nanographites.

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I. INTRODUCTION

Raman spectrum of the graphitic matter is known to give detailed information about its structural features making Raman spectroscopy a widely used tool in the last four decades. It has historically played an important role for the characterization of pyrolitic graphite, carbon fibers,[1,2] glassy carbon, pitch-based graphitic foams,[3,4] nanographite ribbons,[5] carbon nanotubes,[6,7] fullerenes,[8,9] and graphene.[10,11] For instance, a perfect crystalline sp^2 carbon is characterized by a single sharp band centered at 1580 cm^{-1} (the so-called G band) in the first-order Raman spectrum. It is the doubly degenerate phonon mode (E_{2g} symmetry) at the Brillouin zone center that is Raman active for sp^2 carbon networks. However, the introduction of disorder within the structure (doping, edges, defects...) breaks the crystal symmetry and activates certain vibrational modes that would be silent otherwise. These bands of the first-order Raman are called defect bands ($D \sim 1200$–$1400\ \text{cm}^{-1}$) and ($D' \sim 1600$–$1630\ \text{cm}^{-1}$). They are known to be dispersive in frequency due to the double resonance process.[12] Varying efforts have been devoted to determine the carbon "crystallite" diameter L_a based on the ratio between the intensities of the disorder-induced D band and the first-order graphite G band (I_D/I_G). After the pioneering work of Tuinstra and Koenig who performed systematic Raman and x-ray diffraction characterizations showing the proportional relationship between I_D/I_G (using fixed excitation laser energy) and the inverse of L_a determined from various disordered graphitic materials, Knight and White derived an empirical expression to measure the "crystallite" diameter L_a from the I_D/I_G.[13,14] This obtained relation can only be applied to large sp^2 graphitized carbon crystallites, whereas another relationship was proposed by Ferrari and Robertson for highly disordered carbon.[15] Later, a general equation was developed for nanographites ($L_a > 20$ nm) by using any excitation laser energy in the visible range.[16] Great interest is to be attributed to all these correlations. However, this parameter fails in the case of polished graphitized carbon (i.e., unpredictable increase of I_D/I_G leading to the overestimation of the intrinsic structural disorder).[17,18] It is important to underline that the polishing process is usually required for some carbon materials and that the polishing-induced Raman spectra change has been known for many years.[17–21] Consequently, an alternative for this parameter is needed in the case of polished samples. Here, we report on the characterization of sp^2-nanostructured carbon "nanographites" with various excitation laser energies, pyrolysis temperatures, and varying kinds of precursors, and how to determine the "crystallite" diameter from Raman spectra strongly modified by the effect of previous polishing of the sample.

II. EXPERIMENTAL DETAILS

Since the sp^3 phase completely disappears in the carbon matter subjected to heat treatments higher than 1600 °C forming sp^2-nanostructured carbon aggregates,[22] a series of graphitized carbon matter, produced by the pyrolysis of an anthracene-based coke, tar pitch coke, gilsonite, and petroleum coke at temperatures ranging from 1600 °C to 2900 °C was used, including an industrial carbon-carbon composite and a natural "perfect" graphite (from Sri Lanka) as a reference. Among all these different materials, three samples of anthracene-based coke subjected to the temperatures 1600 °C, 2000 °C, and 2900 °C as well as the industrial composite were selected to highlight the effect of the polishing process on Raman spectra. Therefore, millimeter-sized grains of the selected carbons were embedded in an epoxy resin and then polished using 1 μm diamond particles to obtain mirror polished surfaces.

Raman measurements have been performed using an InVia Reflex Renishaw system. The instrument configuration allows for studying the sample with several excitation energies in the visible range (1.58, 1.96, 2.41, 2.54, and 2.71 eV) without necessarily changing the analyzed position of the sample. The spectra were collected under a microscope ($50 \times$ objective), and circular polarization of the excitation lasers was used. The Raman-scattered light was dispersed by a holographic grating with 1800 lines/mm and detected by a charge-coupled device (CCD) camera. Very low incident power (~1 mW) was used to avoid local heating and graphitization effects.[23]

The determination of the coherent domain diameter, during the graphitization process, was achieved using x-ray diffraction (XRD). The patterns were collected at room temperature using a Rigaku ultraX18HFCE diffractometer with a rotating copper anode (Cu$K\alpha$) and an INEL CPS-120 detector, operating at 50 kV and 300 mA in step scan mode between 10° and 90° (in 2θ). The "crystallite" diameter along the a axis, L_a, was calculated from the 11(0) reflection by evaluating the Scherrer relation $L_a = K\lambda/\beta\cos\theta$, where $K = 1.84$, λ is the radiation wavelength (0.154 nm), θ is the reflection position (diffraction angle in rad), and β is the half-height width of the 11(0) peak in 2θ (rad) units.[24] To obtain the angle positions and widths of the measured peaks, the diffraction curves were fitted with pseudo-Voigt functions. To avoid the intrinsic instrumental broadening, the β parameter was corrected using the equation $\beta = \sqrt{\beta_m^2 - \beta_{\mathrm{GGG}}^2}$, where β_m is the half-height width of the measured peak of the samples and β_{GGG} is the half-height width of the peak of a standard gadolinium gallium garnet ($Gd_3Ga_5O_{12}$) powder obtained experimentally.

III. EXCITATION LASER DEPENDENCE ON THE INTENSITY RATIO AND THE FULL WIDTH AT HALF MAXIMUM OF THE *G* BAND

Figure 1(a) displays the first-order Raman spectra of the unpolished anthracene-based coke heat-treated at 2000 °C using five different excitation laser energies (E_L) (1.57, 1.95, 2.41, 2.54, and 2.71 eV). All the spectra were normalized with regard to the D band intensity since this latter was shown to deviate from the E_L^4 dependence as predicted by Raman theory.[16,25] Therefore, in this renormalized view, one can clearly observe the significant increase of the G band intensity, which is the first-order E_{2g} allowed phonon contribution, with increasing E_L. Indeed, a significant upshift of the D band frequency can also be observed upon increasing E_L. This dispersive behavior of both the D and D' bands (47 cm^{-1}/eV determined here for the D band) has already been explained by the double resonance (DR) model.[12,26] According to this model, the D band, being the result in the emission of a photon with the energy $E_L - \hbar\omega(D)$, originates from the process involving electronic states around two inequivalent Dirac points K in the Brillouin zone (BZ) (intervalley DR process), whereas the D' band arises from a process which involves electronic states around the same K (or K') point (intravalley DR process).[12,26,27] The DR condition is reached when the energy is conserved in all these transitions.

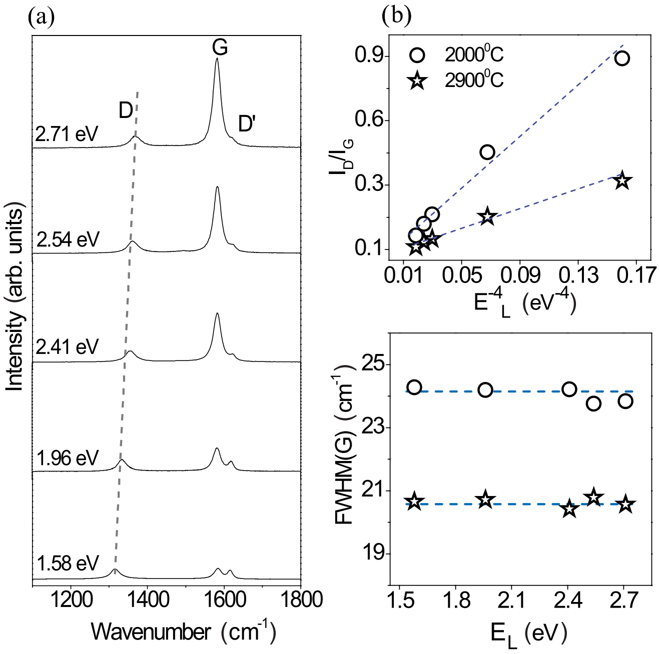

FIG. 1. (Color online) (a) The first-order Raman spectra of the unpolished anthracene-based coke heat-treated at 2000 °C at different excitation laser energies. (b) The band height ratio I_D/I_G and the FWHM of the G band vs the excitation laser energy for unpolished anthracene-based coke heat-treated at two different temperatures.

For the quantitative aspect, Fig. 1(b) displays the evolution of both band height ratio I_D/I_G vs E_L^{-4} and the full width at half maximum (FWHM) of G band vs E_L. A linear relationship is observed between the band height ratio and E_L^{-4} according to the equation $I_D/I_G = c/E_L^4$, where the slope c depends on the disorder degree of the carbon matter (i.e., $c = 3.11$ for the anthracene-based coke heat-treated at 2900 °C and $c = 7.29$ for that pyrolyzed at 2000 °C). However, and as expected, the FWHM(G) remains unchanged by varying E_L since Raman analyses were performed on the same position of the sample (i.e., same local structural order).

IV. DEPENDENCE OF RAMAN PARAMETERS ON PYROLYSIS TEMPERATURE AND POLISHING EFFECT

Figure 2(a) presents Raman spectra recorded with the excitation laser energy ($E_L = 2.41$ eV) and obtained from the unpolished anthracene-based coke heated at 1700 °C, 1900 °C, 2000 °C, and 2900 °C, respectively. Here, all the spectra were normalized with regard to the G band height. It is obvious that the D and D' bands markedly decrease with the pyrolysis temperature augmentation suggesting the increase of the structural order degree. Indeed, many studies of the sp^2-nanostructured carbons showed the dependence of the intensity ratio I_D/I_G on the "crystallite" diameter L_a, and this parameter has been commonly used since 1970.[13–16]

Figure 2(b) shows Raman spectra collected at four selected positions (S1–S4) of the polished sample previously heat-treated at 2900 °C. Significant changes in the intensity of D and D' bands relative to the G band also occur upon polishing in an unpredictable manner. This behavior completely overprints the determination of the intrinsic structural order and consequently prevents the use of this parameter in the case of polished carbon matter. However, a simple visual inspection of Fig. 2(b) shows that the G band width apparently remains unchanged after polishing. Quantitatively, Figs. 2(c) and 2(d) present the evolution of the band height ratio I_D/I_G and the FWHM(G) vs the pyrolysis temperature obtained from the spectra deconvolution by the conventional fitting procedures [WIRE 3.3 program (Renishaw)], after using a linear baseline and Voigt functions. The output parameters are the band position, intensity, FWHM, and integrated area of all the bands (D, D', and G). An additional band, located between 1540 and 1550 cm^{-1}, was required to perfectly fit Raman spectra.[18] One can clearly see the identical behavior for the unpolished carbons of these two

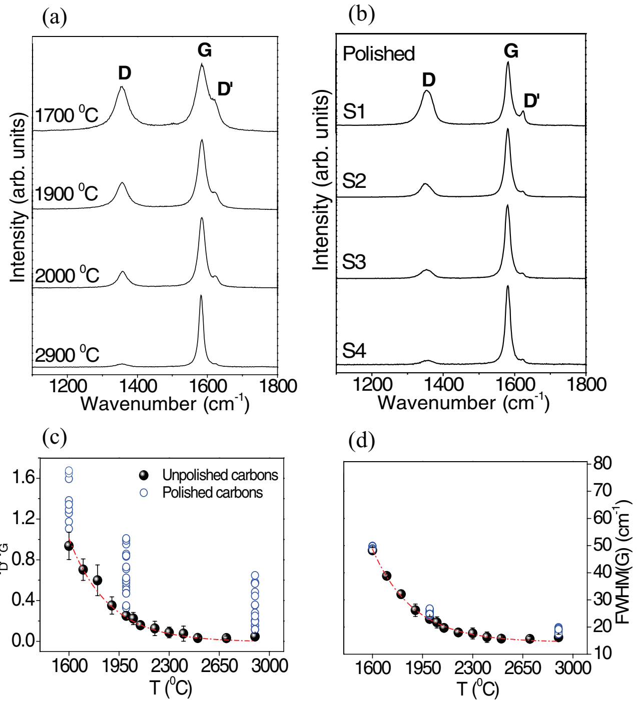

FIG. 2. (Color online) (a) Raman spectra of unpolished anthracene-based coke prepared at different temperatures. All spectra are collected using the laser energy 2.41 eV (514.5 nm). (b) Raman spectra of polished 2900 °C-treated anthracene-based coke obtained at different positions. (c), (d) The band height ratio I_D/I_G and the FWHM of the G band vs the pyrolysis temperatures of unpolished (filled circles) and polished (opened circles) carbons as the result of the deconvolution of Raman spectra.

parameters, I_D/I_G and FWHM(G), which both appear to be graphitization indicators. The band height ratio I_D/I_G and FWHM(G) gradually decrease with increasing the pyrolysis temperature until achieving minimum values around 0 for the I_D/I_G and around 14 cm^{-1} for the FWHM(G).

The identical behavior of these two parameters can be explained as follows: on one hand, the D band differential cross section was already shown to be proportional to the amount of the "crystallite" boundaries in the sp^2-nanostructured carbons[16] or at least an average measure of possible edge structures exhibiting an armchair arrangement,[28] and this is why the D band intensity should be inversely proportional to the "crystallite" diameter L_a. On the other hand, the dependence of Raman linewidths on the inverse of the mean crystallite diameter has also been observed for some nanostructured materials, and the broadening of the Raman line was attributed to the reduction of the phonon lifetime in the nanocrystalline regime as well as the dispersion curves of the material.[29,30] Moreover, Figs. 2(c) and 2(d) also show that while the band height ratios randomly increase in the polished carbon surface, their corresponding G band widths remain almost unchanged. Consequently, the polishing process seems to only modify the resonance conditions without obviously changing the local structural order. Indeed, the very slight increase of FWHM(G) can be avoided by only taking into account the lowest intensity ratio of the analyzed polished sample.

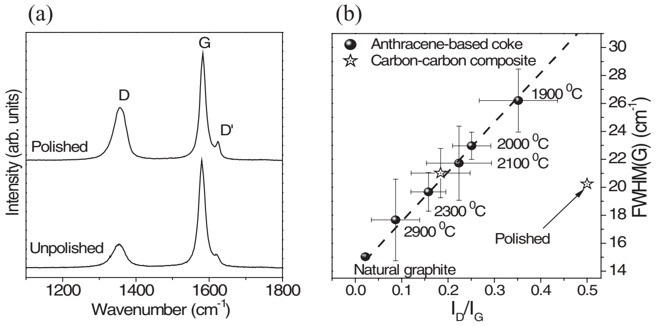

FIG. 3. (a) Raman spectra of polished and unpolished carbon-carbon composite collected using the laser energy 2.41 eV. (b) The I_D/I_G and FWHM(G) values of the unpolished anthracene-based coke treated at different temperatures (filled circles) and carbon-carbon composite (opened stars) both polished and unpolished.

The present results, obtained on the anthracene-based coke, can therefore be expected to be valid for any sp^2-graphitized carbons where the D band is mainly activated by the "crystallite" boundaries. They have to be, nevertheless, assessed and then generalized for sp^2-graphitized carbon nanographites. For that purpose, an industrial graphitized carbon-carbon composite was used. It is composed of petroleum coke grains as filler and a tar-pitch coke as a binder.[31] Figure 3(a) displays Raman spectra of this carbon material (polished and unpolished). The effect of the polishing process is clearly observed (significant increase of the D band). The I_D/I_G and FWHM(G) values of the unpolished carbon-carbon composite seem to perfectly join the FWHM(G) vs I_D/I_G anthracene-based coke profile [Fig. 3(b)] enabling the classification of this material in terms of the structural degree of disorder. Despite the fact that the I_D/I_G value remarkably increases upon polishing of the carbon-carbon composite, the FWHM(G) remains unchanged. For all these reasons, an accurate correlation was needed based on the G band width and the "crystallite" diameter determined by XRD. It is worth noting that these observations do not hold for vacancy-defected nanographites induced, for example, by ion-beam irradiation or for nongraphitizing carbons such as saccharose-based chars.

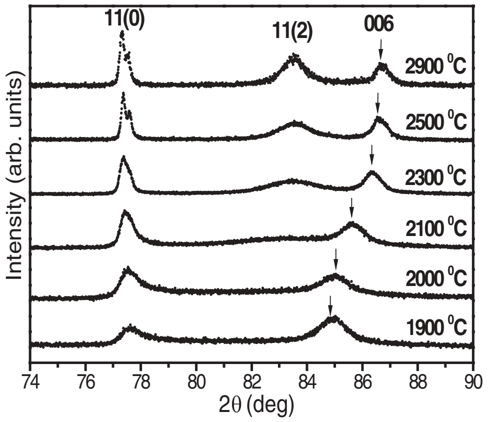

FIG. 4. X-ray diffraction profiles of a series of the anthracene-based carbons heat-treated at different temperatures up to 2900 °C. The 11(0), 11(2), and 006 reflections are indicated.

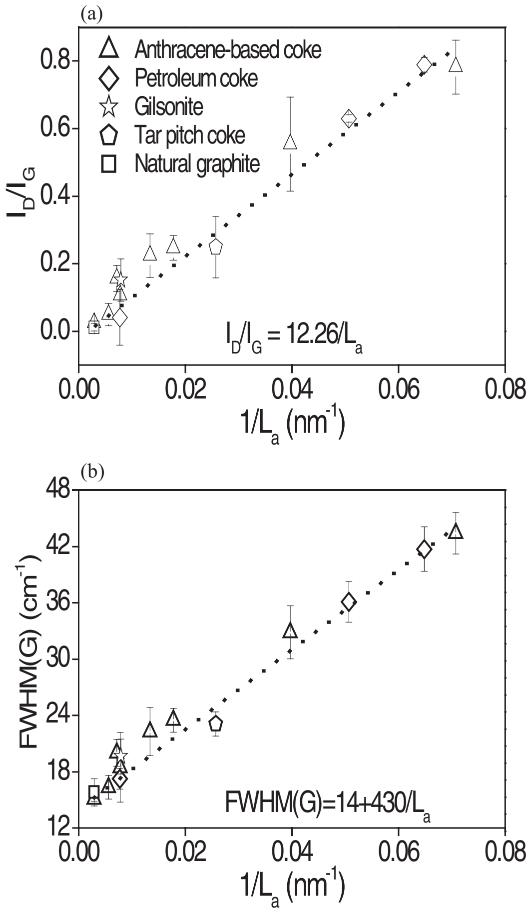

FIG. 5. Dependencies of the (a) I_D/I_G ratio and (b) FWHM of the G band vs the inverse values of "crystallite" diameter for unpolished samples.

V. DEPENDENCE OF CRYSTALLITE DIAMETER ON THE INTENSITY RATIO AND *G*-BAND WIDTH

Figure 4 illustrates the evolution of XRD profiles of sp^2-nanostructured carbons in the 2θ range 74°–90° (here an example of a series of anthracene-based cokes) subjected to increasing heat-treatment temperatures (HTTs). For higher temperatures, the samples exhibit a high degree of crystallinity, as shown by the appearance of distinctive *hkl* reflections, particularly the in-plane peak 11(0) enabling the measurement of the "crystallite" diameter L_a along the basal plane. This peak width continuously decreases with increasing the pyrolysis temperature, which seems to be in good agreement with the results obtained by Raman spectroscopy. The 006 peak, which is due to the stacking of graphene layers, also becomes narrower and its maximum shifts toward larger angles with increasing HTTs indicating an increase in the stacking thickness and improvement of the stacking. Indeed, it is worth mentioning the appearance of the 11(2) peak in the sample profiles prepared at temperatures higher than 2100 °C. The presence of the 11(2) reflections is usually considered as evidence for the tridimensional crystalline order.[32,33]

Figure 5(a) presents the plots of the height intensity ratio I_D/I_G, obtained from the fitting procedure, vs the inverse values of the "crystallite" diameter collected from 14 unpolished samples and characterized by varying precursors and disorder degrees. A linear behavior is thus observed between the band height ratios (obtained from the fitting procedure) and the "crystallite" diameter.

Not unexpectedly, the slope determined in our study (~12.2 nm) noticeably differs from that obtained by Knight and White based on the original data of Tuinstra and Koenig (4.4 nm performed with the laser excitation wavelength/energy $\lambda = 488$ nm/$E_L = 2.54$ eV) and some others gleaned from the literature.[13,34–36] Many references[15,37–39] report the same slope, using either 488 or 514.5 nm wavelengths, which is completely confusing due to a clear dispersive character of I_D/I_G [see Fig. 1(a)]. Indeed, this field usually lacks clear procedures because it is not always clear if the I_D/I_G ratio should be the ratio of the band heights or band areas.

Similarly and interestingly, Fig. 5(b) also illustrates a linear behavior between FWHM(G), obtained from the fitting procedure, versus the inverse values of the "crystallite" diameter of all the samples under consideration, where the crystallite diameters range from $L_a = 15$ nm up to larger values. This linear correlation is expressed by the following function:

$$\mathrm{FWHM}(G) = 14 + 430/L_a \quad (R^2 = 0.97) \tag{1}$$

with L_a (nm) and FWHM(G) (cm^{-1}).

Consequently, FWHM(G) can easily be recovered for carbon matter with "infinite" crystallite diameter such as the highly oriented pyrolitic graphite (HOPG) and where the D band is absent [FWHM(G_{HOPG}) $= 14 \pm 1$ cm^{-1}]. This relationship can then be accurately applied to polished sp^2-nanostructured graphitized carbons.

VI. CONCLUSIONS

In summary, we have reported here a linear correlation between FWHM(G) and the "crystallite" diameter of sp^2-nanostructured carbons "nanographites" obtained from various kinds of precursors, pyrolized at different HTTs. In particular, the influence of polishing on the Raman spectra has clearly been highlighted. It is observed that the relative intensity of the D band unpredictably increases for polished sp^2-nanostructured carbons, leading to the overestimation of the intrinsic structural order in such kind of materials. Moreover, it appears that while the intensity ratio increases, the G band width, which is related to the only effect of sp^2 bonding, remains almost unchanged. Therefore, we have established a linear correlation between the G band width and the "crystallite" diameter larger than $L_a = 15$ nm valid for polished and unpolished graphitizing carbons.

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