Vibrational and Nanoimaging of Eumelanin Superstructures modulated by Atomic-Defects in Micronized Graphene Oxide

Roberto Matassa[1], Sara Mattiello[1], Juan Gabriel Lozano[2], Ana Maria Beltran[2], Costantino Zazza[3], Nico Sanna[3], Jun Wei Phua[4], Jose Mauricio Rosolen[5], Andrea Di Cicco[1], Javid Rezvani[1], and Roberto Gunnella[1]

[1]*Physics Division, School of Science and Technology, University of Camerino, 62032 Camerino, Macerata, Italy.*

[2]*Departamento de Ingeniería y Ciencia de los Materiales y del Transporte, Escuela Técnica Superior de Ingeniería y Escuela Politécnica Superior, Universidad de Sevilla, 41092 Seville Spain.*

[3]*Department for Innovation in Biological, Agro-food and Forest systems, Universita della Tuscia, L.go dell'Universita, 01100 Viterbo, Italy*

[4]*Insectta Pte. Ltd, 8 Cleantech Loop, Singapore, 637145, Singapore.*

[5]*Departamento de Química, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Universidade de São Paulo, Ribeirão Preto, Brazil.*

Abstract: The bioactive nanocarbon assembling revealed interesting vibrational-structural correlations related to the nanometric changes of the biomolecular superstructures, occurring through the modulated dimension of micronized graphene oxide pointing to a topological quantum biomaterial.

The present accomplishment evidences the eumelanin (*e*Mel) molecular units capable of changing nanostructures from its natural origin to self-assembling with the biocompatible micronized graphene oxide (GO_m). Taken together, the hybrid system subject of experiments of high-resolution electron nanoimaging coupled with self-healing vibrational Raman spectroscopy has taken advantage to reveal intriguing and unique features. Indeed, direct imaging-diffraction electron experiments of GO_m, showing twisted (2D band), wrinkling (*D+D'* band), folding (D band), and intercalation (blue-shifted G band) structures, well-matched the response of the corresponding vibrational resonance bands. These finding have shown Raman spectra profile in *e*Mel similar to the atomic-like defected GO_m orientation (*D'', D, D'*, and 2D bands) [1]. The unknown eumelanin superstructure has shown irregular stacked nanosheets of finite-size differently orientated.

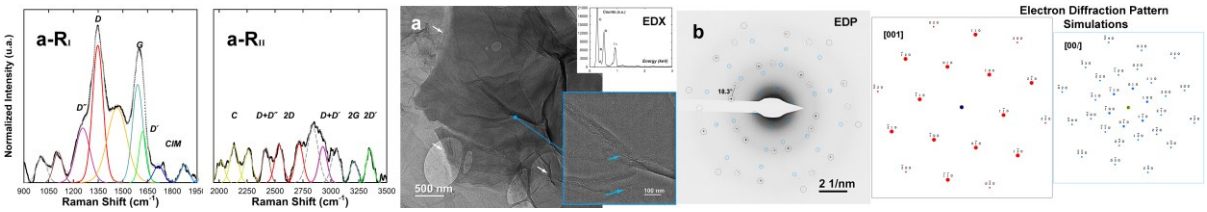

Fig. 1 Structural-vibrational microscopy of GO_m-*e*Mel. **a** BF-TEM images of the GO_m-*e*Mel. Inset: EDX spectroscopy and magnified image. **a-R$_I$ -R$_{II}$** First and second-order resonance Raman spectra showing the fitting and its deconvolution profiles. **b** EDP taken from **a** showing distinct diffraction spots and its simulation patterns (hexagonal symmetry of graphite phase (black circles) and crystalline eumelanin (blue circles).

The readapted eumelanin structure, interacting with defected GO_m sheets, has shown for the first time a morphometric change from nanosheets to smallest nanoparticles (**Fig. 1a**). The structural interaction, technically not visible by HR-TEM, with GO_m surface-edge is mainly validated by the evolution of the sensitive resonant G and D' bands (**Fig. 1a-R$_I$**). Interestingly, the doping/intercalation of increasing interlayers spacing revealed by the 2D band behaviour is successful validated by the complementarity of electron diffraction analyses [2,3] (**Fig. 1b**). The established interlayer hybridization at atomic level induces new exotic electron states and transport phenomena (*D''*, *G*, and *CIM* bands) of different sp^n graphitic hybridizations. To overcome the limited resolution of the HR-TEM and the qualitative Raman analysis, theoretical optimization of the electronic-structure properties (DFT) followed by vibrational calculations of the Raman intensities (DFPT) are needed. Therefore, these spectroscopic observables are derived within the Born-Oppenheimer approximation imposing Periodic Boundary Conditions (PBCs). This relevant achievement concretely completes the complementarity between HR-TEM and Raman analyses by providing quantitative determination of the unknown structural *e*Mel and of the complex excited electronic states of this hybrid system for choosing appropriate dopant species and host biomaterial.

References

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