Functionalized Graphene Bio-Sensing Building-Blocks under Environmental Stimuli

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Abstract: These studies are part of a continuous effort [1,3,4,5] to investigate the main properties of different graphene (G/RGO/GO), and other C allotrope nanostructures used for biosensors design. Successive studies on graphene, reactive-edge graphene, and pore functionalized graphene were conducted throughout the use of the of COMSOL Multiphysics® modules, modeling and simulating either the self-assembling or the environment stimuli responses of the Graphene-C-allotropes nanostructures building-blocks and their functionalization with active biostructures.
The interdisciplinary approach requested on these studies was addressed importing the geometry and field properties of different graphene, carbon nanotubes, fullerenes and biomolecules obtained with ChemBio3D and SolidWorks through Live Link ™ for SolidWorks on Electrochemistry and Multiphysics modules of COMSOL Multiphysics®. The electrical and thermal field properties of C allotrope nanostructures obtained with MATLAB were imported as well through Live Link™ for MATLAB on dedicated modules.

Keywords: graphene, bio-functionalization, bio-sensing, nanosensor

1. Introduction

A realistic process meant to produce functionalized graphene nanosensing structures could be a biomimetic process.

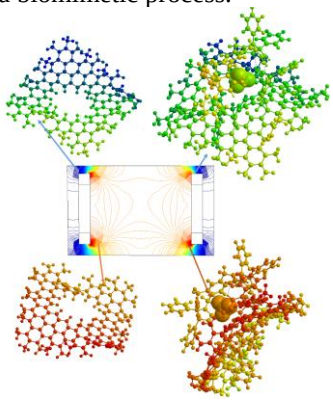
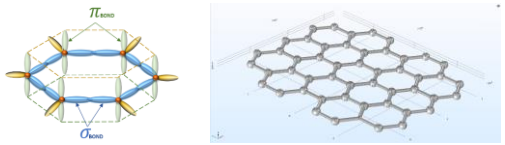


Figure 1. Functionalized G/GO/RGO bio-sensing modules.

Considering the mesoscale related particularities of bio-chemo-electro-thermal processes occurring through ion channels at cellular scale and comparing them with graphene, carbon nanotubes and fullerene size related properties, a self-assembly process under controlled environmental conditions seems possible. This study aims to decipher the self-assembly process requirements for a further scale-up of the biomimetic technique of functionalization of graphene and other C-allotropes for personalized biosensors.
Graphene is a monolayer composed of sp^2 bonded carbon atoms arranged in two dimensional honeycomb lattices. The pristine graphene is a 2D plane sheet of covalent bonded atoms that form ideal crystal lattices (Fig.1a,b) with unique mechanical and transport properties (Table 1). Graphene stands as monolayers attached to the substrates of another layer (SiC or a metal) or as free standing sheets, if the graphene sheet is sufficiently isolated from its environment. Very good quality graphene was made in lab using SiC(001) surface [6].



a b

Figure 2. Graphene studies : (a) unit cell; (b) COMSOL model of G (10,10)

The rate of hopping of adatom per second (R)[8]:

$$R = R_0 exp\left(-E/k_B T\right) \quad (1)$$

where: E= migration energy (eV); T – temperature (K); k_B- Boltzmann constant; R_0-prefactor (R_0 for Si adatom on Si(001) surface: $R_0=1.25x10^{10}$)

The non-linear elastic response of graphene to tensile load [6]:

$$\sigma = E\varepsilon + D\varepsilon^2 \quad (2)$$

where: σ- applied stress; ε- elastic strain; E-Young modulus; D- the third order elastic stiffness

The experimental data [5,6] for graphene shows: *E=1.0 TPa*; *D=-2.0 TPa* (close to CNTs), σ_{int}*=130 GPa* (the highest value ever measured for real materials). The computer simulation [7] resulted data have as well extremely large values: *E=1.05 TPa;* σ_{int}*=110 GPa* .

Using Density Functional Theory (DFT) in ChemBioDraw (running Molecular Dynamics) and importing ChemBioDraw-LiveLink data to MATLAB can be determined the characteristics of the adatom adsorption process on graphene and on other C-allotropes surfaces.

For instance, for a distance of 14.7Å between the graphene sheets (Fig.3) the distance between adatoms (Fig.1) is 7.3Å. The basic unit cell (Fig. 2a) has $a_{C-C} = a_0 = 1.42$Å and vectors $a_{1,2} = \pm\sqrt{3}a_0$~2.4566Å

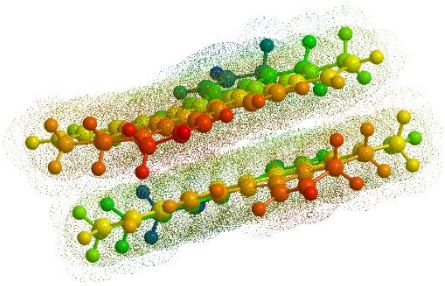


Figure 3. Van der Waals potential for double layer graphene – reactive edges

2. Use of COMSOL Multiphysics® Software

Electrical Potential Profile is a function of distance (x) from graphene surface [2]. The shape of potential function is determined by Modified Poisson-Boltzmann (MPB) equation (Eq.3):

$$\frac{d^2V}{dx^2} - \sum_i \frac{z_i e C_{0i}}{\varepsilon} \cdot \frac{2\sinh\left(\frac{z_i eV}{kT}\right)}{1+2v_i \sinh^2\left(\frac{z_i eV}{2kT}\right)} \qquad (3)$$

where: $v_i=2a^3C_{0i}$; ε_i- permittivity; a- effective ion size; z_i – valence of ion; C_{0i} – bulk concentration of ions

In MATLAB code (P- potential, instead V from Eq.3) all simulation parameters are (Eq.4)[2]:

[x, P, R] = potential_1D(P_0, Zi, Ci, E_R, EFF, MPB) (4)

where: P_0 – applied potential; Zi-array of ion valence values; Ci- array of ion bulk concentration value; E_R- relative permittivity value (78.3 for H_2O); MPB – set to 1 to use MPB formula/ -set to 0 to use regular Poisson-Boltzmann, without modification for steric effect on ion size.

One of the simulation output parameters is ion concentration as a function of the distance from graphene surface (Eq.5):

$$C_i = C_{i0} e^{\frac{-z_i eV(x)}{kT}} \qquad (5)$$

MATLAB application of graphene properties (Fig.2a,b; Fig.4 a) and CNTs (Fig.4b) in specific models and simulations were exported through LiveLink™ in COMSOL Multiphysics® (Fig.3c,4c,5b).

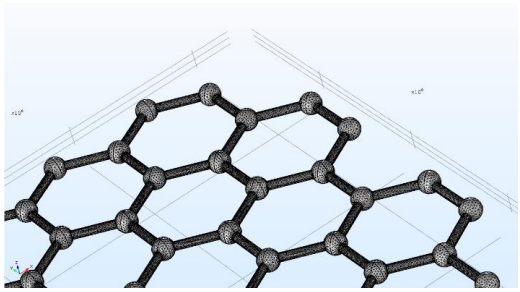
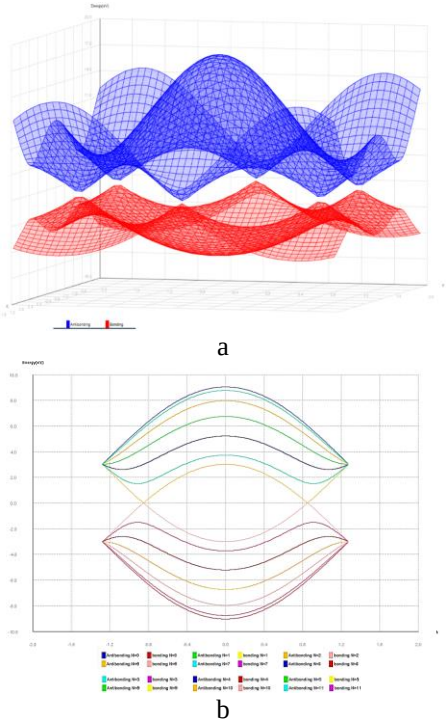


Figure 4 COMSOL mesh structure - G (10,10) reactive edges



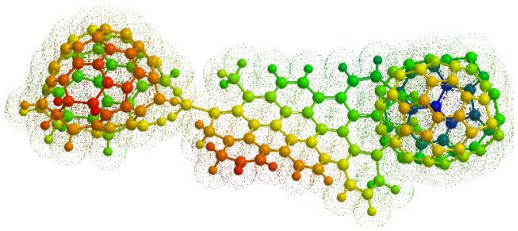
a

b

Figure 5 MATLAB study of electrical properties: (a) G (10, 10) – reactive edges ; (b) CNT (6,6,10)

3. Results

With COMSOL Multiphysics® modules, importing geometry and properties from ChemBio3D on Electrochemistry module.



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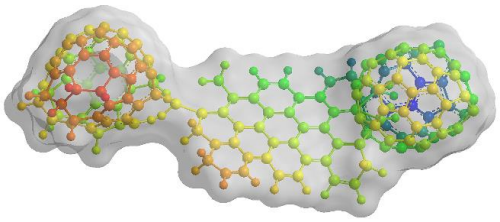

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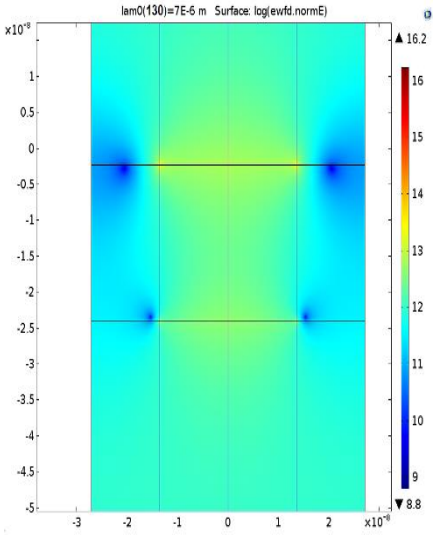
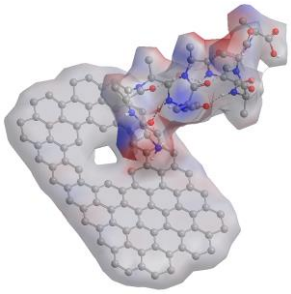


c

Figure 6 RGO- 2xC60 self-assembly:
(a) model; (b) Total Charge Density;
(c) Electrical Potential Profile

The electrical and the thermal properties from MATLAB through LiveLink™ on Multiphysics were performed different functionalization simulations (Fig. 4-5)



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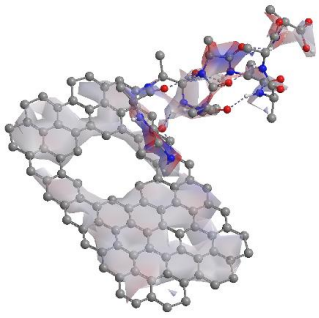

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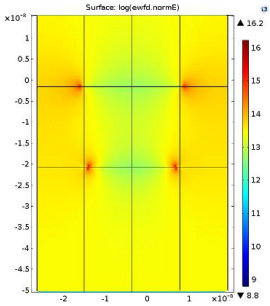

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Figure 7 GO-Alpha-Helix (protein) self-assembly:
(a) model; (b) Total Charge Density;
(c) Electrical Potential Profile

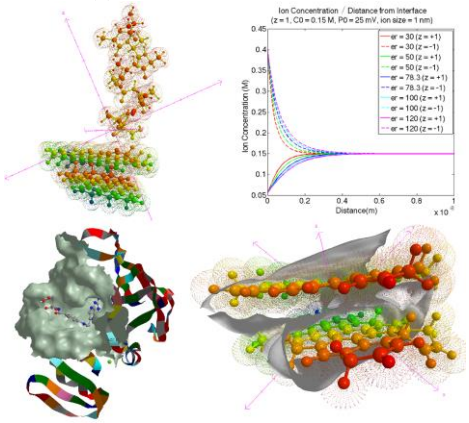
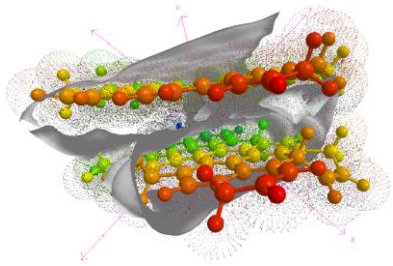


Figure 8. 2x RGO(1-pore)/Alpha-Helix
(a) Self-Assembly model; (b) Ion concentration;
(c) Local Charge Density – Protein-RGO pore;
(d) 2xRGO –Total Charge Density



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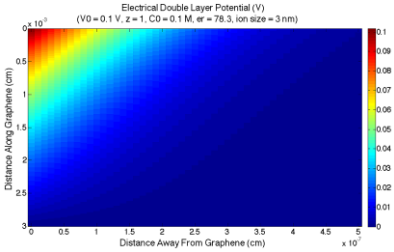

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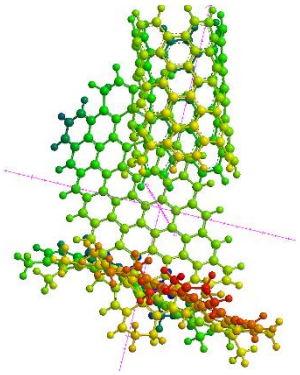
Figure 9 RGO dual-layer study



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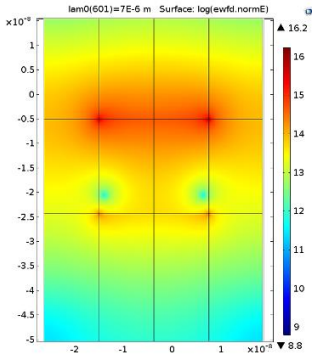

b

Figure 10 Wrinkled (defect) structure studies:
(a) clustered structure RGO/RGO/CNT;
(b) electric properties measured on substrate

4. Conclusions

The mesoscale related particularities of bio-processes at cellular scale can describe a self – assembling process for graphene functionalized structures beginning from MD model output data and calculating the values of all process variables (physical, electrical and chemical) related to the environmental particularities (MATLAB).

C- allotropes (carbon nanotubes and fullerene) can be used on a self-assembly process under controlled environmental conditions on a biomimetic functionalization process simulation.

5. References

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6. Appendix

Table 1: Graphene properties [5]

Property	Symbol	Value
Theoretic specific surface area	SSA	2630 m^2/g
Intrinsic mobility	μ	20.000 cm^2/Vs
Young modulus	E	~1.0 TPa
Thermal conductivity	κ	~5000 W/mK
Transmissivity (transparency to light)	%	~98%