Determination of hydrogen or fluorine coverage in functionalized graphene from a Raman spectrum

T. Fournier[1,2]
I. Arshad[1,2], C. Crespo[3], M. Dubois[4], F. Piazza[5], M. Monthioux[1], B. Lassagne[2], P. Puech[1]
[1]*CEMES, 29 rue Jeanne Marvig, Toulouse, France*
[2]*LPCNO, 135 avenue de Rangueil, Toulouse, France*
[3]*ISM, Université de Bordeaux, 351 CR de la libération, Talence, France*
[4]*ICCF, Université de Clermont Auvergne, 24 avenue Blaise Pascal, Aubiere, France*
[5]*PUCMM, Autopista Duarte, Santiago de los Caballeros, Dominican Republic*
tom.fournier@cemes.fr ; pascal.puech@cemes.fr

Hydrogenation and fluorination modify carbon hybridization in graphene from sp^2 to sp^3, opening an electronic band gap essential for electronic devices [1]. The coverage value is expected to be obtained using Raman spectroscopy, a versatile and non-destructive optical technique successfully applied to point defects created by ion implantation. For ion implantation, the model proposed by Lucchese *et al* [2] assumes that the Raman D mode originates from two circular areas around the point defect: a structurally defective region of radius r_S=1nm and an activated region of radius r_A=3nm (Figure 1a). Although the r_S and r_A values are in good agreement with experimental data from ion implantation, they must be significantly adjusted in an attempt to fit data from hydrogenation or fluorination. Additionally, fluorine coverage can be inhomogeneous [3], complicating calibration. To overcome these difficulties, we propose an adapted model based on Lucchese's framework, introducing a deactivated central area (no D or G band) around the chemisorbed atom (Figure 1b). The sp^3 coverage is derived from the intensity ratio of D over G phonons coming from the unconverted sp^2 region, with radii for deactivated (r_{sp3}), disordered, and activated areas determined by *ab initio* calculations. This model better aligns with the experimental laws and data reported in the literature and outperforms the previous model, which was not adapted to hydrogenation or fluorination (Figure 1c).

References

[1] J. T. Robinson, *et al*, Nano letters, 10 (2010) 3001-3005
[2] M. M. Lucchese, *et al*, Carbon, 5 (2010) 1592-1597
[3] P. V. Bakharev, *et al*, Nature Nanotechnology, 15 (2020) 59-66

Figures

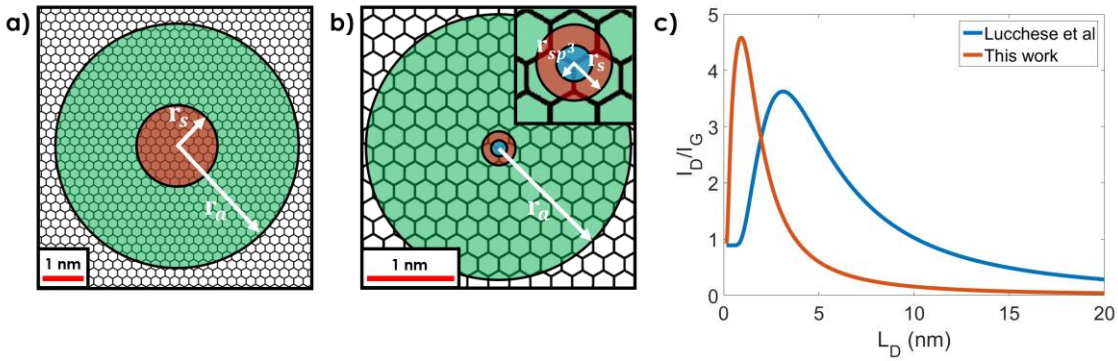

Figure 1: a) Disordered (red) and activated (green) regions from Lucchese's model. b) Deactivated (blue), disordered (red), and activated (green) areas from our model. c) Plot of D over G band intensities (I_D/I_G) as a function of the average distance L_D between point defects for both models valid for 532nm excitation energy.