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Unravelling the Quantum Interactions of Collagen-like Peptides with Carbon-Based Nano-Structures in Aqueous Media

Collagen is the main building-block of connective tissue in animals and the most abundant protein in mammals. Regenerative medicine/tissue engineering is a rapidly growing multidisciplinary field that pursues to develop functional cells and tissue to relieve or partly cure affections deriving from lack or defective production of collagen. Development of novel biomaterials and scaffolds designed to direct the growth, differentiation and organization of the cells in new functional tissue, is a very promising area within this field and biomedicine in general. CNTs and graphene (one-atom thick planar sheet of carbon atoms densely packed in a honeycomb crystal lattice) appear to be gifted materials for this end since apart from presenting very intriguing physical qualities they can be assembled to form three-dimensional porous structures (which encourages bone cell in-growth) and are costly affordable. In a recent work, we have studied in detail the binding of collagen-like peptide units (CPU) to graphene and calcium(Ca)-doped graphene using density functional theory (DFT) as computational method. We found that the binding of CPU to graphene is in general thermodynamically favorable yet very weak (physisorption). Interestingly, we showed that when the carbon surface is doped with Ca impurities the resulting CPU binding is dramatically reinforced as effect of electron-charge transfer between the Ca adatoms and carboxyl groups in the CPU (chemisorption). These findings point towards potential realization of C/Ca-based biomaterials for bio- and nano-technological applications.

The main motivation of this project was to complete our previous work and to fully gauge the potential of CPU-CNS systems as biomaterials. In particular, the specific aims of this project were:

- to characterize the quantum interactions of collagen-like peptide units with CNTs and calcium (Ca)-doped CNTs
- to quantify the effect of water molecules on the quantum interactions of CPU with grahene, Ca-doped nanostructures

In order to achieve the specific aims already cited, we resorted to two different types of first-principles calculations based on density functional theory. Next, we briefly explain the results obtained in our research:

(i) Geometry optimization of CPU adsorbed on CNTs and Ca-doped CNTs

As could have been foreseen, our calculations show that the nature of the interactions between CPU and pristine CNTs is the same than of those observed in CPU-graphene hybrids (e.g. physisorption, E_{bind} ~ 0.1 eV). Nevertheless, when the CNTs are doped with Ca atoms, the interactions of CPU with CNTs turn out to be reinforced substantially with respect to the non-doped cases, and large charge transfers from the metal adatoms to to the amino and carboxyl groups in the CPU are observed (e.g. chemisorption, E_{bind} ~ 1-2 eV, see Fig. 1). Interestingly, the strength of the Ca-mediated CPU-CNT covalent binding increases with increasing CNT radius; the explanation of this effect can be understood in terms of topology since the flatter the carbon surfaces are the largest number of Ca-carboxyl or Ca-amino bonds that can be formed.

(ii) Ab initio molecular dynamics simulations of CPU-CNS and CNS immersed in water

Besides mechanical, chemical and biocompatibility properties, two other essential aspects must be addressed in theoretical design of a biomaterial, namely room-temperature stability and water miscibility. As explained before, we have observed very intense zero-temperature binding of CPU to Ca-doped graphene (corresponding adsorption energies amount to 1-2 eV). Given that these adsorption energies are reasonably large in principle one could expect that the resulting CPU-CNS systems are stable also at room-temperature. Nevertheless, the effect of water molecules, ubiquitous in physiological media, on CPU-CNS interactions cannot be inferred from any of our (or other existent) previous investigations. Therefore, explicit simulation of joint CPU-CNS systems immersed in water is required. In this project, we have performed explicit ab initio molecular dynamics simulations (AIMD) of both CPU/Ca-doped graphene and Ca-doped graphene/water systems considering different temperatures. Our simulations show that the interactions between CPU and Ca-doped nanostructures are strong enough so as to overcome room-temperature ionic excitations (see Fig. 2) and that the effect of calcium atoms in the carbon surfaces is to prevent nanostructure immiscibility in aqueous media.

The whole series of results obtained in this collaboration suggest promising potential of Ca-doped nanostructures for biomaterial and/or protein immobilization application.

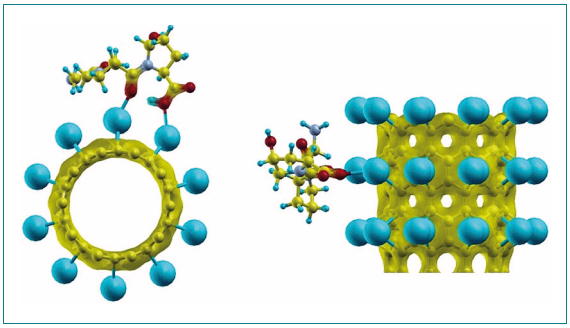

Fig. 1. – Geometry optimized CPU on top of Ca-doped (10,0) CNT. Areas with enhanced electron-charge density with respect to non-doped case are denoted with rough texture.

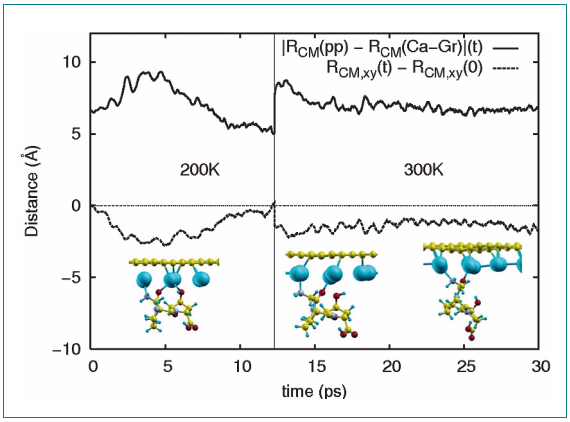

Fig. 2. – Ab initio molecular dynamics simulations of a CPU/Ca-doped graphene system.

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