MULTI-WAVELENGTH RAMAN STUDY OF BALL-MILLED GRAPHITE

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Raman spectroscopy is used as structural tool in the study of carbonaceous materials. Review papers [1,2] provide an analysis of the Raman spectra from the viewpoint that phonons and electrons in a disordered structure can be handled as if the system were structurally perfect and considering the perturbation carried by defects. In fact no graphene layers are truly infinite and the effects of confinement of π electrons within domains with irregular boundaries should be considered. Furthermore these finite sheets (albeit very large on a molecular scale) may contain all sorts of electronic and structural defects such as holes, sp^3 or sp carbon atoms, free radicals, dangling bonds, distortions from planarity, grafted chemical functional groups, CH bonds, etc. [3]. In this work we strive to gain structural insights from Raman spectroscopy on a series of microcrystalline graphite samples with intentionally modulated concentration of defects. Model "graphitic" molecules serve us as representative structures with confined π electrons, which provide spectroscopic signatures related with the G and D Raman signals [4-6].

We carried out a wide series of Raman experiments on crystalline graphite powders obtained from Aldrich. EPR characterization of the samples here investigated is provided in the companion paper [7]. In order to vary the average crystallite size and defects concentration in the sample we have submitted the sample to varying grinding times in ball-milling equipment. Grinding times up to 1200 minutes have been applied. Representative SEM images of the graphite powder obtained from Aldrich and ball milled for 300 and 1080 minutes are reported in Figure 1a. This demonstrates the dramatic effects caused by grinding on graphitic crystallites. As grinding proceeds, smaller crystallites appear which are not observed in pristine graphite. Furthermore, ball milled samples exhibit crystallites with substantially more disrupted and cluttered edges compared with the habitus of crystallites in pristine graphite. Figure 1b reports the variation of the multi-wavelength (458, 514, 785nm) Raman spectra recorded on the ball-milled samples of graphite. A clear increase of D peak with respect to G peak is observed with ball-milling time, furthermore the observed I_D/I_G trends are markedly wavelength-dependent (see Figure 1c).

Within a molecular approach [4-6] deriving from a previous experience on one-dimensional systems (organic polymers) [8], we propose the following picture to help rationalizing these findings. In a given crystallite of average size L_a (simply represented on Figure 1) we can identify three regions:

(i) the core region, sufficiently far from the edge so that its electronic and vibrational properties can not be distinguished from those of the ideal and infinite crystal;

(ii) the electronically perturbed region (of lateral size ξ) which is close enough to the edge so that its local electronic and vibrational structures are affected by confinement effects and are different from those of the bulk material [6];

(iii) the very edge (ultimate edge) where all possible kinds of terminal groups, dangling bonds, and molecular disorder make the system locally different from the ideal sp^2 carbon honeycomb lattice [3].
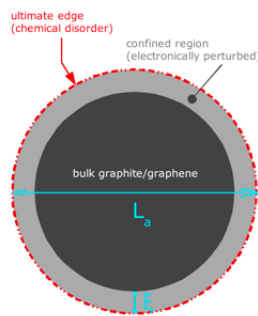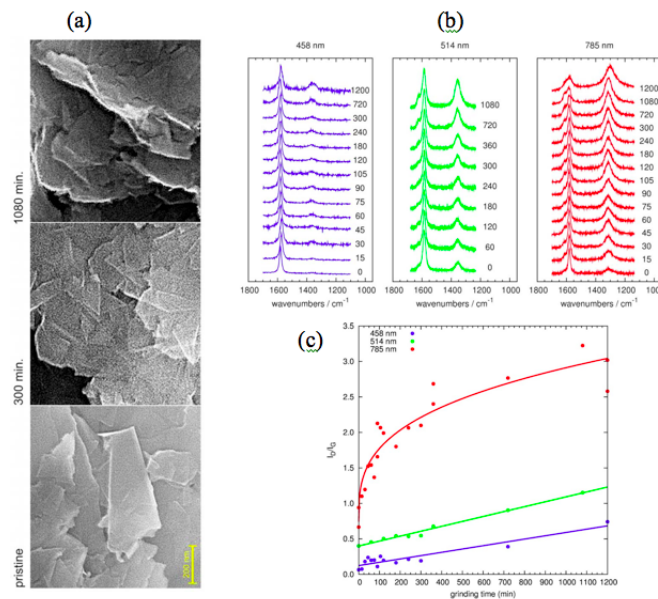

Figure 1: Example of crystallite

Figure 2: (a) SEM images of crystalline graphite powder samples (received from Aldrich, pristine) and subsequently ball milled for increasing times [9]. (b) Raman spectra of ball milled graphite powders recorded with different excitations. Grinding times are reported for each spectrum. (c) I_D/I_G ratios of ball-milled graphite for increasing grinding times and different excitation wavelengths.

The strong variations in the I_D/I_G ratio measured for a given sample with different excitation wavelengths clearly points to the relevance of resonance effects. In principle with all three exciting lines resonance Raman conditions may be reached. The different intensities of the D line at the three excitations do however show that stronger scattering occurs with the 785 nm excitation. The strength may be due either to a larger intrinsic cross section (because of resonance) or to a larger relative concentration in the distribution of "chromophores" or "ramanophores", with energy gaps close or matching the excitation line. These ramanophores arise from the disordered domains and/or edges located in the graphitic particles. The different I_D/I_G curves reported in Figure 1c, demonstrate that the increase in the concentration of resonant ramanophores produced by ball milling does depend on the ramanophore. At early grinding times, ball milling is more effective in producing ramanophores resonant with 785 nm excitation, while at later times the rate of production of these ramanophores sensibly decreases and eventually levels off. On the opposite, when considering the 458 and 514 nm excitations, ball milling maintains a steady rate in producing resonant ramanophores all over the investigated grinding time scale.

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