

Interaction of graphene surfaces with protein: route for effective non-covalent biological functionalization

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Exquisite electronic, mechanical, optical properties of single layer graphene have triggered its integration into a vast ensemble of devices and processes among various applications field. In many of these applications, the graphene basal plane needs to be functionalized with dedicated molecules in order to tune its properties. These functionalization protocol are central in the making of graphene biological sensors as the specific detection of biological target by a biological sensors only can be enabled by grafting of functional sensitive biological molecules (enzymes, proteins, antibodies) onto the graphene basal plane. Grafting of external molecules to a given material is usually achieved through direct covalent grafting to dangling reactive moieties in the first layer of the material one seek to functionalize. In the case of single layer graphene, breaking the carbon lattice to induce chemical reactivity and covalent binding of external molecules drastically modify electronic, optical, mechanical properties to the extent that covalently functionalized graphenes are classified as novel material, (e.g. fluorographene, graphane or graphyne), with very distinct properties¹. In order to attach external molecules to graphene without inducing breaks in the carbon lattice, non-covalent binding has been investigated. In this context, Pi stacking of aromatic moieties to graphene basal plane has been demonstrated as a robust way to bind molecules to graphene. Non covalent functionalization with external aromatic moieties has been successfully applied non-exhaustively for tuning graphene wettability, facile exfoliation from bulk graphite and stabilization of graphene flakes in solution². In the field of biological functionalization, grafting of the biological molecules isn't sufficient on its own and the biological function of the grafted biomolecule needs to be maintained for the bio-functionalization to be operational. Indeed, the interaction between surfaces and biological molecules can have deleterious effect on the biological function of the molecules sought to be grafted. Hydrophobic surfaces in particular are known for inducing protein denaturation through hydrophobic collapse. In this study, we will present

¹ Inagaki, M. & Kang, F.. J. Mater. Chem. A 2, 13193–13206 (2014).

² Zhang, M. et al. Small 6, 1100–1107 (2010).

fundamental considerations on the denaturing nature of graphene surfaces for protein macromolecules. In order to overcome protein denaturation upon adsorption onto graphene lattice, we will compare different routes for a robust non covalent biological functionalization protocol for graphene. We will support our conclusions on the preservation of biological function of grafted biological macromolecules, thus contributing to define an effective route for biological functionalization of graphene surfaces.

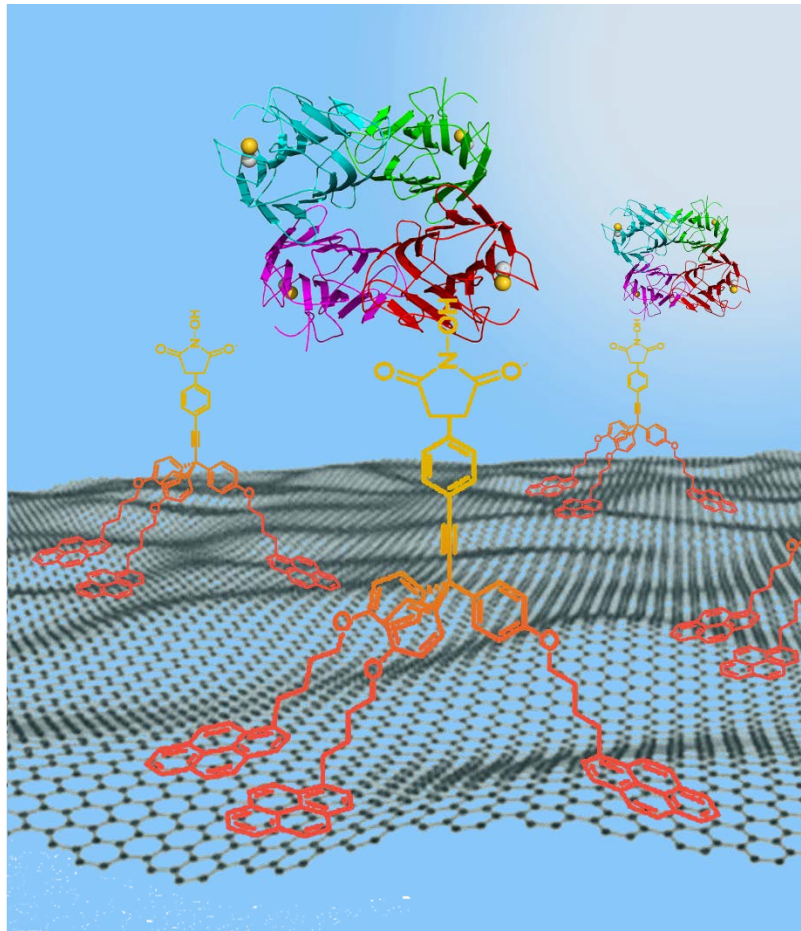


Figure 1 : Artist view depicting the interface between a graphene surface and a protein solution (here Concanavalin A) through the use of specifically designed and synthesized tripodal molecules incorporating N-Hydroxysuccinimide esters at their apex. The tripod bind non covalently to graphene and engage a covalent bond to the protein through the ester. The tripod helps maintaining the protein, although attached to graphene, sufficiently away from it to prevent denaturation.